Chem. Rev. 1983, 83, 135-201

Bridged Hydrocarbyl or Hydrocarbon Binuclear Transition-Metal Complexes: Classification, Structures, and Chemistry

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Received June 7, 1982 (Revised Manuscript Received September 13, 1982)

Contents

I. Introduction, Classification, and General Considerations

Organometallic chemistry, which concerns compounds having metal–carbon bonds, is still expanding rapidly. The simplest molecules are those which contain just one metal atom, the mononuclear compounds. The metal may be uniquely attached to a single carbon atom, the σ-complex, and these are classified according to Table I. Alternatively the metal may be attached more or less equivalently to two or more carbon atoms, the π-complex (η^2 to η^8), which are best known for transition metals,[1] although (for example) η^5-cyclopentadienyls of several main-group elements are well-documented.

In this article we are particularly concerned with binuclear transition-metal complexes in which the two metal atoms are bridged by one or more hydrocarbyl or hydrocarbon ligands, or a simple derivative such as $-CF_2-$ or $-CH_2PR_2CH_2-$. Reference will occasionally also be made to tri- or oligonuclear transition-metal complexes, which are examples of metal clusters, but these will not be discussed extensively. A recent survey deals with electron-deficient μ-alkyl and related μ-hydrocarbyls of main-group metals.[2] We shall also not discuss simple binuclear metal carbonyls or other topics dealt with in recent reviews (Table II).

In sections I–XI the literature is covered to the end of 1980. Section XIII (with an appendix, added at the proof stage, and textual additions elsewhere) and Tables IVa–XIIIa update the available information to the end of 1982.

Di- or oligonuclear transition-metal complexes having μ-hydrocarbyl or μ-hydrocarbon ligands have, for the majority of types, only become prominent in the very recent past; others, such as the μ-CO dimetallic complexes [$Fe_2(CO)_9$] have a longer history. Many of the compounds have structural interest and often are among the exotica of organometallic chemistry. They have significance for theories of (a) bonding, (b) mononuclear metal hydrocarbyl decomposition pathways, (c) certain organometallic mechanisms, e.g., fluxionality of ligand exchange (section XII), and (d) of catalysis, e.g., in Ziegler–Natta α-olefin polymerization.

As for (d) a recently fashionable view was that homogeneous catalysis by metal cluster compounds might

0009-2665/83/0783-0135$06.50/0

TABLE I. Classification of Mononuclear Organo Transition-Metal σ-Complexes

ligand	hybridization of ligating C Atom	examples	ref where available (or recent paper)
1. alkyl	sp^3	$[Hf(CH_2SiMe_3)_4]$	*a*, *b*
2. ylide	sp^3	$[Cr\{CH_2PMe_2CH_2\}_3]$	*c*
3. alkenyl	sp^2	$[Cr(CPh{=}CMe_2)_4]$	*d*
4. aryl	sp^2	$[Lu(C_6H_3Me_2\text{-}2,6)_4]^-$	*a*, *e*
5. carbene	sp^2	$[W\{C(OMe)Ph\}(CO)_5]$, *trans*-$[Rh\{CN(Ph)CH_2CH_2NPh\}Cl(PEt_3)_2]$	*f* *f*
6. acyl	sp^2	$[Re(COMe)(CO)_5]$	*g*
7. iminoacyl	sp^2	$[Zr\{C(NTol\text{-}p)Me\}Me(\eta\text{-}C_5H_5)_2]$	*h*
8. alkynyl	sp	*trans*-$[Pt(C{\equiv}CPh)Cl(PMe_2Ph)_2]$	*i*
9. ketenide	sp	$Ag_2C_2O(py)$	*j*
10. vinylcarbene	sp	$[Mo\{C{=}C(CN)_2\}(\eta\text{-}C_5H_5)Cl(PPh_3)_2]$	*k*
11. carbyne	sp	*trans*-$[W(CPh)(CO)_4I]$	*l*
12. carbonyl	sp	$[Ni(CO)_4]$	*m*
13. isonitrile	sp	$[Fe(CNBu\text{-}t)_5]$	*n*

[a] Davidson, P. J., Lappert, M. F.; Pearce, R. *Chem. Rev.* 1976, *76*, 219. [b] Schrock, R. R., Parshall, G. W. *Chem. Rev.* 1976, *76*, 243. [c] Schmidbaur, H. *Acc. Chem. Res.* 1975, *8*, 62; *Pure Applied Chem.* 1978, *50*, 19. [d] Cardin, C. J.; Cardin, D. J.; Roy, A. *J. Chem. Soc., Chem. Commun.* 1978, 899. [e] Marks, T. J. *Prog. Inorg. Chem.* 1978, *24*, 51. [f] Cardin, D. J.; Cetinkaya, B.; Lappert, M. F. *Chem. Rev.* 1972, *72*, 545. Brown, F. J. *Prog. Inorg. Chem.* 1980, *27*, 1. [g] Wojcicki, A. *Adv. Organomet. Chem.* 1973, *11*, 87. [h] Lappert, M. F.; Milne, C. R. C.; Luong-Thi, N. T. *J. Organomet. Chem.* 1979, *174*, C35. [i] Cetinkaya, B.; Lappert, M. F.; McMeeking, J.; Palmer, D. E. *J. Chem. Soc., Dalton Trans.* 1973, 1202. [j] Blues, E. T., Bryce-Smith, D.; Kettlewell, B.; Roy, M. *J. Chem. Soc., Chem. Commun.* 1973, 921. [k] King, R. B., Saran, M. S. *J. Am. Chem. Soc.* 1973, *95*, 1817. [l] Fischer, E. O.; Schubert, U. *J. Organomet. Chem.* 1975, *100*, 59. [m] Stone, F. G. A.; Abel, E. W. *Quart. Rev.* 1970, *24*, 498; "Transition Metal Clusters" Johnson, B. F. G., Ed.; Wiley; New York, 1980. [n] Treichel, P. M. *Adv. Organomet. Chem.* 1973, *11*, 21. Bassett, J.-M.; Green, M.; Howard, J. A. K.; Stone, F. G. A. *J. Chem. Soc., Dalton Trans.* 1980, 1779.

TABLE II. Recent Reviews Relevant to μ-Hydrocarbyl or μ-Hydrocarbon Binuclear Transition-Metal Complexes

subject/title[r]	section of this review	ref,[t]
bridging phosphorus ylides	II	9
bridging 1,1-alkylidenes (CH_2N_2 as reagent)	III	35
dimetallacycles	II, III, IV, VI, VIII	*a*
bridging 1,1-alkylidenes and 1,1-alkylidynes	III, IV	*b*, *c*
organometallic aspects of Fischer–Tropsch chemistry	III, IV, V	*d*
alkali-metal-transition-metal complexes	V, X	*e*
Ziegler-Natta catalysis	V, X, XII	187
complexes with a bridging unsaturated ligand	VI-IX	*q*
bridging η-allyls and η-cyclopentadienyls	VIII	*f*
bridging pentalenes	VIII	*g*
coordination chemistry of allenes	IX	*h*
carbonyl-cobalt complexes derived from alkynes	IX	*i*
bridging acetylenes in M_2 and M_3 complexes	IX	*j*
$\eta\text{-}C_5H_4\text{-}CH_2\text{-}C_5H_4\text{-}\eta\text{-}Co_2$ complexes	XI	*k*
Fischer-Tropsch reaction	XII	205-208, 218, *l*
olefin metathesis	XII	195
metal clusters	XII	202, 203, *m*
bridged hydrocarbyl intermediates in catalysis	XII	180, 185, *n*
1,1-alkylidyne-Co_3 Clusters	*s*	98
main-group metal organometallic complexes with electron-deficient bridges	*s*	2
complexes with bridging carbonyls	*s*	*o*
complexes with bridging isonitriles	*s*	*p*
carbido cluster complexes	*s*	209

[a] Dyke, A. F.; Finnimore, S. R.; Knox, S. A. R.; Naish, P. J.; Orpen, A. G.; Riding, G. H.; Taylor, G. E. *ACS Symp. Ser.* 1981, *155*, 259. [b] Ashworth, T. V.; Chetcuti, M. J.; Farrugia, L. J., Howard, J. A. K.; Jeffery, J. C.; Mills, R. M., Pain, G. N.; Stone, F. G. A., Woodward, P. *ACS Symp. Ser.* 1981, *155*, 299. [c] Stone, F. G. A. *ACS Symp. Ser.* 1982, in press. Herrmann, W. A. *Adv. Organomet. Chem.* 1982, *20*, 159. [d] Herrmann, W. A. *Angew. Chem., Int. Ed. Engl.* 1982, *21*, 117. [e] Jonas, K.; Krüger, C. *Adv. Organomet. Chem.* 1980, *19*, 520. [f] Werner, H. *J. Organomet. Chem.* 1980, *200*, 335; *Adv. Organomet. Chem.* 1981, *19*, 155. [g] Knox, S. A. R.; Stone, F. G. A. *Adv. Organomet. Chem.* 1974, *7*, 321. [h] Bowden, F. L.; Giles, R. *Coord. Chem. Rev.* 1976, *20*, 81. [i] Dickson, R. S.; Fraser, P. J. *Coord. Chem. Rev.* 1974, *12*, 323. [j] King, R. B. *Ann. N.Y. Acad. Sci.* 1977, *295*, 135. [k] Bergman, R. G. *Acc. Chem. Res.* 1980, *13*, 113. [l] Masters, C. *Adv. Organomet. Chem.* 1979, *17*, 61. [m] Band, E.; Muetterties, E. L. *Chem. Rev.* 1978, *78*, 639. King, R. B. *Progr. Inorg. Chem.* 1972, *15*, 287. Gladfelter, W.; Geoffroy, G. L. *Adv. Organomet. Chem.* 1980, *18*, 207. Chini, P. *J. Organomet. Chem.* 1980, *200*, 37. Muetterties, E. L. *Ibid.* 1980, *200*, 117. [n] Wilke, G. *Pure Appl. Chem.* 1978, *50*, 677. Ugo, R. *Catal. Rev.* 1975, *11*, 225. [o] Colton, R., McCormick, M. J. *Coord. Chem. Rev.* 1980, *31*, 1. [p] Yamamoto, Y. *Coord. Chem. Rev.* 1980, *32*, 193. Treichel, P. M. *Adv. Organomet. Chem.* 1973, *11*, 21. [q] Nesmeyanov, A. N.; Rybinskaya, M. I.; Rybin, L. V., Kaganovich, V. S. *J. Organomet. Chem.* 1973, *47*, 1. [r] Entries in this column are intended to indicate the scope of the cited review in so far as it apertains to the theme of the present article. [s] Additional to review but covering closely related material. [t] Reference numbers in this and subsequent Tables refer to bibliography (section XIV).

John Holton obtained his B.Sc. at the University of Manchester and his D.Phil. (Sussex) in 1976 for his work with M. F. Lappert on alkyls of the lanthanides and early transition metals. He then joined I.C.I. Corporate Laboratory, now the New Science Group, at Runcorn, where he presently heads a small group studying polymerization catalysis as a route to speciality polymers; his other research interests include new organometallic catalysts and new copolymers via novel catalysis improved processes.

Michael Lappert is Professor of Chemistry in the School of Chemistry and Molecular Sciences, University of Sussex. A graduate of the Northern Polytechnic, his B.Sc. was followed by a Ph.D. (with W. Gerrard), to which in 1960 he added a D.Sc. (University of London). He has been at Sussex since 1964, having previously been at UMIST (1959–1964). He was the recipient of the first Chemical Society Award for Main Group Metal Chemistry in 1970 and of the Organometallic Award for 1978. He held a Tilden Lectureship of the Chemical Society, 1972–1973. In 1976 the American Chemical Society presented him with the Frederic Stanley Kipping Award for Organosilicon Chemistry. In 1979 he was elected a Fellow of the Royal Society. He is the author of almost 400 papers on various aspects of inorganic and organometallic chemistry.

Ronald Pearce received his B.Sc. and D.Phil. degrees from the University of Sussex, working for the latter on organosilicon chemistry with C. Eaborn. After postdoctoral work at the University of Toronto with A. G. Brook he joined I.C.I. Corporate Laboratory in 1970. His work on olefin polymerization catalysts included a period with M. F. Lappert on the synthesis of early-transition-metal alkyls. In 1977 he joined I.C.I. Petrochemicals Division, now Petrochemicals and Plastics Division, where his research interests include the metal-catalyzed reactions of synthesis gas.

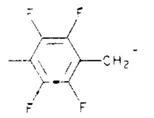
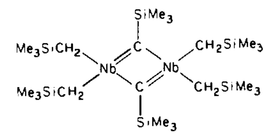
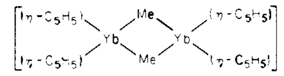
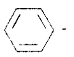
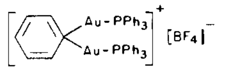
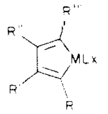
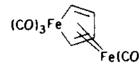
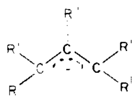
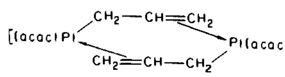
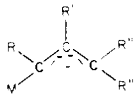
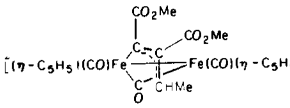
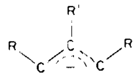
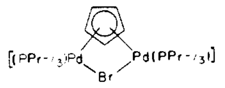
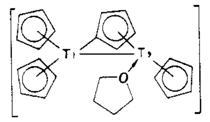
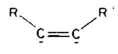
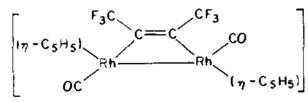
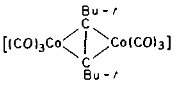
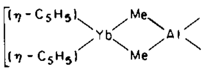
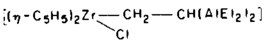
Paul Yarrow received his Bachelor's Degree in Chemistry from the University of Bristol in 1973. Upon completion of his doctoral research with M. F. Lappert he was awarded the degree of D.Phil. (Sussex) for his dissertation on "Cyclopentadienyl Complexes of the Lanthanides and the Early Transition Metals." His interests in catalysis took him to the University of California at Santa Barbara, to do postdoctoral research with P. C. Ford on aspects of the water-gas shift reaction and the chemistry of ruthenium clusters. He then returned to take a postdoctoral position with P. M. Maitlis, with whom he is investigating the chemistry of complexes related to the Fischer–Tropsch reaction. His research interests are in the areas of catalysis of industrially important reactions, reactions of metal–metal bonds, and the chemistry of low-valent early-transition-metal complexes. When not actively involved with chemistry he enjoys sailing, cooking, watching modern dance, and adding to an ever increasing and varied record collection.

not only reveal unusual chemistry and reactivity by means of cooperative effects, but could also provide models for well-known although ill-understood heterogeneous catalytic systems. Enthusiasm for this cause is on the wane, largely because it has been difficult to substantiate all but a handful of claims for such homogeneous cluster catalysis (i.e., systems in which the cluster retains its identity), the most important positive result being the potentially industrially important conversion of carbon monoxide and hydrogen into ethylene glycol, e.g., using $[Rh_4(CO)_{12}]$.[3] We shall not pursue this theme here, since we are mainly concerned with bimetallic rather than cluster systems. However, the search for bimetallic catalysts, having two, possibly different, metal–substrate binding sites is an exciting prospect. Synthetic problems are considerable and an important objective of this Review is to reveal these.

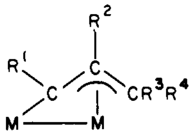
Tables of compounds are a significant feature of this work and have the following functions: (i) to identify the known compounds, which for each ligating mode are listed according to the nature of the central metal(s), using the Periodic Table as the basis for subdivision; (ii) to indicate the method of synthesis; (iii) to note which physical methods have been used in their study; and (iv) to provide the appropriate references.

Bridged hydrocarbyl or hydrocarbon binuclear complexes may be classified in various ways. We prefer to adopt a method based on the nature of the ligand rather than the metals (see Table III). Thus, sections II–XI relate to various types of thermally robust and generally well-characterized complexes, whereas section XII concerns the now quite numerous organometallic re-

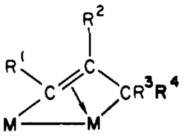
TABLE III. Classification of Bridged Hydrocarbyl or Hydrocarbon Transition-Metal Complexes

section	ligand type	examples of ligand	bonding characteristics of bridging C's	examples of complex
II	μ-vicinal (1,*n*;*n* $\geqslant$ 2) alkylidene and related ligands	$^{-}CH_2\text{-}CH_2^{-}$	$(sp^3)^2$, σ, σ	$[Zr_2(\eta\text{-}C_5H_5)_4(\mu\text{-}CH_2CH_2)(ClAlEt_3)_2]$
		$^{-}CF_2\text{-}CF_2\text{-}CF_2^{-}$	$(sp^3)^2$, σ, σ	$[Mn_2(\mu\text{-}C_3F_6)(CO)_{10}]$
			sp^3, sp^2, σ, σ	$[Fe_2(\mu\text{-}C_7H_2F_4)(\eta\text{-}C_5H_5)_2(CO)_4]$
		$^{-}CH{=}CH\text{-}CH{=}CH^{-}$	$(sp^2)^2$, σ, σ	$[Fe_2(\mu\text{-}C_4H_4)(\eta\text{-}C_5H_5)_2(CO)_4]$
			$(sp^2)^2$, σ, σ	$[Co_2(\mu\text{-}C_6H_4)(dmg)_2(PPh_3)_2]$
III	μ-geminal (1,1−) alkylidene	$RR'C^{2-}$	$(sp^3)^2$, σ, σ	$[Fe_2(\mu\text{-}CH_2)(\mu\text{-}CO)_2(CO)_6]$
IV	μ-geminal (1,1−) alkylidyne	RC^{3-}	(sp^2), σ, σ, π $(sp^2)^2$	
			$(sp^3)^3$, σ, σ, σ	$[Co_3(\mu\text{-}CR)(CO)_9]$
V	μ-alkyl	$RR'R''C^{-}$	σ, σ	
	μ-aryl		$(sp^3)^2$, σ, σ	
VI	μ-alkenyl	$RR'C{=}CR''^{-}$	(sp^2, p), σ, π	$[Fe_2(\mu\text{-}CH{=}CHBr)(\mu\text{-}Br)(CO)_6]$
	μ-metallocyclopentadienyl		$(sp^2, p)^2$, σ, π	
VII	μ-alkynyl	$RC{\equiv}C^{-}$	(sp, p), σ, π	$[Fe_2\{\mu\text{-}C{\equiv}CPh\}(\mu\text{-}PPh_2)(CO)_6]$
VIII	μ-allyl and related compounds		$(sp^3, p)^2$, σ, π	
			σ, π	
			π	$[Mo\{\mu\text{-}C_3H_5\}_2(\eta\text{-}C_3H_5)_2]$
	μ-cyclopentadienyl		$(p)^2$, π, π	
			$(sp^2, p)^2$, σ, π	
X	μ-acetylene		$(sp^2)^2$, σ, σ	
		$R\text{-}C{\equiv}C\text{-}R'$	$(sp^3)^2$, σ, σ (or π,π)	
X	μ-hydrocarbyl main-group-transition-metal	e.g., $RR'R''C^{-}$	$(sp^3)^2$, σ, σ	
		e.g., $^{-}CH_2\text{-}CH_2^{-}$	$(sp^3)^2$, σ, σ	 $[(\eta\text{-}C_5H_5)_2Zr(Cl)\text{—}CH_2\text{—}CH(AlEt_2)_2]$
XI	μ^2-bis(carbene)	$=C(Z)C=$	$(sp^2)^2$, σ, σ	$[W_2(\mu^2\text{-}CC_6H_4C\text{-}p)(CO)_8(Br)_2]$
XI	μ^2-bis(carbyne)	$\equiv C(Z)C\equiv$	$(sp)^2$, σ, σ	$[Cr_2\{\mu^2\text{-}C(OEt)(CH_2C_6H_4CH_2\text{-}o)C\text{-}(OEt)\}(CO)_{10}]$

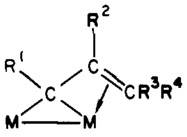
[a] There is considerable difficulty in unambiguously classifying the bridging ligands in a number of complexes. For example, the three representations (A) (allyl), (B) (alkenyl), and (C) (alkylidene type) are useful in describing various aspects of the structures, spectroscopic data, and reactions of the complexes $[Ru_2\{\mu\text{-}\eta^1,\eta^3\text{-}C(O)CPhCPh\}(\mu\text{-}CO)(CO)(\eta\text{-}C_5H_5)_2]$,[260] $[Fe_2(\mu\text{-}\eta^1,\eta^3\text{-}C(COOMe)C(COOMe)CHMe)(\mu\text{-}CO)(CO)(\eta\text{-}C_5H_5)_2]$,[198] and $[Ru_2(\mu\text{-}\eta^1,\eta^3\text{-}CMeCMeCH_2)(\mu\text{-}CO)(CO)(\eta\text{-}C_5H_5)_2]$,[215] and their analogues. The authors expressed no particular preference for any of (A), (B), or (C). For some complexes our categorizations have, in consequence, been somewhat arbitrary and readers are cautioned that apparently related species may be differently located in the tables that follow.



A

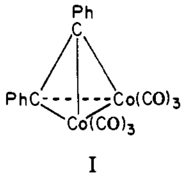


B

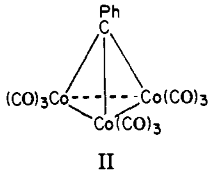


C

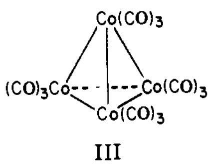
actions in which bridged dimetal complexes are believed to be implicated as intermediates. The compounds considered in sections II–IX are generally homonuclear (although in sections II–V we shall cover the special case of bridges between a transition metal and aluminum), while section X concerns the particular heteronuclear complexes in which one of the metals belongs to the d or f block elements whereas the other is a main-group metal, often Li or Al (except for those covered in sections II–V). The bridging ligands discussed in sections II–IV are polyanionic, e.g., $^-CH_2CH_2^-$ or CH_2^{2-}, or CH^{3-}; those in sections V–VIII are monoanionic, e.g., $^-CH_3$ (with σ–,σ– connectivities to each metal), $^-CH{=}CH_2$ (σ–,π–), $^-CH_2{-}C{\equiv}CH$ (σ–,π–), or $^-CH_2{-}CH{=}CH_2$ (σ–,π–). Section IX refers to complexes in which the bridge is neutral, e.g., C_6H_4 (benzyne) or $CH{\equiv}CH$. As to whether the ligand to metal bonds are described as, σ–,σ– or π–π– is largely a matter of taste; our preference is marginally for the former. Thus, it seems convenient to describe (μ-acetylene)dimetal complexes as dimetallatetrahedranes, e.g., I for $[Co_2(\mu\text{-}C_2Ph_2)(CO)_6]$.



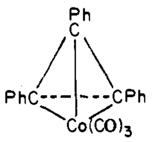
I



II

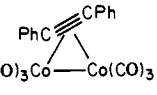


III

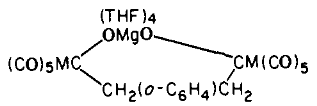


IV

The relationship to a trimetalla or tetrametalla analogue, e.g., II or III, then becomes clear, and this focuses on an interesting challenge—the synthesis of the remaining organometallic member of the series, e.g., IV; two complexes of this type are known: $[M(C_3Ph_3)(PPh_3)_2]^+$ (M = Ni[4] or Pt[5]). The usefulness of descriptions of this type will also become apparent in later sections, particularly those dealing with bridging alkylidynes where identifying μ_2-CR species as dimetallocyclopropenes allows a simple understanding in organic chemical terms of their preparation from mononuclear complexes (metallaalkynes) and their conversion to μ_3-CR complexes. (In adopting this method we are following the Isolobal Relationships originally described in 1938[6] and more recently revived.[7]) The more traditional formulation is the π–,π– mode, as in V. There seems to be, as yet, only isolated examples of a bridging neutral bis(carbene) ligand, as in VI (M = Cr or W),[8a] $[M_2\{\mu\text{-}C(Ph)OC(Ph)\text{-}\}(\eta\text{-}C_5H_5)_2(CO)_4]$ [M = Mn (X-ray) or Re],[8b] (two other examples are in



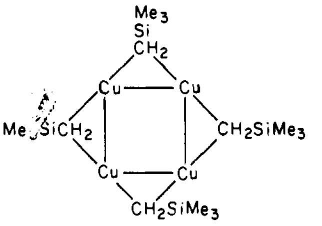
V



VI

Table XIII), or a bridging bis(carbyne) ligand $[M_2(\mu\text{-}p\text{-}CC_6H_4C\text{-})(CO)_8Br_2]$ [M = Cr or W (X-ray)].[8c]

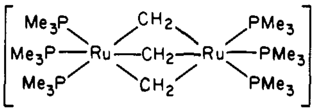
Alternative or complementary methods (i)–(viii) of classifying μ-hydrocarbyl or μ-hydrocarbon polymetallic complexes are worth noting based on: (i) the number of metal centers—here we are particularly concerned with binuclear complexes rather than higher aggregates or clusters, (ii) homo- or heteronuclear assemblies, (iii) the number of bridges between the two metal centers, (iv) the number of metals connected to a bridging ligand, (v) homo- or heterobridges, (vi) bonding characteristics, e.g., (σ–,σ–), (σ–,π–), (π–,π–), electron-precise or electron-deficient, (vii) the number of carbon atoms separating the two metal centers, and (viii) bridges which incorporate atoms other than C. As for (iii), complexes may have a single-, double-, or triple-ligating atom, as in VII, VIII, or IX. As for (iv), a bridging ligand may be shared by two metal centers, e.g., VII–IX, three metal centers as in II, or four to six metal centers as in carbido complexes such as $[Fe_6(CO)_{16}(\mu\text{-}C)]$.



VII

$[Y(\eta\text{-}C_5H_5)_2(\mu\text{-}Me)_2AlMe_2]$

VIII



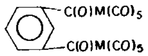
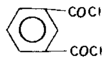
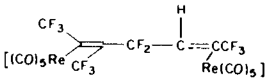
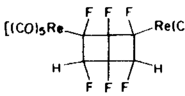
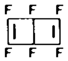
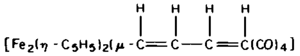
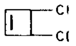
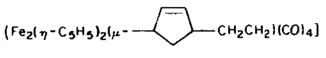
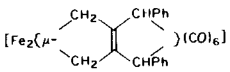
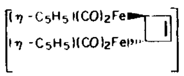
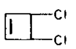
IX

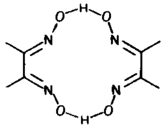
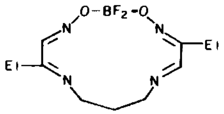
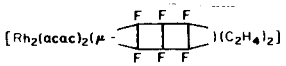
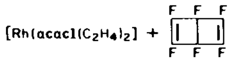
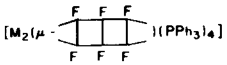
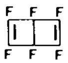
II. μ-Vicinal (1, n; n ≥ 2) Alkylidenedimetal and Related Complexes [M–(C<)ₙ–M′]

A. Stoichiometry, Structures, and Bonding

As evident from Table III the compounds considered in this section have σ-connectivities between each metal atom and each of two vicinal carbon atoms of a bidentate dianionic organic ligand, the two metal–carbon assemblies being essentially 2-electron 2-center bonds. Well-characterized compounds are listed in Table IV. The bidentate hydrocarbyl ligand may have functionality, e.g., $^-CH_2C({:}O)CH_2^-$ or the ylides $^-CH_2PR_2CH_2^-$.

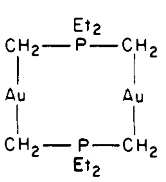
TABLE IV. μ-Vicinal ($1, n; n > 2$) Alkylidenedimetal Complexes (See Also Table IVa)

compound	preparation	comments	ref
$[M_2(\eta\text{-}C_5H_5)_4(\mu\text{-}CH_2\text{-}CH_2)(ClAlEt_3)_2]$	$[M(\eta\text{-}C_5H_5)_2Cl_2] + Al_2Et_6$	M = Ti or Zr, cannot remove $AlClEt_2$ for M = Ti. X-ray analysis M = Zr (Figure 1)	22 32
$[Zr_2(\eta\text{-}C_5H_5)_4(\mu\text{-}CH_2\text{-}CH_2)Cl_2]$	$[Zr(\eta\text{-}C_5H_5)_2Cl_2] + Al_2Et_6$ + THF	complexed $AlClEt_2$ removed by THF (Figure 1)	16
$[Mo_2(\eta\text{-}C_5H_5)_2(\mu\text{-}CO(CF_2)_3CO)(CO)_6]$	$2Na[Mo(\eta\text{-}C_5H_5)(CO)_3] + ClCO(CF_2)_3COCl$	hydrogen analogues do not exist	*a*
$[Mo_2(\eta\text{-}C_5H_5)_2(\mu\text{-}(CF_2)_3)(CO)_6]$	$[Mo_2(\eta\text{-}C_5H_5)_2\{\mu\text{-}CO(CF_2)_3CO\}(CO)_6]/\Delta$	hydrogen analogues do not exist	*a*
$[Mn_2\{\mu\text{-}CO(CF_2)_3CO\}(CO)_{10}]$	$2Na[Mn(CO)_5] + ClCO(CF_2)_3COCl$		18
$[Mn_2\{\mu\text{-}(CF_2)_3\}(CO)_{10}]$	$[Mn_2\{\mu\text{-}CO(CF_2)_3CO\}(CO)_{10}]/\Delta$		18
	2Na(M(CO)5] + 	M = Mn or Re, para isomer also prepared	*b*
$[M_2(\mu\text{-}C_6H_4)(CO)_{10}]$	$[Mn_2\{\mu\text{-}CO(CF_2)_3CO\}(CO)_{10}]/\Delta$	M = Mn or Re	*b*
	$Na[Re(CO)_5] + CF_3C{\equiv}CCF_3$		*c*
	HRe(CO)5 + 	para isomer also formed	*c*
$[Fe_2(\eta\text{-}C_5H_5)_2(\mu\text{-}(CH_2)_n)(CO)_4]$	$2Na[Fe(\eta\text{-}C_5H_5)(CO)_2] + Br\text{-}(CH_2)_n\text{-}Br$	n = 3, 4, 5, or 6; X-ray analysis n = 3 (Figure 3) and n = 4 (Figure 4)	17, 18, *d*
$[Fe_2(\eta\text{-}C_5H_5)_2\{\mu\text{-}CO(CF_2)_3CO\}(CO)_4]$	$2Na[Fe(\eta\text{-}C_5H_5)(CO)_2] + ClCO(CF_2)_3COCl$		*a*
$[Fe_2(\eta\text{-}C_5H_5)_2\{\mu\text{-}(CF_2)_3\}(CO)_4]$	$[Fe_2(\eta\text{-}C_5H_5)_2\{\mu\text{-}CO(CF_2)_3CO\}(CO)_4] \xrightarrow{h\nu}$		*a*
$[Fe_2\{\mu\text{-}CF_2CF_2\}(\mu\text{-}SMe)_2(CO)_6]$	$[Fe(\mu\text{-}SMe)(CO)_3]_2 + F_2C{=}CF_2 \xrightarrow{h\nu}$	X-ray	*e*
$[Fe_2(\eta\text{-}C_5H_5)_2(\mu\text{-}CH_2C{\equiv}CCH_2)(CO)_4]$	$2Na[Fe(\eta\text{-}C_5H_5)(CO)_2] + ClCH_2C{\equiv}CCH_2Cl$	cannot be hydrogenated to $(\text{-}CH_2\text{-})_4$ bridged complex	*f*
$[Fe_2(\eta\text{-}C_5H_5)_2(\mu\text{-}C{\equiv}C\text{-})_2(CO)_4]$	$[Fe(\eta\text{-}C_5H_5)(CO)_2C{\equiv}CH] \xrightarrow[TMEDA]{CuCl,\ O_2}$		*g*
$K_8[Fe_2(\mu\text{-}C{\equiv}C\text{—}C{\equiv}C)(CN)_{10}]\cdot(NH_3)_2$	$K_4[Fe(CN)_5C{\equiv}CH]\cdot NH_3 + 6NH_2NO$		*h*
 $[Fe_2(\eta\text{-}C_5H_5)_2(\mu\text{-}\overset{H}{C}{=}\overset{H}{C}\text{—}\overset{H}{C}{=}\overset{H}{C}(CO)_4]$	$2Na[Fe(\eta\text{-}C_5H_5)(CO)_2]$ + 	X-ray structure (Figure 2)	23, 24
$[Fe_2(\eta\text{-}C_5H_5)_2(\mu\text{-}CH_2\text{—}CH{=}CH\text{—}CH_2CH_2)(CO)_4]$	$[Fe(\eta\text{-}C_5H_5)(CO)_2C_2H_4]^+ +$ $[Fe(\eta\text{-}C_5H_5)(CO)_2(C_2H_5)] \rightarrow$	cis:trans isomers (1.1)	31
	$[Fe(\eta\text{-}C_5H_5)(CO)_2C_2H_4]^+ +$ $[Fe(\eta\text{-}C_5H_5)(CO)_2\underbrace{CHCH_2CH{=}CHCH_2}]$		31
	$[Fe_2(CO)_9] + PhCH{=}C{=}CH_2$	mixture of 3 isomers	*i*
$[Fe_2D_2\{\mu\text{-}CD_2C(O)CD_2\}(Me_2PCH_2CH_2PMe_2)_4]$	$(CD_3)_2CO + [FeH(Me_2PCH_2CH_2PMe_2)_2\text{-}(\alpha\text{-Naphthyl})]$		*j*
	$2Na[Fe(\eta\text{-}C_5H_5)(CO)_2]$ + 	also prepared  [Fp = $Fe(CO)_2(\eta\text{-}C_5H_5)$]	*k*

$[Fe_2(\eta\text{-}C_5H_5)_2(\mu\text{-}C_6F_4)(CO)_4]$	$Li_2C_6F_4 + [Fe(\eta\text{-}C_5H_5)(CO)_2I]$	1,3 and 1,4 isomers prepared but not 1,2 species due to steric crowding	29, *l* *m*
$[Fe_2(\eta\text{-}C_5H_5)_2(\mu\text{-}CH_2C_6F_4)(CO)_4]$	$Na[Fe(\eta\text{-}C_5H_5)(CO)_2] + BrCH_2C_6F_5$	low yield, stable complex sublimes at 200 °C, X-ray	*n*
$[Co_2(\eta\text{-}C_5H_5)_2(\mu\text{-}(CH_2)_3)(\mu\text{-}CO)_2]$	$[Co_2(\eta\text{-}C_5H_5)_2(CO)_2]^-\cdot Na^+ + ICH_2CH_2CH_2I$		*o*
$[Co_2(dmg)_2(\mu\text{-}(CH_2)_n)(py)_2]$	$[Co(dmg)(py)]^- + Br(CH_2)_nBr$	dmg =  $n = 3$ or 4	*p*
$[Co_2(\mu\text{-}CF_2CF_2)(CO)_8]$	$[Co_2(CO)_8] + C_2F_4$		*q*
$K_6[Co_2(\mu\text{-}CF_2CF_2)(CN)_{10}]\cdot(H_2O)_2$	$K_3[Co(H)(CN)_5]_{aq} + C_2F_4$		*r*
$[Co_2(\mu\text{-}(CF_2)_3)(CO)_8]$	$Na[Co(CO)_4] + ClCO(CF_2)_3COCl$		*q*
$[Co_2(dmg)_2(\mu\text{-}C_6H_4)(PPh_3)_2]$	$[Co(dmg)(PPh_3)Cl] + [ArN_2]_2SO_4$	1,3 and 1,4 isomers prepared; also 4,4'-biphenyl derivative	*s*
$[Co_2(\mu\text{-}(CF_3)C{=}CH(CF_3)C{=}CH{-}CH{=}C(CF_3))(CO)_6]$	$CF_3C{\equiv}CH + [Co_2(CO)_8]$	both metal atoms interact with central double bond	*t*
$[Rh_2(L)_2(\mu\text{-}CH_2)_n)Cl_2]$	$LRh + Cl(CH_2)_nCl$	$n = 2\text{-}6$, yield 65% $n = 10$, mixture obtained (plus monomeric *w*-chloroalkyl) L = 	21
			*u*
$[Ni_2(\eta\text{-}C_5H_5)_2\{(\mu\text{-}C{\equiv}C\text{-})_n\}(PPh_3)_2]$	$[Ni(\eta\text{-}C_5H_5)_2\{\text{-}(C{\equiv}C\text{-})_nH\}] \xrightarrow[O_2,\ TMEDA]{CuCl}$	$n = 2\ \ 3\ \ 4$	*g*
$[M(PBu_3)_2(\mu\text{-}C{\equiv}C{-}C{\equiv}C)M(PBu_3)_2(\mu\text{-}C{\equiv}C\text{--}C{\equiv}C)]_n$	$[M(PBu_3)_2C{\equiv}C{-}C{\equiv}CH] + [M(PBu_3)_2Cl_2]$	M = Pd, Pt, or Pt/Pd mixed samples	*v*
$[Ni_2(\mu\text{-}C_6H_4\text{-}o)_2(PEt_3)_4]$	$[Ni(PEt_3)_2Cl(C_6H_4Br)] + 2Li$	equilibrium with the diphosphine adduct	30
$[Ni_2(\mu\text{-}C_6H_4)(PPh_3)_4Br_2]$	$[Ni(PPh_3)_2Br_2] + LiC_6H_4Li$		*w*
$[Ni_2(\mu\text{-}CH_2C_6H_4CH_2)(PPh_3)_4Cl_2]$	$2[Ni(PPh_3)_2(C_2H_2)] + ClCH_2C_6H_4CH_2Cl$	ortho complex not isolated, only para and meta analogues	*w*
$[Pd_2\{\mu\text{-}2,4\text{-}C_6H_2(CH_2NEt_2)_2\}Cl_2]$	$2,4\text{-}C_6H_4(CH_2NEt_2)_2 + [PdCl_4]^{2-}$	1,2, 1,3, and 1,4 derivatives	*x*
$[Pt_2(\mu\text{-}CF_2CF_2)(COD)_2]$	$[Pt(COD)_2] + C_2F_4$	can displace COD by L_2 where L = PEt_3 or $L_2 = 1,2\text{-}C_6H_4(AsMe_2)$	66
	$[M(PPh_3)_4)]$ + 	M = Pd or Pt	*u*

[a] King, R. B.; Bisnette, M. B. *J. Organomet. Chem.* **1964**, *2*, 15. [b] Nesmeyanov, A. N.; Anisimov, K. N.; Kolobova, N. E.; Ioganson, A. A. *Dokl. Akad. Nauk SSSR, Ser. Khim.* **1967**, *175*, 627. [c] Goodfellow, R. J.; Green, M.; Mayne, N.; Rest, A. J.; Stone, F. G. A. *J. Chem. Soc. A* **1968**, 177. Cook, D. J., Green, M.; Mayne, N.; Stone, F. G. A. *Ibid.* **1968**, 1771. [d] King, R. B.; Bisnette, M. B. *J. Organomet. Chem.* **1967**, *7*, 311. For related species ($n = 5$) see also: Wegner, P. A.; Sterling, G. P. *Ibid.* **1978**, *162*, C31. [e] Bonnet, J. J.; Mathieu, R., Poilblanc, R.; Ibers, J. A. *J. Am. Chem. Soc.* **1979**, *101*, 7487. [f] Bauch, T. A., Konowitz, H., Giering, W. P. *J. Organomet. Chem.* **1976**, *114*, C15 [g] Kim, J. P.; Masai, H.; Sonogashira, K.; Hagihara, N. *Inorg. Nucl. Chem. Lett.* **1970**, *6*, 181. [h] Nast, Von R.; Urban, F. *Z. Anorg. Allg. Chem.* **1957**, *289*, 244. [i] Otsuka, S.; Nakamura, N.; Tani, K. *J. Chem. Soc. A* **1968**, 2248. [j] Ittel, S. D.; Tolman, C. A.; English, A. D.; Jesson, J. P. *J. Am. Chem. Soc.* **1978**, *100*, 7577. [k] Sanders, A.; Giering, W. P. *J. Am. Chem. Soc.* **1974**, *96*, 5247. [l] Bruce, M. I. *J. Organomet. Chem.* **1970**, *21*, 415. [m] Blackmore, T.; Bruce, M. I.; Davidson, P. J., Iqbal, M. Z.; Stone, F. G. A. *J. Chem. Soc. A* **1970**, 3153. [n] Bruce, M. I. *J. Organomet. Chem.* **1967**, *10*, 495. [o] Theopold, K. H.; Bergman, R. G. *J. Am. Chem. Soc.* **1980**, *102*, 5694; *Organometallics* **1982**, *1*, 1571. [p] Schrauzer, G. N., Windgassen, R. J. *J. Am. Chem. Soc.* **1966**, *88*, 3738. [q] Hoehn, H. H.; Pratt, L.; Watterson, K. F.; Wilkinson, G. *J. Chem. Soc.* **1961**, 2738. Booth, B. L.; Haszeldine, R. N.; Inglis, T. *J. Chem. Soc., Dalton Trans.* **1975**, 1449. [r] Mays, M. J.; Wilkinson, G. *Nature (London)* **1964**, *203*, 1167. [s] Bekaröglu, O. *Chim. Acta. Turc.* **1974**, *2*, 131; *Chem. Abstr.* **1976**, *84*, 90272b. [t] Harbourne, D. A.; Rosevear, D. T.; Stone, F. G. A. *Inorg. Nucl. Chem. Lett.* **1966**, *2*, 247. [u] Booth, B. L.; Haszeldine, R. N., Tucker, N. I. *J. Chem. Soc., Dalton Trans.* **1975**, 1439. [v] Sonogashira, K.; Kataoka, S.; Takahashi, S.; Hagihara, N. *J. Organomet. Chem.* **1978**, *160*, 319. [w] Hipler, B.; Uhlig, E., Vogel, J. *J. Organomet. Chem.* **1981**, *218*, Cl. [x] Trofimenko, S. *J. Am. Chem. Soc.* **1971**, *93*, 1808.

The latter are not discussed further here, since excellent reviews are available,[9] but an example of a derived dinuclear complex is compound X, for which there is



X

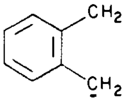
crystallographic supporting evidence,[10] as there is for $[Ti_2\{\mu\text{-}(CH_2)_2PMe_2\}_2(\mu\text{-}OMe)_2(OMe)_4]$,[11] and $[Cr_2\{\mu\text{-}(CH_2)_2PMe_2\}_4]$.[12] Some further binuclear complexes have the bridging ligands $Me_2{}^+As(CH_2{}^-)_2$ or $Me_2Si(CH_2{}^-)_2$. Thus, treatment of $[Au(AsMe_3)Cl]$ with 2 mol $AsMe_3CH_2$ furnished $[Au_2\{\mu\text{-}(CH_2)_2AsMe_2\}_2]$ with elimination of $AsMe_3$ and $[AsMe_4]Cl$,[10] whereas $[Mo_2\{\mu\text{-}OCOCH_3\}_4]$ with an excess of $Mg(CH_2SiMe_3)_2$ and PMe_3 yielded $[Mo_2\{\mu\text{-}(CH_2)_2SiMe_2\}(CH_2SiMe_3)_2(PMe_3)_3]$;[13] X-ray analysis showed that both the CH_2SiMe_3 groups were attached to one of the molybdenum atoms with three PMe_3 groups on the other.[14]

It is to be expected that some of the factors which influence the stability of these compounds are similar to those governing mononuclear transition-metal hydrocarbyls.[15] It is not surprising therefore that, for example, vicinal dialkylidenedimetal complexes having β-hydrogen atoms are somewhat rare, as β-hydride elimination may be a favored decomposition pathway unless the metal environment is somewhat crowded. Additionally, the transition state for β-elimination is quite sterically demanding and also requires a readily available metal coordination site, and this may account for the existence of compounds such as XI[16] or XII ($n = 3\text{–}4$).[17] The relative abundance of perfluoro bridged

$[\{Zr(\eta\text{-}C_5H_5)_2(ClAlEt_3)CH_2\}_2]$
XI

$[\{Fe(\eta\text{-}C_5H_5)(CO)_2\}_2(CH_2)_n]$
XII

compounds (bridging fluorocarbyl dianions) is attributed in part to the strength of the $sp^3C\text{—}F$ bond and also to the energetic disadvantage of forming a metal–fluorine bond, especially for a low-oxidation-state (soft) metal center as in $[\{Mn(CO)_5\}_2(CF_2)_3]$.[18] A further general problem with regard to obtaining stable binuclear complexes arises simply because the ligand is bidentate, and relates to ring–chain equilibria. For example, whereas a ligand such as XIII may in principle



XIII

bridge two metal centers, it may also act as a chelate, as in $[Zr(\eta\text{-}C_5H_5)_2(CH_2C_6H_4CH_2\text{-}o)]$.[19] As has been noted, especially for bidentate diphosphines,[20] ring formation is disfavored by increasing the chain length between two donor sites. The largest dimetal separation so far reported for an alkylidenedimetal complex is by 10 carbon atoms in $[\{Rh(L)Cl\}_2(CH_2)_{10}]$ (see Table IV).[21]

X-ray crystallographic data are available on six compounds. Figure 1 provides a comparison of corresponding structural features of three related molecules

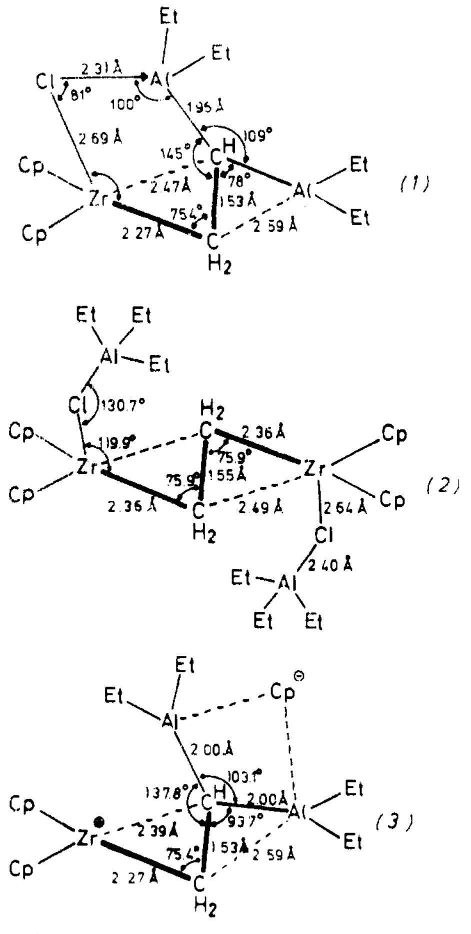


Figure 1. A comparison of corresponding structural elements of $[Zr(\eta\text{-}C_5H_5)_2\{CH_2CH(AlEt_2)_2\}Cl]$, (1), $[Zr_2(\eta\text{-}C_5H_5)_4(\mu\text{-}CH_2CH_2)(ClAlEt_3)_2]$, (2), and $[Zr(\eta\text{-}C_5H_5)_2\{CH_2CH(AlEt_2)_2\}][C_5H_5]$, (3); the cyclopentadienyl anion of 3 is not shown; and is arranged symmetrically in the lattice between two neighboring Zr centers. Reproduced, with permission, from: Kaminsky, W.; Kopf, J.; Sinn, H.; Vollmer, H.-J. *Angew. Chem., Int. Ed. Engl.* **1976**, *15*, 629. Copyright 1976, Verlag Chemie GmbH.

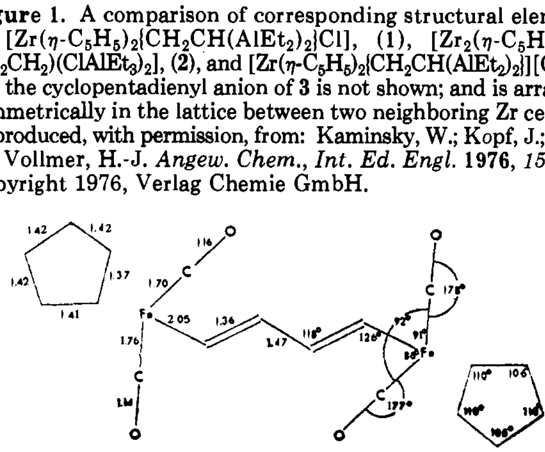


Figure 2. Structural parameters for *trans*-$[Fe_2(\eta\text{-}C_5H_5)_2(\mu\text{-}C_4H_4)(CO)_4]$. Reproduced, with permission, from: Davis, R. E. *J. Chem. Soc., Chem. Commun.* **1968**, 1218. Copyright 1968, Chemical Society, London.

$[Zr(\eta\text{-}C_5H_5)_2\{CH_2CH(AlEt_2)_2\}Cl]$,[16,22] $[Zr_2(\eta\text{-}C_5H_5)_4(\mu\text{-}CH_2CH_2)\{ClAlEt_3\}_2]$,[16] and $[Zr(\eta\text{-}C_5H_5)_2\{\mu\text{-}CH_2CH(AlEt_2)_2\}][C_5H_5]$;[16] in the first and last of these compounds a $^-CH_2CH^{2-}$ ligand bridges a Zr atom and two Al atoms, and in the other complex there is a $^-CH_2CH_2{}^-$ bridge between two Zr atoms. The most interesting structural feature is that the σ-bonded atomic grouping $Zr\text{–}CH_2\text{–}C$ is invariably characterized by an angle of only 76° at the CH_2 group. By contrast X-ray analysis of three binuclear iron(II) compounds reveals no such distortions in the *trans*-$^-CH{=}CH\text{—}CH{=}CH^-$,[23,24] or $^-CH_2(CH_2)_nCH_2{}^-$ ($n = 1$ or 2)[17] bridging units (Figures 2–4). Dynamic NMR measurements on $[Zr(\eta\text{-}C_5H_5)_2\{CH_2CH(AlEt_2)_2\}Cl]$ (Figure 1) show that the Cl→Al

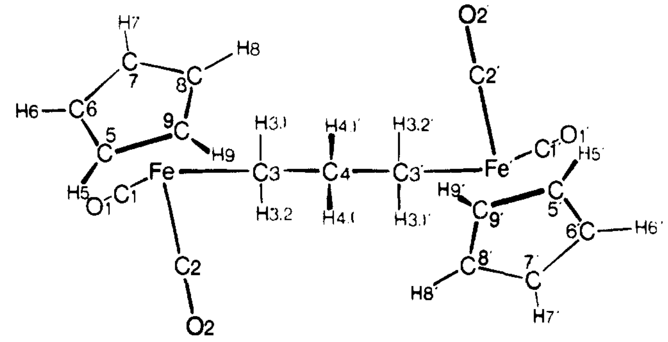


Figure 3. Schematic representation of the molecular structure of $[Fe_2(\eta\text{-}C_5H_5)_2\{\mu\text{-}(CH_2)_3\}(CO)_4]$. Reproduced, with permission, from: Pope, L.; Sommerville, P.; Laing, M.; Hindson, K. J.; Moss, J. R. *J. Organomet. Chem.* **1976**, *112*, 309. Copyright 1976, Elsevier Sequoia SA.

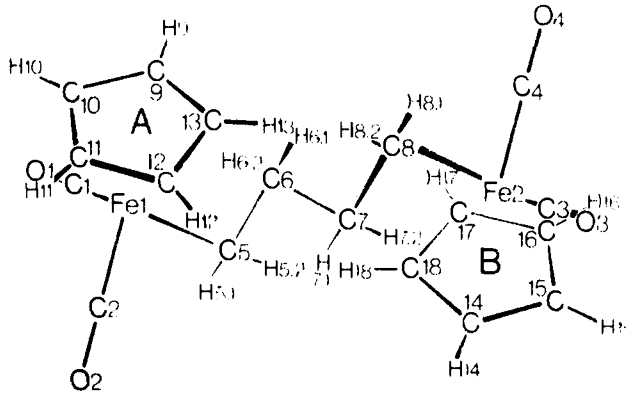


Figure 4. Schematic representation of the molecular structure of $[Fe_2(\eta\text{-}C_5H_5)_2\{\mu\text{-}CH_2)_4\}(CO)_4]$. Reproduced, with permission, from: Pope, L.; Sommerville, P.; Laing, M.; Hindson, K. J.; Moss, J. R. *J. Organomet. Chem.*, **1976**, *112*, 309. Copyright 1976, Elsevier Sequoia SA.

bond is weak. It would be interesting to compare the ethylene bridge in $[Zr_2(\eta\text{-}C_5H_5)_4\{\mu\text{-}CH_2CH_2\}(AlClEt_3)_2]$ with the related bridged species $[Zr_2\{\mu\text{-}CH_2CHR\}(Cl)_6(PEt_3)_4]$ (R = H or Me) but to date no crystallographic data are available on the latter complexes.[25] The room temperature ^1H NMR spectrum of $[Fe_2(\eta\text{-}C_5H_5)_2(\mu\text{-}C_4H_4)(CO)_4]$ shows unexpectedly two sharp singlets at τ 3.76 and 5.05 (relative intensity 2:5), with the former signal being broadened at −65 °C;[23] it was suggested that the molecule is stereochemically nonrigid leading to interconversion of C(1) and C(1′) with C(2) and C(2′) (see Figure 2). In each of the complexes $[Fe_2(\eta\text{-}C_5H_5)_2\{\mu\text{-}(CH_2)\}_m(CO)_4]$ ($m = 3$, Figure 3 and $m = 4$, Figure 4) the iron atoms are joined by simple chains of σ-bonded CH_2 groups. Bond lengths are similar in both: Fe–CO 1.75, C–O 1.15, Fe–C(cp) 2.11, Fe–CH_2 2.08, (cp)C–C(cp) 1.41, and CH_2–CH_2 1.55 Å; bond angles at Fe–CH_2–CH_2 average 114°.[17]

B. Synthesis and Chemical Properties

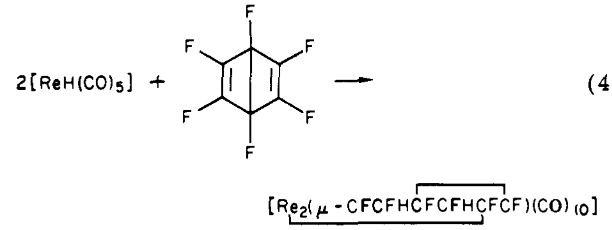
Synthetic procedures may be divided into seven categories: (a) salt elimination, (b) hydrogen halide elimination, (c) dihydrogen elimination, (d) alkane elimination, (e) insertion of an unsaturated hydrocarbon into a metal–metal or metal–hydrogen bond, (f) oxidative addition of an α,ω-dihalide or an unsaturated fluorocarbon to a low oxidation-state mononuclear metal complex, and (g) oxidative addition of a coupled unsaturated hydro- or fluorocarbon to a low oxidation-state mononuclear metal complex. These are illustrated in eq 1–7, more detail being provided in Table IV.

As for (a), many of the salt eliminations involve a metalate anion, such as $[Mo(\eta\text{-}C_5H_5)(CO)_3]^-$, $[Mn(CO)_5]^-$, or $[Fe(\eta\text{-}C_5H_5)(CO)_2]^-$, and an α,ω-dihalide, but of course only a limited number of compounds having significant metal-centered nucleophilicity exist.[26]

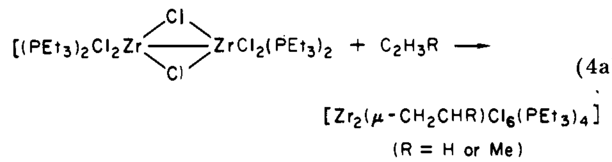
$$2Na[Mo(\eta\text{-}C_5H_5)(CO)_3] + ClC(O)(CF_2)_3C(O)Cl \rightarrow [\{Mo(\eta\text{-}C_5H_5)(CO)_3\}_2\{\mu\text{-}C(O)(CF_2)_3CO\}] + 2NaCl \quad (1)$$

$$2[CoCl(dmg)(PPh_3)] + {}^1/_2[PhN_2]_2[SO_4] \rightarrow [Co_2(\mu\text{-}C_6H_4\text{-}p)(dmg)_2(PPh_3)_2] + 2HCl \quad (2)$$

$$2K_3[CoH(CN)_5] + C_2F_4 \rightarrow K_6[Co_2(\mu\text{-}CF_2CF_2)(CN)_{10}] + H_2 \quad (3)$$

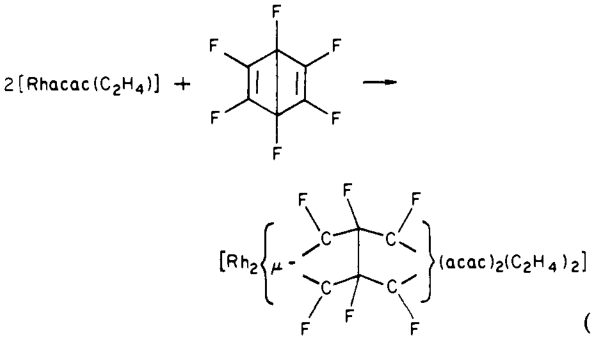


(4)

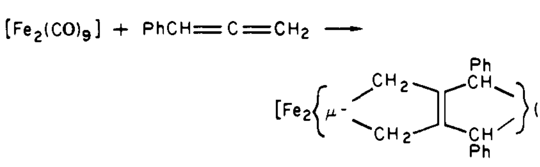


(4a)

$$[Zr(\eta\text{-}C_5H_5)_2Cl(Et)] + (AlEt_3)_2 \rightarrow [Zr(\eta\text{-}C_5H_5)_2\{CH_2CH(AlEt_2)_2\}Cl] + 2C_2H_6 \quad (5)$$



(6)



(7)

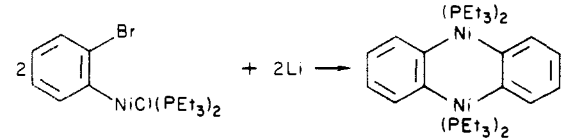
Complications may involve an intramolecular nucleophilic attack on a coordinated acyl group, as in eq 8,[27]

$$Na[Mn(CO)_5] + Br(CH_2)_3Br \rightarrow [Mn(CO)_5Mn(\overline{COCH_2CH_2CH_2})(CO)_4] \quad (8)$$

(possibly via $[Mn(CO)_5{-}M\{C({=}O)CH_2CH_2CH_2Br\}(CO)_4]$), or failure to obtain more than a monosubstitution product, as in eq 9.[28] Alternatively, the organic

$$Na[Mo(\eta\text{-}C_5H_5)(CO)_3] + Br(CH_2)_nBr \rightarrow [Mo(\eta\text{-}C_5H_5)(CO)_3\{(CH_2)_nBr\}] \quad (9)$$

substrate may be α,ω-metalated and this is caused to react with a metal halide complex, as in the p-LiC_6F_4Li + $2[Fe(\eta\text{-}C_5H_5)CO_2I]$ system.[29] A further variant involves a bifunctional substrate such as XIV and Würtz coupling, as in eq 10.[30]



XIV (10)

A rather unusual hydrogen halide elimination involves coordinated ligands, as shown in eq 11.[31]

$$[Fe(\eta\text{-}C_5H_5)(CO)_2(C_2H_4)]^+ + [Fe(\eta\text{-}C_5H_5)(CO)_2(C_3H_5)] \xrightarrow{-H^+} [Fe_2(\eta\text{-}C_5H_5)_2\{\mu\text{-}CH_2CH{=}CHCH_2CH_2\}(CO)_4] \quad (11)$$

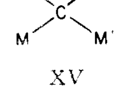
A remarkable series of reactions, involving bimolecular ethane elimination, leads inter alia to some crystallographically characterized zirconium(IV) complexes (Figure 1).[32] The starting materials are $[Zr(\eta\text{-}C_5H_5)_2Cl_2]$ and $(AlEt_3)_2$ and the first formed product is $[Zr(\eta\text{-}C_5H_5)_2Cl(Et)]$, which reacts with more triethylalane to yield the three compounds of Figure 1; one of these, $[Zr(\eta\text{-}C_5H_5)_2\{CH_2CH(AlEt_2)_2\}Cl]$, is converted into $[Zr_2(\eta\text{-}C_5H_5)_4(\mu\text{-}CH_2CH_2)Cl_2]$ upon treatment with tetrahydrofuran, whereby $AlEt_3.(THF)$ is eliminated. It appears that the β-hydrogen atoms of $[Zr(\eta\text{-}C_5H_5)_2(CH_2CH_3)Cl]$ are sufficiently acidic to cleave the Al–Et bond of triethylalane, and this is borne out by labeling experiments; thus, use of $[Al(CH_2CD_3)_3]_2$ or $[Al(CD_2CH_3)_3]_2$ afforded CD_3CH_2D or CH_3CHD_2, respectively. Detailed kinetic studies of these reactions, including the determination of kinetic isotope effects, have been carried out.[33] Corresponding binuclear titanium compounds were insufficiently stable to be characterized.[32]

There are relatively few data concerning the chemical behavior of the alkylidenedimetal complexes. However, the Zr/Al complexes were studied in part in connection with their potential as soluble Ziegler–Natta polymerization catalysts. The complex $[Zr(\eta\text{-}C_5H_5)_2\{CH_2CH(AlEt_2)_2\}][C_5H_5]$ (Figure 1) is soluble in hydrocarbons and inserts α-olefins or 1,3-dienes but the products have not yet been characterized.[16] The chlorine-containing complexes $[Zr(\eta\text{-}C_5H_5)_2\{CH_2CH(AlEt_2)_2\}Cl]$ and $[Zr_2(\eta\text{-}C_5H_5)_4(\mu\text{-}CH_2CH_2)(ClAlEt_3)_2]$ react with these unsaturated hydrocarbons upon addition of excess $(AlEt_3)_2$, and especially on addition of the triethylalane and water; dechlorination takes place, presumably with formation of aluminoxanes, to give very active homogeneous catalysts for the polymerization of α-olefins, particularly of ethylene.

III. μ-Geminal (1,1-) Alkylidenedimetal Complexes, [M–(C<)–M′]

A. Stoichiometry, Structures, and Bonding

Like the μ-vicinal alkylidenedimetal complexes, the bimetalic compounds considered in this section have σ-connectivities between each metal atom and bridging CH_2^{2-} group(s), or substituted methylene group(s), and are electron precise, i.e., there are 2-electron 2-center bonds (see Table III); the relevant structural unit is that shown in XV. Well-documented compounds are listed in Table V. Complexes of this type are sometimes referred to as having "bridging carbene" ligands. However, we shall not use this classification and reserve the term carbene–metal complex[34] to one in which the three coordinate ligating carbon atom is sp^2-hybridized. The ligand may be found in mononuclear species, as in $[W\{C(OMe)Ph\}(CO)_5]$, or as a metallacarbene as in the dinuclear complex $[Nb_2(CH_2SiMe_3)_4(\mu\text{-}CSiMe_3)_2]$ (see section IV); for this reason such compounds are almost unique to the transition metals, double bonding to main-group metalloids being confined to those (P, As, or S) which form ylides.



XV

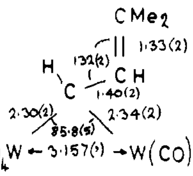


Figure 5. Selected parameters and schematic representation of the molecular structure of $[W_2(\mu\text{-}CHCH{=}CMe_2)(CO)_8]$.[49]

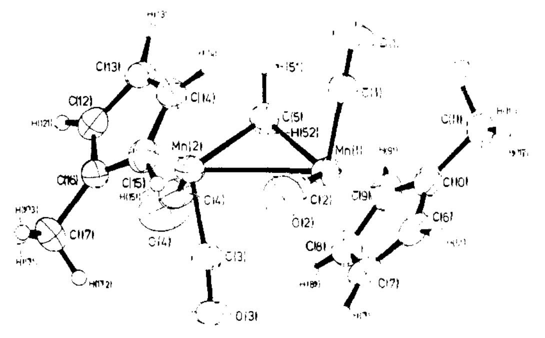


Figure 6. Schematic representation of the molecular structure of $[Mn_2(\eta\text{-}C_5H_4Me)_2(\mu\text{-}CH_2)(CO)_4]$: Mn–Mn 2.779 (1) Å, Mn–C(5) 2.013 (5) Å, Mn(1)–C(5)–Mn(2) 87.3 (2)°, H(51)–C(5)–H(52) 92 (8)°, C(5)–Mn(2)–Mn(1) 46.4 (1)°. Reproduced, with permission, from: Creswick, M.; Bernal, I.; Herrmann, W. A. *J. Organomet. Chem.* **1979**, *172*, C39. Copyright 1979; Elsevier Sequoia SA.

The "bridging carbene" nomenclature is useful, nevertheless, in drawing attention to their isoelectronic relationship to "bridging carbonyls". This is significant and probably accounts for the fact that many of the known μ-geminal alkylidenedimetal complexes (a) contain carbonyl coligands, (b) alternatively or additionally have tertiary phosphine ligands, (c) are found in low metal oxidation state complexes, and (d) are often conveniently prepared using a diazoalkane (as a carbenoid) and a carbonylmetal complex as starting materials. Items (a) to (c) are reasonably rationalized in terms of the preference for binding of the soft CO, CRR′, or PR''_3 ligands to a soft metal center. The importance of point (d) is emphasized by the existence of a substantial review devoted in large part to this topic.[35] Like the many carbonyl–metal complexes, the μ-CRR′-dimetal complexes are generally rather stable and air-insensitive, which may account for the large amount of structural data now available (on more than 25 compounds, see Figures 5–32). The simplest type of compound which may be classified as a 1,1-alkylidenedimetal complex has a single CH_2 bridge, the first example of which was $[Mn_2(\eta\text{-}C_5H_4Me)_2(\mu\text{-}CH_2)(CO)_4]$, Figure 6, obtained in 1975,[36] from $[Mn(\eta\text{-}C_5H_4Me)(CO)_2(THF)]$ and diazomethane.[36] A quite different type of complex has a CH_2 bridge between an early transition metal in high oxidation state and aluminium, as in $[TiAl\{\mu\text{-}CH_2\}(\eta\text{-}C_5H_5)_2Me_2(\mu\text{-}Cl)]$, (XXIII),[37,38] and

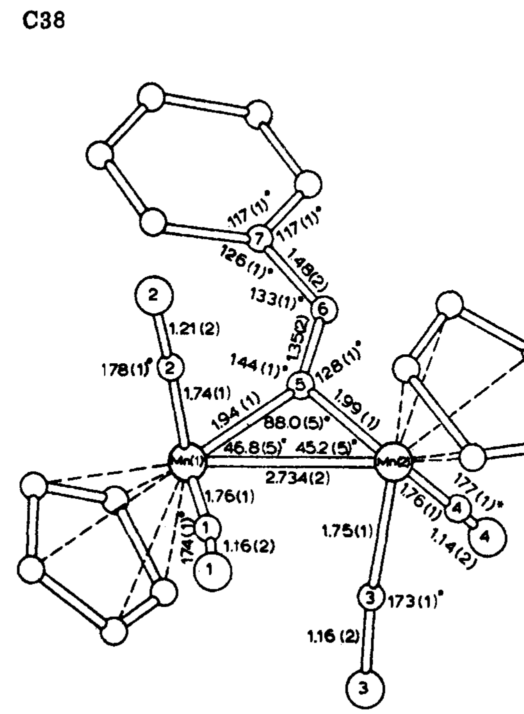


Figure 7. Schematic drawing of the molecular structure of $[Mn_2\{\mu\text{-}C(CHPh)\}(\eta\text{-}C_5H_5)_2(CO)_4]$. Reproduced, with permission, from: Nesmeyanov, A. N.; Aleksandrov, G. G.; Antonova, A. B.; Anisimov, K. N.; Kolobova, N. E.; Struchkov, Yu. T. *J. Organomet Chem.* **1976**, *110*, C36. Copyright 1976, Elsevier Sequoia SA.

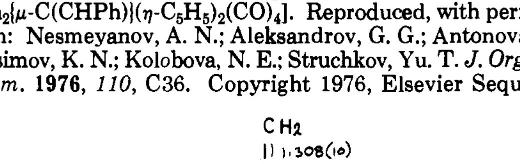


Figure 8. Schematic representation of the molecular structure of $[Mn_2\{\mu\text{-}C(CH_2)\}(\eta\text{-}C_5H_5)_2(CO)_4]$.[51] There is an 11° twist of the CCH_2 ligand about the double bond. The two η-C_5H_5 ligands are trans to one another.

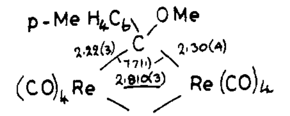
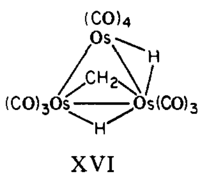


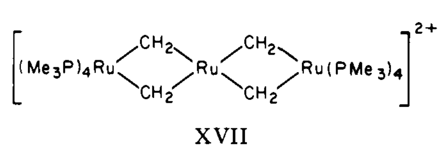
Figure 9. Schematic representation of the molecular structure of $[Re_2\{\mu\text{-}C(OMe)C_6H_4Me\}_2(CO)_8]$.[50]

$[TaAl\{\mu\text{-}CH_2\}(\eta\text{-}C_5H_5)_2Me_4]$, (XXIV).[39] The μ-CH_2 chemical shifts are at 1.51 τ (^1H) and 188 ppm (^{13}C) (or 0.90 τ and 204 ppm for the analogue having μ-CH_3 rather than μ-Cl) for the former,[37] and 2.32 τ and 177 ppm for the latter.[39] The $AlMe_3$ moiety may be considered as inhibiting "the catastrophic decomposition of $[\{Ti(\eta\text{-}C_5H_5)_2CH_3\}_2]$ and dictates the abstraction of hydrogen from methyl rather than cyclopentadienyl groups.[37]

As elsewhere in this Review, trinuclear complexes are excluded: the majority of these are triangular, e.g., the seminal compound XVI,[40] but a rare chain cation XVII[41] has also been structurally characterized. Compound XVI is of interest for (a) its mode of preparation, insertion of CH_2 (from CH_2N_2) into $[Os_3(\mu\text{-}H)_2(CO)_{10}]$; (b) the neutron diffraction results; (c) its conversion to a μ-CH_3 isomer; and (d) its conversion into a μ-CH complex (see section IVA).



XVI



XVII

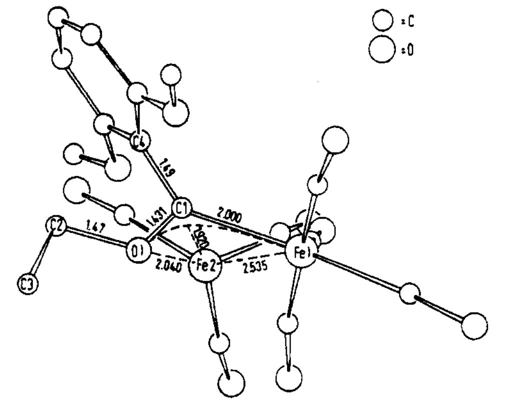


Figure 10. Schematic representation of the molecular structure of $[Fe_2\{\mu\text{-}C(OEt)C_6H_3(OMe)_2\text{-}2,6\}(CO)_7]$. Reproduced, with permission, from: Fischer, E. O.; Winkler, E.; Huttner, G.; Regler, G.; *Angew. Chem., Int. Ed. Engl.* **1972**, *11*, 238. Copyright 1972, Verlag Chemie GmbH. (See also Huttner, G.; Regler, G. *Chem. Ber.* **1972**, *105*, 2726.) The molecule appears to be two electrons short of satisfying EAN requirements, and thus an Fe(1)→Fe(2) dative bond is suggested.

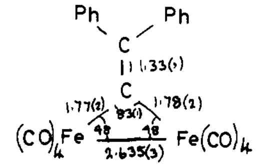


Figure 11. Selected parameters and schematic representation of the molecular structure of $[Fe_2(\mu\text{-}C{=}CPh_2)(CO)_8]$.[55]

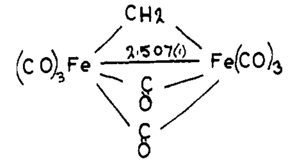


Figure 12. Schematic representation of the molecular structure of $[Fe_2(\mu\text{-}CH_2)(\mu\text{-}CO)_2(CO)_6]$ {"isostructural" with $[Fe_2(CO)_9]$};[47] μ-CH_2 and (μ-CO)'s disordered.

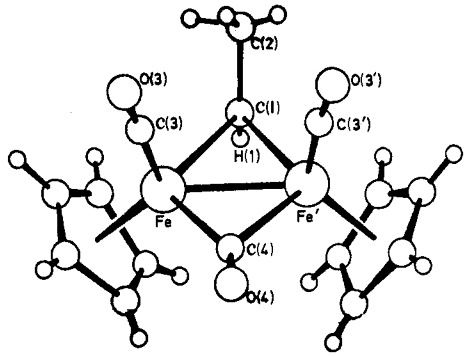
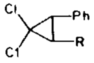
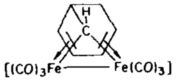


Figure 13. Schematic representation of the molecular structure of *cis*-$[Fe_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CHMe)(\eta\text{-}C_5H_5)_2]$. Bond lengths: Fe–Fe′ 2.520 (1), Fe–C(1) 1.986 (3), Fe–C(3) 1.747 (3), Fe–C(4) 1.902 (3), C(1)–C(2) 1.513 (6), C(3)–O(3) 1.151 (4), C(4)–O(4) 1.183 (5) Å. Angles: Fe–C(1)–Fe′ 78.8 (1), Fe–C(4)–Fe′ 83.0 (1), H(1)–C(1)–C(2) 112 (2.5)°. Reproduced, with permission, from: Dyke, A. F.; Knox, S. A. R.; Naish, P. J.; Orpen, A. G. *J. Chem. Soc., Chem. Commun.* **1980**, 441. Copyright 1980, The Chemical Society, London.

As evident from the illustrated structural data of

Table V. μ-Geminal (1,1-) Alkylidenedimetal Complexes (See Also Table Va)

compound	preparation	comments	ref
$[Ta_2(\eta\text{-}C_5Me_4Et)_2Cl_4(\mu\text{-}CHPMe_3)(\mu\text{-}O)(H)]$	$[[Ta(\eta\text{-}C_5Me_4Et)_2Cl_2]_2(H)(\mu\text{-}CHO)] + PMe_3$	X-ray shows Ta–Ta asymmetrically bridged by a $>CHPMe_3$ phosphonium ylide fragment	*a*
$[CrPt\{\mu\text{-}C(CO_2Me)Ph\}(CO)_4(PMe_3)_3]$	$[L_4L'Cr(\mu\text{-}CPh)PtL'_4] + MeO^-$ ($L = CO$, $L' = PMe_3$)	X-ray analysis (Figure 31), *p*-tolyl derivative prepared for Cr and W	46
$[Mo_2(\eta\text{-}C_5H_5)_2(CO)_4\{\mu\text{-}C(C_6H_4Me\text{-}p)_2\}]$	$[Mo_2(\eta\text{-}C_5H_5)_2(CO)_4] + N_2CR_2$	X-ray, semibridging carbonyl	*b*
$[Mo_2(\eta\text{-}C_5H_5)_2(\mu\text{-}CHCH{=}CMe_2)(\mu\text{-}CO)(CO)_3]$	$[Mo_2(\eta\text{-}C_5H_5)_2(CO)_4] +$ 	X-ray	*c*
$[W_2(\mu\text{-}CHCH{=}CMe_2)(CO)_n]$ ($n = 8$ or 9)	$MeLi + [MeOC(Me){=}W(CO)_5]$	X-ray (Figure 5, $n = 8$)	*d*, 49 ($n = 9$)
$[WRe\{\mu\text{-}C(PMe_3)(Ph)\}(\mu\text{-}CO)(CO)_8]$	$[WRe(CPh)(CO)_9] + PMe_3$	X-ray (Figure 59). Cr analogue also prepared	60
$[Mn_2(\eta\text{-}C_5H_4R)_2(\mu\text{-}CH_2)(CO)_4]$	$[Mn(\eta\text{-}C_5H_4R)(CO)_2(THF)] + CH_2N_2$	cis and trans isomers formed, R = H or Me (Figure 6)	36
$[Mn_2(\eta\text{-}C_5H_5)_2(\mu\text{-}C{=}CHPh)(CO)_4]$	$[Mn(\eta\text{-}C_5H_5)(CO)_2(THF)] + PhC{\equiv}CPh/h\nu$	X-ray, Re_2 and Mn/Re complexes also prepared (Figure 7)	83, 84, *e*
$[Mn_2(\eta\text{-}C_5H_5)_2(\mu\text{-}C{=}CHCO_2Me)(CO)_4]$	$[Mn(\eta\text{-}C_5H_5)(CO)_2(C{=}CHCO_2Me)] + [Mn(\eta\text{-}C_5H_5)(CO)_2(OEt_2)]$		85
$[Mn_2(\eta\text{-}C_5H_5)_2(\mu\text{-}C{=}C{=}CR_2)(CO)_4]$	$[Mn(\eta\text{-}C_5H_5)(CO)_2(OEt_2)] + [Mn(\eta\text{-}C_5H_5)(CO)_2\text{-}(C{=}C{=}CR_2)]$	R = Bu-*t*, C_6H_{11}, Ph, CH_2Ph	86
$[Mn_2(\eta\text{-}C_5H_5)_2(\mu\text{-}C{=}CH_2)(CO)_4]$	$[Mn(\eta\text{-}C_5H_5)(CO)_2(THF)] + HC{\equiv}CH$	X-ray (Figure 8)	51
$[Re_2\{\mu\text{-}C(OMe)R\}_2(CO)_8]$	$[Re_2(CO)_{10}] + \xrightarrow[(2)\ [Me_3O]\ [BF_4]]{(1)\ 2LiR}$	X-ray, R = $p\text{-}C_6H_4Me$ (Figure 9)	50
$[Fe_2(\mu\text{-}CH_2)(\mu\text{-}CO)_2(CO)_6]$	$[Fe_2(CO)_8]^{2-} + CH_2I_2$	X-ray (Figure 12); μ-CHR analogues also (e.g., R = Me, *i*-Pr, OMe, CO_2Et)	47
$[Fe_2(\eta\text{-}C_5H_5)_2(\mu\text{-}CHMe)(\mu\text{-}CO)(CO)_2]$	$[M_2(\eta\text{-}C_5H_5)_2(CO)_2\{CH{=}CHC(O)\}] + \xrightarrow[2.\ NaBH_4]{1.\ HBF_4}$	X-ray (Figure 13)	79
$[Fe_2(\mu\text{-}CHPh)(CO)_8]$	$[Fe(CO)_4(C(Ph)OLi)] + [Me_3O][BF_4]$		*f*
$[Fe_2(\eta\text{-}C_5H_5)_2\{\mu\text{-}C(CN)_2\}(\mu\text{-}CO)(CO)_2]$	$Na[Fe(\eta\text{-}C_5H_5)(CO)_2] + Br_2C(CN)_2$	low yield	72
$[Fe_2(\mu\text{-}CF_2)_2(\mu\text{-}CO)(CO)_6]$	$[Fe(CO)_5] + CF_2Br_2/h\nu$		64
$[Fe_2(\mu\text{-}C{=}CPh_2)(CO)_8]$	$[Fe_2(CO)_9] + Ph_2C{=}C{=}O/h\nu$	X-ray (Figure 11)	55
$[Fe_2(\mu\text{-}CFCF_3)(\mu\text{-}SMe)_2(CO)_6]$	$[Fe_2\{\mu\text{-}CF_2CF_2\}(\mu\text{-}SMe)_2(CO)_6]/\Delta$	X-ray (cf. reaction of $[\{Fe(\mu\text{-}SMe)(CO)_3\}_2]$ and CF_2CF_2 at low temperatures gives $[Fe_2\{\mu\text{-}CF_2CF_2\}\text{-}(\mu\text{-}SMe)_2(CO)_6]$	*g*
$[Fe_2(\eta\text{-}C_5H_5)_2(\mu\text{-}CHCO_2R)(CO)_2(\mu\text{-}CO)]$	$[\{Fe(\eta\text{-}C_5H_5)(CO)_2\}_2] + N_2CHCO_2R \xrightarrow{h\nu}$	R = Et or Bu-*t* (X-ray)	*h*
$[Fe_2(\eta\text{-}C_5H_5)_2\{\mu\text{-}C{=}C(CN)_2\}(\mu\text{-}CO)(CO)_2]$	$Na[Fe(\eta\text{-}C_5H_5)(CO)_2] + Cl_2C{=}C(CN)_2$	X-ray, 2 isomers (Figure 15)	72, *i*
$[Fe_2(\eta\text{-}C_5H_5)_2\{\mu\text{-}C{=}C(Ph)CH_2R\}(\mu\text{-}CO)(CO)_2]$	$Na[Fe(\eta\text{-}C_5H_5)(CO)_2] +$ 	R = H or Ph	*j*
	$[Fe(CO)_5] +$  $/h\nu$	X-ray (Figure 14)	68
$[Fe_2\{\mu\text{-}C(C_6H_3(OMe)_2\text{-}2,6)OEt\}(CO)_7]$	$[Fe(CO)_5] + \xrightarrow[2.\ [Et_3O][BF_4]]{1.\ C_6H_3(OMe)_2Li}$	X-ray (Figure 10)	88
$[Fe_2(\mu\text{-}C{=}NEt_2)_2(CO)_6]$	$[Fe(CO)_5] + Et_2NC{\equiv}CNEt_2$	X-ray, reaction involves the breaking of a C≡C bond	115
$[Ru_2(\mu\text{-}CH_2)_3(PMe_3)_6]$	$[Ru_3O(OAc)_6(H_2O)_3]OAc + MgMe_2 + PMe_3$	X-ray (Figure 16)	75
$[Ru_2(\mu\text{-}CH_2)_2(\mu\text{-}CH_3)(PMe_3)_6]^+$	$[Ru_3O(OAc)_6(H_2O)_3]OAc + MgMe_2 + PMe_3 + H[BF_4]$	X-ray (Figure 17)	75
$[Ru_2(\mu\text{-}CH_2)_2(PMe_3)_6]^{2+}$	$[Ru_3O(OAc)_6(H_2O)_3]OAc + MgMe_2 + PMe_3 + 2H[BF_4]$	X-ray (Figure 18)	75

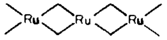
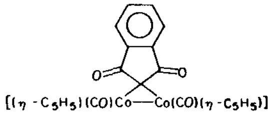
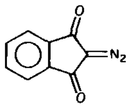
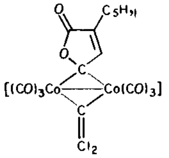
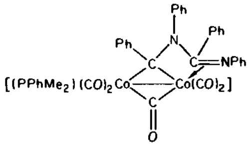
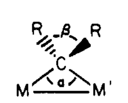
$[Ru_2(\eta-C_5H_5)_2(\mu-CMe_2)_2(\mu-CO)(CO)_2]$	$[Ru(\eta-C_5H_5)(CO)_2(\mu-C_3H_4)] + \xrightarrow[2.\ H^-]{1.\ H^+}$		81
$[Ru_2(\eta-C_5H_5)_2(\mu-C{=}CH_2)(\mu-CO)(CO)_2]$	$[Ru_2(CO)_2(\mu-CCH_2)(\eta-C_5H_5)_2] + \xrightarrow[2.\ H^-]{1.\ HBF_4}$	X-ray (Figure 19)	80
$[Ru_3(\mu-CH_2)_4(PMe_3)_8]^{2+}$	$[Ru_3O(OAc)_6(H_2O)_3OAc] + MgMe_2$ $PMe_3 + H[BF_4]_{aq}$	X-ray, linear structure 	41
$[M_2(\eta-C_5H_5)_2(\mu-CRR')(CO)_2]$	$[M(\eta-C_5H_5)(CO)_2] + N_2CRR'$ or $[M_2(\eta-C_5H_5)_2(CO)_3] + ONN(CH_2R)C(O)NH_2$	M = Co, R = R' = H, X-ray (Figure 20) R = R' = CO_2Et R = H, R = CO_2Et, X-ray (Figure 21) R = H, R' = CO_2Bu-*t* R = R' = CO_2Me M = Rh, R = R' = H, X-ray (Figure 27) R = R' = Me R = R' = CO_2Et	*k*, *l*, 44, 50, 58
	$[Co(\eta-C_5H_5)(CO)_2]$ + 	X-ray	*m*
$[Co_2(\mu-CH_2)(\eta-C_5Me_5)_2(\mu-CO)]$	$CoCl_2 + LiC_5Me_5 + LiCH_2CHO$	X-ray (Figure 20)	43
$[Co_2(\eta-C_5H_5)_2(\mu-CPh_2)(\mu-CO)]$	$[Co(\eta-C_5H_5)(CO)_2] + N_2CPh_2$		44
$[Co_2(\mu-CF_2)_2(CO)_6]$	$[Co_2(CO)_8] + CF_2Br_2/h\nu$		64
$[Co_2\{\mu-C(CF_3)X\}(\mu-CO)(CO)_6]$	$[Co_2(CO)_8] + (CF_3)_2CN_2$ or $+ C_2F_4/\Delta$	X = CF_3 or F	65, *n*
$[Co_2\{\mu-COC(O)CR'CR\}(\mu-CO)(CO)_6]$	$[Co_2(CO)_6CH{=}CH] + CO$	R = H, R' = H (Figure 24, X-ray) R = H, R' = Me, Pr, *n*-C_6H_{13}, Ph, $SiMe_3$, or steroid derivatives	52, *o*
	[μ-carbene-μ-CO complex](cf, above) + IC≡CI	X-ray (Figure 22)	56
	$[Co(CO)_4]^- + PhC(Cl)NPh$	X-ray, $PPhMe_2$ can be replaced by CO (Figure 23)	73
$[Rh_2(\eta-C_5H_5)_2(\mu-CPh_2)_2(\mu-CO)]$	$[Rh(CO)_2Cl]_2 + Ph_2C{=}C{=}O + NaCp$	X-ray (Figure 26)	57
$[Rh_2(\eta-C_5H_5)_2(\mu-CPh_2)_2]$	$[Rh(CO)_2Cl]_2 + Ph_2C{=}C{=}O + NaCp$		57
$[Rh_2(\eta-C_5Me_5)_2(CO)_2(\mu-CRR')]$	$[Rh_2(\eta-C_5Me_5)_2(CO)_2] + N_2CRR'$	R = H, R' = H, Me, or CO_2Et; R = R' = Ph; Δ/R = R' = Ph → $[Rh_2(\eta-C_5Me_5)_2(\mu-CO)\{\mu-CPh_2\}]$	45, 46
$[Rh_2(\mu-CPh_2)_2(\mu-CO)Cl_2py_2]$	$[[Rh(CO)_2Cl]_2] + Ph_2C{=}C{=}O + py$	X-ray (Figure 25)	*p*
$[Ir_2(\eta-C_8H_{12})_2(\mu-CH_2)]$	$[[Ir(\eta-C_8H_{12})Cl]_2] + MeLi$	formed by decomposition of the methyl bridged dimer via α-hydrogen abstraction	*q*

Table V (*Continued*)

compound	preparation	comments	ref
$[Pt_2(\mu\text{-}CH_2)(\mu\text{-}Ph_2PCH_2PPh_2)_2Cl_2]$	$[Pt(Ph_2PCH_2PPh_2)_2Cl_2] + CH_2N_2$	X-ray	54, *r*
$[Pt_2\{\mu\text{-}C(CF_3)X\}(COD)_2]$	$[Pt(COD)_2] + CF_3CF{=}CF_2$ (or $+ CF_2{=}CFH$)	COD = cyclooctadiene, Pd complex also isolated ($X = CF_3$), $X = CF_3$ or H	66
$[Pt_2(\mu\text{-}CHCF_3)_2(COD)_2]$	as above	not isolated, characterized by ^{19}F NMR	66
$[Pt_2\{\mu\text{-}C(OMe)Ph\}(CO)_2(PMeBu\text{-}t_2)_2]$	reaction byproduct in prepn. of Pt_2Cr complex (see below)	low yield byproduct	71, *s*
$[PtM\{\mu\text{-}C(OMe)R\}(CO)_5(PMe_3)_2]$	$[M(CO)_5{=}C(OMe)R] + [Pt(C_2H_4)_3] + 2PMe_3$	M = Cr, Mo, or W, X-ray (M = W, R = Ph) (Figure 32) R = Me or Ph	69, 70
$[MMn(\eta\text{-}C_5H_5)\{\mu\text{-}C(OMe)Ph\}(CO)_2(PMe_3)_2]$	$[Mn(\eta\text{-}C_5H_5)(CO)_2(C(OMe)Ph)] + PMe_3 + [Pt(C_2H_4)_3]$ or $+ [Ni(COD)_2]$, or $+ [Pd(dibenzylideneacetone)_2]$	M = Ni, Pd, or Pt, general reaction: $\equiv M{=}CRR^1 + M(O)$, adding a metal(O) complex across a metal-carbene double bond	69, 70
$[PtMn(\mu\text{-}\overline{C{=}CHCH_2CH_2O})(CO)_4(PMe_3)_2]$	$[Mn_2(CO)_9(\overline{COCH_2CH_2CH_2})] + [Pt(C_2H_4)_3] + 2PMe_3$	X-ray, 2 isomers	70, *t*
$[Pt_2\{\mu\text{-}C(O)(CPh)_2\}(Bu\text{-}t\text{-}NC)_4]$	$[Pt_3(Bu\text{-}t\text{-}NC)_6]$ $Ph\overline{C{=}CPhC}(O)$	X-ray, can replace 2Bu-*t*-NC by COD; HBF_4 protonates C=O (Figure 28)	67
$[U_2(\eta\text{-}C_5H_5)_4\{(\mu\text{-}CH)PPh_2CH_2\}_2]$	$[U(\eta\text{-}C_5H_5)_3Cl] + Li(CH_2)_2PPh_2$	X-ray, the normal mode of ylide bonding is $M\text{-}CH_2\text{-}P(<)\text{-}CH_2\text{-}M$ (Figure 29)	59
$[Au(PPh_3)]_2[\mu\text{-}C(CN)_2]$	$CH_2(CN)_2 + [Au(PPh_3)]_3O[BF_4] + K_2CO_3$	X-ray	*w*
Selected Examples of Trimetallic Complexes			
$[H_2Os_3(\mu\text{-}CH_2)(CO)_{10}]$	$[H_2Os_3(CO)_{10}] + CH_2N_2$	X-ray	40
$[H_2Os_3\{\mu\text{-}C(PEt_2)R\}(CO)_9]$	$[Os_3(CO)_{12}] + PEt_3/\Delta$	can replace one CO by PEt_3, R = H or Me	*u*
$[Ni_3\{\mu\text{-}C(OMe)Ph\}_3(CO)_3]$	$[Ni(CO)_4] + [Mo(\eta\text{-}C_5H_5)NO(CO)\{C(OMe)Ph\}]$	not well-characterized	*v*
$[Pt_3\{\mu\text{-}C(OMe)Ph\}(\mu\text{-}CO)_2(PR_3)_3]$	reaction byproduct in prepn. of Pt_2Cr complex (see below)	analogous complexes isolated with one or both bridging carbonyls replaced by the carbene ligand $\{C(OMe)Ph\}$	71, *s*
$[Pt_2M\{\mu\text{-}C(OMe)Ph\}(\mu\text{-}CO)_2(CO)_4(PR_3)_2]$	$[Pt(C_2H_4)_2PR_3] + [M(CO)_5\{C(OMe)Ph\}]$	M = Cr or W X-ray, M = W $PR_3 = P(cyclohexyl)_3$ or $PBu\text{-}t_2Me$	71, *s*

[a] Belmonte, P.; Schrock, R. R.; Churchill, M. R.; Youngs, W. J. *J. Am. Chem. Soc.* 1980, *102*, 2858. [b] Messerle, L.; Curtis, M. D. *J. Am. Chem. Soc.* 1980, *102*, 7789. [c] Barker, G. K.; Carroll, W. E.; Green, M.; Welch, A. J. *J. Chem. Soc., Chem. Commun.* 1980, 1071. [d] Levisalles, J.; Rudler, H.; Dahan, F.; Jeannin, Y. *J. Organomet. Chem.* 1980, *187*, 233. [e] Antonova, A. B.; Kolobova, N. E., Petrovsky, P. V.; Lokshin, B. V.; Obezyuk, N. S. *J. Organomet. Chem.* 1977, *137*, 55. Nesmeyanov, A. N.; Aleksandrov, G. G.; Antonova, A. B.; Anisimov, K. N.; Kolobova, N. E.; Struchkov, Yu. T. *Ibid.* 1976, *110*, C36. Kolobova, N. E.; Antonova, A. B.; Khitrova, O. M. *Ibid.* 1978, *146*, C17. [f] Fischer, E. O.; Kiener, V.; Fischer, R. D. *J. Organomet. Chem.* 1969, *16*, P60; 1970, *23*, 215. [g] Bonnet, J. J.; Mathieu, R.; Poilblanc, R.; Ibers, J. A. *J. Am. Chem. Soc.* 1979, *101*, 7487. [h] Herrmann, W. A.; Plank J.; Bernal, I.; Creswick, M. *Z. Naturforsch B:Anorg. Chem., Org. Chem.* 1980, *35B*, 680. [i] Kirchner, R. M.; Ibers, J. A. *J. Organomet. Chem.* 1974, *82*, 243. [j] Marten, D. F.; Dehmlow, E. V.; Hanlon, D. J.; Hossain, M. B.; Helm, D. van der *J. Am. Chem. Soc.* 1981, *103*, 4940. [k] Herrmann, W. A.; Huggins, J. M.; Reiter, B.; Bauer, C. *J. Organomet. Chem.* 1981, *214*, C19. [l] Herrmann, W. A. *Chem. Ber.* 1978, *111*, 1077. [m] Creswick, M.; Bernal, I.; Herrmann, W. A.; Steffl, I. *Chem. Ber.* 1980, *113*, 1377. [n] Cooke, J.; Cullen, W. R.; Green, M.; Stone, F. G. A. *J. Chem. Soc. A* 1969, 1872. Booth, B. L.; Haszeldine, R. N.; Inglis T. *J. Chem. Soc., Dalton Trans.* 1975, 1449. [o] Pályi, G.; Váradi, G.; Vizi-Orosz, A.; Markó, L. *J. Organomet. Chem.* 1975, *90*, 85. Guthrie, D. J. S.; Khand, I. U.; Knox, G. R.; Hollmeier, J.; Pauson, P. L.; Watts, W. E. *Ibid.* 1975, *90*, 93. [p] Yamamoto, T.; Garber, A. R.; Wilkinson, J. R.; Boss, C. R.; Streib, W. E.; Todd, L. J. *J. Chem. Soc., Chem. Commun.* 1974, 354. [q] Schmidt, G. F.; Muetterties, E. L.; Beno, M. A.; Williams, J. M. *Proc. Natl. Acad. Sci. U.S.A.* 1981, *78*, 1318. [r] Brown, M. P.; Fisher, J. R.; Puddephatt, R. J.; Seddon, K. R. *Inorg. Chem.* 1979, *18*, 2808. [s] Ashworth, T. V.; Berry, M.; Howard, J. A. K.; Laguna, M.; Stone, F. G. A. *J. Chem. Soc., Chem. Commun.* 1979, 45; *J. Chem. Soc., Dalton Trans.* 1980, 1615. [t] Ashworth, T. V.; Berry, M.; Howard, J. A. K.; Laguna, M.; Stone, F. G. A. *J. Chem. Soc., Chem. Commun.* 1979, 43. [u] Deeming, A. J. *J. Organomet. Chem.* 1977, *128*, 63. [v] Fisher, E. O.; Beck, H. J. *Angew. Chem., Int. Ed. Engl.* 1970, *9*, 72. [w] Smyslova, E. I.; Perevalova, E. G.; Dyadchenko, V. P.; Grandberg, K. I.; Slovokhotov, Yu. L.; Struchkov, Yu. T. *J. Organomet. Chem.* 1981, *215*, 269.



XVIII

Figures 5–32, for some μ-alkylidenedimetal complexes there is a single CRR′ bridge, whereas for others there is an additional CRR′ bridge, a μ-CO, or other connectivity. For the first type, extended Hückel MO calculations suggest a dimetallacyclopropane structure XVIII with significant MM′ bonding and a relatively high electron density at the bridgehead carbon.[42] Consistent with this description are the protonation reactions (section IIIC) and ^{13}C NMR data;[35] e.g., the carbon-13 chemical shift for μ-CH_2 in $[Mn_2(\mu\text{-}CH_2)(\eta\text{-}C_5H_4Me)_2(CO)_4]$ is at 150 ppm and is generally found in the range 100–200 ppm for related μ-CRR′ complexes, in contrast to the 240–440 ppm for terminal RR′C═metal complexes.[34] However, as stated earlier, such comparison is unrealistic, because hybridization in XVIII approximates to sp^3 whereas in RR′C═metal complexes C_{carb} is sp^2. In $[Co_2\{\mu\text{-}CH_2\}(\eta\text{-}C_5H_5)_2(\mu\text{-}CO)]$,[43] $[Co_2\{\mu\text{-}CPh_2\}(\eta\text{-}C_5H_5)_2(\mu\text{-}CO)]$,[44] or $[Rh_2\{\mu\text{-}CH_2\}(\eta\text{-}C_5Me_5)_2(\mu\text{-}CO)]$[45] a metal–metal double bond has been proposed, on the basis of analogy with $[Co_2(\eta\text{-}C_5H_5)_2(\mu\text{-}CO)_2]$ and the EAN rule, whence such compounds might be described as dimetallacyclopropenes.

The μ-CRR′ ligand may be semibridging rather than symmetrical, as in $[CrPt\{\mu\text{-}C(CO_2Me)Ph\}(CO)_4(PMe_3)_3]$, Figure 31;[46] this is a further parallel with a μ-CO ligand. Another example is $[Fe_2\{\mu\text{-}CH_2\}(\mu\text{-}CO)_2(CO)_6]$, which has a solid state geometry (Figure 12) isostructural with $[Fe_2(CO)_9]$;[47] although in solution the IR spectrum shows only terminal CO's, hence probably the structure is of the isomer $[Fe_2\{\mu\text{-}CH_2\}(CO)_8]$. In contrast with $[Rh_2(\mu\text{-}CH_2)(\eta\text{-}C_5H_5)_2(CO)_2]$,[35] some analogues $[Rh_2(\mu\text{-}CRR')(\eta\text{-}C_5Me_5)_2(CO)_2]$, readily decarbonylate to yield the carbonyl-bridged complex $[Rh_2(\mu\text{-}CRR')(\mu\text{-}CO)(\eta\text{-}C_5Me_5)_2]$.

For complexes of the type XVIII, it has been noted that (a) the M–M′ distance is similar to that of the $(\mu\text{-}CO)_2$ analogue, and (b) the internal angle α is far less sensitive than the external angle β to changes in the variables M, M′, R, and R′:[48a] e.g., $\alpha = 81.7\ (1)°$ and $\beta = 115.9\ (4)°$ in $[Mn_2\{\mu\text{-}CH_2\}(\eta\text{-}C_5H_4Me)_2(CO)_4]$,[48b] (Figure 6), but $\alpha = 86.9\ (2)°$ and $\beta = 92\ (2)°$ in $[Rh_2\{\mu\text{-}CH_2\}(\eta\text{-}C_5H_5)_2(CO)_2]$,[48c] (Figure 27).

B. Synthesis

The first compound having a μ-alkylidene type structure, $[Co_2\{\mu\text{-}COC(O)CH{=}CH\}(\mu\text{-}CO)(CO)_6]$, Figure 24, a γ-lactone-derived complex, was prepared in 1959[52a] from $[Co_2(\mu\text{-}HCCH)(CO)_6]$ and CO but not recognized as such until 1967;[52b] the first μ-vinylidenedimetal complex was $[Fe_2(\mu\text{-}C{=}CPh_2)(CO)_8]$, Figure 11, obtained by a deoxygenation of diphenylketene, (eq 12).[53] This may be regarded as a *carbene insertion*

$$2[Fe(CO)_5] + Ph_2C{=}C{=}O \xrightarrow[C_6H_6]{h\nu} [Fe_2\{\mu\text{-}C{=}CPh_2\}(CO)_8] \quad (12)$$

reaction (if it is assumed that the first formed binuclear complex is $[Fe_2(CO)_9]$) into a metal–metal bond, in this case of a vinylidenecarbene $Ph_2C{=}C$:. As mentioned in section IIIA., diazoalkanes provide an alternative source of carbene,[35] as in eq 13 (dppe = $Ph_2PCH_2CH_2PPh_2$),[54] and 14;[48a] for the latter, when the

$$[Pt_2Cl_2(\mu\text{-}dppe)_2] + CH_2N_2 \rightarrow [Pt_2\{\mu\text{-}CH_2\}Cl_2(\mu\text{-}dppe)_2] \quad (13)$$

$$2[Co(\eta\text{-}C_5H_5)(CO)_2] + N_2CHCO_2Et \rightarrow [Co_2\{\mu\text{-}CH(CO_2Et)\}(\eta\text{-}C_5H_5)_2(CO)_2] \quad (14)$$

reaction was carried out in THF at −90 °C an intermediate XIX was isolated which undergoes dynamic behavior in solution via pairwise scrambling (^{13}C NMR)[48a] yielding $[Co_2\{\mu\text{-}CH(CO_2Et)\}(\eta\text{-}C_5H_5)_2(CO)_2]$ by an intramolecular first-order process. This shows that the designation "carbene insertion reaction" should be regarded as a convenient formalism rather than a

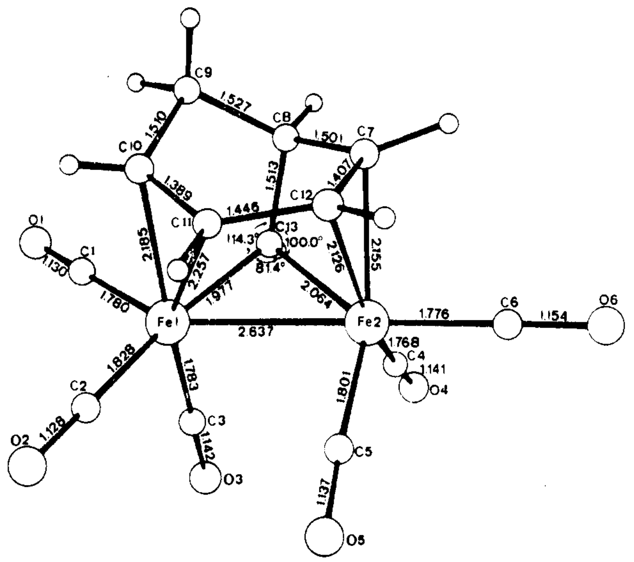


Figure 14. Schematic representation of the molecular structure of a (μ-methylidyne)(μ-cyclohexa-η^2-diene)diiron(0) complex $[Fe_2(\mu\text{-}CH)(\mu\text{-}\eta^2,\eta^2\text{-}CHCH{=}CHCH{=}CHCH_2)(CO)_6]$. Reproduced, with permission, from: Aumann, R.; Wörmann, H.; Krüger, C. *Angew. Chem., Int. Ed. Engl.* **1976**, *15*, 609. Copyright 1976, Verlag Chemie GmbH.

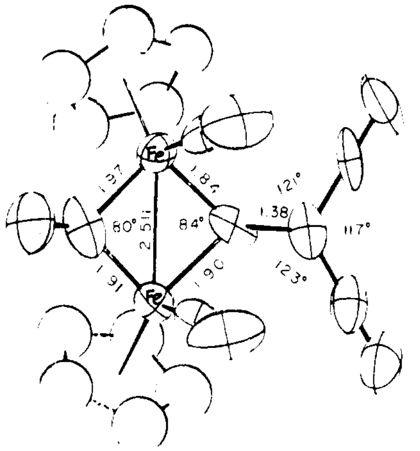
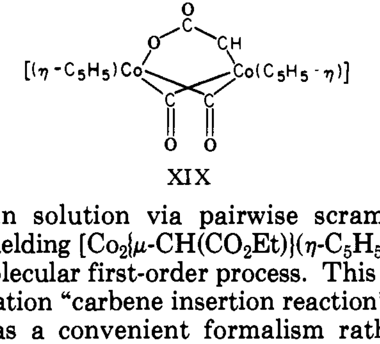


Figure 15. ORTEP drawing of *cis*-$[Fe_2\{\mu\text{-}C{=}C(CN)_2\}(\eta\text{-}C_5H_5)_2(\mu\text{-}CO)(CO)_2]$. Reproduced, with permission, from: Kirchner, R. M.; Ibers, J. A. *J. Organomet. Chem.* **1974**, *82*, 243. Copyright 1979, Elsevier Sequoia SA.



XIX

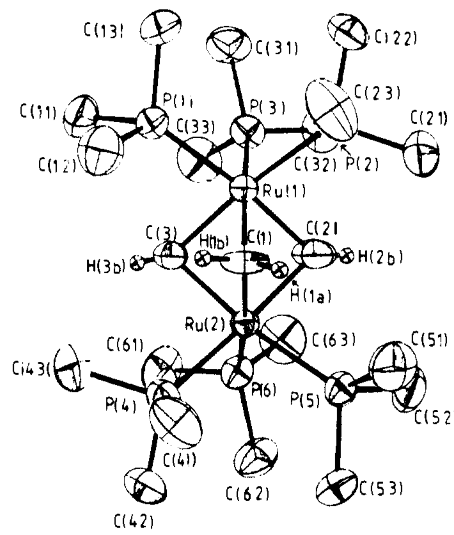


Figure 16. ORTEP drawing of the molecule $[Ru_2(\mu\text{-}CH_2)_3(PMe_3)_6]$. Reproduced, with permission, from: Hursthouse, M. B.; Jones, R. A.; Malik, K. M. A.; Wilkinson, G. *J. Am. Chem Soc.* **1979**, *101*, 4128. Average Ru–C and Ru–P distances are 2.107 and 2.336 Å, respectively, Ru–Ru = 2.650 (1) Å, and RuCRu angle ≃ 78°.

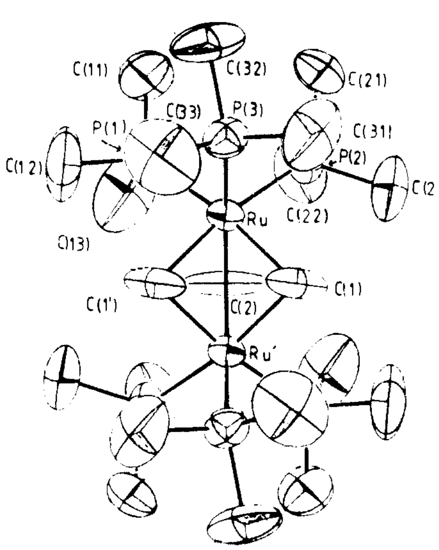


Figure 17. ORTEP drawing of the $[Ru_2(\mu\text{-}CH_2)_2(\mu\text{-}CH_3)(PMe_3)_6]^+$ cation. Reproduced, with permission, from: Hursthouse, M. B.; Jones, R. A.; Malik, K. M. A.; Wilkinson, G. *J. Am. Chem. Soc.* **1979**, *101*, 4128. A $\mu\text{-}CH_2$ in C_2 axis and second CH_2 and CH_3 disordered.

statement of mechanistic significance. From the $[Mn_2(CO)_{10}]\text{-}CH_2N_2$ system, $[(OC)_5MnNN({=}CH_2)\text{-}Mn(CO)(CO)_4]$ was isolated.[62] An *N*-alkyl-*N*-nitrosourea $H_2NCON(NO)Me$ has also been used as a convenient methylene-transfer reagent, converting $[Rh_2(\eta\text{-}C_5H_5)_2(\mu\text{-}CO)(CO)_2]$ into $[Rh_2\{\mu\text{-}CH_2\}(\eta\text{-}C_5H_5)_2(CO)_2]$.[58]

A further carbene insertion reaction is shown in eq 15, the carbenoid being $Ph_2C{=}C{=}O$;[63] the Rh(I)

$$\tfrac{1}{2}[\{Rh(CO)_2Cl\}_2] + Ph_2C{=}C{=}O \longrightarrow$$

$$(1/n)[\{Rh(\mu\text{-}CPh_2)(CO)Cl\}_n] \xrightarrow{py} [Rh_2(\mu\text{-}CPh_2)(\mu\text{-}CO)Cl_2py_2]$$

(see Figure 25)

$$\Big\downarrow{\scriptstyle NaC_5H_5}$$

$$\tfrac{1}{2}[Rh_2(\mu\text{-}CPh_2)(\eta\text{-}C_5H_5)(\mu\text{-}CO)] \underset{+CO}{\overset{-CO}{\rightleftharpoons}} \tfrac{1}{2}[Rh_2(\mu\text{-}CPh_2)(\eta\text{-}C_5H_5)_2] \qquad (15)$$

(see Figure 26)

reagent may have a dual role, as a decarbonylating

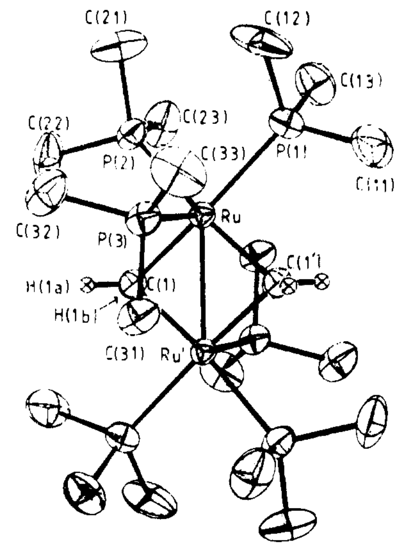


Figure 18. ORTEP drawing of the $[Ru_2(\mu\text{-}CH_2)_2(PMe_3)_6]^{2+}$ cation. Reproduced, with permission, from: Hursthouse, M. B.; Jones, R. A.; Malik, K. M. A.; Wilkinson, G. *J. Am. Chem. Soc.* **1979**, *101*, 4128. Planar C-Ru-C-Ru with mean Ru–C 2.071 (5) Å.

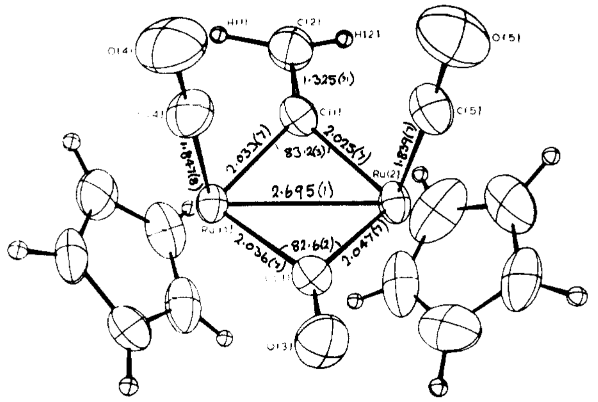


Figure 19. ORTEP drawing of the molecule $[Ru_2(\mu\text{-}CCH_2)(\eta\text{-}C_5H_5)_2(CO)_2(\mu\text{-}CO)]$. Reproduced, with permission, from: Davies, D. L.; Dyke, A. F.; Endesfelder, A.; Knox, S. A. R.; Naish, P. J.; Orpen, A. G.; Plaas, D.; Taylor, G. E. *J. Organomet. Chem.* **1980**, *198*, C43. Copyright 1980, Elsevier Sequoia SA. For comparison with the protonated μ-CMe complex, see Figure 40.

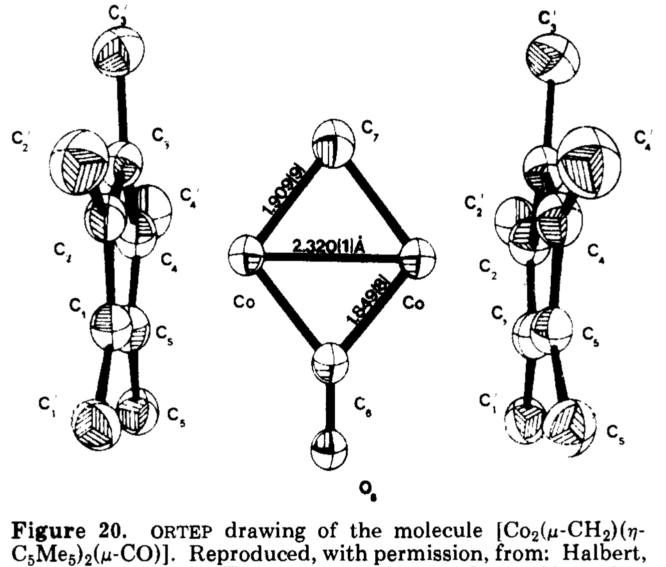


Figure 20. ORTEP drawing of the molecule $[Co_2(\mu\text{-}CH_2)(\eta\text{-}C_5Me_5)_2(\mu\text{-}CO)]$. Reproduced, with permission, from: Halbert, T. R.; Leonowicz, M. E.; Maydonovitch, D. J. *J. Am. Chem. Soc.* **1980**, *102*, 5101. A double CoCo bond is suggested.

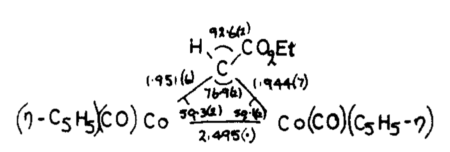


Figure 21. Schematic representation of the molecular structure of *trans*-$[Co_2\{\mu\text{-}CH(CO_2Et)\}(\eta\text{-}C_5H_5)_2(CO)_2]$.[48a]

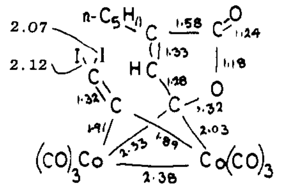


Figure 22. Schematic representation of the molecular structure of $[Co_2(\mu\text{-}CCl_2)\{\mu\text{-}\overline{COC(O)C(\eta\text{-}C_5H_{11})CH}\}(CO)_6]$;[56] each Co atom is pseudooctahedral, the $Co_2(CO)_6$ group is markedly asymmetric, and the plane of the lactone ring is perpendicular to CI_2.

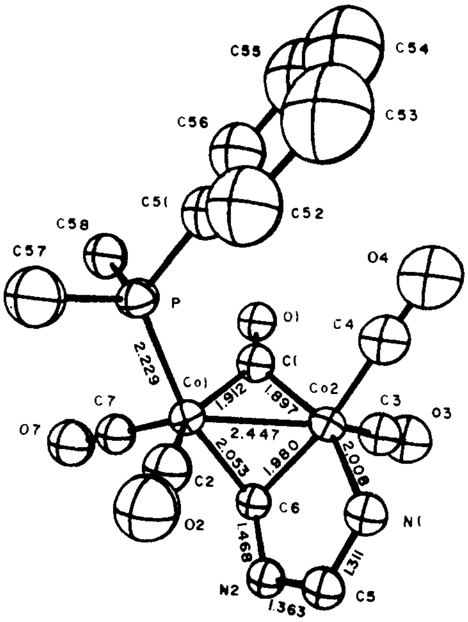
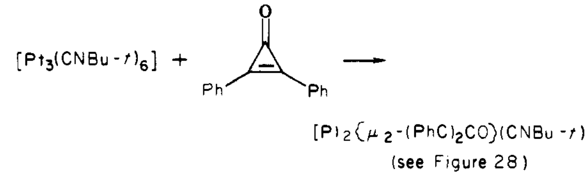


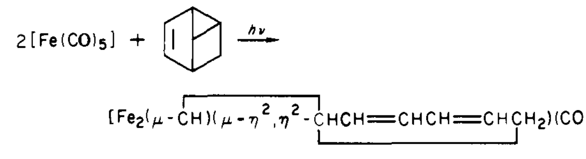
Figure 23. ORTEP drawing of the molecule $[Co_2\{\mu\text{-}C(Ph)N\text{-}(Ph)C(Ph)N\text{-}\}(Ph)\}(\mu\text{-}CO)(CO)_4(PMe_2Ph)]$ (the 4Ph groups of the bridging ligand are not shown). Reproduced, with permission, from: Adams, R. D.; Chodosh, D. F.; Golembski, N. M. *J. Organomet. Chem.* **1977**, *139*, C39. Copyright 1977, Elsevier Sequoia SA.

agent thus generating Ph_2C:, and as substrate.

Other variants of reactions which may be viewed as carbene insertions are (a) that between $[Fe(CO)_5]$ and CF_2Br_2 with UV irradiation to afford $[Fe_2\{\mu\text{-}CF_2\}_2(\mu\text{-}CO)(CO)_6]$,[64] (b) $[Co_2\{\mu\text{-}CF_2\}_2(CO)_6]$ from $[Co_2(CO)_8]$, (c) the formation of $[Co_2\{\mu\text{-}CF(CF_3)\}(\mu\text{-}CO)(CO)_6]$ from $[Co_2(CO)_8]$ and C_2F_4 (via $[Co_2\{\mu\text{-}CF_2CF_2\}(\mu\text{-}CO)(CO)_7]$,[65] and (d) the preparation of $[Pt_2\{\mu\text{-}CR(CF_3)\}(COD)_2]$ (e.g., R = CF_3) from $[Pt(COD)_2]$ and $CF_3CF{=}CF_2$.[66]



(16)



(17)

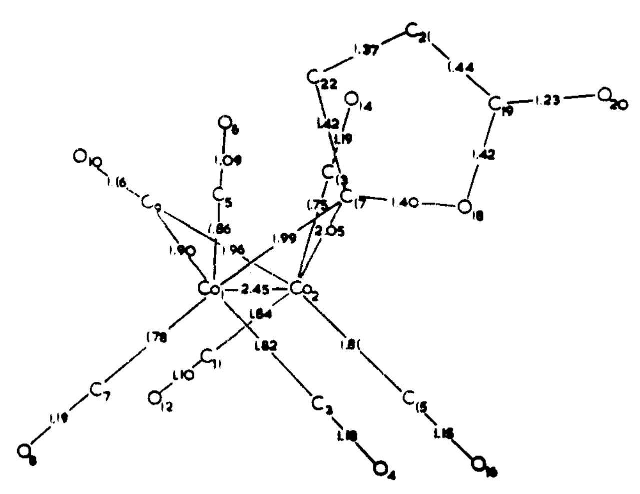


Figure 24. Schematic representation of the molecular structure of $[Co_2\{\mu\text{-}\overline{COC(:O)CH:CH}\}(\mu\text{-}CO)(CO)_6]$, showing interatomic distances (Å). Reproduced, with permission, from: Mills, O. S.; Robinson, G. *Inorg. Chim. Acta* **1967**, *1*, 61. Copyright 1967, Elsevier Sequoia SA. The μ-alkylidene ligand is a γ-lactone derivative. The structure is similar to that of $[Co_2(\mu\text{-}CO)_2(CO)_6]$.

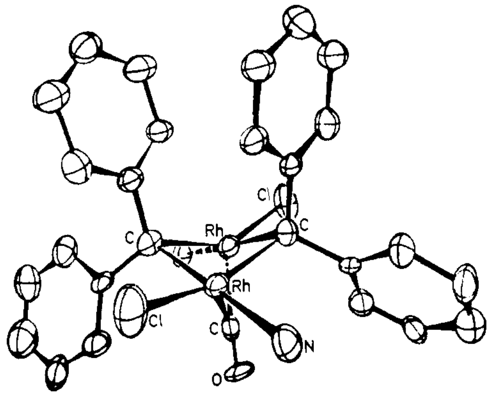


Figure 25. ORTEP drawing of the molecular structure of $[Rh_2(\mu\text{-}CPh_2)_2(\mu\text{-}CO)Cl_2(NC_5H_5)_2]$; only the nitrogen atoms of the pyridine rings are included for clarity. Reproduced, with permission, from: Yamamoto, T.; Garber, A. R.; Wilkinson, J. R.; Boss, C. R.; Streib, W. E.; Todd, L. J. *J. Chem. Soc., Chem. Commun.* **1974**, 354. Copyright 1974, Chemical Society, London. The RhRh distance is 2.51 Å; this is a preliminary structure.

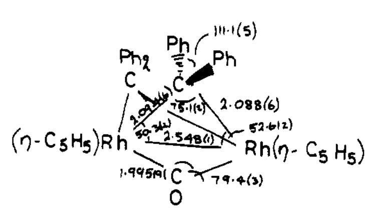


Figure 26. Schematic representation of the molecular structure of $[Rh_2\{\mu\text{-}CPh_2\}_2(\eta\text{-}C_5H_5)_2(\mu\text{-}CO)]$.[57] The molecule has C_2 symmetry, the two C_5H_5 rings are staggered about the RhRh bond, and the two Ph rings are roughly orthogonal, the dihedral angle being 85.3°. The C_2 axis passes through μ-CO and is perpendicular to the Rh–Rh bond.

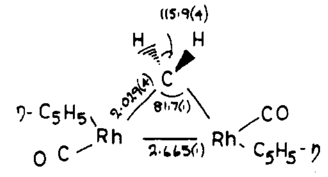


Figure 27. Schematic representation of the molecular structure of *trans*-$[Rh_2(\mu\text{-}CH_2)(\eta\text{-}C_5H_5)_2(CO)_2]$.[58]

A second type of reaction leading to (μ-1,1-alkylidene)dimetal complexes is that of *metal-promoted ring-opening*, but this has had only limited application,

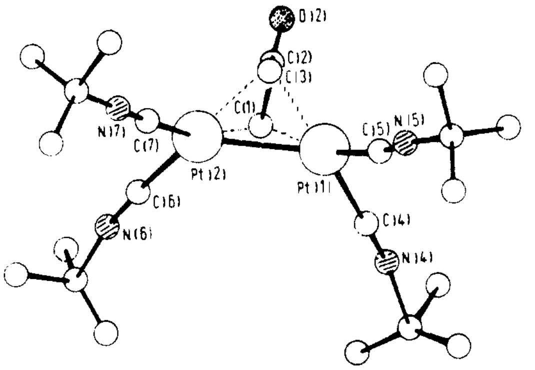


Figure 28. The molecular structure of $[Pt_2\{\mu_2\text{-}(PhC)_2CO\}(CNBu\text{-}t)_4]$; the two phenyl groups at C(1) and C(3) are omitted for clarity. Reproduced, with permission, from: Carrol, W. E.; Green, M.; Howard, J. A. K.; Pfeffer, M.; Stone, F. G. A. *Angew. Chem., Int. Ed. Engl.* **1977**, *11*, 793. Copyright 1977, Verlag Chemie GmbH.

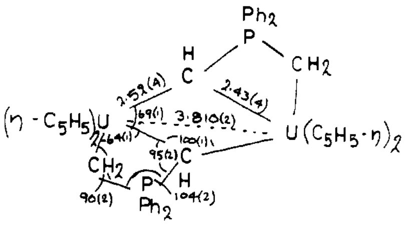


Figure 29. Schematic representation of the molecular structure of $[U_2\{(\mu\text{-}CH)PPh_2CH_2\}_2(\eta\text{-}C_5H_5)_4]$.[59] The molecule crystallizes as the OEt_2 adduct, CH_2-U-CH 130(1)°, P-CH-U 142(2)°; each U atom is approximately tetrahedral, and each U atom may be regarded as quasi-nine-coordinate.

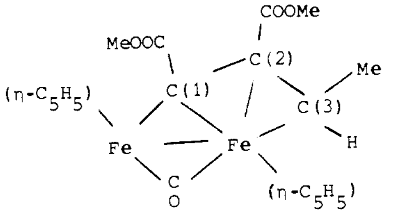


Figure 30. Schematic representation of the molecular structure of $[Fe_2\{\mu\text{-}\eta^1,\eta^3\text{-}C(COOMe)C(COOMe)CHMe\}(\mu\text{-}CO)(\eta\text{-}C_5H_5)_2]$. Bond lengths: Fe–Fe, 2.540 (2); Fe–C(1), 1.969 (12); Fe–C(2), 2.042 (12); Fe–C(3), 2.111 (13) Å. Angle C(1)–C(2)–C(3), 119.3(1.1)°.[198]

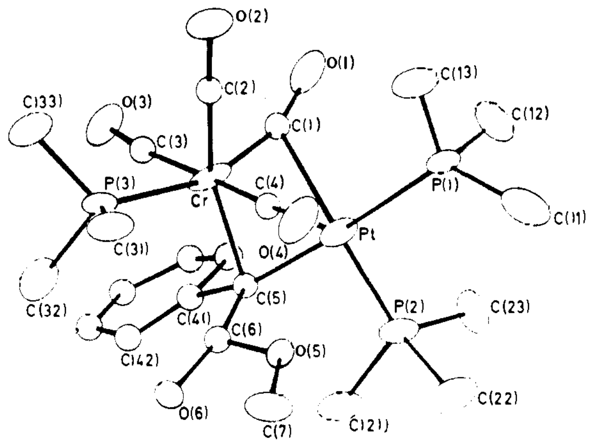
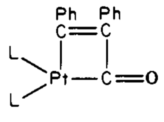
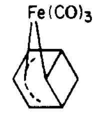


Figure 31. The molecular geometry of $[CrPt\{\mu\text{-}C(CO_2Me)Ph\}(CO)_4(PMe_3)_3]$, including the atomic numbering scheme. Bond lengths: Cr–Pt, 2.646 (7); Cr–C(5), 2.27 (4); Pt–C(5), 1.98 (4); Pt–C(1), 2.19 (4); Cr–C(1), 1.75 (5); C(1)–O(1), 1.31 (5) Å. Angles: Cr–C(1)–O(1), 157 (4); Cr–C(1)–Pt, 84 (2)°. Reproduced, with permission, from: Howard, J. A. K.; Jeffery, J. C.; Laguna, M.; Navarro, R.; Stone, F. G. A. *J. Chem. Soc., Chem. Commun.* **1979**, 1170. Copyright 1979, The Chemical Society, London. The $C(CO_2Me)Ph$ ligand asymmetrically bridges the Cr–Pt bond.

eq 16[67] and 17.[68] The former may require an intermediate platinacyclobutenone (XX), a type known for



XX



XXI

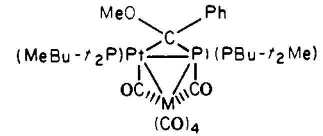
stronger σ-donor ligands (L) than *t*-BuNC, and insertion of a further Pt(0) moiety into the C=C bond thereof. The latter may arise by reaction of $[Fe(C_6H_{10}\text{-}\eta^2)(CO)_4]$ and XXI.

An important and rather general method of forming (μ-1,1-alkylidene)dimetal complexes has analogy with the cyclopropanation reaction involving an olefin and a carbene. Thus, a carbene–metal complex may be transformed into a dimetallacyclopropane $[L_m\overline{M\text{-}(C<)\text{-}M'}L_n]$, by insertion of a low-oxidation-state metal fragment $M'L_n$ into the M=C bond. We may, therefore, designate this a *dimetallacyclopropanation*, and it has wide generality. The carbene–metal complex has been of type $[M\{C(OR')R\}(CO)_5]$ (M = Cr, Mo, or W)[69] or $[Mn(\eta\text{-}C_5H_5)\{C(OR')R\}(CO)_2]$[70] and the metallocarbene analogue a Ni(0), Pd(0), or Pt(0) species. An example is in eq 18.[69] However, a more complicated

$$[W\{C(OMe)Ph\}(CO)_5] \xrightarrow[2.\ 2PMe_3]{1.\ [Pt(COD)_2],\ (-C_2H_4)} [\overline{W\{\mu\text{-}C(OMe)Ph\}(CO)_5Pt}(PMe_3)_2] \quad (18)$$

reaction has also been observed, wherein a *carbene transfer reaction* from one metal center onto another occurs, as in eq 19 (M = Cr or W).[71] There are a

$$[M\{C(OMe)Ph\}(CO)_5] + 2[Pt(\eta\text{-}C_2H_4)_2(PBu\text{-}t_2Me)] \longrightarrow$$



(19)

number of variants of *salt elimination*, as exemplified by eq 20,[72] 21,[73], 22,[59] 23,[43] and 24.[47] The coupling of

$$2Na[Fe(\eta\text{-}C_5H_5)(CO)_2] + Cl_2C{=}C(CN)_2 \rightarrow [Fe_2\{\mu\text{-}C{=}C(CN)_2\}(\eta\text{-}C_5H_5)_2(\mu\text{-}CO)(CO)_2] + 2NaCl \quad (20)$$

$$2Na[Co(CO)_4] + 2ClC(Ph){=}NPh \rightarrow [Co_2\{\mu\text{-}\underline{C(Ph)N(Ph)C(Ph)(N)}(Ph)\}(\mu\text{-}CO)(CO)_6] + 2NaCl \quad (21)$$

$$2[U(\eta\text{-}C_5H_5)_3Cl] + 2Li(CH_2)_2PPh_2 \rightarrow [U_2\{(\mu\text{-}CH)PPh_2CH_2\}_2(\eta\text{-}C_5H_5)_4] + 2LiCl + 2C_5H_6 \text{ (see Figure 29)} \quad (22)$$

$$2CoCl_2 + 2LiCH_2CHO + 2Li[C_5Me_5] \rightarrow [Co_2(\mu\text{-}CH_2)(\eta\text{-}C_5Me_5)_2(\mu\text{-}CO)] + 4LiCl \quad (23)$$

$$Na_2[Fe_2(CO)_8] + CH_2I_2 \rightarrow [Fe_2(\mu\text{-}CH_2)(\mu\text{-}CO)_2(CO)_6] + 2NaI \quad (24)$$

the imidoyl fragments to yield the product of Figure 23 (eq 21) has precedent in a nonbridging context (eq 25).[74]

$$^1/_2[\{Rh(CO)_2Cl\}_2] + 2ClC(Ph){=}NPh \rightarrow [\overline{RhCl_3\{C(Ph)N(Ph)C(Ph)N}(Ph)\}(CO)] \quad (25)$$

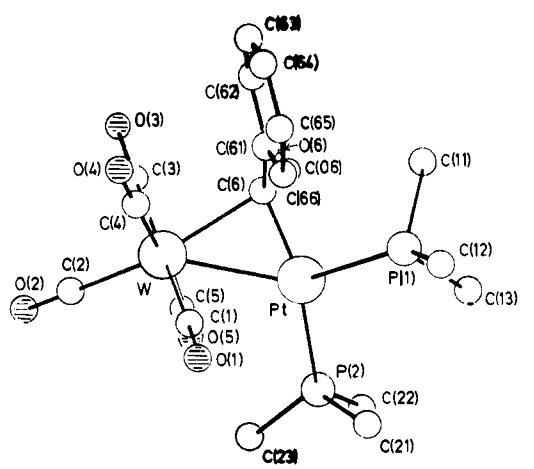


Figure 32. Molecular structure of [W{μ-C(OMe)Ph}(CO)$_5$Pt(PMe$_3$)$_2$]. reproduced, with permission, from: Ashworth, T. V.; Howard, J. A. K.; Laguna, M.; Stone, F. G. A. *J. Chem Soc., Dalton Trans.* **1980**, 1593. Copyright 1980, The Chemical Society, London.

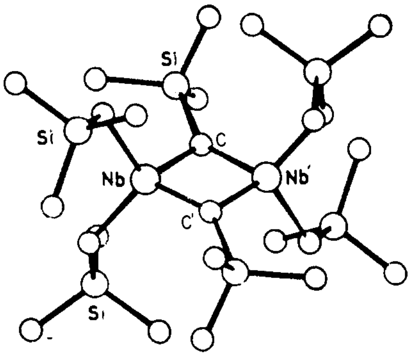
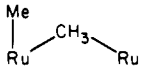


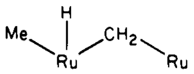
Figure 33. Schematic representation of the molecular structure of [Nb$_2${μ-C(SiMe$_3$)}$_2$(CH$_2$SiMe$_3$)$_4$]. Reproduced, with permission, from: Huq, F.; Mowat, W.; Skapski, A. C.; Wilkinson, G. *J. Chem. Soc., Chem. Commun.* **1971**, 1477. Copyright 1971, The Chemical Society, London. Bond lengths (Å): NbC, 1.995 (9); Nb'C, 1.954 (9); Nb–CH$_2$, 2.160 (9) (av.); Nb...Nb', 2.897 (2); C...C', 2.684 (13). Angles (°): CNbC', 85.6 (4); NbCNb', 94.4 (4); NbCSi, 119.8 (6); Nb'CSi, 142.4 (5). C is ca. 0.2 Å out of the NbNb' Si plane.

The reaction according to eq 23 is particularly interesting;[43] it seems likely that both the bridging CH$_2$ and CO groups of the compound represented in Figure 20 arise from the enolate of acetaldehyde.

An intriguing stepwise *sequential methylation and α-hydride elimination*, involving methane loss from an intermediate such as (XXIIa) or (XXIIb), may account



XXIIa



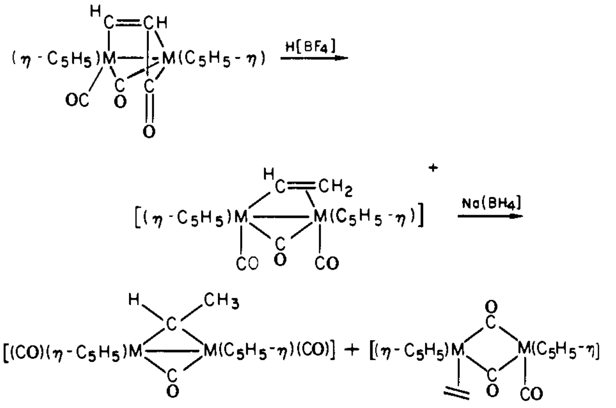
XXIIb

for the formation of the (μ-CH$_2$)$_3$–diruthenium complex (Figure 16) by the reaction according to eq 26.[75] The

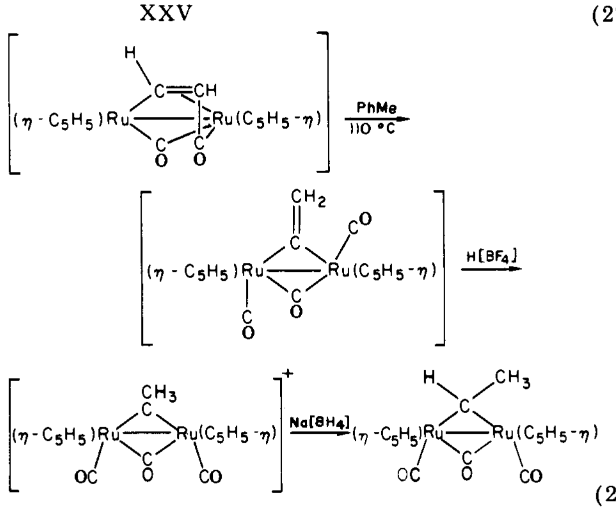
$$[Ru_3O(O_2CMe)_6][MeCO_2] + 2MgMe_2 + PMe_3\ (excess) \rightarrow [Ru_2(\mu\text{-}CH_2)_3(PMe_3)_6] + cis\text{-}[RuMe_2(PMe_3)_4] \quad (26)$$

triply bridged complex reacts with 2 equiv of fluoroboric acid with *methane elimination* to generate [Ru$_2${μ-CH$_2$}$_2$(PMe$_3$)$_4$][BF$_4$]$_2$.[75,76] The reverse type of reaction, the conversion of a μ-CH$_2$-μ-H-Rh$_2$ into a MeRhRh complex has been demonstrated (see eq 42, section IIIC);[77] and the tautomerism [Os$_3$(μ-CH$_2$)(μ-H)$_2$(CO)$_{10}$] $\rightleftharpoons$ [Os$_3$(μ-Me)(μ-H)(CO)$_{10}$] has already been mentioned.[78]

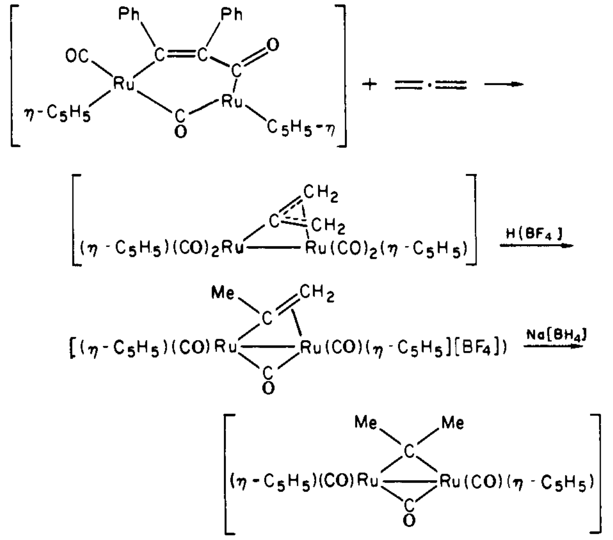
Reaction according to eq 26 probably involves a (μ-methyl)dimetal precursor and this is just one of a number of syntheses in which the nature of the bridge between two metal centers is modified so as to transform to an (μ-alkylidene)dimetal complex. Notable examples of such *bridge modifications* are the *sequential protonation and hydride addition* of eq 27 [M =



XXV (27)

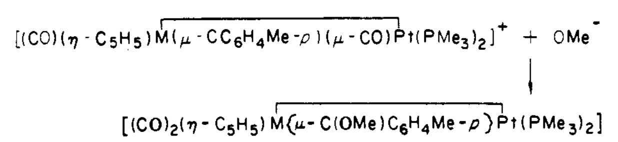


(28)

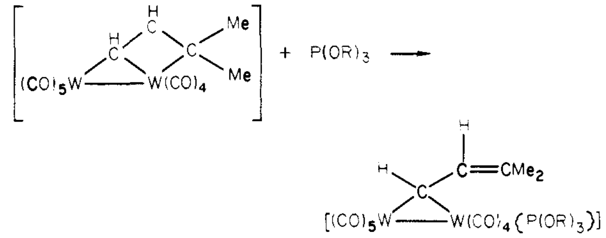


(29)

Fe or Ru],[79] the *hydride additions* of eq 28[80] and to the {σ,π-C(Me)=CH$_2$} bridge of [Ru$_2${μ-C(Me)=CH$_2$}(η-C$_5$H$_5$)$_2$(μ-CO)(CO)$_2$]$^+$,[81] the *proton addition* of eq 29,[77] the *methoxide addition* of eq 30 (M = Mn or Re),[46] the phosphite addition of eq 31 (R = Me or Et),[82] and the



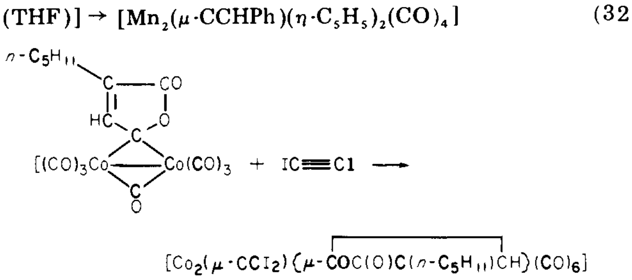
$$[(CO)(\eta\text{-}C_5H_5)M(\mu\text{-}CC_6H_4Me\text{-}p)(\mu\text{-}CO)Pt(PMe_3)_2]^+ + OMe^- \rightarrow [(CO)_2(\eta\text{-}C_5H_5)M\{\mu\text{-}C(OMe)C_6H_4Me\text{-}p\}Pt(PMe_3)_2] \quad (30)$$



(31)

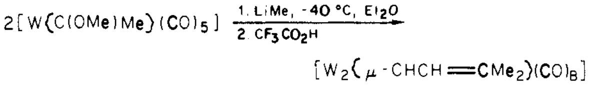
1,2 shift of a bridging acetylene, eq 32 (also for a MnRe analogue),[84] or α-haloacetylene (a presumed intermediate) as exemplified by eq 33.[56] A reaction similar to that of eq 32 has also been carried out with acetylene itself.[51] A related reaction is that between $[Mn\{C{=}C(R)R'\}(\eta\text{-}C_5H_5)(CO)_2]$ and $[Mn(\eta\text{-}C_5H_5)(CO)_2(OEt_2)]$ to yield $[Mn_2\{\mu\text{-}C{=}C(R)R'](\eta\text{-}C_5H_5)_2(CO)_4]$ (R = H, R′ = CO_2Me[85] or R′ = Ph[83]) or a bridging allenedimetal complex, e.g., $[Mn_2\{\mu\text{-}C{=}C{=}CR(R')\}(\eta\text{-}C_5H_5)_2(CO)_4]$.[86]

$$[Mn(\eta\text{-}PhC{\equiv}CH)(\eta\text{-}C_5H_5)(CO)_2] + [Mn(\eta\text{-}C_5H_5)(CO)_2(THF)] \rightarrow [Mn_2(\mu\text{-}CCHPh)(\eta\text{-}C_5H_5)_2(CO)_4] \quad (32)$$

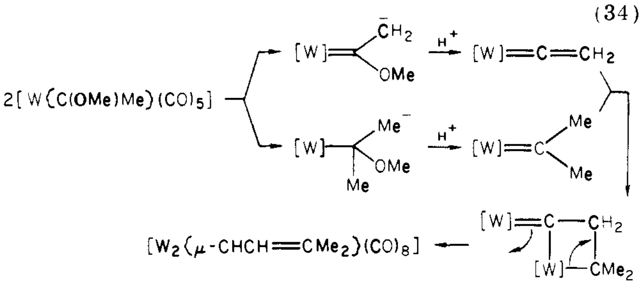


(33)

The remarkable *sequential alkylation and protonation of a carbene–tungsten* complex of eq 34 may have a bearing on certain olefin dismutation reactions;[87] various ^{2}H-labeling experiments are consistent with the reaction pathway of eq 35. A somewhat related reaction (eq 36) had been described earlier;[88] similarly, $[Re_2\{\mu\text{-}C(OMe)Ar\}_2(CO)_8]$ (Ar = Ph or C_6H_4Me-*p*) was obtained from $[Re_2(CO)_{10}]$ and successive treatment with 2LiAr and $2[OMe_3][BF_4]$.[50]



$$2[W\{C(OMe)Me\}(CO)_5] \xrightarrow[2.\ CF_3CO_2H]{1.\ LiMe,\ -40\ °C,\ Et_2O} [W_2\{\mu\text{-}CHCH{=}CMe_2\}(CO)_8] \quad (34)$$

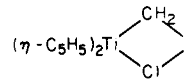


(35)

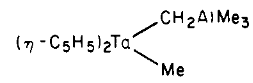
$$2[Fe(CO)_5] \xrightarrow[2.[OEt_3][BF_4]]{1.Li[C_6H_3(OMe)_2\text{-}2,6],\ THF} [Fe_2\{\mu\text{-}C(OEt)C_6H_3(OMe)_2\text{-}2,6\}(CO)_7] \quad (36)$$

An interesting *μ-vinylidene–μ-alkylidyne exchange reaction* is in eq 58 (see section IVB). The transformation of $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_4]$ into $[Fe_2\{\mu\text{-}CCH_2\}(\eta\text{-}C_5H_5)_2(\mu\text{-}CO)(CO)_2]$ by treatment successively with LiMe and CF_3COOH may involve water elimination from a C(OH)Me group.[89]

The interesting methylene-bridged compounds XXIII[37] and XXIV[39] may be regarded as transition-metal ylide complexes stabilized by *coordination of the ylide carbon to an aluminum Lewis acid site.* An analogue of the former compound, $[TiAl(\mu\text{-}CH_2)(\eta\text{-}C_5H_5)_2Cl_2Me]$, was made by methane elimination from $[Ti(\eta\text{-}C_5H_5)_2Cl_2]$ and $^1/_2(AlMe_3)_2$.[32] Using an equimolar proportion of $(AlMe_3)_2$ yielded XXIII,[37] which was also accessible from $[Ti(\eta\text{-}C_5H_5)_2Me_2]$ and $^1/_2(AlClMe_2)_2$, or from the metallacycle $[Ti\{CH_2CH(CH_2Bu\text{-}t)CH_2(\eta\text{-}C_5H_5)_2]$ by reaction with $^1/_2(AlClMe_2)_2$ at −40 °C.[90] Reaction between $[Ti(\eta\text{-}C_5H_5)_2Me_2]$ and $^1/_2(AlMe_3)_2$ gave a compound formulated as XXIII but with μ-CH_3 in place of μ-Cl.[37] Similar compounds having $TiCH_2Zn$ units were believed to form when $ZnMe_2$ was used in place of $^1/_2(AlMe_3)_2$. Reaction of $[Ta(CH_2)(CH_3)(\eta\text{-}C_5H_5)_2]$ and $^1/_2(AlMe_3)_2$, or $[Ta(CH_3)_3(\eta\text{-}C_5H_5)_2]$ and $^1/_2(AlMe_3)_2$ gave compound XXIV;[39] in the latter reaction $[Ta(\eta\text{-}C_5H_5)_2Me_2][AlMe_4]$ may have been an intermediate.



XXIII



XXIV

C. Chemical Properties

Complexes which possess a CH_2 group bridging two bonded transition-metal atoms are of interest, inter alia, because of their possible relationship to methylene groups on metal surfaces in heterogeneous reactions. In this context some of the reactions outlined below may serve as models for elementary steps in certain heterogeneous catalytic reactions of olefins. We distinguish two principal types of behavior: those in which the bridging alkylidene group is implicated and others in which it maintains its integrity.

Protonation may involve attack at the μ-CH_2 group, as in eq 37,[41,75] at the β-atom of a μ-vinylidene [e.g., eq

$$[Ru_2(\mu\text{-}CH_2)_3(PMe_3)_6] \underset{LiMe}{\overset{H^+}{\rightleftharpoons}} [Ru_2(\mu\text{-}CH_2)_2(\mu\text{-}CH_3)(PMe_3)_6]^+ \underset{LiMe}{\overset{H^+(-CH_4)}{\rightleftharpoons}} [Ru_2(\mu\text{-}CH_2)_2(PMe_3)_6]^{2+} \quad (37)$$

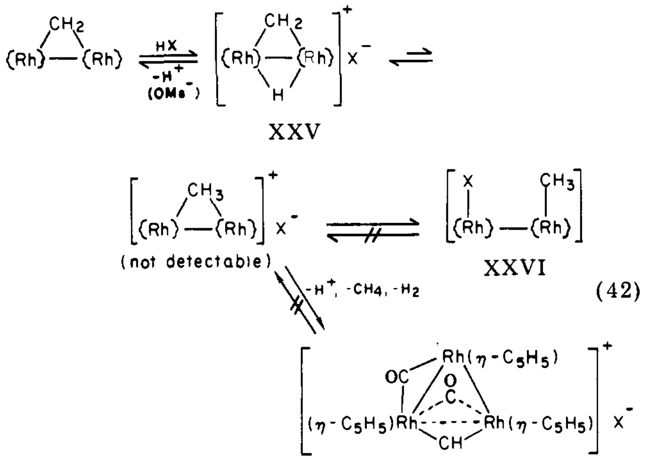
$$[Ru_2(\mu\text{-}CCH_2)(\eta\text{-}C_5H_5)_2(\mu\text{-}CO)(CO)_2] \xrightarrow{H^+} [Ru_2(\mu\text{-}CCH_3)(\eta\text{-}C_5H_5)_2(\mu\text{-}CO)(CO)_2]^+ \quad (38)$$

$$[Mn_2\{\mu\text{-}CCHR\}(\eta\text{-}C_5H_5)_2(CO)_4] \xrightarrow{H^+} [Mn_2(\mu\text{-}CCH_2R)(\eta\text{-}C_5H_5)_2(CO)_4]^+ \quad (39)$$

$$[Rh_2\{\mu\text{-}CH_2\}(\eta\text{-}C_5H_5)_2(CO)_2] \underset{OMe^-}{\overset{H^+}{\rightleftharpoons}} [Rh_2\{\mu\text{-}CH_2\}(\eta\text{-}C_5H_5)_2(CO)_2(\mu\text{-}H)]^+ \quad (40)$$

$$[Pt_2\{\mu_2\text{-}(PhC)_2CO\}(CNBu\text{-}t)_4] \xrightarrow{H^+} [Pt_2\{\mu_2\text{-}(PhC)_2COH\}(CNBu\text{-}t)_4]^+ \quad (41)$$

38 (M = Fe[89] or Ru[80]) or 39 (R = H or Me)[91]], or at the metal centers [e.g., eq 40[77,92,93]], or at a remote site as in eq 41.[67] The μ-CH_2-μ-H dirhodium cation XXV of eq 42 is unstable and if X = Cl or Br rearranges irreversibly into a methyldirhodium halide, XXVI[77] or if H = $OOCCF_3$ or SO_3CF_3 into a Rh_3 cluster XXVII,[93] as depicted in eq 42 {Rh} = [Rh (η-C_5H_5)(CO)]. A protonation of a singly bridged alkylidene (eq 43) has not apparently yet been reported; however, a related electrophilic methylation shows that a cationic alkyldimetal cation may suffer elimination to yield a bridging alkylidynedimetal cation, as in eq 44.[46] There is, of course, a close analogy with the conversion of an (alkoxycarbene)nickel complex into a carbyne–nickel cation.[94] A μ-vinylidene/μ-alkylidyne exchange reaction is shown in eq 58 (section IVB).

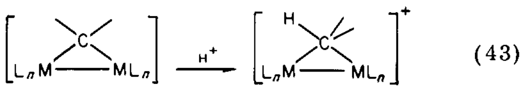


XXV

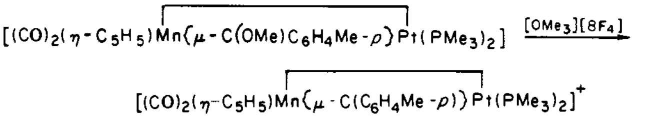
XXVI

(42)

XXVII



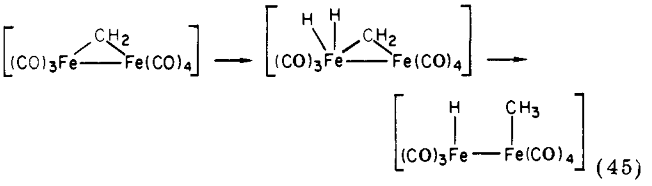
(43)



$$[(CO)_2(\eta\text{-}C_5H_5)Mn(\mu\text{-}C(OMe)C_6H_4Me\text{-}p)Pt(PMe_3)_2] \xrightarrow{[OMe_3][BF_4]} [(CO)_2(\eta\text{-}C_5H_5)Mn(\mu\text{-}C(C_6H_4Me\text{-}p))Pt(PMe_3)_2]^+ \quad (44)$$

Deprotonation of cationic complexes has been observed, cf. reverse of eq 37[41] and 40[77,92,93] using LiMe or NaOMe; with the former reagent, *methylation* (reverse of eq 37) has also been noted.

An interesting *hydrogenolysis* results from the reaction of $[Fe_2(\mu\text{-}CH_2)(\mu\text{-}CO)_2(CO)_6]$ with dihydrogen (200 psi) in benzene at 60 °C when methane (81%), acetaldehyde (5%), and $[Fe_3(CO)_{12}]$ are formed.[47] As the reaction rate decreases, although the organic products are unaltered {$[Fe(CO)_5]$ is the coproduct}, when the reaction is carried out in the presence of CO (400 psi), it is likely that there is initial CO loss, as in eq 45; formation of CH_3CHO may result from CO insertion into the Fe–CH_3 bond, the organic products resulting from a final 1,3-hydrogen shift.

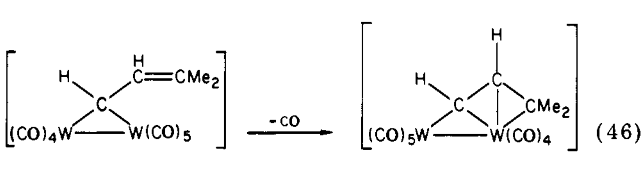


(45)

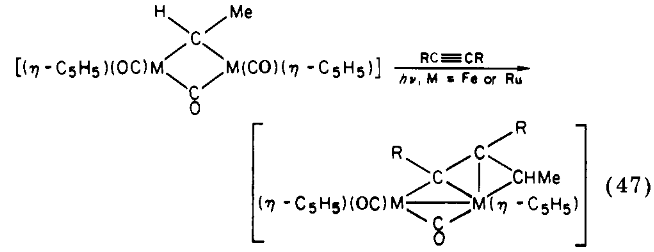
Carbonylation of $[Ru_2(\mu\text{-}CH_2)_3(PMe_3)_6]$ takes place upon reaction with CO (5 atm) at 60 °C in benzene or toluene to yield *trans*-$[Ru(CO)_3(PMe_3)_2]$, but methane was not detected.[41,75]

Carbene transfer from $[Fe_2(\mu\text{-}CH_2)(\mu\text{-}CO)_2(CO)_6]$ to an olefin (olefin homologation) was observed.[47] Thus, C_2H_4 (400 psi in C_6H_6 at 55 °C) gave C_3H_6 (>90%) and C_3H_6 gave mainly isobutene but also n-C_4H_8; sequential metallocyclic intermediates, such as a $[Fe_2\{\mu\text{-}(CH_2)_3\}(CO)_7]$ and $[Fe_2(\mu\text{-}CH_2CH{=}CH_2)(CO)_7H]$ for the C_2H_4 reaction, may be involved. Some of these complexes are *hydrogenation catalysts*, e.g., $[Ru_2(\mu\text{-}CH_2)_2(PMe_3)_6]^{2+}$ [41,75] and $[Fe_2(\mu\text{-}CH_2)(\mu\text{-}CO)_2(CO)_6]$;[47] as for the latter, reaction with C_2H_4 and H_2 gave CH_4 (66%), C_3H_6 (6%), and C_2H_6 (ca. 600%).

Treatment with a neutral ligand may result in simple *ligand displacement*, as in the replacement of CO by PPh_3 in $[(OC)_5M\{\mu\text{-}C(OMe)Ph\}Pt(PMe_3)_2]$ (M = Cr or W),[69] or *change the nature of the bridging ligand*, as in eq 46[49] or 47,[80a] [which exemplifies insertion of an alkyne (M = Fe or Ru, R = H or COOMe)], or eq 48[83] (where fragmentation to mononuclear species has occurred). Reactions of the latter type may be implicated in olefin metathesis (see section XIIE). Sublimation of $[Rh_2(\mu\text{-}CPh_2)(\eta\text{-}C_5Me_5)_2(CO)_2]$ gave $[Rh_2(\mu\text{-}CPh_2)(\mu\text{-}CO)(\eta\text{-}C_5Me_5)_2]$.[45]



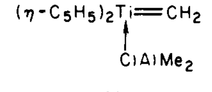
(46)



(47)

$$[Mn_2(\mu\text{-}C{=}CHPh)(\eta\text{-}C_5H_5)_2(CO)_4] + 2PPh_3 \longrightarrow [Mn(C{=}CHPh)(\eta\text{-}C_5H_5)(CO)(PPh_3)] + [Mn(\eta\text{-}C_5H_5)(CO)_2(PPh_3)] \quad (48)$$

Finally, we come to the reactions of $[TiAl(\mu\text{-}CH_2)(\eta\text{-}C_5H_5)_2Me_2(\mu\text{-}Cl)]$, XXIII, and $[TaAl(\mu\text{-}CH_2)(\eta\text{-}C_5H_5)_2Me_4]$, XXIV. The only reaction recorded for the latter is the *bridge splitting* with NMe_3 to yield $[Ta(CH_2)(CH_3)(\eta\text{-}C_5H_5)_2]$ and $AlMe_3.NMe_3$.[39] Compound XXIII undergoes Me/Y *exchange reactions* with $^1/_2$-$(AlY_3)_2$ to yield $[TiAl(\mu\text{-}CH_2)(\eta\text{-}C_5H_5)_2Y_2(\mu\text{-}Cl)]$ (Y = Cl, CD_3, or CH_2CMe_3);[37] a process which may involve the intermediate XXVIII, the formation of which is enhanced by addition of a base such as NMe_3. This postulate also accounts for the ability of compounds XXIII to undergo *olefin homologation* or act as *olefin methathesis catalysts*. Thus, XXIII reacts under ambient conditions in PhMe with (i) C_2H_4, to yield C_3H_6 (32% in 18 h); (ii) C_3H_6, to give i-C_4H_8 (59%) and a trace of methylcyclopropane; (iii) i-C_4H_8, to give 1,2-dimethylcyclopropane (2% with another C_5H_{10}), pro-



XXVIII

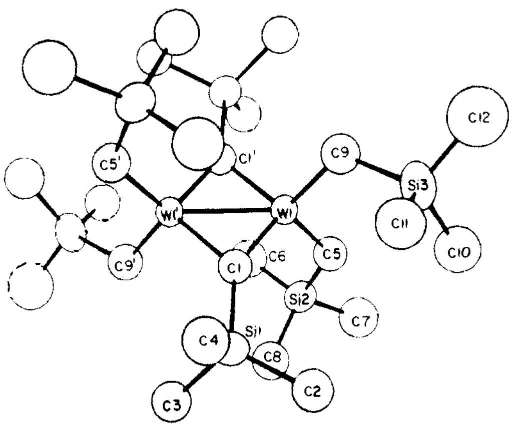
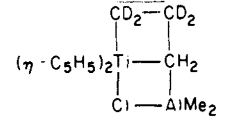


Figure 34. ORTEP drawing of the molecular structure of $[W_2\{\mu\text{-}C(SiMe_3)\}_2(CH_2SiMe_3)_4]$. Reproduced, with permission, from: Chisholm, M. H.; Cotton, F. A.; Extine, M. W.; Murillo, C. A. *Inorg. Chem.* **1978**, *17*, 696. Bond lengths (Å): WW, 2.549 (2); W(1)C(1), 1.85 (3); W(1)C(1′), 1.97 (2); W(1)C(5), 2.13 (3); W(1)C(9), 2.05 (3). Angles (°): WC(1)W, 84 (1); C(1)W(1)C(1′), 96 (1); W(1)C(1)Si, 146 (2); W(1′)C(1)Si, 130 (2).

vided that NMe_3 or THF is present; and (iv) C_2D_4, to give $CD_3CH{=}CH_2$ (1.4 parts) + $CH_2DCD{=}CD_2$ (1 part). A d_6 analogue of XXIII, $[TiAl(\mu\text{-}CH_2)(\eta\text{-}C_5H_5)_2(CD)_3)_2(\mu\text{-}Cl)]$, similarly reacts with C_2H_4 to yield C_3H_6. These results show that sequential intermediates in these olefin reactions are XXVIII and XXIX (shown



XXIX

for the C_2D_4 reaction, which can undergo β-hydrogen transfer to either of the two metal-bound CH_2 or CD_2 groups). These experiments were extended to show that (i) XXIII + $^{13}CH_2{=}CMe_2$ equilibrate in ca. 30 h in C_6D_6 at 52 °C with $[TiAl(\mu\text{-}^{13}CH_2)(\eta\text{-}C_5H_5)_2Me_2(\mu\text{-}Cl)]$ and $i\text{-}C_4H_8$, and (ii) XXIII catalyzes the $^{13}CH_2/^{12}CH_2$ exchange between $^{13}CH_2{=}CMe_2$ and $^{12}CH_2{=}C(CH_2)_5$.[38] Similarly, in the systems XXIII–$CD_2{=}CMe_2$ and $[TiAl(\mu\text{-}CD_2)(\eta\text{-}C_5H_5)_2(CD_3)_2(\mu\text{-}Cl)]\text{-}CH_2{=}CMe_2$, exchange was limited to the hydrogens of the $\mu\text{-}CH_2$ or $\mu\text{-}CD_2$ group and the $\alpha\text{-}CH_2$ or $\text{-}CD_2$ groups of the olefin. Thus compound XXIII is an *olefin metathesis catalyst* and an experiment relevant to the mechanism is its reaction with $t\text{-}BuCH_2CH{=}CH_2$ in presence of pyridine (or 4-vinylpyridine–styrene copolymer) to yield the metallacycle $[Ti\{CH_2CH(CH_2Bu\text{-}t)CH_2\}(\eta\text{-}C_5H_5)_2]$.[90] Compound XXIII acts as a Wittig reagent, converting cyclohexanone into methylenecyclohexane,[37] ethyl acetate into ethyl isopropenyl ether, or esters (generally) or lactones[95] into vinyl ethers. With $PhC{\equiv}CPh$, the titanacyclobutene $[Ti(CH_2CPhCPh)(\eta\text{-}C_5H_5)_2]$ is formed.[38]

IV. μ-Geminal (1,1-) Alkylidynedimetal Complexes, [M-(C-)-M′]

A. Stoichiometry, Structures, and Bonding

The complexes considered in this section have σ-connectivities between each metal atom and the bridging CH group(s) or substituted methyne group(s),

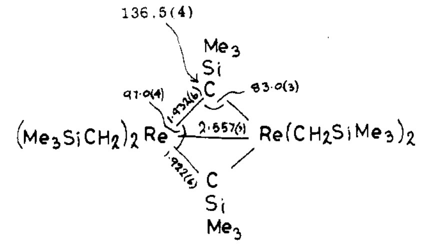
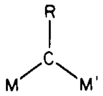


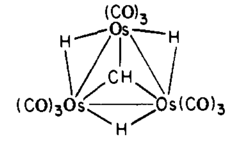
Figure 35. Schematic representation of the molecular structure of $[Re_2\{\mu\text{-}C(SiMe_3)\}_2(CH_2SiMe_3)_4]$.[100] Unlike for the isoleptic Nb (Figure 33) or W (Figure 34) compounds, the bridging is symmetrical. The average Re–CH_2 length is 2.076 (8) Å.

and may formally be regarded as triply anionic, i.e., CH^{3-}. Such compounds are sometimes said to have "bridging carbyne" ligands which is possibly useful in that certain of the synthetic methods are similar to those employed for a terminally bonded carbyne–metal complex such as *trans*-$[W(CPh)(CO)_4I]$; however, we shall not adopt this classification and indeed prefer to regard the compounds as carbene–metal complexes since the bridging carbon atom is approximately sp^2 hybridized, as shown in the basic structural unit XXX.

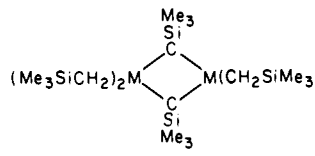


XXX

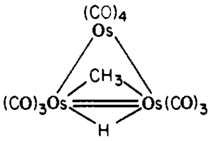
The first alkylidynedimetal complex to have been described was in 1971,[96] XXXI (M = Nb or Ta), and



XXXII



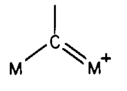
XXXI

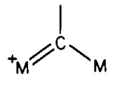


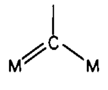
XXXIII

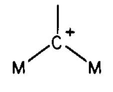
well-characterized compounds are listed in Table VI. Trinuclear compounds are once more excluded, but complex XXXII is particularly interesting, not least because of its synthesis from an equilibrium mixture of the tautomers (XXXIII and XVI), by heating in xylene at 110 °C.[97] The archetypal tetrahedral cluster is that of the $[Co_3(\mu\text{-}CX)(CO)_9]$ family, cf. II.[98] Complexes such as XXXI, as well as similar (μ-alkylidyne)dimetal complexes, may serve as models for a binuclear decomposition pathway of metal alkyls;[15] this is illustrated by the synthesis of XXXI from $Mg(CH_2SiMe_3)Cl + MCl_5$. The terminally bonded alkylidenemetal complexes are, of course, often made by a similar reaction, e.g., $[Ta(CHCMe_3)(CH_2CMe_3)_3]$ from $TaCl_5$ and $LiCH_2CMe_3$.[99]

X-ray diffraction data are now available on a significant number of compounds, see Figures 33–44. In some complexes, the nature of the bridging is unsymmetrical, as in XXXIV, whereas in others the bridging carbon atom is equidistant from the two metal centers, as in XXX. For the former, structure XXXIV provides an adequate account of the bonding, whereas for the latter a valence bond description requires contributions from three principal canonical forms XXXIVa ↔ XXXIVb ↔ XXXV.[80] In complexes XXXI the

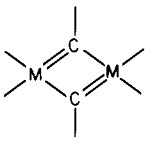

XXXIVa

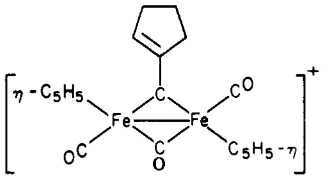

XXXIVb


XXXIV

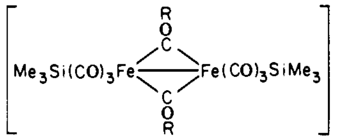

XXXV

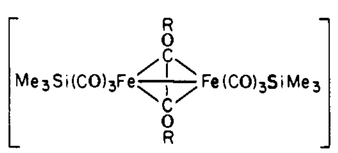
MCMC ring has been described as quasiaromatic,[96,103] in order to account for the observed diamagnetism; a dimetallacyclobuta-1,3-diene formalism, XXXVI (M = Nb or Ta), is an alternative statement, and leaves the metal in the d^0 configuration (see also ref 104). A consequence of the above resonance proposal is that the bridging carbon should be electrophilic. This is borne out by the hydride and methoxide addition, eq 28 and 30, and by the extremely shielded bridging carbon atoms. The outstanding example is the 448.27 ppm carbon-13 NMR chemical shift in XXXVII;[105] the cationic nature of the complex may make its own contribution. This value may be compared with 406 in the Nb and Ta complexes XXXI, 354 in the isoleptic W analogue (Figure 34),[106] 336.5 in the WPt complex of Figure 42,[107] and 201.2 ppm in $[Re_2(\mu\text{-CPh})(\mu\text{-Br})(CO)_8]$.[108]


XXXVI


XXXVII

The isoleptic series of complexes $[M_2\{\mu\text{-C(SiMe}_3)\}_2(CH_2SiMe_3)_4]$ (M = Nb,[96] Ta,[96] W,[109] or Re[100]) is particularly interesting because of the available structural data (Figures 33–35). The presence of M–M(W) and M═M(Re) and absence of a metal bond (Nb, Ta) is reflected not only in the MM lengths, but also in a contraction of the MCM angle for W or Re. It is curious that only in the rhenium complex is the bridge symmetrically situated. The complexes formulated as $[M_2\{\mu\text{-C(CMe}_3)\}_2(CH_2CMe_3)_6]$ (M = Mo or W) have a similar MCMC ring.[110] Another complex in which there may well be a metal–metal double bond is $[CrW\{\mu\text{-C}(C_6H_4Me\text{-}p)\}(\eta\text{-}C_5H_5)(\eta\text{-}C_6Me_6)(CO_4]$, Figure 41.[111] The compounds $[Fe_2\{\mu\text{-C(OR)}\}_2(CO)_6(SiMe_3)_2]$ (R = $SiMe_3$ or H) may have structures XXXIX, but alternatives XL were considered.[112] The AlR_3 adducts of (bridged-carbonyl)dimetal complexes, e.g., $[Fe_2\{\mu\text{-C(OAlR}_3)\}_2(\eta\text{-}C_5H_5)_2(CO)_2]$,[113,114] are somewhat related.


XXXIX


XL

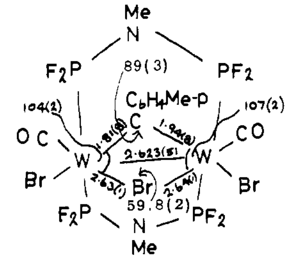


Figure 36. Schematic representation of the molecular structure of $[W_2\{\mu\text{-C}(C_6H_4Me\text{-}p)\}Br_2(CO)_2\{\mu\text{-}(PF_2)_2NMe\}_2]$.[101]

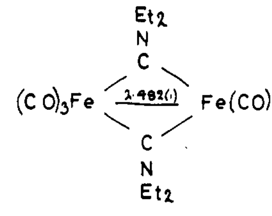
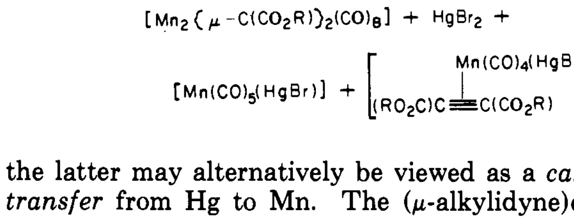


Figure 37. Schematic representation of the molecular structure of $[Fe_2\{\mu\text{-C(NEt}_2)\}_2(CO)_6]$.[102] Bond lengths (Å): FeC_b (av), 1.903 (4); C_bN (av), 1.282 (4); Bond angles (°): FeC_bFe', 81.3 (2); $C_bFe'_bC'_b$, 73.2 (2). FeFe bond is considered to be bent. The short CN distance indicates considerable double bond character.

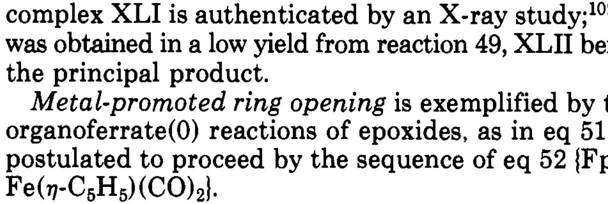
B. Synthesis

We shall consider synthetic processes in a similar sequence to those discussed in section IIIB for (μ-alkylidene)dimetal complexes.

Reactions which might be regarded as *carbyne insertions* are shown in eq 49[115] and 50 (R = Et or Bu^n);[119]



(49)



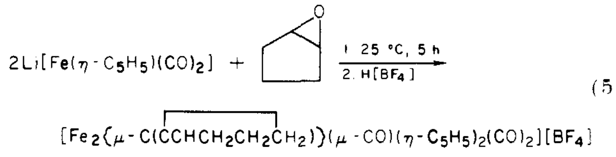
$$2[MnBr(CO)_5] + 2Hg[N_2C(CO_2R)]_2 \longrightarrow [Mn_2\{\mu\text{-C(CO}_2R)\}_2(CO)_8] + HgBr_2 + [Mn(CO)_5(HgBr)] + \left[\begin{array}{c} Mn(CO)_4(HgBr) \\ | \\ (RO_2C)C{\equiv}C(CO_2R) \end{array}\right]$$

(50)

the latter may alternatively be viewed as a *carbyne transfer* from Hg to Mn. The (μ-alkylidyne)diiron complex XLI is authenticated by an X-ray study;[102] it was obtained in a low yield from reaction 49, XLII being the principal product.

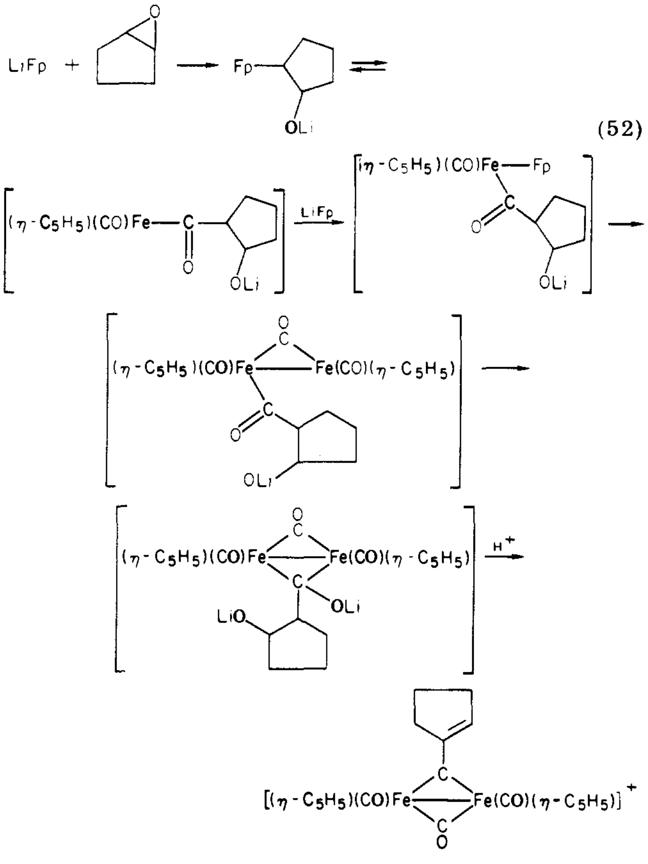
Metal-promoted ring opening is exemplified by the organoferrate(0) reactions of epoxides, as in eq 51,[105] postulated to proceed by the sequence of eq 52 {Fp = $Fe(\eta\text{-}C_5H_5)(CO)_2$}.

The reaction of a carbynemetal complex with a low-oxidation-state metal fragment may be termed *dimetallacyclopropenation*. It was first demonstrated for the process shown in eq 53 [L_n = $(\eta\text{-}C_5H_5)(CO)_2$ or $(OC)_4Br$, R = Me or Ph].[107] Further examples relate



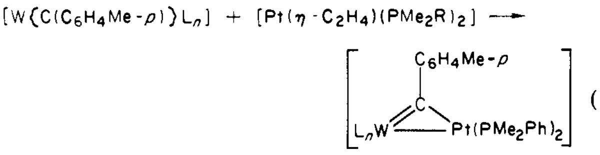
(51)

XLIII



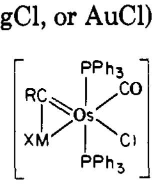
(52)

XLIII



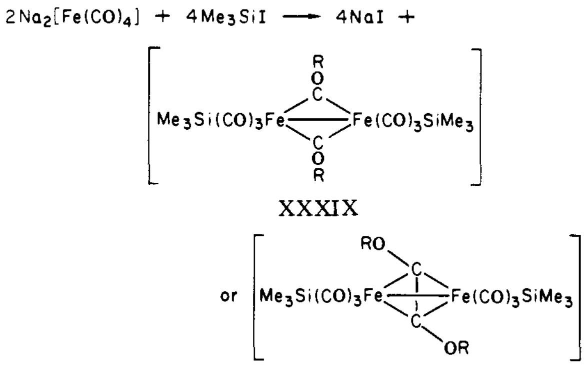
(53)

to the moieties ML_m = $Mn(\eta\text{-}C_5H_4Me)(CO)_2$, $Re(\eta\text{-}C_5H_5)(CO)_2$, $Cr(\eta\text{-}C_6Me_6)(CO)_2$, $Co(\eta\text{-}C_5H_5)(\mu\text{-}CO)$, and $Rh(\eta\text{-indenyl})(CO)$ in place of $Pt(PR_3)_2$ and were generated from $[W\{C(C_6H_4Me\text{-}p)\}(\eta\text{-}C_5H_5)(CO)_2]$ and $[M(CO)L_m]$ by photolysis or (for the Rh compound) a thermal reaction.[111] The Os-coinage metal clusters XLIV (MX = CuI, AgCl, or AuCl) were similarly made from $[Os\{C(C_6H_4Me\text{-}p)\}(CO)(Cl)(PPh_3)_2]$ and CuI, AgCl or $Ag[ClO_4]$–LiCl, or $[AuCl(PPh_3)]$, respectively.[117]



XLIV

A single, but incompletely established (see XXXIX or XL, R = $SiMe_3$) *salt elimination* reaction exists and involves a crucial *migration of an $SiMe_3$ group from metal to oxygen* of a coordinated carbonyl group (eq 54);[112] reaction with dry HCl afforded the analogue with R = H, which was reconverted to its progenitor by treatment with Me_3SiCl/NEt_3.



XXXIX (54)

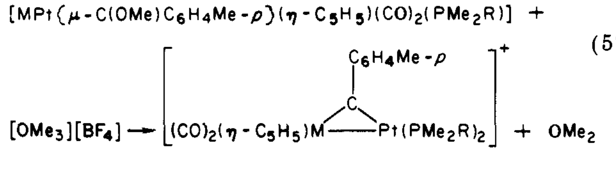
XL

Sequential alkylation and α-hydride abstraction is the route for the synthesis of the isoleptic complexes $[M_2\{\mu\text{-}C(SiMe_3)\}_2(CH_2SiMe_3)_4]$ (M = Nb, Ta, W, or Re): using $NbCl_5$ or $TaCl_5$ and $Mg(CH_2SiMe_3)Cl$,[103] WCl_4 and $Mg(CH_2SiMe_3)_2$ in THF (in petroleum $[W_2(CH_2SiMe_3)_6]$ was obtained),[106] or $Mg(CH_2SiMe_3)Cl$,[118] or $[ReCl_4(THF)_2]$ and $Mg(CH_2SiMe_3)Cl$ (only a trace yield was obtained, the principal product being $[Re_2(CH_2SiMe_3)_8(\mu\text{-}N_2)]$).[100] Similarly, compounds formulated as $[M_2\{\mu\text{-}C(CMe_3)\}_2(CH_2CMe_3)_6]$ (M = Mo or W) were obtained, together with $[M_2(CH_2CMe_3)_6]$, from $MoCl_5$ or WCl_6 and $Li(CH_2CMe_3)$.[110]

We now come to syntheses in which the starting material already has a bridge, between the two metal atoms, which becomes transformed into an alkylidyne bridge. *β-Protonation* of a (μ-vinylidene)dimetal complex to yield $[M_2(\mu\text{-}CMe)(\eta\text{-}C_5H_5)_2(\mu\text{-}CO)(CO)_2]^+$ has already been noted (eq 38);[80,89] see also eq 39 for $[Mn_2(\mu\text{-}CCH_2R)(\eta\text{-}C_5H_5)_2(CO)_4]^+$ (R = H or Me).[91] β-Protonation of a μ-CNMe group is featured in eq 55.[119] *α-Methoxide elimination* from a (μ-methoxyalkylidene)dimetal complex is demonstrated in eq 56[108] and 57 (M = Mn or Re, R = Me or Ph).[46] The other example is (*μ-alkylidyne*) *exchange* (eq 58),[91] the facility of which is in part attributable to the acidity of the β-hydrogens in the alkylidynedimetal cations.

$$[Fe_2\{\mu\text{-}CNMe\}(\eta\text{-}C_5H_5)_2(\mu\text{-}CO)(CO)_2] + H^+ \rightarrow [Fe_2\{\mu\text{-}C(NHMe)\}(\eta\text{-}C_5H_5)_2(\mu\text{-}CO)(CO)_2]^+ \quad (55)$$

$$[Re_2\{\mu\text{-}C(OMe)Ph\}(CO)_9] + Al_2Br_6 \rightarrow [Re_2\{\mu\text{-}CPh\}(\mu\text{-}Br)(CO)_8] + CO + Al_2Br_5OMe \quad (56)$$



(57)

$$[Mn_2\{\mu\text{-}CEt\}(\eta\text{-}C_5H_5)_2(CO)_4][SO_3CF_3] + [Mn_2\{\mu\text{-}C{=}CH_2\}(\eta\text{-}C_5H_5)_2(CO)_4] \xrightarrow{MeNO_2} [Mn_2\{\mu\text{-}C{=}CHMe\}(\eta\text{-}C_5H_5)_2(CO)_4] + [Mn_2\{\mu\text{-}CMe\}(\eta\text{-}C_5H_5)_2(CO)_4][SO_3CF_3] \quad (58)$$

The reaction of the terminal carbyne–metal complex and the chelating ligand $MeN(PF_2)_2$ (eq 59)[101] may be

$$[WBr\{C(C_6H_4Me\text{-}p)\}(CO)_4] + MeN(PF_2)_2 \xrightarrow{h\nu, CH_2Cl_2} [W_2(\mu\text{-}Br)Br_2\{\mu\text{-}C(C_6H_4Me\text{-}p)\}\{\mu\text{-}MeN(PF_2)_2\}_2(CO)_2] \quad (59)$$

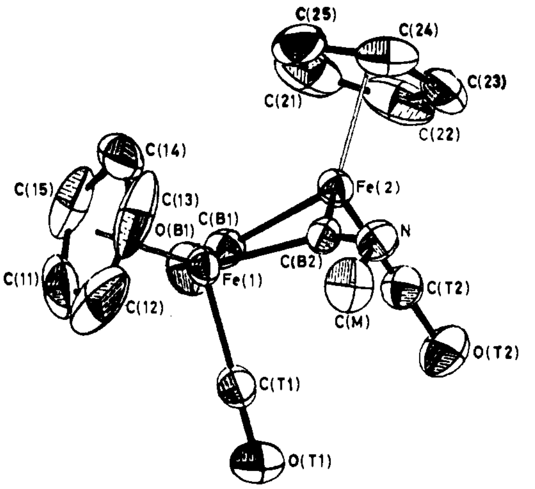


Figure 38. ORTEP drawing of the cation *cis*-$[Fe_2\{\mu\text{-}C(NHMe)\}(\eta\text{-}C_5H_5)_2(\mu\text{-}CO)(CO)_2]^+$. Reproduced, with permission, from: Willis, S.; Manning, A. R.; Stephens, F. S. *J. Chem. Soc., Dalton Trans.* **1979**, 23. Copyright 1979, The Chemical Society, London. Bond lengths (Å): FeFe′, 2.521 (1); FeC(T), 1.78; FeC(B2), 1.87; FeC(B1), 1.95; C(B2)N, 1.28 (1). Bond angles (°): FeC(B2)Fe′, 84.6 (4).

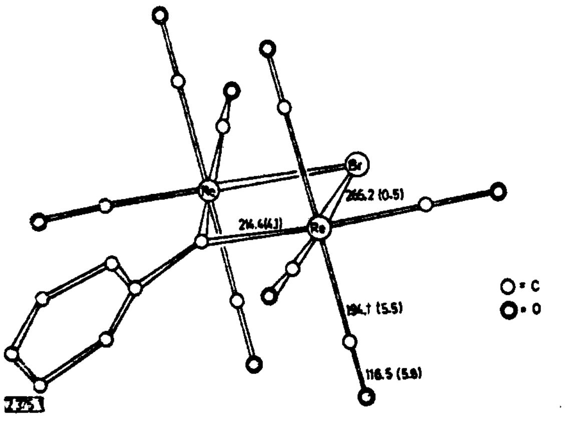


Figure 39. Schematic representation of the molecular structure of $[Re_2(\mu\text{-}CPh)(\mu\text{-}Br)(CO)_8]$. Reproduced, with permission, from: Fischer, E. O., Huttner, G.; Lindner, T. L.; Frank, A.; Kreissl, F. R. *Angew. Chem., Int. Ed. Engl.* **1976**, *15*, 231. Copyright 1976, Verlag Chemie GmbH. Bond lengths (pm): ReC, 214.4 (4.1); ReBr, 265.2 (05). The Ph ring is twisted 72° about the almost planar $Re_2(\mu\text{-}Br)(\mu\text{-}C)(CO)_4$ moiety.

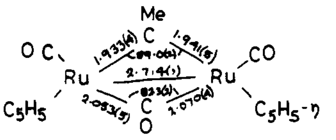


Figure 40. Schematic representation of the molecular structure of the cation in $[Ru_2(\mu\text{-}CMe)(\eta\text{-}C_5H_5)_2(\mu\text{-}CO)(CO)_2][BF_4]$.[80] It is of interrest to compare this with that of the deprotonated $\mu\text{-}CCH_2$ complex of Figure 19.

a further example of a dimetallacyclopropenation. The pathway for eq 60 may involve an intermediate, $[Fe(\eta\text{-}C_5H_5)(COCH_2Ph)CO]$.[105]

$$[Fe(\eta\text{-}C_5H_5)(CH_2Ph)(CO)_2] \xrightarrow[2.H^+]{1.Li[Fe(\eta\text{-}C_5H_5)(CO)_2]} [Fe_2\{\mu\text{-}C(CH_2Ph)\}(\eta\text{-}C_5H_5)_2(\mu\text{-}CO)(CO)_2]^+ \quad (60)$$

C. Chemical Properties

We have already noted (section IIIB) that *nucleophilic addition at the bridging carbon* atom of a (μ-alkylidyne)dimetal complex may provide a route to a (μ-alkylidene)dimetal analogue. Thus, there is simple *methoxide addition* as in eq 30, although this may be accompanied by a CO migration, cf., eq 61;[46] *PMe_3 addition* as in eq 83 (section XI);[60] and *hydride addition* (see final step of eq 28).[80] The *acidity of the β-hydrogen atoms* of a (μ-alkylidyne)dimetal complex is shown by the ready *bridge exchange* in $[Mn_2\{\mu\text{-}C(CH_2R)\}(\eta\text{-}C_5H_5)_2(CO)_4]^+$ (R = H or Me) with $CF_3CO_2^-$ or with a μ-vinylidene analogue, see eq 58.[91]

$$[CrPt\{\mu\text{-}CPh\}(CO)_4(PMe_3)_3]^+ + OMe^- \rightarrow [CrPt\{\mu\text{-}C(CO_2Me)Ph\}(CO)_4(PMe_3)_3] \quad (61)$$

The (μ-alkylidyne)dimetal complexes are often robust for low oxidation states of metals. However, the isoleptic series $[M\{\mu\text{-}C(SiMe_3)\}_2(CH_2SiMe_3)_4]$ (M = Nb,[103]

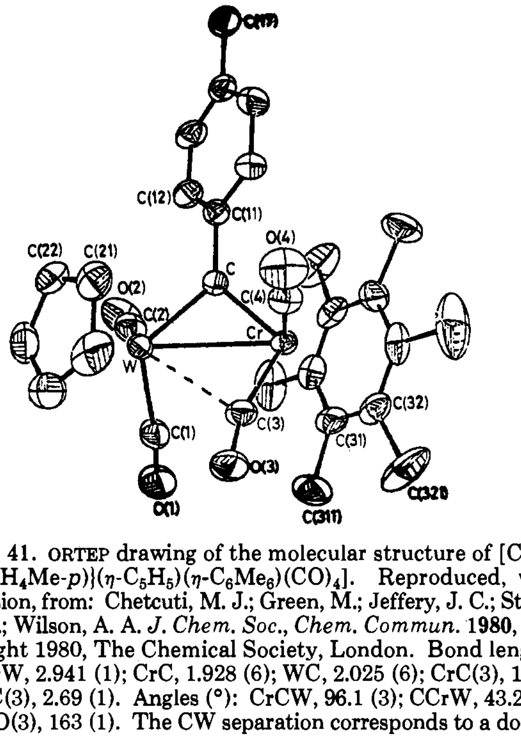


Figure 41. ORTEP drawing of the molecular structure of $[CrW\{\mu\text{-}C(C_6H_4Me\text{-}p)\}(\eta\text{-}C_5H_5)(\eta\text{-}C_6Me_6)(CO)_4]$. Reproduced, with permission, from: Chetcuti, M. J.; Green, M.; Jeffery, J. C.; Stone, F. G. A.; Wilson, A. A. *J. Chem. Soc., Chem. Commun.* **1980**, 948. Copyright 1980, The Chemical Society, London. Bond lengths (Å): CrW, 2.941 (1); CrC, 1.928 (6); WC, 2.025 (6); CrC(3), 1.840 (6); WC(3), 2.69 (1). Angles (°): CrCW, 96.1 (3); CCrW, 43.2 (2); CrC(3)O(3), 163 (1). The CW separation corresponds to a double bond.

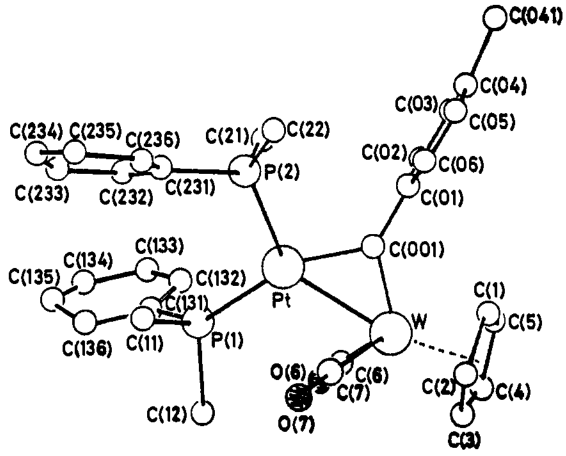


Figure 42. Schematic representation of the molecular structure of $[WPt\{\mu\text{-}C(C_6H_4Me\text{-}p)\}(\eta\text{-}C_5H_5)(CO)_2(PMe_2Ph)_2]$. Reproduced, with permission, from: Ashworth, T. V.; Howard, J. A. K.; Stone, F. G. A. *J. Chem. Soc., Dalton Trans.* **1980**, 1609. Copyright 1980, The Chemical Society, London. WPt, 2.751 (1) Å; WC(001), 1.967 (6) Å, PtC(001), 1.997 (9) Å; the *p*-tolyl ring is inclined at 88.1° to the W-Pt-C plane.

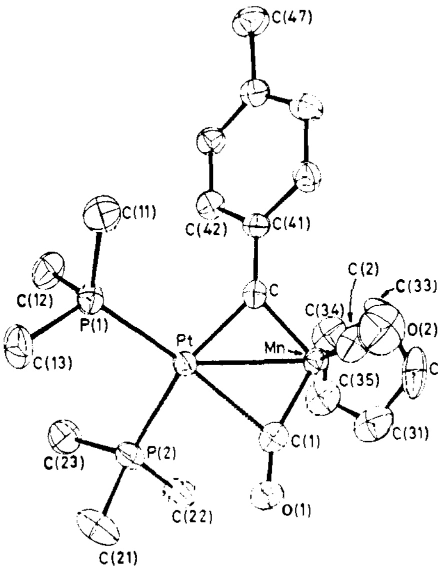


Figure 43. ORTEP drawing of the molecular geometry of the cation $[MnPt\{\mu\text{-}C(C_6H_4Me\text{-}p)\}(\eta\text{-}C_5H_5)(CO)_2(PMe_3)_2]^+$. Reproduced, with permission, from: Howard, J. A. K.; Jeffery, J. C.; Laguna, M.; Navarro, R. Stone, F. G. A. *J. Chem. Soc., Chem. Commun.* **1979**, 1170. Copyright 1979, The Chemical Society, London. The MnC bond was regarded as Mn═C. The plane of the tolyl group is inclined 43° to the Mn(μ-C)Pt plane.

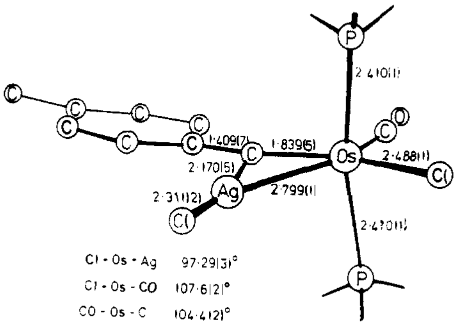


Figure 44. Schematic representation of the molecular structure of $[OsAg\{\mu\text{-}C(C_6H_4Me\text{-}p)\}(CO)(\mu\text{-}Cl)(Cl)(PPh_3)_2]$. Reproduced, with permission, from: Clark, G. R.; Cochrane, C. M.; Roper, W. R.; Wright, L. J. *J. Organomet. Chem.* **1980**, *199*, C35. Copyright 1980, Elsevier Sequoia SA.

Ta,[103] W,[106] or Re[100]) are *air- and moisture-sensitive*, as is the bis(μ-siloxyalkylidyne)diiron complex XXXIX.[112] The latter reacts with hydrogen chloride and the derived (μ-hydroxyalkylidyne)diiron compound is resilylated to the starting material by treatment with Me_3SiCl and NEt_3.

A *metal fragmentation* has been observed, involving transformation of $[Fe_2\{\mu\text{-}C(NEt_2)\}_2(CO)_6]$ into tetrakis(diethylamino)cyclopentadienone–tricarbonyliron complex (XLII) (see eq 49).[115] The complex XLIV (MX = AgCl) with perchloric acid reacted according to eq 62.[117]

$$[OsAg\{\mu\text{-}C(C_6H_4Me\text{-}p)\}(CO)(Cl)_2(PPh_3)_2] + HClO_4 \rightarrow [Os\{C(C_6H_4Me\text{-}p)H\}(CO)(Cl)ClO_4(PPh_3)_2] + AgCl \quad (62)$$

V. (μ-Hydrocarbyl)dimetal and Related Electron-Deficient Complexes, [M(R or Ar)M′]

A. Stoichiometry, Structures, and Bonding

The existence of electron-deficient alkyl-bridging of main-group metals has long been known.[15] Prominent illustrations include $(LiMe)_4$, in which each methyl group is equivalently linked to three metal atoms, XLV, and $(AlMe_3)_2$, in which the bridging is of the type shown in XLVI. The first examples of alkyl-bridged transition-metal complexes were obtained in 1966, but their structural identification awaited later spectroscopic[120]

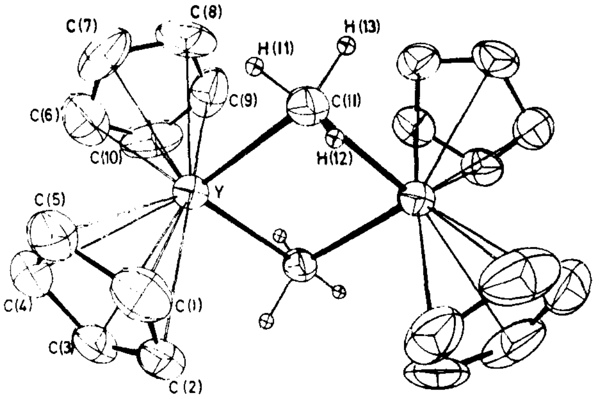


Figure 45. ORTEP drawing of the molecule $[Y_2(\mu\text{-}CH_3)_2(\eta\text{-}C_5H_5)_4]$; the Yb analogue is isostructural. Reproduced, with permission, from: Holton, J.; Lappert, M. F.; Ballard, D. G. H.; Pearce, R.; Atwood, J. L.; Hunter, W. E. *J. Chem. Soc., Dalton Trans.* **1979**, 54. Copyright 1979, The Chemical Society, London. Bond lengths (Å) (Yb in parentheses): YC(Cp), 2.655 (18) [2.613 (13)]; Y–CH_3, 2.545 (11) [2.511 (35)]; C(11)H(11), 0.93; C(11)H(12), 0.86; C(11)H(13), 1.15. Bond angles (°): YCY′, 87.7 (3) [86.6 (3)]; MeYMe′, 92.3 (3) [93.4 (4)]; H(11)C(11)H(12), 111; H(11)C(11)H(13), 95; H(12)C(11)H(13), 118.

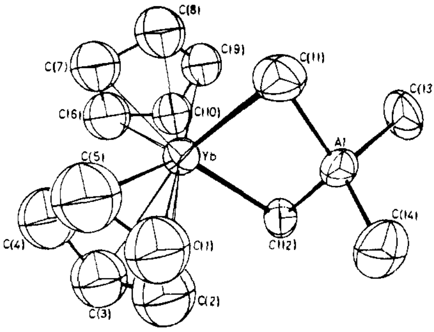


Figure 46. ORTEP drawing of the molecule $[YbAl(\mu\text{-}CH_3)_2(\eta\text{-}C_5H_5)_2Me_2]$. Reproduced, with permission, from: Holton, J.; Lappert, M. F.; Ballard, D. G. H.; Pearce, R.; Atwood, J. L.; Hunter, W. E. *J. Chem. Soc., Dalton Trans.* **1979**, 45. Copyright 1979, The Chemical Society, London. Bond lengths (Å): YbC(Cp), 2.61 (3); YbC_b, 2.59 (3); AlC_b, 2.18 (5); AlC_t, 2.00 (1). Bond angles (°): YbCAl, 78.9 (1.6); C(12)YbC(11), 87.1 (6); C(11)AlC(12), 113.8. The yttrium compound, $[YAl(\mu\text{-}CH_3)_2(\eta\text{-}C_5H_5)_2Me_2]$, is isostructural, the average bridging bond distances being 2.10 (2) Å for CAl and 2.58 (3) Å for CY; the Y...Al separation being 3.056 (6) Å.[129,130]

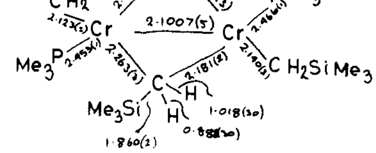
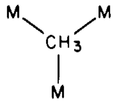
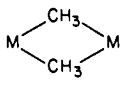


Figure 47. Schematic representation of the molecular structure of $[Cr_2(\mu\text{-}CH_2SiMe_3)_2(CH_2SiMe_3)_2(PMe_3)_2]$.[125] Bond angles (av) (°): PCrCr′, 108.3; C_μCrCr′; 61.7; C_μCrP, 167.1; C_μCrC′$_\mu$, 85.1; CCrCr′, 125.1; C_μCrP, 94.9; CCrP, 88.5; C_μCrC, 169.4. The two bridging groups are in a cis configuration; the chromium atoms are believed to be joined by a quadruple bond.


XLV

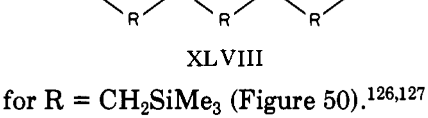

XLVI

M—CH$_3$—M

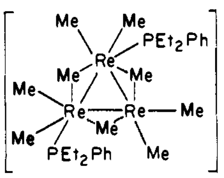
XLVII

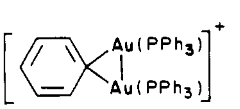
and eventually (1978) X-ray[121] studies (Figure 52). The first case of a single alkyl bridge, as in XLVII, was provided by [{Cu(CH$_2$SiMe$_3$)}$_4$][122,123] (VII). For binuclear metal complexes, bridges of type XLVI have received X-ray verification: Y and Yb (Figure 45),[124,129] Cr (Figure 47),[125] Mn (Figure 51),[126,127] and Ni (Figure 52).[121] In [Y$_2$(μ-CH$_3$)$_2$(η-C$_5$H$_5$)$_4$], the carbon-13 chemical shift of the bridging methyl ligand is at 23.0 ppm,[124] J (^{89}Y–C^{1}H$_3$ = 3.6 Hz and J (^{89}Y–^{13}CH$_3$) = 25.0 Hz. Related to the dimeric metallocene methyls of Y and Yb are the tetramethylaluminates [MAl(μ-CH$_3$)$_2$(η-C$_5$H$_5$)$_2$(CH$_3$)$_2$] (Figure 46).[128,129,130]

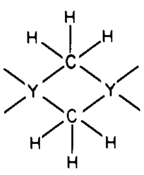
It is interesting that the degree of molecular aggregation of dialkylmanganese [{MnR$_2$}$_n$], is strongly dependent on the nature of the alkyl group, being the dimer for R = CH$_2$CMe$_2$Ph (neophyl) (Figure 51), tetramer for R = CH$_2$CMe$_3$ (neopentyl, XLVIII), or

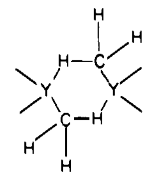

XLVIII

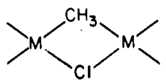
polymer for R = CH$_2$SiMe$_3$ (Figure 50).[126,127] The frozen solution ESR spectrum indicates high spin Mn^{2+}. The unit XLVII has also been established for XLIX[131]


XLIX


LIII


L


LI


LII

and may well be present in [Re$_3$Me$_9$],[132,133] [Re$_3$(CH$_3$)$_9$(PEt$_2$Ph)$_3$],[75] and [Re$_6$(μ-CH$_3$)$_6$(CH$_3$)$_6$(μ-O$_2$CMe)$_6$].[132,133] A methyl bridge is confirmed by X-ray analysis of a salt containing the cation [Ru$_2$(μ-CH$_2$)$_2$(μ-CH$_3$)(PMe$_3$)$_6$]$^+$ (Figure 17).[75] Reference has already been made to [Ru$_2$(μ-CH$_3$)(η-C$_5$H$_5$)$_2$(μ-CO)(CO)$_2$]$^+$ (eq 28),[80] [Os$_3$(μ-CH$_3$)(μ-H)(CO)$_{10}$] (XXXIII),[97] and [TiAl(μ-CH$_2$)(μ-CH$_3$)(η-C$_5$H$_5$)$_2$Me$_2$].[37]

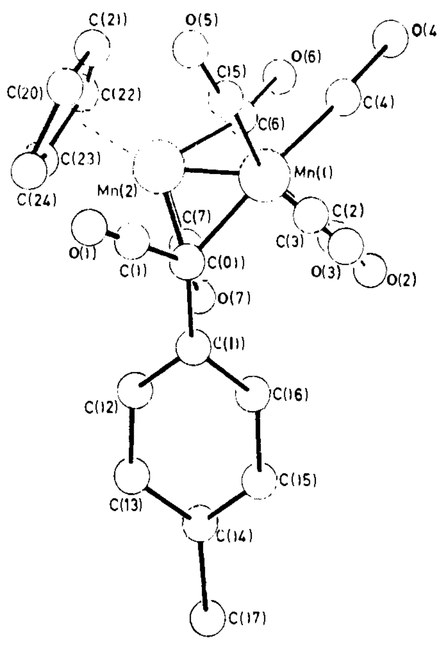


Figure 48. Schematic drawing of the molecular structure of [Mn$_2${μ-C(Tol-p)=CO}(η-C$_5$H$_5$)(CO)$_6$]. Reproduced, with permission, from: Martin-Gil, J.; Howard, J. A. K.; Navarro, R.; Stone, F. G. A. *J. Chem. Soc., Chem. Commun.* **1979**, 1168. Copyright 1979, The Chemical Society, London. Bond lengths (Å): MnMn′, 2.735 (1); Mn(1)C(01) = Mn(2)C(01), 2.128 (4); C(01)C(1), 1.326 (6); C(1)O(1), 1.167 (5). These data suggest a symmetrically sited μ-ketene bridge rather than an ylide bridge (i.e., the CO bond of the bridge is C=O rather than $^-$C≡O$^+$). The corresponding MnRe complex in which Re replaces Mn(1) and Ph replaces p-Tol has been characterized by E. O. Fischer et al. (cited by Martin-Gil et al.).

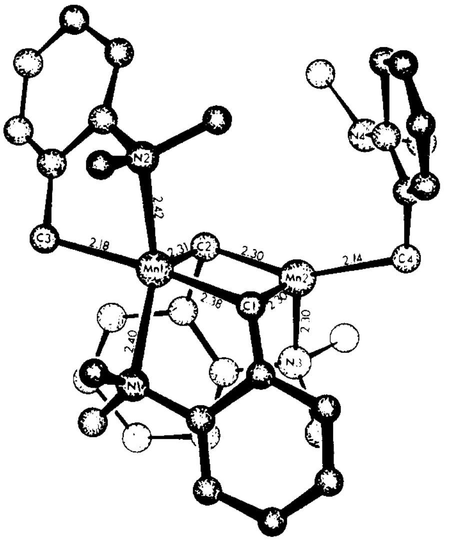


Figure 49. ORTEP drawing of the molecular structure of [Mn$_2$(μ-CH$_2$C$_6$H$_4$NMe$_2$-o)$_2$(CH$_2$C$_6$H$_4$NMe$_2$-o)$_2$]. Reproduced, with permission, from: Manzer, L. E.; Guggenberger, L. J. *J. Organomet. Chem.* **1977**, *139*, C34. Copyright 1977, Elsevier Sequoia SA. Additional parameters: MnMn′, 2.810 (3) Å; Mn(C(1) or C(2),av)Mn′, 74.4°; C(2)MnC(1)(av), 105.6°; Mn(1)C(2)Mn(2)C(1) planar to 0.02 Å.

For [Y$_2$(μ-CH$_3$)$_2$(η-C$_5$H$_5$)$_4$], X-ray diffraction located the bridge hydrogen atoms (Figure 45) and confirmed the symmetrical arrangements (L),[124] rather than the alternative LI which had at one time been considered for (AlMe$_3$)$_2$. Bridge hydrogen atoms were also identified in [Cr$_2$(μ-CH$_2$SiMe$_3$)$_2$(CH$_2$SiMe$_3$)$_2$(PMe$_3$)$_2$] (Figure 47).[125] A mixed μ-Me-μ-Cl bridge (LII has been considered for the unstable [TiAl(η-C$_5$H$_5$)$_2$Me$_3$Cl],[124,134,135] the yttrium analogue,[124] [Ni(η-allyl){MgMe$_2$Cl(OEt$_2$)}],[120] and some tetranuclear Ru$_2$M$_2$ (M = Zn or Mg) complexes.[136] The o-(dimethylamino)benzyl ligand R$^-$ was first introduced for the paramagnetic CrR$_2$ and MnR$_2$; for the latter, the molecular structure in Figure 49 shows that the nitrogen atom is also involved in bonding.[137] The X-ray crystal structures of two further binuclear complexes are noteworthy. That shown in Figure 53 for a (μ-ferrocenyl)digold(I) cation,[138,139] might be the prototype for a wider series of μ-aryl complexes; LIII resembles

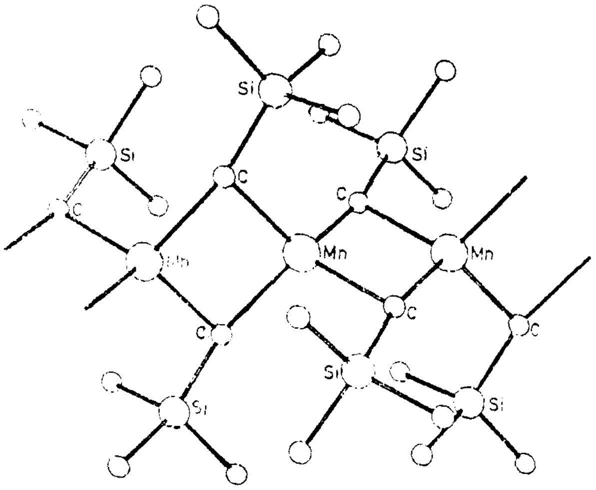


Figure 50. Schematic representation of the molecular structure $[\{Mn(\mu\text{-}CH_2SiMe_3)_2\}_n]$. Reproduced, with permission, from: Andersen, R. A.; Carmona-Guzman, E.; Gibson, J. F.; Wilkinson, G. *J. Chem. Soc., Dalton Trans.* **1976**, 2204. Copyright 1976, The Chemical Society, London. (Citing X-ray data of Hursthouse, M. B. and Raithby, P. R..) No details for this polymer.

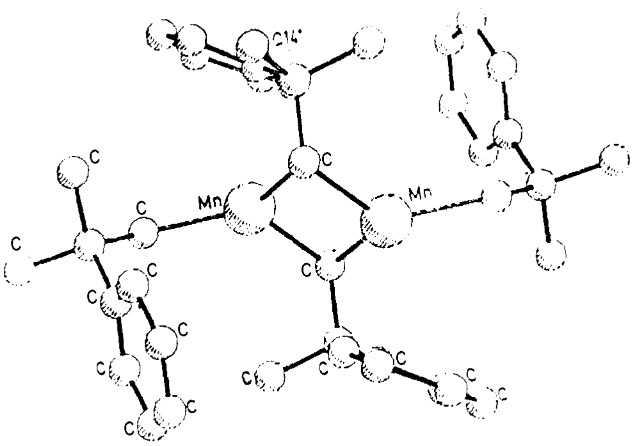


Figure 51. Schematic representation of the molecular structure of $[Mn_2(\mu\text{-}CH_2CMe_2Ph)_2(CH_2CMe_2Ph)_2]$. Reproduced, with permission, from: Andersen, R. A.; Carmona-Guzman, E.; Gibson, J. F.; Wilkinson, G. *J. Chem. Soc., Dalton Trans.* **1976**, 2204. Copyright 1976, The Chemical Society, London. (Citing X-ray data of Hursthouse, M. B.; Raithby, P. R..) The MnC(1) and MnC(2) lengths of ca. 2.7 Å indicate some η^2-interaction of Ph rings with Mn; the ortho-H has close contact to Mn. MnMn′ of 2.719 Å indicates negligible metal–metal interaction.

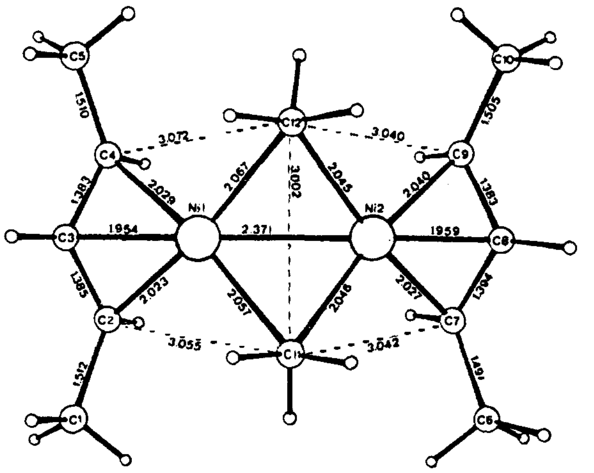


Figure 52. Schematic representation of the molecular structure of $[Ni_2(\mu\text{-}CH_3)_2(\eta\text{-}C_3H_3Me_2\text{-}1,3)_2]$. Reproduced, with permission, from: Krüger, C.; Sekutowski, J. C.; Berke, H.; Hoffmann, R. *Z. Naturforsch. B: Anorg. Chem., Org. Chem.* **1978**, *33*, 1110. Copyright 1978, Verlag der Zeitschrift für Naturforschung. The molecule is folded about its center, the two $\eta^3\text{-}C_5H_9$ lying cis with respect to NiNi′, but trans to the two mutually *cis*-μ-Me bridges. Each Ni atom is in approximately square planar environment; the two $NiMe_2$ planes are at 117.5° with respect to one another.

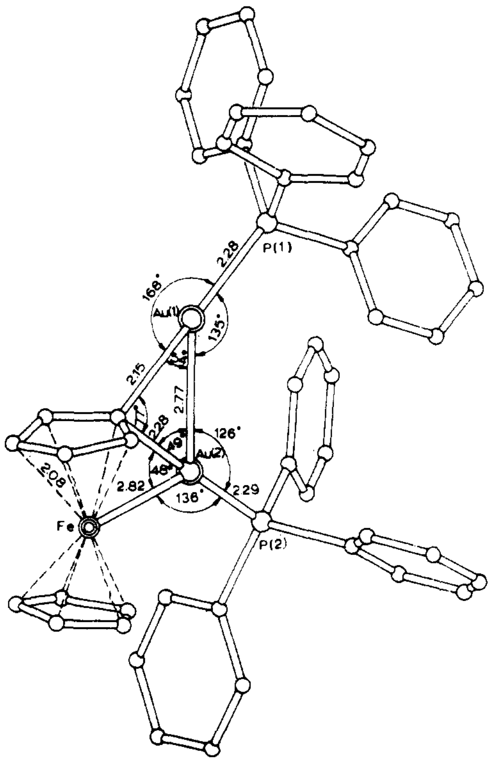
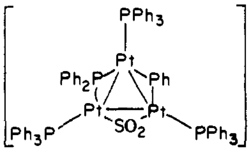


Figure 53. Schematic drawing of the molecular structure of the cation $[Au_2\{\mu\text{-}(\eta\text{-}C_5H_4)Fe(\eta\text{-}C_5H_5)\}(PPh_3)_2]^+$. Reproduced, with permission, from: Nesmeyanov, A. N.; Perevalova, E. G.; Grandberg, K. I.; Lemenovskii, D. A.; Baukova, Y. V.; Afanassova, O. B. *J. Organomet. Chem.* **1974**, *65*, 131. Copyright 1974, Elsevier Sequoia SA. See also: Andrianov, V. G.; Struchkov, Yu. T.; Rossinskaya, E. R. *J. Chem. Soc., Chem. Commun.* **1973**, 338. In the tri-*p*-tolylphosphine analogue, ^{31}P NMR data show that the two $Au(PAr_3)$ units are equivalent, whereas the $Au(PPh_3)$ groups are inequivalent not only in the crystal but also in solution.

a Wheland intermediate in electrophilic aromatic substitution, and is established (X-ray) for the trinuclear complex LIV,[140] and for $[Fe_2\{\mu\text{-}\overline{C(CHO)(PPh_2}\}(\eta\text{-}C_6H_4)(CO)_6]$ (Figure 59).[141] For these complexes the plane of the aryl ring is perpendicular to that of the $\overline{\mathrm{MCM}}$ triangle. Two chelating ortho substituents in $^-C_6H_3(OMe)_2\text{-}2,6$ force the two entities to become coplanar giving the unusual planar five-coordinate carbon atom in the complex of Figure 62, $[V_2\{\mu\text{-}C_6H_3(OMe)_2\text{-}2,6\}_4]$.[142] Aryl bridging by the ligand $^-C_6H_4CH_2NMe_2\text{-}o$ (Ar^-) (in which nitrogen donation is also implicated) is confirmed for $[\{CuAr\}_4]$,[143,144] and is likely in various other arylcopper(I),[146] and arylsilver(I) complexes (often trimers in benzene solution).[145] Similar bridging may be found in $[\{Sc(\eta\text{-}C_5H_5)_2(C{\equiv}CPh)\}_2]$.[147] The structure illustrated in Figure 48 shows a bridging ketenide ligand, $\mu\text{-}^-C(Tol\text{-}p){=}C{=}O$.[148] The ketenide carbonyl bond was also



LIV

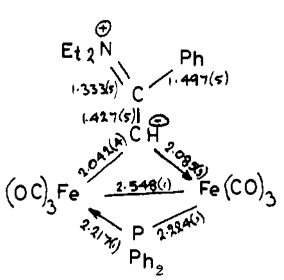


Figure 54. Schematic representation of the molecular structure of $[Fe\{\mu\text{-}CHC(Ph)NEt_2\}(CO)_6(\mu\text{-}Ph_2P)]$.[158] The coordination geometry about the bridging C atom is approximately tetrahedral, whereas about the adjacent C atom and the N atom, it is planar.

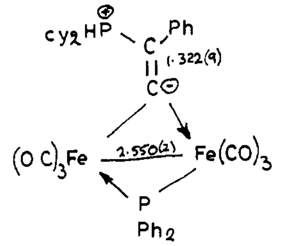


Figure 55. Schematic representation of the molecular structure of $[Fe_2\{\mu\text{-}CC(Ph)PCy_2H\}(CO)_6(\mu\text{-}Ph_2P)]$.[159] The coordination geometry about the bridging C atom approximates to trigonal planes.

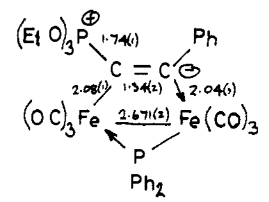


Figure 56. Schematic representation of the molecular structure of $[Fe_2\{\mu\text{-}C(Ph)C[P(OEt)_3]\}(CO)_6(\mu\text{-}PPh_2)]$.[161]

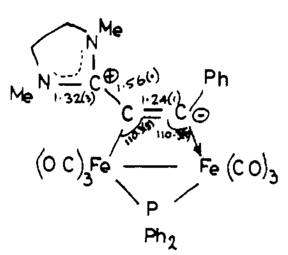


Figure 57. Schematic representation of the molecular structure of $[Fe_2\{\mu\text{-}C(Ph)C[CN(Me)(CH_2)_2NMe]\}(CO)_6(\mu\text{-}PPh_2)]$.[160]

identified by a CO stretching band at 1850 cm^{-1} and a carbon-13 NMR chemical shift at 162.4 ppm; thus, an alternative formulation as a bridging ylide is less attractive.

The Zr^{III} complex $[\{Zr(\eta\text{-}C_5H_5)_2Me\}_2]$ is not well-characterized.[149] The titanium analogue is certainly exceedingly unstable,[124] although a monoetherate is somewhat more robust.[150] There is evidence for a *n*-butyl bridge in $[\{Y(\eta\text{-}C_5H_4Me)_2Bu^n\}_2]$ from NMR spectroscopy.[151]

For tetramethylaluminates of formula $[MAl(\mu\text{-}CH_3)_2(\eta\text{-}C_5H_4R)_2(CH_3)_2]$ (M = Sc,[128] Y,[128,152] Gd,[128] Dy, Ho, Er, Tm, Yb, or Ti,[152]) there are a number of interesting features. IR bands at 1250 and 1235 cm^{-1} arise from vibrations associated with bridging methyl groups, cf., 1368 and 1195 cm^{-1} in the corresponding $[M_2(\mu\text{-}CH_3)_2(\eta\text{-}C_5H_5)_4]$.[124] The Sc compound (R = H) is nonfluxional at ambient temperatures, there being distinct NMR signals for both bridging and terminal methyl groups, but at +100 °C these environments become coincident. For the Y analogue rapid site exchange is already apparent at +40 °C and $\Delta G^{\ddagger}_{392K}$ for site ex-

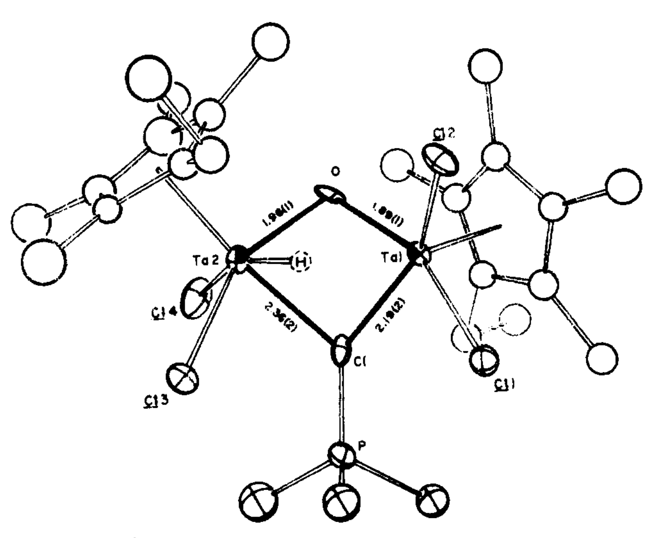


Figure 58. Schematic representation of the molecular structure of $[Ta_2\{\mu\text{-}CH(PMe_3)\}(\eta\text{-}C_5Me_4Et)_2Cl_4(H)(\mu\text{-}O)]$. Reproduced, with permission, from: Belmonte, P.; Schrock, R. R.; Churchill, M. R.; Young, W. J. *J. Am. Chem. Soc.* **1980**, *102*, 2858. The terminal hydride ligand on Ta(2) is shown in its deduced position. The coordination environment about Ta(1) is of the "four legged piano stool type" with equivalent Cp–Ta(1)–L angles (mean 105°). The Ta(1)–Ta(2) distance is 2.992 (1) Å. The mean P–Me distance is 1.84 Å and the Me_3PCH moiety is regarded as a phosphonium ylide.

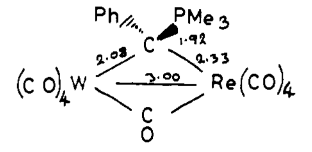


Figure 59. Schematic representation of the molecular structure of $[WRe\{\mu\text{-}C(Ph)PMe_3\}(\mu\text{-}CO)(CO)_8]$.[60] The Re and W atoms cannot be distinguished; however, the assignment is preferred based on M–C bond lengths.

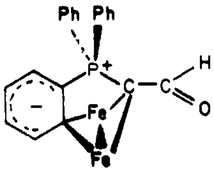


Figure 60. Valence bond representation of the molecular structure of $[Fe_2\{\mu\text{-}C(CHO)PPh_2\}(\mu\text{-}C_6H_4)(CO)_6]$. Reproduced, with permission, from: Churchill, M. R.; Rotella, F. J. *Inorg. Chem.* **1978**, *17*, 2614. There are two crystallographically independent molecules within the asymmetric unit. Bond lengths (Å): FeFe′, 2.471 (1) and 2.466 (1); Fe–C_6H_4, 2.001 (6) and 2.159 (5) for molecule 1 and 1.986 (6) and 2.185 (6) for molecule 2; Fe–C-CHO, 2.037 (6) and 2.047 (6) for molecule 1 and 2.036 (6) and 2.052 (6) for molecule 2. The C_6H_4 ring resembles a Meisenheimer intermediate as found in nucleophilic aromatic substitution.

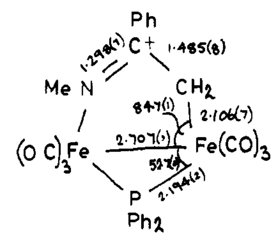
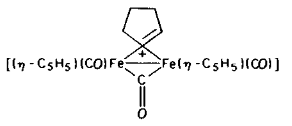
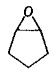
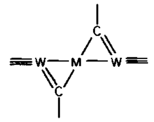


Figure 61. Schematic representation of the molecular structure of $[Fe_2\{\mu\text{-}CH_2\text{-}CPh\text{-}N(Me)\}(CO)_6(\mu\text{-}PPh_2)]$.[158]

Table VI. μ-Geminal (1,1-) Alkylidynedimetal Complexes (See Also Table VIa)

compound	preparation	comments	ref
$[M_2(\mu\text{-}CSiMe_3)_2(CH_2SiMe_3)_4]$	$Me_3SiCH_2MgCl + MCl_5$	M = Nb or Ta X-ray (M = Nb) (Figure 33)	96, 103
$[CrPt(\mu\text{-}CPh)(CO)_4(PMe_3)_3][BF_4]$	$[CrPt\{C(OMe)Ph\}(CO)_4(PMe_3)_3] + Me_3O[BF_4]$	X-ray, tungsten analogue containing $\mu\text{-}CC_6H_4Me\text{-}p$	46, *a*
$[W_2(\mu\text{-}CSiMe_3)_2(CH_2SiMe_3)_4]$	$Mg(CH_2SiMe_3)_2 + WCl_6/THF$ or WCl_4	X-ray (Figure 34)	109
$[M_2(\mu\text{-}CCMe_3)_2(CH_2CMe_3)_4]$	$LiCH_2CMe_3 + MCl_x$	M = Mo or W structure by analogy with Me_3SiCH_2 derivatives	110
$[W_2\{\mu\text{-}C(C_6H_4Me\text{-}p)\}Br_2(CO)_2\{\mu\text{-}(PF_2)_2NMe\}_2]$	$[W(CC_6H_4Me\text{-}p)Br(CO)_4] + F_2PN(Me)PF_2/h\nu$	X-ray (Figure 36)	101
$[WPt(\eta\text{-}C_5H_5)\{\mu\text{-}C(C_6H_4Me\text{-}p)\}(CO)_2(PR_3)_2]$	$[W(\eta\text{-}C_5H_5)(CO)_2\{C(C_6H_4Me\text{-}p)\}] + [Pt(C_2H_4)(PR_3)_2]$	$PR_3 = PMe_3$ or PMe_2Ph (X-ray) (Figure 42)	107, *b*
$[CrW(\eta\text{-}C_5H_5)\{\mu\text{-}C(C_6H_4Me\text{-}p)\}(\eta\text{-}C_6Me_6)(CO)_4]$	$[W(\eta\text{-}C_5H_5)_2(CO)_2\{C(C_6H_4Me\text{-}p)\}] + [Cr(\eta\text{-}C_6Me_6)(CO)_3]$	X-ray (Figure 41)	111
$[WM(\eta\text{-}C_5H_5)\{\mu\text{-}C(C_6H_4Me\text{-}p)\}(CO)_2L_x]$	$[W(\eta\text{-}C_5H_5)(CO)_2\{C(C_6H_4Me\text{-}p)\}] + ML_x + h\nu$	$ML_x = [Mn(\eta\text{-}C_5H_4Me)(CO)_3]$, $[Re(\eta\text{-}C_5H_5)(CO)_3]$, $[Rh(\eta\text{-}indenyl)(CO)_2]$ (X-ray), $[Co(\eta\text{-}C_5H_5)(CO)_2]$	111
$[Mn_2(\eta\text{-}C_5H_5)_2(\mu\text{-}CR)(CO)_4][CF_3CO_2]$	$[Mn_2(\eta\text{-}C_5H_5)_2(CO)_4(\mu\text{-}CCHR)] + CF_3CO_2H$	R = Me or Et	91
$[Mn_2(\mu\text{-}CCO_2R)_2(CO)_8]$	$[Mn(CO)_5Br] + Hg(N_2CCO_2R)_2$	R = Et or But	*c*
$[MPt(\eta\text{-}C_5H_5)\{\mu\text{-}C(C_6H_4Me\text{-}p)\}(CO)_2(PMe_3)_2]\cdot[BF_4]$	$[M(\eta\text{-}C_5H_5)(CO)_2\{\mu\text{-}C(OMe)C_6H_4Me\text{-}p\}\text{-}Pt(PR_3)_2] + Me_3O[BF_4]$	M = Mn(X-ray) or Re (Figure 43)	46, *a*
$[Re_2(\mu\text{-}CPh)(\mu\text{-}Br)(CO)_8]$	$[Re_2(CO)_8C(OMe)Ph] + Al_2Br_6$	X-ray (Figure 39)	108
$[Re_2(\mu\text{-}CSiMe_3)_2(CH_2SiMe_3)_4]$	$ReCl_4(THF)_2 + MgCH_2SiMe_3(Cl)$	X-ray (Figure 35)	100
$[Fe_2(\mu\text{-}COSiMe_3)_2(Me_3Si)_2(CO)_6]$	$Me_3SiI + Na_2[Fe(CO)_4]$		112
$[Fe_2(\mu\text{-}COH)_2(Me_3Si)_2(CO)_6]$	acidification of the $\mu\text{-}COSiMe_3$ complex	X-ray	112
$[Fe_2(\eta\text{-}C_5H_5)_2(\mu\text{-}COAlEt_3)(CO)_2]$	$[\{Fe(\eta\text{-}C_5H_5)(CO)_2\}_2] + AlEt_3$	X-ray	*d*
$[Fe_2\{\mu\text{-}C(NEt_2)\}_2(CO)_6]$	$[Fe(CO)_5] + Et_2NC\equiv CNEt_2/h\nu$	X-ray (Figure 37)	115
$[Fe_2(\eta\text{-}C_5H_5)_2\{\mu\text{-}C(NHMe)\}(\mu\text{-}CO)(CO)_2]^+$	$[Fe_2(\eta\text{-}C_5H_5)_2(CO)_{4\text{-}n}(CNR)_n] + H[BF_4]$	X-ray, $n = 1$ or 2 (Figure 38)	119, *c*
$[Ru_2(\eta\text{-}C_5H_5)_2(\mu\text{-}CMe)(\mu\text{-}CO)(CO)_2][BF_4]$	$[Ru_2(\eta\text{-}C_5H_5)_2(CO)_2(\mu\text{-}CO)(\mu\text{-}C{=}CH_2)] + H[BF_4]$	X-ray (Figure 40)	80
	$Li[Fe(\eta\text{-}C_5H_5)(CO)_2]$ +  + $H[BF_4]$		105
$[M\{W(\eta\text{-}C_5H_5)(CO)_2(\mu\text{-}CC_6H_4Me\text{-}p)\}_2]$	$[W(\eta\text{-}C_5H_5)(CO)_2\{\equiv CC_6H_4Me\}] + [Pt(C_2H_4)_3]$, $[Pd(C_7H_{10})_3]$, or $[Ni(\eta\text{-}C_8H_{12})_2]$	M = Ni, Pd, or Pt X-ray (M = Ni and Pt) linear structure 	*f*
	Miscellaneous Trimetallic Complexes		
$[Fe_3(\eta\text{-}C_5H_2Me_2C_2H_3)(\mu\text{-}CEt)(CO)_8]$	$[Fe_3(CO)_{12}] + MeC\equiv CH$	X-ray	*g*
$[HFe_3(\mu\text{-}COMe)(CO)_{10}]_2(DMTED)$	$[DMTED][Fe_3(CO)_{11}] + CH_3SO_3F$	X-ray (DMTED = *N,N'*-dimethyltriethylenediamine cation(2+)	*h*
$[HM_3(\mu\text{-}COMe)(CO)_{10}]$	$[HM_3(\mu\text{-}CO)(CO)_{10}]^- + MeSO_3F$	M = Fe, Ru or Os X-ray (M = Fe and Ru)	105, *i*
$[H_3M_3(\mu\text{-}COMe)(CO)_9]$	H_2 + monohydrido complex		105, *i*
$[H_3M_3(\mu\text{-}CMe)(CO)_9]$	$[H_4M_4(CO)_{12}] + C_2H_4$	M = Fe, Ru, or Os, X-ray (M = Fe and Ru)	*j*
$[Ru_3(\eta\text{-}C_5H_5)(\mu\text{-}CCH_2Bu\text{-}t)(CO)_8]$	$[HRu_3(CO)_9C_2Bu\text{-}t] + C_5H_6$		*k*
$[H_3Os_3(\mu\text{-}CH)(CO)_9]$	$[HOs_3(CO)_{10}CH_3] \rightleftharpoons$		78
$[Co_3(\mu\text{-}CR)(CO)_9]$	e.g., $[Co_2(CO)_8] + CRCl_3$ or $[HCCo(CO)_9] + HgR_2$	R = Hal, Alk, Ar, etc	98
$[M_3(\eta\text{-}C_5H_5)_3(\mu\text{-}CNEt_2)_2]$	$[M(\eta\text{-}C_5H_5)(CO)_2] + Et_2NC\equiv CNEt_2$	M = Co or Rh	115
$[Ni_3(\eta\text{-}C_5H_4R)(\eta\text{-}C_5H_5)_2(\mu\text{-}CPh)]$	$[Ni(\eta\text{-}C_5H_5)_2] + PhCH_2MgCl$	R = H or CH_2Ph	*l*
$[PtWFe(\eta\text{-}C_5H_5)\{\mu\text{-}C(C_6H_4Me\text{-}p)\}(CO)_6(PR_3)]$	$[Fe_2(CO)_9] + [PtW(\eta\text{-}C_5H_5)\{\mu\text{-}C(C_6H_4Me\text{-}p)\}\text{-}(CO)_2(PR_3)_2]$	$PR_3 = PEt_3$ or $PMePh_2$, X-ray	*m*

$[FeRhW(\eta\text{-}C_5H_5)(\eta\text{-}C_9H_7)\{\mu\text{-}C(C_6H_4Me\text{-}p)\}\text{-}(\mu\text{-}CO)(CO)_5]$	$[RhW(\eta\text{-}C_5H_5)(\eta\text{-}C_9H_7)\{\mu\text{-}C(C_6H_4Me\text{-}p)\}\text{-}(CO)_3] + [Fe_2(CO)_9]$	X-ray; Co and Rh analogues also prepared via reaction with $[Co_2(CO)_8]$ and $[Rh_2(\eta\text{-}C_5H_5)_2(\mu\text{-}CO)_2]$, respectively	*m*
$[Mo_3O(\mu\text{-}CMe)(OAc)_6(H_2O)_3]^+$	$[Mo(CO)_6] + AcOH/(AcO)_2O/\Delta$	X-ray, W complexes also prepared	*n*
$[HFe_4(\mu\text{-}CH)(CO)_{12}]$	$[Fe_4C(CO)_{12}] + H_2$	X-ray	*o*
$[Rh_3(\eta\text{-}C_5H_5)_3(\mu\text{-}CH)(CO)_2][PF_6]$	$[Rh(\eta\text{-}C_5H_5)_2(CO)_2(\mu\text{-}CH_2)] + CF_3CO_2H$	X-ray	*p*
$[Ni_3(\eta\text{-}C_5H_5)_3(\mu\text{-}CR)]$	$[Ni(\eta\text{-}C_5H_5)_2] + RCH_2Li$	R = CMe_3 or $SiMe_3$	*q*

[a] Howard, J. A. K.; Jeffery, J. C.; Laguna, M.; Navarro, R.; Stone, F. G. A. *J. Chem. Soc., Dalton Trans.* 1981, 751. [b] Ashworth, T. V.; Howard J. A. K.; Stone, F. G. A. *J. Chem. Soc., Chem. Commun.* 1979, 42. [c] Herrmann, W. A. *Angew. Chem., Int. Ed. Engl.* 1974, *13*, 812; *J. Organomet. Chem.* 1975, *97*, 1. [d] Kim, N. E.; Nelson, N. J.; Shriver, D. F. *Inorg. Chim. Acta.* 1973, 7, 393. [e] Willis, S.; Manning, A. R.; Stephens, F. S. *J. Chem. Soc., Dalton Trans.* 1979, 23. [f] Ashworth, T. V.; Chetcuti, M. J.; Howard, J. A. K.; Stone, F. G. A.; Wisbey, S. J.; Woodward, P. *J. Chem. Soc., Dalton Trans.* 1981, 763. [g] Aime, S.; Milone, L.; Sappa, E.; Tiripicchio, A. *J. Chem. Soc., Dalton Trans.* 1977, 227. [h] Shriver, D. F.; Lehman, D.; Strope, D. *J. Am. Chem. Soc.* 1975, *97*, 1594. [i] Keister, J. B. *J. Chem. Soc., Chem. Commun.* 1979, 214. [j] Wong, K. S.; Fehlner, T. P. *J. Am. Chem. Soc.* 1981, *103*, 966. Sheldrick, G. M.; Yesinowski, J. P. *J. Chem. Soc., Dalton Trans.* 1975, 873. Deeming, A. J.; Underhill, M. *J. Chem. Soc., Chem. Commun.* 1973, 277. [k] Raverdino, V.; Aime, S.; Milone, L.; Sappa, E. *Inorg. Chim. Acta.* 1978, *30*, 9. [l] Voyevodskaya, T.; Pribytkova, I. M.; Ustynyuk, Y. A. *J. Organomet. Chem.* 1972, *37*, 187. [m] Chetcuti, M.; Green, M.; Howard, J. A. K.; Jeffery, J. C.; Mills, R. M.; Pain, G. N.; Porter, S. J.; Stone, F. G. A.; Wilson, A. A.; Woodward, P. *J. Chem. Soc., Chem. Commun.* 1980, 1057; *J. Chem. Soc., Dalton Trans.* 1982, 1757, 2475; see also Chetcuti, M. J.; Marsden, K.; Moore, I.; Stone, F. G. A.; Woodward, P. *Ibid.* 1982, 1749. [n] Bino, A.; Cotton, F. A.; Dori, Z. *J. Am. Chem. Soc.* 1981, *103*, 243. [o] Beno, M. A.; Williams, J. M.; Tachikawa, M.; Muetterties, E. L. *J. Am. Chem. Soc.* 1981, *103*, 1485. [p] Dimas, P. A.; Duesler, E. N.; Lawson, R. J.; Shapley, J. R. *J. Am. Chem. Soc.* 1980, *102*, 7787. Herrmann, W. A.; Plank, J.; Guggolz, E.; Ziegler, M. L. *Angew. Chem., Int. Ed. Engl.* 1980, *20*, 651. [q] Booth, B. L.; Casey, G. C. *J. Organomet. Chem.* 1979, *178*, 371.

TABLE VII. μ-Alkyl or Aryl Electron-Deficient Dimetal Complexes (See Also Table VIIa)

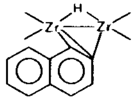
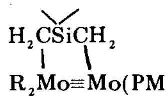
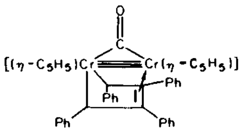
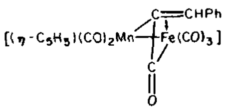
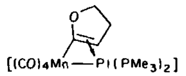
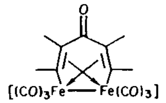
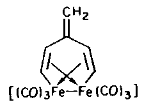
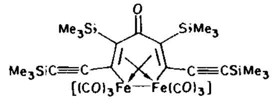
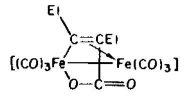
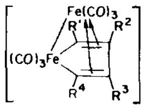
compound	preparation	comments	ref
$[Ti\{C_6H_5\}_2]_n$	$[Ti(\eta\text{-}C_5H_5)_2R_2] + C_6H_5Li$	polymeric probably aryl-bridged	*a*
$[Ti\{CH_2C_6H_5\}_2]_2$	$[Ti(\eta\text{-}C_5H_5)_2R_2] + C_6H_5CH_2Li$	dimeric probably aryl-bridged	*a*
$[Zr_2(\eta\text{-}C_5H_5)_4\{\mu\text{-}CH_3\}_2]$	$[Zr(\eta\text{-}C_5H_5)_2Me_2] + H_2$	characterized by IR and molecular weight data	149
$[Zr_2(\eta\text{-}C_5H_5)_4\{\mu\text{-}CH_2O\}Cl_2]$	$Zr(\eta\text{-}C_5H_5)_2(H)Cl + CO$	bridge structure not well-characterized	*b*
$[Zr_2(\eta\text{-}C_5H_5)_4\{\mu\text{-}C_{10}H_7\}(\mu\text{-}H)]$	$[Zr(\eta\text{-}C_5H_5)_2Cl_2] + K[C_{10}H_8]$	X-ray shows bridging hydride and bridging naphthyl  	*c*
$[V_2\{\mu\text{-}C_6H_3(OMe)_2\text{-}2,6\}_4]$	$[VCl_3(THF)_3] + 4LiC_6H_3(OMe)_2\text{-}2,6$	two types of bridge identified by X-ray (Figure 63): (1) aryl bridge; (2) —C—C—O	142
$[Cr_2\{\mu\text{-}CH_2SiMe_3\}_2(CH_2SiMe_3)_2(PMe_3)_2]$	$[Cr_2(OAc)_4] + Mg(CH_2SiMe_3)_2 + PMe_3$	X-ray (Figure 47) shows alkyl-bridged structure. The molybdenum complex has a different structure  H_2CSiCH_2 $R_2Mo{\equiv}Mo(PMe_3)_3$	13, 76
$[[Mn(\mu\text{-}CH_2SiMe_3)_2]_n]$	$MnCl_2 + Mg(CH_2SiMe_3)Cl$	polymeric structure (Figure 50), cf. $(BeMe_2)_n$ reacts with PMe_3 to give $[Mn_2(\mu\text{-}CH_2SiMe_3)_2(CH_2SiMe_3)_2(PMe_3)_2]$ (X-ray)	126
$[Mn_4\{\mu\text{-}CH_2CMe_3\}_6(CH_2CMe_3)_2]$	$MnCl_2 + Mg(CH_2CMe_3)Cl$	linear tetramer, end Mn atom 3-coordinate with terminal alkyl	126
$[Mn_2\{\mu\text{-}CH_2C(Ph)Me_2\}_2(CH_2C(Ph)Me_2)_2]$	$MnCl_2 + Mg(CH_2C(Ph)Me_2)Cl$	X-ray (Figure 51) shows alkyl-bridged structure	126
$[Mn_2\{\mu\text{-}CH_2C_6H_4NMe_2\text{-}o\}_2(CH_2C_6H_4NMe_2\text{-}o)_2]$	$MnI_2 + LiCH_2C_6H_4NMe_2\text{-}o$	X-ray (Figure 49), Cr analogue associated in solution	137
$[M_2(\eta\text{-}C_5H_5)\{\mu\text{-}C(C_6H_4Me\text{-}p){=}C{=}O\}(CO)_6]$	$[M(\eta\text{-}C_5H_5)(CO)_2(CC_6H_4Me\text{-}\rho)][BF_4] + [N(PPh_3)_2][Mn(CO)_5]$	M = Mn or Re X-ray (M = Mn) (Figure 48)	148
$[Ru_2(\mu\text{-}CH_3)(\mu\text{-}CH_2)_2(PMe_3)_6]^+$	$[Ru_2(\mu\text{-}CH_2)_3(PMe_3)_6] + H[BF_4]$		75
$[Rh_2(\eta\text{-}C_8H_{12})(\mu\text{-}Me)_2]$	$[\{Rh(\eta\text{-}C_8H_{12})Cl\}_2] + MeLi$	X-ray	*d*
$[Ru_2(CO)_3H\{P(OC_6H_4)(OPh)_2\}_2[OP(OPh)_2]]$	$[Ru_3(CO)_9\{P(OPh)_3\}_3] \xrightarrow[\text{decalin}]{\Delta}$	X-ray, OC_6H_4 bridges the two metal centers	*e*
$[Ni_2\{\mu\text{-}CH_3\}_2(\eta\text{-}C_3H_3R_2\text{-}1,3)_2]$	$[\{Ni(\eta\text{-}C_3H_3R_2)Br\}_2] + Mg(Me)Cl$	R = H or Me(X-ray, Figure 52)	121
$[M_2(\eta\text{-}C_5H_5)_4\{\mu\text{-}CH_3\}_2]$	$[M(\eta\text{-}C_5H_5)_2(\mu\text{-}CH_3)_2Al(CH_3)_2] +$ pyridine	M = Y, Dy, Ho, Er, Tm, or Yb (X-ray, M = Y or Yb) Figure 45	124

TABLE VII (*Continued*)

$[Au_2\{\mu\text{-}(\eta\text{-}C_5H_3X)Fe(\eta\text{-}C_5H_5)\}(PPh_3)_2][BF_4]$	$[Au\{\mu\text{-}(\eta\text{-}C_5H_4X)Fe(\eta\text{-}C_5H_5)\}(PPh_3)]$ + $H[BF_4]$	X-ray (X = H) (Figure 53) X = H, Cl, OMe, or CH_2NMe_2	138
$[Au_2\{\mu\text{-}R\}(Ph_3P)_2][BF_4]$	$[Ar(R)(PPh_3)]$ + $H[BF_4]$	R = $CH{=}CH_2$, C_6H_5, or C_6H_4Me-4	138, *f*
	Selected Examples of Polymetallic Complexes		
$[Re_6\{\mu\text{-}CH_3\}_6(CH_3)_6(L)_6]$	$[Re_3Me_9]$ + LH	Structure proposed from spectral data L = CO_2Me, CO_2CH_2Ph, $CF_3COCHCOCH_3$	133
$[Re_3\{\mu\text{-}CH_3\}_3(CH_3)_6]$	$[Re_3Cl_9]$ + MeMgCl		132
$[Re_3\{\mu\text{-}CH_3\}_3(CH_3)_3(L^1)_3]$	$[Re_3Me_9]$ + L^1H	L^1 = MeCOCHCOMe, PhCOCHCOMe, $C_4H_3SCOCHCOCF_3$	133
$[Re_3(\mu\text{-}CH_3)_3(CH_3)_6(PEt_2Ph)_n]$ (n = 2, 3)	$[Re_3Cl_9]$ + MgMeCl + PEt_2Ph	X-ray	131
$[Re_3Cl_3(\mu\text{-}CH_2SiMe_3)_3(CH_2SiMe_3)_3]$	$[Re_3Cl_9]$ + Me_3SiCH_2MgCl	X-ray shows alkyl bridges	*g*
$[HOs_3\{\mu\text{-}CH_3\}(CO)_{10}]$	$[H_2Os_3(CO)_{10}]$ + CH_2N_2	equilibrium with methylene bridged species.	78
$[Os_3(\mu\text{-}Ph)(CO)_8(\mu\text{-}PPh_2)(\mu\text{-}PPhC_6H_4)]$	$[Os_3(CO)_{12}]$ + PPh_3, Δ	X-ray	*h*
$[Cu_4\{\mu\text{-}CH_2SiMe_3\}_4]$	CuI + $LiCH_2SiMe_3$	X-ray	123
$[M_4(\mu\text{-}Ar)_4]_m$	general preparative method: (1) $ZnAr_2$ + MX (2) LiR + MX	M = Cu or Ag; Ar = C_6H_5, C_6H_4Me-*o* (*m* or *p*), $C_6H_3Me_2$-2,4, $C_6H_3(OMe)_2$-2,6, $C_6H_2(OMe)_3$-2,4,6, $C_6H_4(CH_2NMe_2)$-*o*, C_6H_3Me-5-CH_3NMe_2-2, C_6H_3OMe-5-CH_2NMe_2-2, $C_6H_2Me_2$-3,5-CH_2NMe_2-2, X-ray: M = Cu, Ar = C_6H_3Me-5-CH_2NMe_2-2; M = Ag, Ar = C_6F_5; M = Au, Ar = $C_6H_2Me_2$-3,5-CH_2NMe_2-2	143, 144, 145, 146, *i*
$[Cu_6(\mu\text{-}C_6H_4NMe_2\text{-}2)_4(\mu\text{-}Br)_2]$	$[Cu(C_6H_4NMe_2\text{-}2)]$ + CuBr	X-ray For Cu or Ag the CH_2NMe_2 substituted phenyl complexes have been prepared.	*j*
$[Cu_6(\mu\text{-}C_6H_4NMe_2\text{-}2)_4(\mu\text{-}CCC_6H_4Me\text{-}2)_2]$	$[CuAr_4Br_2]$ + $LiCCAr^1$	X-ray	*k*
$[Cu_4Ag_2(\mu\text{-}C_6H_4NMe_2\text{-}2)_4][CF_3SO_3]_2$	CuAr + $Ag[CF_3SO_3]$	Cu_4Cu_2, Cu_4Au_2, Ag_4Al_2 complexes also prepared	*l*
$[Au_2Zn_2(\mu\text{-}C_6H_4R)_6]$	AuCl + Ar_2Zn $[Au(CO)Cl]$ + Ar_2Zn	R = H or 4-Me	*m*

[a] Thiele, K.-H.; Roder, A.; Mörke, W. *Z. Anorg. Allg. Chem.* 1978, *441*, 13. [b] Fachinetti, G.; Floriani, C.; Roselli, A.; Pucci, S. *J. Chem. Soc., Chem. Commun.* 1978, 269. [c] Pez, G. P.; Putnik, C. F.; Suib, S. L.; Stucky, G. D. *J. Am. Chem. Soc.* 1979, *101*, 6933. [d] Schmidt, G. F.; Muetterties, E. L.; Beno, M. A.; Williams, J. M. *Proc. Natl. Acad. Sci. U.S.A.* 1981, *78*, 1318. [e] Bruce, M. I.; Howard, J. A. K.; Nowell, I. W.; Shaw, G.; Woodward, P. *J. Chem. Soc., Chem. Commun.* 1972, 1041. [f] Schmidbaur, H.; Inoguchi, Y. *Chem. Ber.* 1980, *113*, 1646. [g] Mertis, K.; Edwards, P. G.; Wilkinson, G.; Malik, K. M. A.; Hursthouse, M. B. *J. Chem. Soc., Dalton Trans.* 1981, 705. [h] Bradford, C. W.; Nyholm, R. S.; Gainsford, G. J.; Guss, J. M.; Ireland, P. R.; Mason, R. *J. Chem. Soc., Chem. Commun.* 1972, 87. [i] Koten, G. van; Leusink, A. J.; Noltes, J. G. *J. Organomet. Chem.* 1974, *85*, 105; 1973, *56*, 379; 1974, *80*, C56. Boersma, J.; Tombe, F. J. A.; Weijers, F.; Kerk, G. J. M. van der *Ibid.* 1977, *124*, 229. Camus, A.; Marsich, N.; Nardin, G.; Randaccio, L. *Ibid.* 1979, *174*, 121. Usón, R.; Laguna, A.; Brun, P. *Ibid.* 1980, *197*, 369. [j] Koten, G. van; Noltes, J. G. *J. Chem. Soc., Chem. Commun.* 1974, 575. Guss, J. M.; Mason, R.; Thomas, K. M.; Koten, G. van; Noltes, J. G. *J. Organomet. Chem.* 1972, *40*, C79. [k] Hoedt, R. W. M.; Noltes, J. G.; Koten, G. van; Spek, A. L. *J. Chem. Soc., Dalton Trans.* 1978, 1800. [l] Koten, G. van; Jastrzebski, J. T.; Noltes, J. G. *Inorg. Chem.* 1977, *16*, 1782. [m] Graaf, P. W. J. de; Boersma, J.; Kerk, G. J. M. van der *J. Organomet. Chem.* 1977, *127*, 391.

Table VIII. (μ-Alkenyl)dimetal Complexes Including Metallocyclopentadienyl Metal Complexes (See Also Table VIIIa)

compound	preparation	comments	ref
	$[(Cr(\eta\text{-}C_5H_5)(CO)_2)_2] + PhC{\equiv}CPh/\Delta$	X-ray	*a*
$[Mo_2(\eta\text{-}C_5H_5)_2(OCOCF_3)(CO)_4(\mu\text{-}CH{=}CH_2)]$	$[Mo_2(\eta\text{-}C_5H_5)_2(CO)_4(\mu\text{-}CH{\equiv}CH)] + \xrightarrow[2.\ ^-OCOCF_3]{1.\ H^-}$	X-ray	*b*
	$[Mn(\eta\text{-}C_5H_5)(CCHPh)(CO)_2] + [Fe_2(CO)_9]$	X-ray	*c*
$[Mn_2(\mu\text{-}CFCF_2)_2(CO)_8]$	$[Mn(CO)_5SnMe_3] + F_2CCF_2$		*d*
	$[Mn(\eta\text{-}C_5H_5)(CO)_2\{C(OMe)Ph\}] + [Pt(C_2H_4)_3] + PMe_3$	X-ray, 2 isomers (red and yellow)	*e*
$[Fe_2\{\mu\text{-}CHCHBr\}(\mu\text{-}Br)(CO)_6]$	$[Fe_2(CO)_9] + BrCHCHBr$	X-ray	*f*
$[Fe_2(\eta\text{-}C_5H_5)(\mu\text{-}CH{=}CHR)(\mu\text{-}CO)(CO)_4]$	$[Fe_2(CO)_9] + [Fe(\eta\text{-}C_5H_5)(CHCHR)(CO)_2]$	R = H, Ph, MeCO, or PhCO Fe/W analogue also prepared	*g*
$[Fe_2\{\mu\text{-}C(NR')CR_2\}(CO)_6]$	$[Fe_3(CO)_{12}] + R_2C{=}C{=}NR'$		*h*
	$[Fe_2(CO)_9] + MeC{\equiv}CMe$	X-ray, $(CHCPh)_2CO$ analogue also prepared (X-ray) and related $(CMeCMe)_2SiPh_2$ analogue	*i*
	$[Fe_3(CO)_{12}] + HC{\equiv}CH$	X-ray	*j*
	$Me_3SiC{\equiv}C\text{-}C{\equiv}CSiMe_3 + [Fe(CO)_5]$	X-ray	*k*
	$[Fe_3(CO)_{12}] + EtC{\equiv}CEt$	X-ray	*l*
$[Fe\{\mu\text{-}\overline{FeCR^1CR^2CR^3CR^4}\}(CO)_6]$ 	$RC{\equiv}CR' + [Fe(CO)_5]$	$R^1 = R^2 = R^3 = R^4 = H$ (X-ray) $R^1 = R^2 = R^3 = R^4 = Ph$ (X-ray) $= OSiMe_3$ (X-ray) $R^1 = Et, R^2 = R^3 = R^4 = H$ $R^1 = OH, R^2 = R^3 = R^4 = H$ $R^1 = R^4 = CO_2Me, R^2 = R^3 = H$ $R^1 = R^4 = OMe, R^2 = R^3 = H$ $R^1 = R^3 = C{\equiv}CMe, R^2 = R^4 = Me$ $R^1 = R^4 = OH, R^2 = R^3 = Me$ (X-ray) $R^1\text{-}R^4 = (CH_2)_n, R^2\text{-}R^3 = (CH_2)_m$ $R^1 = CHPh_2, R^2 = H, R^3 = R^4 = OMe$ (X-ray)	*m*

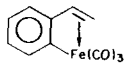
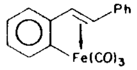
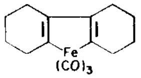
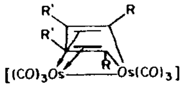
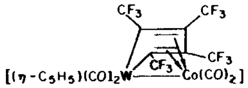
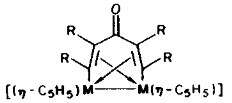
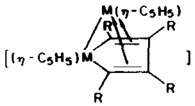
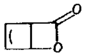
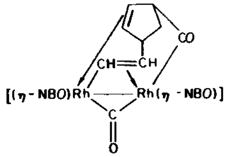
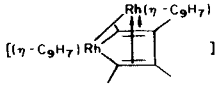
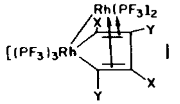
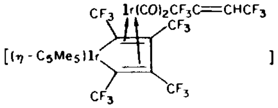
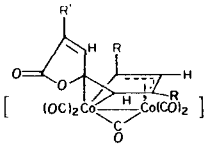
$[Fe\{\mu\text{-}(MR(CO)_3)\}(CO)_3]$	alkyne + $[Fe_2(CO)_9]$	$MR(CO)_3$ =  Os analogue also prepared	*n*
			*o*
			*p*
$[Ru_2(\eta\text{-}C_5H_5)_2(\mu\text{-}CMeCMeCH_2)(\mu\text{-}CO)(CO)]$	$[Ru_2(\eta\text{-}C_5H_5)_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CMe)]^+$ + $MeCH{=}CH_2/h\nu$	X-ray	*q*
$[M_2(\eta\text{-}C_5H_5)_2(CO)(\mu\text{-}CO)\{\mu\text{-}RC{=}CRC(O)\}]$	$[\{M(\eta\text{-}C_5H_5)(CO)_2\}_2]$ + $RC{\equiv}CR/h\nu$	M = Fe or Ru, R = H, Me, Ph, CO_2Me(Fe only), X-ray; M = Ru, R = Ph	*r*
	$[Os_3(CO)_{12}]$ + $MeC{\equiv}CH$ $[Os_3(CO)_{12}]$ + $MeC{\equiv}CMe$	X-ray (R = R′ = Me *or* R = H, R′ = Me)	*s* *t*
	$[W(\eta\text{-}C_5H_5)Cl(CF_3C{\equiv}CCF_3)_2]$ + $[Co_2(CO)_8]$	X-ray, molybdenum analogue also prepared	*u*
	$[M_2(\eta\text{-}C_5H_5)_2(RC{\equiv}CR)(CO)_2]$ + $RC{\equiv}CR$	M = Co or Rh, R = CF_3 or Me	*v*
	$[Co(\eta\text{-}C_5H_5)(CO)_2]$ +  $[Rh(\eta\text{-}C_5H_5)(C_2H_4)_2]$ + $CF_3C{\equiv}CCF_3$	R = H R = CF_3	*w* *w*
	$[Rh_6(CO)_{12}(NBD)_3]/\Delta$	NBD = norbornadiene	*x*
	$[Rh(\eta\text{-}C_9H_7)(C_2H_4)_2]$ + $MeC{\equiv}CMe$		*y*
	$[Rh_2(PF_3)_8]$ + $XC{\equiv}CY$	X = Y = CO_2Me X = H and Y = CO_2Me	*z*
$[Rh_2(\eta\text{-}C_9H_7)_2(\mu\text{-}CH{=}CH_2)(\mu\text{-}CMeCHMe)]$	$[Rh(\eta\text{-}C_9H_7)(C_2H_4)_2]$ + $MeC{\equiv}CMe$	X-ray (C_9H_7 = indenyl)	*y*
	$[Ir(\eta\text{-}C_5Me_5)(CO)_2]$ + $CF_3C{\equiv}CCF_3$	X-ray	*v*
	$[Co_2(\mu\text{-}CO)(\mu\text{-}C_4O_2R')(CO)_6]$ + $RC{\equiv}CH$	R = Me, Pr, Bu, Ph, CH_2OMe R′ = H, Pr, Bu, C_5H_{11}, Ph X-ray (R = Ph, R′ = Me or Bu)	*am*

Table VIII (*Continued*)

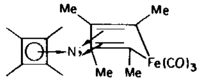
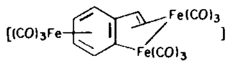
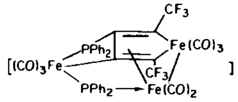
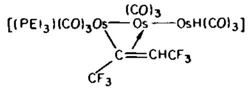
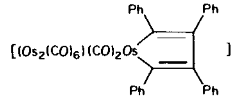
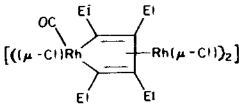
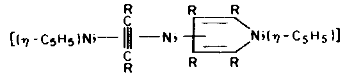
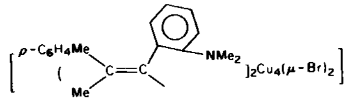
compound	preparation	comments	ref
	$[Fe_3(CO)_{12}] + [Ni(\eta\text{-}C_4Me_4)Cl_2]$	X-ray	*aa*
	Selected Examples of Polymetallic Compounds		
	$[Fe_3(CO)_{12}]$ + alkyne	X-ray	*ab*
	$Ph_2PC{\equiv}CCF_3 + [Fe_3(CO)_{12}]$	X-ray	*ac*
$[Os_3(\mu\text{-}CR{=}CHR')(\mu\text{-}H)(CO)_{10}]$	$[H_2Os_3(CO)_{10}] + RC{\equiv}CR'$	R = R' = H (X-ray) R = H R' = Et (X-ray) R = CF_3 R' = CF_3 (X-ray)	*ad* *ae* *af*
$[Os_3H(CO)_{10}(PEt_3)(\mu\text{-}CF_3C{=}CHCF_3)]$	$[HOs_3(CO)_{10}(CF_3C{=}CHCF_3)] + PEt_3$	X-ray, linear Os_3 unit 	*ag*
$[Os_3\{\mu\text{-}C(PEt_2)CH_2\}(\mu\text{-}H)(CO)_9]$	$[Os_3(CO)_{11}PEt_3]/\Delta$		*ah*
	$[Os_3(CO)_{12}] + PhC{\equiv}CPh$	X-ray, reaction with CO gives the $Os_3(CO)_9$ analogue	*ai*
	$[[Rh(CO)_2Cl]_2] + EtC{\equiv}CEt$	X-ray	*aj*
	$[Ni(\eta\text{-}C_5H_5)_2] + RC{\equiv}CR$	R = CF_3 (complex bridged molecule of general formula $[Ni(\eta\text{-}C_5H_5)(RCCR)]_4$ also isolated, X-ray	*ak*
	CuR + CuBr		*al*

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TABLE IX. (μ-Alkynyl)dimetal Complexes (See Also Table IXa)

compound	preparation	comments	ref
$[Ti_2(\eta\text{-}C_5H_4R)_4(\mu\text{-}C{\equiv}CPh)_2]$	$[Ti(\eta\text{-}C_5H_4R)_2Cl_2] + NaC{\equiv}CPh$	R = H or Me (X-ray)	*a*
$[TiPt(\eta\text{-}C_5H_5)_2(\mu\text{-}C{\equiv}CPh)_2PR_3]$	$[Ti(\eta\text{-}C_5H_5)_2(C{\equiv}CPh)_2] + [Pt(C_2H_4)_2PR_3]$	X-ray. $PR_3 = P(c\text{-}C_6H_{11})_3$, PMe_2Ph, $PMePh_2$, PPh_3, $PPr\text{-}i_2Ph$	*b*
$[TiNi(\eta\text{-}C_5H_5)_2(\mu\text{-}C{\equiv}CPh)_2(CO)]$	$[Ti(\eta\text{-}C_5H_5)_2(C{\equiv}CPh)_2] + [Ni(CO)_4]$		*c*
$[CuPPh_3][Re(\mu\text{-}C{\equiv}CC_6F_5)_2(CO)_3(PPh_3)]$	$[Re(CO)_3(PPh_3)_2Cl] + CuC{\equiv}CC_6F_5$	X-ray	*d*
$[Fe_2(\mu\text{-}C{\equiv}CPh)(\mu\text{-}PPh_2)(CO)_6]$	$[Fe_2(CO)_9] + Ph_2PC{\equiv}CPh$	X-ray; can replace one CO with PPh_3 (X-ray).	*e*
			f
$[[FeCu(\eta\text{-}C_5H_5)(\mu\text{-}C{\equiv}CPh)(\mu\text{-}Cl)(CO)_2]_2]$	$[Fe(\eta\text{-}C_5H_5)(CO)_2Cl] + CuC{\equiv}CPh$	X-ray	*g*
$[RuCu(\eta\text{-}C_5H_5)(\mu\text{-}C{\equiv}CPh)(\mu\text{-}Cl)(PPh_3)_2]$	$[Ru(\eta\text{-}C_5H_5)Cl(PPh_3)_2] + CuC{\equiv}CPh$	X-ray	*h*
$[Pt_2(\sigma\text{-}C{\equiv}CPh)(\mu\text{-}C{\equiv}CPh)(\mu\text{-}SiMe_2)(PR_3)_2]$	$[Pt(C_2H_4)_2PR_3] + Me_3SiC{\equiv}CPh$	X-ray	*b*
$[M_2(\eta\text{-}C_5H_5)_4(\mu\text{-}C{\equiv}CPh)_2]$	$[\{M(\eta\text{-}C_5H_5)_2Cl\}_2] + LiC{\equiv}CPh$	M = Gd, Ho, Er, or Yb	*j*
$[RhAg(\mu\text{-}C{\equiv}CC_6F_5)_4(PPh_3)_3]$	$[Rh(PPh_3)_3Cl] + Ag(C{\equiv}CC_6F_5)$	X-ray	*k*
$[IrCu(\mu\text{-}C{\equiv}CAr)_4(PPh_3)_3]$	$[IrCl(CO)(PPh_3)_2] + CuC{\equiv}CAr$	Ar = C_6F_5	*l*
	Selected Examples of Polymetallic Compounds		
$[Fe_3(\eta\text{-}C_5H_5)(\mu\text{-}C{\equiv}CPh)(CO)_7]$	$[Fe_2(CO)_9] + [FeCu(\eta\text{-}C_5H_5)(\mu\text{-}C{\equiv}CPh)(\mu'\text{-}Cl)(CO)_3]_2$		*m*
$[Fe_2Ru(\eta\text{-}C_5H_5)(\mu\text{-}C{\equiv}CPh)(CO)_6(PPh_3)_2]$	$[Fe_2(CO)_9] + [RuCu(\eta\text{-}C_5H_5)(\mu\text{-}C{\equiv}CPh)(\mu'\text{-}Cl)(PPh_3)_2]$		*h*
$[Ru_3(\mu\text{-}C{\equiv}CBu^t)(\mu\text{-}H)(CO)_9]$	$[Ru_3(CO)_{12}] + t\text{-}BuC{\equiv}CH$		*n*
$[Ru_3(\mu\text{-}C{\equiv}CBu^t)(\eta\text{-}\eta\text{-}C_6H_{10})(\mu\text{-}H)(CO)_9]$	reaction of the nonacarbonyl complex with hexadiene	X-ray	*n*
$[Os_3(\mu\text{-}C{\equiv}CPh)(\mu\text{-}H)(CO)_{10}]$	$[H_2Os_3(CO)_{10}] + HC{\equiv}CPh$		*o*
$[Os_3(\mu\text{-}C{\equiv}CR)(\mu\text{-}H)(CO)_9]$	$[H_2Os_3(CO)_{10}] + HC{\equiv}CR/\Delta$	R = H or Me	*o*
$[Co_5(\mu\text{-}CC{\equiv}CH)(CO)_{15}]$	$[Co_3(CO)_9CCl] + 1,3,5\text{-}C_6H_3Me_3$	X-ray, one of many reaction products	*p*
$[RhAg_2(\mu\text{-}C{\equiv}CC_6F_5)_5(PPh_3)_3]$	$[Rh(PPh_3)_3Cl] + Ag(C{\equiv}CC_6F_5)$	X-ray	*k*
$[Ir_2Cu_4(\mu\text{-}C{\equiv}CPh)_8(PPh_3)_2]$	$[IrCl(CO)(PPh_3)_2] + PhC{\equiv}CH$	X-ray, Rh_2Ag_4 analogue also prepared	*q*
$[Cu_6(\mu\text{-}C_6H_4CH_2NMe_2\text{-}2)_4(\mu\text{-}C{\equiv}CC_6H_4Me\text{-}2)_2]$	$[Cu_6R_4X_2] + LiC{\equiv}CAr$	X-ray	*r*
$[(Yb(\eta\text{-}C_5H_5)_2(\mu\text{-}C{\equiv}CPh))_3]$	$[\{Yb(\eta\text{-}C_5H_5)_2Cl\}_2] + LiC{\equiv}CPh$	R = *n*-alkyl, e.g., *n*-C_6H_{13} or *n*-C_4H_9; also R = alkynyl	*s*

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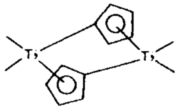
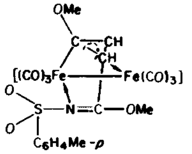
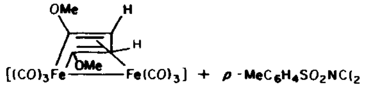
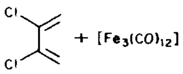
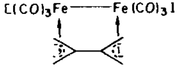
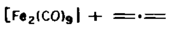
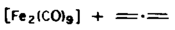
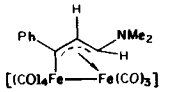
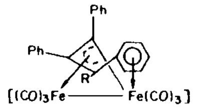
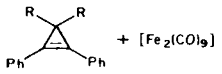
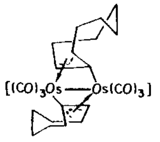
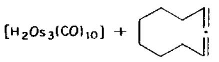
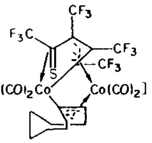
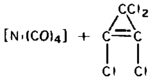
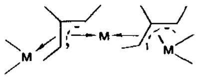
TABLE X. μ-Allyl, μ-Cyclopentadienyl and Related Dimetal Complexes[as] (See Also Table Xa)

compound	preparation	comments	ref
$[Ti_2(\mu\text{-}\eta^1\text{-}\eta^5\text{-}C_5H_4)_2(\eta\text{-}\eta'\text{-}C_{10}H_8)(HAlEt_2)_2]$	$[Ti(\eta\text{-}C_5H_5)_2] + AlEt_3/\Delta$	X-ray 	*a*
$[Ti_2(\eta\text{-}C_5H_5)_3(\mu\text{-}\eta^1\text{-}\eta^5\text{-}C_5H_4)]$	$[Ti(\eta\text{-}C_5H_5)_2Cl_2] + K[C_{10}H_8]$	X-ray	*b*
$[Zr_2(\eta\text{-}C_5H_5)_2(\mu\text{-}\eta^1\text{-}\eta^5\text{-}C_5H_4)_2L_2]$	$[Zr(\eta\text{-}C_5H_5)_2L_2]/\Delta$	L = PMe_2Ph or $PMePh_2$	*c*
$[Nb_2(\eta\text{-}C_5H_5)_2(\mu\text{-}\eta^1\text{-}\eta^5\text{-}C_5H_4)_2H_2]$	$[Nb(\eta\text{-}C_5H_5)_2H_3]/\Delta$	X-ray	*d*
$[M_2(\mu\text{-}C_3H_5)_2(\eta\text{-}C_3H_5)_2]$	$MCl_x + Mg(C_3H_5)Cl$	X-ray, M=Cr or Mo (cf. analogous $[Re_2(C_3H_5)_4]$ does not contain bridging allyl groups)	*e*
$[Mo_2(\eta\text{-}C_5H_5)_2(\mu\text{-}\eta^1\text{-}\eta^5\text{-}C_5H_4)_2H_2]$	$[[Mo(\eta\text{-}C_5H_5)_2HLi]_4] + N_2O$	tungsten analogue also prepared	*f*
$[Mo_2(\eta\text{-}C_5H_5)_2(\mu\text{-}\eta^1\text{-}\eta^5\text{-}C_5H_4)_2]$	$[Mo(\eta\text{-}C_5H_5)_2H_2]/h\nu$		*g*
$[MoMn(\eta\text{-}C_5H_5)(\mu\text{-}\eta^1\text{-}\eta^5\text{-}C_5H_4)(CO)_5]$	$[Mo(\eta\text{-}C_5H_5)_2H_2] + [Mn(CO)_5Me]$	X-ray, tungsten analogue also prepared	*h*
$[WIr(\eta\text{-}C_5H_5)(\mu\text{-}\eta^1\text{-}\eta^5\text{-}C_5H_4)(\mu\text{-}H)_2H(L)_2]$	$[W(\eta\text{-}C_5H_5)_2H_2] + [IrH_2L_2(EtOH)_2][PF_6]$	L = PEt_3, PMe_2Ph, PPh_2Me, PPh_3	*i*
$[W_2(\eta\text{-}C_5H_5)_2(\mu\text{-}\eta^1\text{-}\eta^5\text{-}C_5H_4)_2H(CH_2SiMe_3)]$	$[W(\eta\text{-}C_5H_5)_2H_2] + SiMe_4$		*j*
$[ReMn(\eta\text{-}C_5H_5)(\mu\text{-}\eta^1\text{-}\eta^5\text{-}C_5H_4)H(CO)_4]$	$[Re(\eta\text{-}C_5H_5)_2H] + [Mn(CO)_5Me]$		*h*
$[\{Mn(\eta\text{-}C_5H_5)(\mu\text{-}C_5H_5)\}_n]$	$Mg(\eta\text{-}C_5H_5)Br + MnCl_2$	X-ray, ionic structure	*k*
$[Fe_2(\eta\text{-}C_5H_5)_2(\mu\text{-}C_3H_5)(CO)_4]^+$	$[[Fe(\eta\text{-}C_5H_5)(CO)_2]_2(CH_2)_3] + [Ph_3C][BF_4]$		*l*
$[Fe_2(\mu\text{-}C_3Ph_3R)(CO)_6]$	$[Fe_2(CO)_9] + CPhCPhCPhR$	X-ray, R=H, Me, or Ph	*m*
$[Fe_2\{\mu\text{-}MeCCHCHCHCHC(O)Me\}(CO)_6]$	$[Fe(CO)_5] + CH_3C(CHCHC(O)CH_3)CHCH$		*m*
$[Fe_2(\mu\text{-}C_3H_4)(CO)_7]$	$[Fe_2(CO)_9] + C_3H_4$		*n*
			*o*
			*p*
			*n*
		X-ray of the PPh_3 analogue	*q*
	$PhCH{=}CHCONMe_2 + [Fe_3(CO)_{12}] + Et_3O[BF_4]$	X-ray	*r*
		R = H (X-ray), Me, or Ph	*m*

		X-ray	*s*
	$[\{Co(CO)_3SC_6F_5\}_2] + CF_3C{\equiv}CCF_3$	X-ray	*t*
$[Ni_2(\eta\text{-}C_5H_5)_2(\mu\text{-}C_5H_5)][BF_4]$	$[Ni(\eta\text{-}C_5H_5)_2] + H[BF_4]$	X-ray	*u*
$[Ni_2(\eta\text{-}C_5Ph_5)(\mu\text{-}C_3Ph_3)(\eta\text{-}C_4Ph_4)]$	$NiBr_2 + [Ph_5C_4Al]Li_2$	X-ray	*v*
$[\{Ni_2(\mu\text{-}C_3Cl_3)(CO)_2(\mu\text{-}Cl)\}_2]$		X-ray	*w*
$[Pd_2(\mu\text{-}C_5H_5)_2(PR_3)_2]$	$[Pd_2(PR_3)_2Cl_2(MeCO_2)_2] + 2TlC_5H_5 + Na/K$	R = Me, Ph, or Pr-*i*; or R = Et (X-ray)	*x*
$[Pd_2(\mu\text{-}C_5H_5)(\mu\text{-}C_3H_4R)(PR'_3)_2]$	$[Pd(\eta\text{-}C_5H_5)(\eta\text{-}C_3H_4R)] + Pd(PR'_3)_2$	X-ray (R = Me, R′ = Ph); R = H, Me, or Bu-*t*, R′ = e.g., Pr-*i*, C_6H_{11}, or Ph	*y*
$[Pd_2(\mu\text{-}C_3H_4R)(\mu\text{-}X)(PR'_3)_2]$	$[Pd(\mu\text{-}C_3H_4R)X]_2 + Pd(PR'_3)_2$	X-ray (X = I, R = H, R′ = Ph)	*ac*, *z*
$[Pd_2(\mu\text{-}C_3H_4R)_2(PR'_3)_2]$	$[Pd(\mu\text{-}C_3H_4R)_2] + Pd(PR'_3)_2$	R′ = e.g., Pr-*i*, R = e.g., Me, in plane bridging alkyl, i.e., ; cf. bridging C_5H_5: 	*ac*
$[Pd_2(\mu\text{-}C_5H_5)(\mu\text{-}Br)(PPr\text{-}i_3)_2]$	$[Pd(\eta\text{-}C_5H_5)Br(PPr\text{-}i_3)] + Mg/THF$	X-ray	*aa*
$[Pt_2(\mu\text{-}C_3H_5)_2(acac)_2]$	$[\{PtCl(\eta\text{-}C_3H_5)\}_2] + Tl(acac)$	X-ray	*ab*
$[\{Pt_2(\mu\text{-}C_3H_5)_2Cl_2\}_2]$	$[Pt(\eta\text{-}C_3H_5)_2] + HCl$	X-ray	*ab*
$[Pt_2\{\mu\text{-}CPhC(O)CPh\}(t\text{-}BuNC)_4]$	$[Pt_3(CNBu\text{-}t)_6] + \overline{CPhCPhCO}$	X-ray, can protonate carbonyl with HBF_4	*ad*
$[Au\{\mu\text{-}(C_5H_3R)Fe(\eta\text{-}C_5H_5)\}PPh_3]$	$[Au(Cl)PPh_3] + LiR$	copper analogue known, R = H, Cl, OMe, or CH_2NMe_2	*ae*
$[Au_2\{\mu\text{-}(C_5H_3R)Fe(\eta\text{-}C_5H_5)\}(PPh_3)_2]^+$	$[AuR'PPh_3] + H[BF_4]$	X-ray (R = H, Cl, OMe, or CH_2NMe_2)	*ae*
$[\{Sc(\eta\text{-}C_5H_5)_2(\mu\text{-}\eta'\text{-}C_5H_5)\}_n]$	$ScCl_3 + Na[C_5H_5]$	X-ray, samarium analogue also prepared (X-ray)	*af*, *ag*
$[Th_2(\eta\text{-}C_5H_5)_4(\mu\text{-}\eta^1\text{-}\eta^5\text{-}C_5H_4)_2]$	$[Th(\eta\text{-}C_5H_5)_3R]/\Delta$	X-ray	*ah*
	Selected Examples of Trimetallic Complexes		
$[HM_3(\mu\text{-}MeCCHCH)(CO)_9]$	$[M_3(CO)_{10}CHCMe]/\Delta$	M = Ru or Os	*ai*
$[HRu_3(\mu\text{-}MeCCHCEt)(CO)_9]$	$[Ru_3(CO)_{12}] + C_6H_{10}$	X-ray	*aj*
$[Rh_3(\eta\text{-}C_5H_5)_3(\mu\text{-}C_5H_5)H]$	$RhCl_3 + Mg(C_5H_5)Br$	X-ray, C_5H_5 bridges the Rh_3 triangle	*ak*
$[M_3(\mu\text{-}C_3RR'_2)_2(acac)_2]$	$[M_3(\mu\text{-}C_3RR'_2)_2Br_2] + Tl(acac)$	X-ray, linear structure, M = Pd or Pt, R′ = R = *p*-$MeOC_6H_4$; R = Ph, R′ = *p*-$MeOC_6H_4$	*al*
$[M_3(\mu\text{-}C_3R_3)_2Br_2]$	$[M_2\{PhCHCHC(O)CHCHPh\}_3Solv] + [CRCR'CR']Br$	R = Ph, R′ = *p*-$MeOC_6H_4$, M = Pd or Pt, the Pd_3 and Pt_3 allyl clusters contain bridging allyl groups, i.e., 	*am*

[a] Guggenberger, L. J.; Tebbe, F. N. *J. Am. Chem. Soc.* 1973, *95*, 7870. [b] Pez, G. P. *J. Am. Chem. Soc.* 1976, *98*, 8072. [c] Gell, K. I.; Schwartz, J. *J. Chem. Soc., Chem. Commun.* 1979, 244. Gell, K. I.; Harris, T. V.; Schwartz, J. *Inorg. Chem.* 1981, *20*, 481. [d] Guggenberger, L. J. *Inorg. Chem.* 1973, *12*, 294. [e] Aoki, T.; Furusaki, A.; Tomiie, Y.; Ono, K.; Tanaka, K. *Bull. Chem. Soc. Jpn.* 1969, *42*, 545. Cotton, F. A.; Pipal, J. F. *J. Am. Chem. Soc.* 1971, *93*, 5441. [f] Cooper, N. J.; Green, M. L. H.; Couldwell, C.; Prout, K. *J. Chem. Soc., Chem. Commun.* 1977, 145. [g] Berry, M.; Cooper, N. J.; Green, M. L. H.; Simpson, S. J. *J. Chem. Soc. Chem. Commun.* 1978, 99; *J. Chem. Soc., Dalton Trans.* 1980, 29. Carmen, M.; Green, M. L. H.; Jimenez, R. *Ibid.* 1982, 2495. [h] Hoxmeier, R.; Deubzer, B.; Kaesz, H. D. *J. Am. Chem. Soc.* 1971, *93*, 536. Hoxmeier, R. J.; Blickensderfer, J. R.; Kaesz, H. D. *Inorg. Chem.* 1979, *18*, 3453. Hoxmeier, R. J.; Knoble, C. B.; Kaesz, H. D. *Ibid.* 1978, *18*, 3462. [i] Pregosin, P. S.; Togni, A.; Venanzi, L. M. *Angew. Chem., Int. Ed. Engl.* 1981, *20*, 668. [j] Berry, K.; Elmitt, K.; Green, M. L. H. *J. Chem. Soc., Dalton Trans.* 1979, 1950. [k] Bunder, W.; Weiss, E. *Z. Naturforsch., B Anorg.*

TABLE X (*Continued*)

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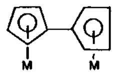
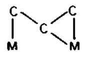
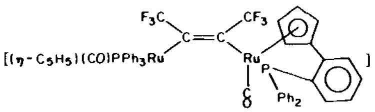


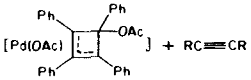
I



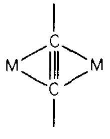
II

TABLE XI. (μ-Acetylene)dimetal Complexes (Selected, Well-Characterized Examples)[ag,ah]

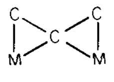
compound	preparation	comments	ref
$[Ta_2Cl_4(\mu\text{-}Cl)_2(\mu\text{-}Me_3CC{\equiv}CCMe_3)(THF)_2]$	$[Ta_2Cl_6(SC_4H_8)_3]$ + $t\text{-}BuC{\equiv}CBu\text{-}t$	X-ray, (tetrahedral)[ag] Ta–Ta 2.677 Å, very short, i.e., a double bond	*a*
$[Mo_2(\eta\text{-}C_5H_5)_2(\mu\text{-}HC{\equiv}CH)(CO)_4]$	$[[Mo(\eta\text{-}C_5H_5)(CO)_2]_2]$ + $HC{\equiv}CH$	X-ray, X-ray also on Et_2C_2 and Ph_2C_2 analogues (tetrahedral)	*b*
$[W_2(\mu\text{-}MeC{\equiv}CMe)(\mu\text{-}Br)(Br)(CO)_5(Ph_2As)_2CH_2]$	$[WCMe(Br)(CO)_4]$ + $(Ph_2As)_2CH_2$	X-ray, (tetrahedral)	*c*
$[Fe_2(\mu\text{-}Bu\text{-}t\text{-}C{\equiv}CBu\text{-}t)(CO)_6]$	$[Fe_2(CO)_9]$ + $t\text{-}BuC{\equiv}CBu\text{-}t$	X-ray, (tetrahedral)	*d*
$[Fe_2(\mu\text{-}Bu\text{-}t\text{-}C{\equiv}CBu\text{-}t)_2(CO)_4]$	$[Fe_3(CO)_{12}]$ + $t\text{-}BuC{\equiv}CBu\text{-}t$	X-ray, (tetrahedral)	*e*
$[Fe_2(\mu\text{-}F_3CC{\equiv}CCF_3)(\mu\text{-}SCF_3)_2(CO)_6]$	$[\{Fe(CO)_3SCF_3\}_2]$ + $F_3CC{\equiv}CCF_3$	X-ray, (in plane)	*f*
$[Fe_2(\mu\text{-}C_6F_4)(CO)_8]$	$Li[(CO)_4Fe(C(O)C_6F_5)]$ + Me_3SiCl	X-ray, low yield byproduct; for other examples of this type of complex see Table IV	*g*
	$[RuMe(CO)PPh_3(\eta\text{-}C_5H_5)]$ + $(F_3C)_2C_2$	(in plane)	*h*
$[CoNi(\mu\text{-}PhC{\equiv}CPh)(\eta\text{-}C_5H_5)(CO)_3]$	$[Ni_2(\eta\text{-}C_5H_5)_2(PhC{\equiv}CPh)]$ + $[Co_2(CO)_8]$	X-ray, (tetrahedral)	*i*
$[Co_2(\mu\text{-}t\text{-}BuC_2Bu\text{-}t)(CO)_6]$	$[Co_2(CO)_8]$ + $t\text{-}BuC_2Bu\text{-}t$	X-ray, many examples known with different acetylenes, (tetrahedral)	*d*
$[Co_2(\mu\text{-}H_2C_2)(CO)_4(PMe_3)_2]$	$[Co_2(CO)_6(HC_2H)]$ + PMe_3	X-ray, substituted alkyne complexes known, (tetrahedral)	*j*
$[Co_2(\eta\text{-}C_5H_5)_2(\mu\text{-}Me_3SiC_2SiMe_3)(\mu\text{-}CO)]$	$[Co(\eta\text{-}C_5H_5)(CO)_2]$ + $Me_3SiC_2SiMe_3$		*k*
$K_6[Co_2(\mu\text{-}R_2C_2)(CN)_{10}]$	$[Co(CN)_5]^{3-}$ + R_2C_2	various acetylenes, e.g., R = CO_2Me, CO_2Et, CN, H	*l*
$[Co_2(\mu\text{-}PhC_2Ph)(CO)_4(Ph_2PCH_2PPh_2)]$	$[Co_2(\mu\text{-}PhC_2Ph)(CO)_6]$ + $Ph_2PCH_2PPh_2$	X-ray, (tetrahedral)	*m*

$[Co_2(\mu\text{-}CCCF_2CF_2CFCF)(CO)_6]$	$[Co_2(CO)_8] + CCCF_2CF_2CFCF$	X-ray, cis cyclic alkyne stabilized by coordination	*n*
$[Rh_2(\eta\text{-}C_5H_5)_2(\mu\text{-}F_3CC_2CF_3)(CO)_2]$	$[Rh(\eta\text{-}C_5H_5)(CO)_2] + F_3CC_2CF_3$	X-ray, (in plane)	*o*
$[Rh_2(\eta\text{-}C_5H_5)_2(\mu\text{-}F_3CC_2CF_3)(\mu\text{-}CO)]$	$[Rh_2(\eta\text{-}C_5H_5)_2(\mu\text{-}F_3CC_2CF_3)(CO)_2] + Me_3NO$	preparation involves the interconversion of an in-plane to a tetrahedral complex	*p*
$[Rh_2(\mu\text{-}PhC_2Ph)_2(PF_3)_4(PPh_3)_2]$	$[Rh_2(PF_3)_8] + PhC{\equiv}CPh + 2PPh_3$	X-ray, various substituted acetylene derivatives known, (tetrahedral)	*q*
$[Rh_2(\mu\text{-}CF_3C_2CF_3)(F_3CCC(CF_3)CH[C(O)Bu\text{-}t]_2)_2]$	$[Rh(dpm)(CO)_2] + F_3CC_2CF_3$	X-ray, (in plane), dpm = dipivaloylmethanato	*r*
$[Rh_2\{(Ph_2P)_2CH_2\}_2(\mu\text{-}F_3CC{\equiv}CCF_3)(Cl)_2]$	$[(RhCl(C_8H_{12})]_2] + DPM + HC{\equiv}CH$	X-ray, (in plane)	*s*
$[Ir_2(\mu\text{-}PhC{\equiv}CH)(PPh_3)_2(CO)_4]$	$[Ir(CO)_3(PPh_3)] + HC{\equiv}CPh$	X-ray, (tetrahedral)	*t*
$[Ir_2(\mu\text{-}F_3CC_2CF_3)_2(NO)_2(PPh_3)_2]$	$[Ir(PPh_3)_3NO] + F_3CC_2CF_3$	X-ray, (in plane)	*u*
$[Ni_2(\eta\text{-}C_5H_5)_2(\mu\text{-}HC_2H)]$	$[Ni(\eta\text{-}C_5H_5)_2] + HC_2H$	X-ray, (tetrahedral)	*v*
$[Ni_2(\eta\text{-}C_5H_5)_2(\mu\text{-}Ph_2PC_2R)]$	$[Ni(\eta\text{-}C_5H_5)_2] + Ph_2PC_2R$	R = Bu-*t* or Ph (tetrahedral)	*w*
$[Ni_2(\eta\text{-}C_5H_5)_2(\mu\text{-}Ph_2P(O)C_2CF_3)]$	$[Ni(\eta\text{-}C_5H_5)_2] + Ph_2PC_2R$	X-ray, (tetrahedral), one of six products separated by chromatography	*x*
$[Ni_2(\eta\text{-}C_8H_{12})_2(\mu\text{-}PhC_2Ph)]$	$[Ni(\eta\text{-}C_8H_{12})_2] + PhC_2Ph$	X-ray, (tetrahedral)	*y*
$[Ni_2(\eta\text{-}C_5H_5)_2]_2[\mu\text{-}CC(CH_2)_nCC(CH_2)_mCH_2]$	$[Ni(\eta\text{-}C_5H_5)_2]$ + cyclic diacetylene	Co analogue also prepared	*z*
$[NiFe(\eta\text{-}C_5H_5)(\mu\text{-}CHCPPh_3)(CO)_3]$	$[Ni(\eta\text{-}C_5H_5)(C{\equiv}CH)(PPh_3)] + [Fe_2(CO)_9]$	X-ray, (tetrahedral), rare example of heterobimetallic	*aa*
$[Pd_2(\eta\text{-}C_5Ph_5)_2(\mu\text{-}PhC{\equiv}CPh))$	$Pd(OAc)_2 + PhC{\equiv}CPh$	X-ray, (tetrahedral) many related examples known	*ab*
			
$[Pd_2\{(Ph_2P)_2CH_2\}_2(\mu\text{-}RC{\equiv}CR)(Cl)_2]$	$[Pd_2\{(Ph_2P)_2CH_2\}_2(Cl)_2] + RC{\equiv}CR$	X-ray (R = CF_3), also R = CO_2Me or CO_2Et	*ac*
$[Pt_2(\eta\text{-}C_8H_{12})_2(\mu\text{-}F_3CC{\equiv}CCF_3)_2]$	$[PtC(CF_3)_2{\cdot}O{\cdot}Pt(C_8H_{12})] + F_3CC{\equiv}CCF_3$	X-ray, (in plane)	*ad*
$[Pt_2(\eta\text{-}PhC{\equiv}CPh)(\mu\text{-}PhC{\equiv}CPh)(PMe_3)_2]$	$[Pt(\eta\text{-}C_8H_{12})_2] + PhC{\equiv}CPh + PMe_3$	X-ray, (tetrahedral), cf. with above	*ae*
$[Pt_2\{(Ph_2P)_2CH_2\}_2(\mu\text{-}RC{\equiv}CR)(X)(\sigma\text{-}RC{=}CHR)]$	$[Pt_2\{(Ph_2P)_2CH_2\}_2H_2(\mu\text{-}H)]^+ + 2RC{\equiv}CR$	R = CO_2Me or CF_3	*af*

[a] Cotton, F. A.; Hall, W. T. *Inorg. Chem.* 1980, *19*, 2354. [b] Bailey, W. I.; Chisholm, M. H.; Cotton, F. A.; Rankel, L. A. *J. Am. Chem. Soc.* 1978, *100*, 5764. [c] Fischer, E. O.; Ruhs, A.; Friedrich, P.; Huttner, G. *Angew. Chem., Int. Ed. Engl.* 1977, *16*, 465. [d] Cotton, F. A.; Jamerson, J. D.; Stults, B. R. *J. Am. Chem. Soc.* 1976, *98*, 1774. [e] Nicholas, N.; Bray, L. S.; Davis, R. E.; Pettit, R. *J. Chem. Soc., Chem. Commun.* 1971, 608. [f] Davidson, J. L.; Harrison, W.; Sharp, D. W. A.; Sim, G. A. *J. Organomet. Chem.* 1973, *46*, C47. [g] Bennett, M. J.; Graham, W. A. G.; Stewart, R. P.; Tuggle, R. M. *Inorg. Chem.* 1973, *12*, 2944. [h] Bruce, M. I.; Gardener, R. C. F.; Stone, F. G. A. *J. Chem. Soc., Dalton Trans.* 1979, 906. [i] Freeland, B. H.; Hux, J. E.; Payne, N. C.; Tyers, K. G. *Inorg. Chem.* 1980, *19*, 693. [j] Bonnet, J. J.; Mathieu, R. *Inorg. Chem.* 1978, *17*, 1973. [k] Sakurai, H.; Hayashi, J. *J. Organomet. Chem.* 1972, *39*, 365. [l] Kimball, M. E.; Martella, J. P.; Kaska, W. C. *Inorg. Chem.* 1967, *6*, 414. [m] Bird, P. H.; Fraser, A. R.; Hall, D. N. *Inorg. Chem.* 1977, *16*, 1923. [n] Bailey, N. A.; Churchill, M. R.; Hunt, R.; Mason, R.; Wilkinson, G. *Proc. Chem. Soc.* 1964, 401. [o] Dickson, R. S.; Kirsch, H. P.; Lloyd, D. J. *J. Organomet. Chem.* 1975, *101*, C48. [p] Dickson, R. S.; Pain, G. N. *J. Chem. Soc., Chem. Commun.* 1979, 277. See also Dickson, R. S.; Fallon, G. P.; Nesbit, R. J.; Pain, G. N. *J. Organomet. Chem.* 1982, *236*, C61. [q] Bennet, M. A.; Johnson, R. N.; Robertson, G. B.; Turney, T. W.; Whimp, P. O. *Inorg. Chem.* 1976, *15*, 97. [r] Jarvis, A. C.; Kemmitt, R. D. W.; Russell, D. R.; Tucker, P. A. *J. Organomet. Chem.* 1978, *159*, 341. [s] Cowie, M.; Dickson, R. S. *Inorg. Chem.* 1981, *20*, 2682. [t] Angoletta, M.; Bellon, P. L.; Demartin, F.; Sansoni, M. *J. Organomet. Chem.* 1981, *208*, C12. [u] Clemens, J.; Green, M.; Kuo, M. C.; Fritchie, C. J.; Mague, J. T.; Stone, F. G. A. *J. Chem. Soc., Chem. Commun.* 1972, 53. [v] Wang, Y.; Coppens, P. *Inorg. Chem.* 1976, *15*, 1122. [w] Carty, A. J.; Paik, N. H.; Ng, T. W. *J. Organomet. Chem.* 1974, *74*, 279. [x] Restivo, R. J.; Ferguson, G.; Ng, T. W.; Carty, A. J. *Inorg. Chem.* 1977, *16*, 172. [y] Day, V. W.; Abdel-Meguid, S. S.; Dabestani, S.; Thomas, M. G.; Pretzer, W. R.; Muetterties, E. L. *J. Am. Chem. Soc.* 1976, *98*, 8289. [z] King, R. B.; Haiduc, I.; Efraty, A. *J. Organomet. Chem.* 1973, *47*, 145. [aa] Yasufuku, K.; Yamazaki, H. *Bull. Chem. Soc. Jpn.* 1972, *45*, 2664. Yasufuku, K.; Aoki, K.; Yamazaki, H. *J. Organomet. Chem.* 1975, *84*, C28. [ab] Jack, T. R.; May, C. J.; Powell, J. *J. Am. Chem. Soc.* 1977, *99*, 4707. [ac] Lee, C. L.; Hunt, C. T.; Balch, A. I. *Inorg. Chem.* 1981, *20*, 2498. [ad] Smart, L. E.; Browning, J.; Green, M.; Laguna, A.; Spencer, J. L.; Stone, F. G. A. *J. Chem. Soc., Dalton Trans.* 1977, 1777. [ae] Green, M.; Grove, D. M.; Howard, J. A. K.; Spencer, J. L.; Stone, F. G. A. *J. Chem. Soc., Chem. Commun.* 1976, 759. [af] Puddephatt, R. J.; Thomson, M. A. *Inorg. Chim. Acta.* 1980, *45*, L281; *Inorg. Chem.* 1982, *21*, 725. [ag] The alkyne can bridge in two distinct modes: (a) Tetrahedral-μ_2-η^2 geometry, i.e., I in which the alkyne lies perpendicular to the M–M axis, (b) in plane- cis-dimetalated olefin, i.e., the alkyne lies in the plane of the M–M axis (II). The two modes of bonding are interconvertible, *cf.* Dickson, R. S.; Pain, G. N. *J. Chem. Soc., Chem. Commun.* 1979, 277. [ah] Hoffmann, D. M.; Hoffmann, R. *Organometallics* 1982, *1*, 1299; *J. Chem. Soc., Dalton Trans.* 1982, 1471.



I



II

TABLE XII. μ-Hydrocarbyl Main-Group Metal-Transition-Metal Complexes (See Also Table XIIa)

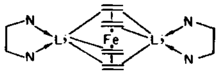
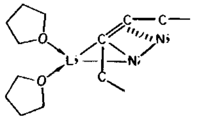
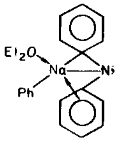
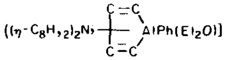
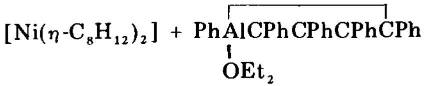
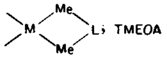
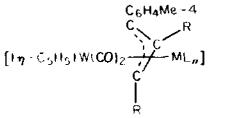
compound	preparation	comments	ref
$[TiAl(\eta\text{-}C_5H_5)_2(\mu\text{-}CH_2)(\mu\text{-}Cl)(CH_3)_2]$	$[Ti(\eta\text{-}C_5H_5)_2Cl_2] + Al_2Me_6$	terminal alkyl exchange with Al_2R_6	37
$[TiAl(\eta\text{-}C_5H_5)_2\{\mu\text{-}CH_3\}\{\mu\text{-}CH_2\}(CH_3)_2]$	$[Ti(\eta\text{-}C_5H_5)_2Me_2] + Al_2Me_6$		*a*
$[TiAl(\eta\text{-}C_5H_5)_2(\mu\text{-}CH_3)_2(CH_3)_2]$	$[\{Ti(\eta\text{-}C_5H_5)_2Cl\}_2] + Li[AlMe_4]$		128
$[TiAl(\eta\text{-}C_5H_5)_2(\mu\text{-}CH_3)(\mu\text{-}Cl)(CH_3)_2]$	$[\{Ti(\eta\text{-}C_5H_5)_2Cl\}_2] + Al_2Me_6$	unstable complex	128
$[Ti_2Zn(\eta\text{-}C_5H_5)_4(\mu\text{-}C_6H_5)_2]$		spectroscopic characterization	*b*
$[Ti_2(\mu\text{-}\eta\text{-}C_5H_4AlEt_2H)_2(\eta\text{-}C_5H_5)_2]$	$[Ti(\eta\text{-}C_5H_5)_2] + Al_2Et_6/\Delta$	X-ray	*c*
$[Zr(\eta\text{-}C_5H_5)_2\{\mu\text{-}CH_2CH(AlEt_2)_2\}(Cl)]$	$[Zr(\eta\text{-}C_5H_5)_2Cl_2] + Al_2Et_6$	X-ray, Cl^- may be replaced by $[C_5H_5]^-$ (X-ray), spectroscopic characterization of titanium analogues, a variety of Zr–Al bridged species have been prepared from the reaction of $[Cp_2ZrCl_2]$ and Al_2Et_6 (see ref 187)	16, *d* *e*
$[Ta(\eta\text{-}C_5H_5)_2\{\mu\text{-}CH_2AlMe_3\}(Me)]$	$[Ta(\eta\text{-}C_5H_5)_2(CH_2)(CH_3)] + Al_2Me_6$		39
$[Ta(\mu\text{-}CCMe_3LiL)(CH_2CMe_3)_3]$	$[Ta(CH_2CMe_3)_3CHCMe_3] + BuLi$	X-ray $L = MeNCH_2CH_2N(Me)CH_2CH_2$	*f*
$[CrNa_2\{\mu\text{-}C_6H_5\}_4(C_6H_5)(THF)(Et_2O)_3]$	$CrCl_3 + Na[C_6H_5]$	X-ray	*g*
$[CrLi_3(\mu\text{-}CH_3)_6(dioxane)_3]$	$CrCl_3 + LiMe$	X-ray	*h*
$[M_2Li_4(\mu\text{-}CH_3)_8(Et_2O)_4]$	$MCl_x + LiMe$	M = Cr or W (X-ray)	*i*
$[CrLi_2(\mu\text{-}C_6H_4CH_2NMe_2\text{-}2)_2Cl_2(THF)_2]$	$CrCl_2 + LiC_6H_4CH_2NMe_2\text{-}2$	Mn analogue prepared from MnI_2	137
$[[Mo(\eta\text{-}C_5H_5)(\eta\text{-}C_5H_4)H]_2Al_3Me_5]$	$[Mo(\eta\text{-}C_5H_5)_2H_2] + Al_2Me_6$	X-ray	*j*
$[\{Mo(\eta\text{-}C_5H_4)_2Al_2Me_3\}_2]$	$[Mo(\eta\text{-}C_5H_5)_2H_2] + Al_2Me_6$	X-ray	*j*
$[W(\mu\text{-}CH)(Cl)(PMe_3)_3(AlMe_2Cl)]$	$[W(CH)(Cl)(PMe_3)_4] + (AlMe_2Cl)_2 + PMe_3$	X-ray, shows 82% Me and 18% Cl bridged structure	*k*
$[Re_2\{\mu\text{-}CSn(TPP)C\}(CO)_5]$	$Sn(TPP)Cl_2 + [Re_2(CO)_{10}]$	X-ray, (TPP = tetraphenylporphinato)	*l*
$[FeLi_2(C_2H_4)_4(TMEDA)_2]$	$[Fe(\eta\text{-}C_5H_5)_2] + Li + C_2H_4 + TMEDA$	X-ray 	*m*
$[OsAg(\mu\text{-}CC_6H_4Me\text{-}p)(Cl)_2(CO)(PPh_3)_2]$	$[Os(CC_6H_4Me)(Cl)(CO)(PPh_3)_2] + AgCl$	X-ray, Cu and Ag analogues also prepared (Figure 44)	117
$[CoLi(\eta\text{-}C_8H_{12})_2(THF)_2]$	$[Co(\eta\text{-}C_5H_5)(\eta\text{-}C_8H_{12})] + Li(\eta\text{-}C_8H_{12})$	X-ray, Ni analogue also prepared	*n*
$[CoLi(\eta\text{-}C_8H_{12})_2Li(\mu\text{-}Ph)(THF)_2]$	$[Co(\eta\text{-}C_8H_{12})(\eta\text{-}C_8H_{14})] + LiPh$	X-ray	*o*
$[Ni(\mu\text{-}C_{12}H_{17}NiLi)_2(THF)_4]$	$[Ni(\eta\text{-}C_{12}H_{18})Li_2] + 2C_{12}H_{18}Ni$	X-ray shows the bridging unit:  the carbon chain being part of the C_{12} chain	*p*
$[Ph[Na(OEt_2)]_2[Ph_2Ni]_2N_2NaLi_6(Et_2O)_4\cdot OEt_2]_2$	$PhLi + [(ttt\text{-}C_{12}H_{18})Ni] + N_2 + NaPh$	X-ray, complex structure containing side on dinitrogen, numerous phenyl bridges are present, e.g., 	*q*
	$[Ni(\eta\text{-}C_8H_{12})_2] + PhAlCPhCPhCPhCPh$ with OEt_2 on Al	X-ray	*r*
$[NiAl(\mu\text{-}CH_3)_2(CH_3)_3(bipy)]$	$[Ni(bipy)Me_2] + Al_2Me_6$		*s*
$[Cu_2Li_2(\mu\text{-}CH_3)_4]$	$CuI + MeLi$	spectroscopic characterization, see also $LiCu_2Me_3$, $Li_2Cu_2Me_5$, and Li_2CuMe_3, butyl analogues also prepared	*t*

TABLE XII (*Continued*)

$[CuLi_2(\mu\text{-}CH_3)_3]$	CuI + MeLi	spectroscopic characterization, butyl compound also prepared	*t*
$[M_2Li_2(\mu\text{-}C_6H_4CH_2NMe_2\text{-}2)_4]$	$MX + LiC_6H_4CH_2NMe_2\text{-}2$	M = Cu, Ag, or Au	*u*
$[AgLi(\mu\text{-}Ar)_2]$	AgX + ArLi	Ar = C_6H_5, *o*-, *m*-, *p*-tolyl, C_6F_5, 2,6-dimethylphenyl	*v*
$[\{AuM(\mu\text{-}Ar)Cl\}_x]$	$[Au(CO)Cl] + MAr_2$	M = Zn, Ar = Ph, $C_6H_4Me\text{-}o$, $C_6H_4(CH_2CH_2)\text{-}o$, $C_6H_3(OMe)_2\text{-}2,6$; M = Cd or Hg, Ar = Ph	*aa*
$[MAl(\eta\text{-}C_5H_5)_2(\mu\text{-}CH_3)_2(CH_3)_2]$	$[\{M(\eta\text{-}C_5H_5)_2Cl\}_2] + Li[AlMe_4]$	M = Sc, Y, Gd, Dy, Ho, Er, Tm, or Yb X-ray (M = Y and Yb, Figure 46)	128, 130
$[MAl(\eta\text{-}C_5H_5)_2(\mu\text{-}CH_2CH_3)_2(CH_2CH_3)_2]$	$[\{M(\eta\text{-}C_5H_5)_2Cl\}_2] + Li[AlEt_4]$	M = Sc, Y, or Ho	128
$[YbLi(\eta\text{-}C_5Me_5)_2(\mu\text{-}Me)(\mu\text{-}X)(Et_2O)_2]$	$[\{Yb(\eta\text{-}C_5Me_5)_2Cl\}_2] + LiMe$	X = Cl, I, or Me	*w*
$[MLi(\mu\text{-}Bu\text{-}t)_2(Bu\text{-}t)_2(THF)_x]$	$LiBu\text{-}t + MCl_3$	M = Sm, Er, or Yb	*x*
$[MLi_3\{\mu\text{-}Me\}_6(TMEDA)_3]$	$MCl_3 + LiMe$	X-ray (M = Er), M = Pr, Nd, Sm, Tm, Yb, Er, or Lu  	*y*
$[ULi_2R_6L_8]$	$UCl_4 + LiR + TMEDA\ (L)$	R = Me, CH_2SiMe_3, Ph, or $C_6H_4CH_2NMe_2\text{-}o$	*z*
$[ULi_3R_8]\cdot L_3$	$UCl_4 + LiR + O(CH_2CH_2)_2O\ (L)$	R = Me, CH_2SiMe_3, or CH_2CMe_3	*z*

[a] Tebbe, F. N.; Parshall, G. W.; Zeile, J. V.; Reddy, G. S.; Harlow, R. L. *Abstr. Pap.—Am. Chem. Soc.* 1978, 176th. [b] Vyshinskaya, L. I.; Razuvaev, G. A.; Latyaeva, V. N.; Lineva, A. N. *Proc. Conf. Coord. Chem.* 1973, *15*, 262. [c] Wailes, P. C.; Weigold, H. *J. Organomet. Chem.* 1970, *24*, 713. [d] Kaminsky, W.; Sinn, H. *Justus Liebigs Ann. Chem.* 1975, 424. Kaminsky, W.; Vollmer, H.-J. *Ibid.* 1975, 438. [e] (X-ray), Kaminsky, W.; Kopf, J.; Thirase, G. *Justus Liebigs Ann. Chem.* 1974, 1531. [f] Guggenberger, L. J.; Schrock, R. R. *J. Am. Chem. Soc.* 1975, *97*, 2935. [g] Müller, E.; Krausse, J.; Schmiedeknecht, K. *J. Organomet. Chem.* 1972, *44*, 127. [h] Krausse, J.; Marx, G. *J. Organomet. Chem.* 1974, *65*, 215. [i] Collins, D. M.; Cotton, F. A.; Koch, S. A.; Millar, M.; Murillo, C. A. *Inorg. Chem.* 1978, *17*, 2017. [j] Retting, S. J.; Storr, A.; Thomas, B. S.; Trotter, J. *Acta. Crystallogr., Sect. B* 1974, *B30*, 666. Forder, R. A.; Prout, K. *Ibid.* 1974, *B30*, 2312. [k] Sharp, P. R.; Holmes, S. J.; Schrock, R. R. *J. Am. Chem. Soc.* 1981, *103*, 965. Churchill, M. R.; Rheingold, A. L.; Wasserman, H. J. *Inorg. Chem.* 1981, *20*, 3392. [l] Noda, I.; Kato, S.; Mizuta, M.; Yasuoka, N.; Kasai, N. *Angew. Chem., Int. Ed. Engl.* 1979, *18*, 83. [m] Jonas, K.; Schieferstein, L. *Angew. Chem., Int. Ed. Engl.* 1979, *18*, 549. Jonas, K.; Schieferstein, L.; Krüger, C.; Tsay, Y. H. *Ibid.* 1979, *18*, 550. [n] Jonas, K.; Mynott, R.; Krüger, C.; Sekutowski, J. C.; Tsay, Y. H. *Angew. Chem., Int. Ed. Engl.* 1976, *15*, 767. [o] Bönnemann, H.; Krüger, C.; Tsay, Y. H. *Angew. Chem., Int. Ed. Engl.* 1976, *15*, 46. [p] Jonas, K.; Krüger, C.; Sekutowski, J. C. *Angew. Chem., Int. Ed. Engl.* 1979, *18*, 487. [q] Jonas, K.; Brauer, D. J.; Krüger, C.; Roberts, P. J.; Tsay, Y. H. *J. Am. Chem. Soc.* 1976, *98*, 74. [r] Krüger, C.; Sekutowski, J. C.; Hoberg, H.; Krause-Göing, R. *J. Organomet. Chem.* 1977, *141*, 141. [s] Jolly, P. W.; Jonas, K.; Krüger, C.; Tsay, Y. H. *J. Organomet. Chem.* 1971, *33*, 109. [t] Pearson, R. G.; Gregory, C. D. *J. Am. Chem. Soc.* 1976, *98*, 4098. Ashby, E. C.; Lin, J. J.; Watkins, J. J. *J. Org. Chem.* 1977, *42*, 1099. [u] Koten, G. van; Noltes, J. G. *J. Organomet. Chem.* 1979, *174*, 367. Leusink, A. J.; Koten, G. van; Marsman, J. W.; Noltes, J. G. *Ibid.* 1973, *55*, 419. Koten, G. van; Noltes, J. G. *Ibid.* 1974, *82*, C53. [v] Blenkers, J.; Hofstee, H. K.; Boersma, J.; Kerk, G. J. M. van der *J. Organomet. Chem.* 1979, *168*, 251. Smith, V. B.; Massey, A. G. *Ibid.* 1970, *23*, C9. [w] Watson, P. L. *J. Chem. Soc., Chem. Commun.* 1980, 652. [x] Wayda, A. L.; Evans, W. J. *J. Am. Chem. Soc.* 1978, *100*, 7119. [y] Schumann, H.; Pickardt, J.; Brucks, N. *Angew. Chem., Int. Ed. Engl.* 1981, *20*, 120. [z] Sigurdson, E. R.; Wilkinson, G. *J. Chem. Soc., Dalton Trans.* 1977, 812. [aa] Graaf, P. W. J. de; Konig, A. J. de; Boersma, J.; Kerk, G. J. M. van der. *J. Organomet. Chem.* 1977, *141*, 345.

TABLE XIII. Miscellaneous μ-Hydrocarbyl- or μ-Hydrocarbon-Dimetal Complexes (See Also Table XIIIa)

compound	preparation	comments	ref
$[M(\mu\text{-}MeOC_6H_3OMe\text{-}2,6)_4]$	$[VCl_3(THF)_3] + LiC_6H_3(OMe)_2\text{-}2,6$	M = V (X-ray, Figure 63)	167, 142
	$[M_2(OAc)_4] + LiC_6H_3(OMe)_2\text{-}2,6$	M = Cr or Mo (Figure 64) these complexes also contain an aryl bridge (see Table VII)	169
 	$[RhW(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_3(\eta\text{-}C_5H_5)(\eta\text{-}C_9H_7)] + PhC{\equiv}CPh$	ML_n = $Rh(\eta\text{-}C_9H_7)$, R = Ph	*a*
	$[CoW(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_3(\eta\text{-}C_5H_5)(\eta\text{-}C_5Me_5)] + PhC{\equiv}CPh$ or $MeC{\equiv}CMe$	ML_n = $Co(\eta\text{-}C_5Me_5)$, R = Ph or Me	
	$[Fe_2W(\mu\text{-}CC_6H_4Me\text{-}4)(\mu\text{-}CO)(CO)_8(\eta\text{-}C_5H_5)] + RC{\equiv}CR$	ML_n = $Fe(CO)_3$, R = Me(X-ray), Ph, CF_3, or $C_6H_4Me\text{-}4$	

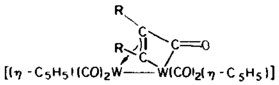
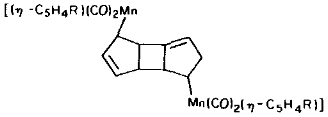
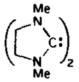
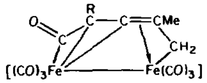
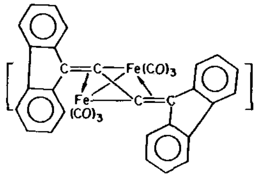
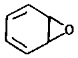
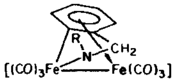
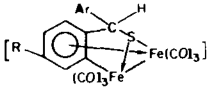
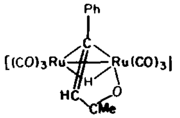
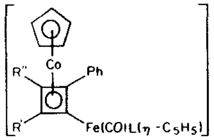
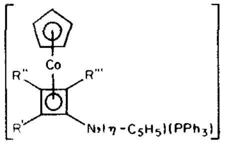
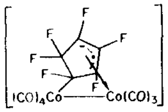
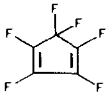
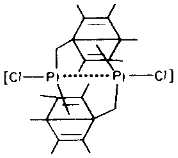
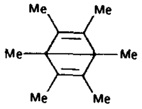
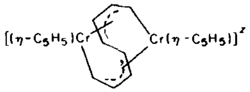
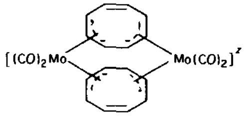
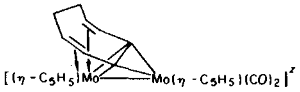
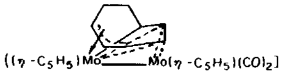
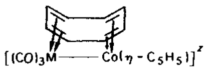
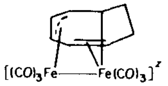
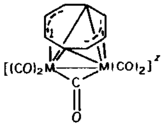
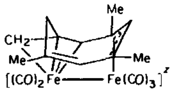
	$[\{W(\eta\text{-}C_5H_5)(CO)_3\}_2]$ + RC≡CR/$h\nu$	R = CO_2Me, X-ray, fluxional molecule	*b*
	$(Mn(\eta\text{-}C_5H_4R)(CO)_2(THF)]$ + 	R = H or Me(X-ray)	*d*
$[Fe_2\{\mu\text{-}CHC(Ph)NEt_2\}(CO)_6(\mu\text{-}PPh_2)]$	$[Fe_2(CO)_6(\mu\text{-}C{\equiv}CPh)(\mu\text{-}PPh_2)]$ + NEt_2H	X-ray (Figure 54)	159
$[Fe_2\{\mu\text{-}C{=}C(Ph)(Pcy_2H)\}(CO)_6(\mu\text{-}PPh_2)]$	$[Fe_2(CO)_6(\mu\text{-}C{\equiv}CPh)(\mu\text{-}PPh_2)]$ + Pcy_2H	X-ray (Figure 55)	160
$[Fe_2\{\mu\text{-}C(Ph)C[P(OEt)_3]\}(CO)_6(\mu\text{-}PPh_2)]$	$[Fe_2(CO)_6(\mu\text{-}C{\equiv}CPh)(\mu\text{-}PPh_2)]$ + $P(OEt)_3$	X-ray (Figure 56)	161
$[Fe_2\{\mu\text{-}C(Ph)CCN(Me)(CH_2)_2NMe\}(CO)_6(\mu\text{-}PPh_2)]$	$[Fe_2(CO)_6(\mu\text{-}C{\equiv}CPh)(\mu\text{-}PPh_2)]$ + 	X-ray (Figure 57)	162
$[Fe_2\{\mu\text{-}C(CHO)PPh_2\}(\mu\text{-}C_6H_4)(CO)_6]$	$[Fe_3(CO)_{12}]$ + $(Me_3Sn)_2C{=}PPh_3$	X-ray (Figure 60)	164, *c*
$[Fe_2(\mu\text{-}CH_2CPhNMe)(CO)_6(\mu\text{-}PPh_2)]$	$[Fe_2(CO)_6(\mu\text{-}C{\equiv}CPh)(\mu\text{-}PPh_2)]$ + $NMeH_2$/Florisil, C_6H_6	X-ray (Figure 61)	158
$[Fe_2\{\mu\text{-}C(Ph)O\}_2(CO)_6]$	$[Fe(CO)_5]$ + $\xrightarrow{\text{1. LiPh}}$ $\xrightarrow{\text{2. }Ph_3CCl}$	X-ray (Figure 62)	165
	$[Fe_2(CO)_9]$ + $CH_2{=}CMeC{\equiv}CR$	X-ray (R = Et and Bu-*t*) H_2CCMeC moiety = allyl CCRCO = 3-electron donor	*e*
	$[Fe_2(CO)_9]$ + $Ph_2C{=}C{=}C{=}CPh_2$	X-ray	*f*
	$[Fe(CO)_5]/h\nu$ + 	X-ray	*g*
$[M_2\{\mu^2\text{-}C(OEt)(CH_2C_6H_4CH_2\text{-}o)C(OEt)\text{-}\}(CO)_{10}]$	$[M(CO)_6]$ + $o\text{-}C_6H_4(CH_2MgCl)_2$, then $[Et_3O][BF_4]$	X-ray (M = Cr), also M = Mo or W	*aa*
$[\{Rh(COD)Cl\}_2\{\mu^2\text{-}CN(R)(CH_2)_3N(CH_2)_2\text{-}N(CH_2)_3N(R)C\text{-}\}]$	$[\{Rh(COD)Cl\}_2]$ + $RN(CH_2)_3NC{=}CN(CH_2CH_2)(CH_2)_3NR$	X-ray (R = CH_2Ph)	*ab*
	$[Fe_2(CO)_9]$ + Schiff base (e.g., toluidine + benzaldehyde)	X-ray, R = $p\text{-}MeC_6H_4$	*h*
	$[Fe_2(CO)_9]$ + $Ar_2C{=}S$	Ar = C_6H_5, C_6H_4OMe or $C_6H_4NMe_2$	*i*
	$[Ru(\eta\text{-}C_8H_{12})(CO)_3]$ + $PhCH_2C(O)Me$	X-ray	*j*

TABLE XIII (*Continued*)

compound	preparation	comments	ref
	[Co(η-C_5H_5)(PPh_3)(R'C≡CR'')] + [Fe(η-C_5H_5)(CO)L(C≡CPh)]	R' = R'' = Ph or CO_2Me and L = CO R' = R'' = CO_2Me; L = CO R' = Ph, R'' = CO_2Me; L = CO or PPh_3	*k*
	[Co(η-C_5H_5)(PPh_3)(R'C≡CR'')] + [Ni(η-C_5H_5)(PPh_3)(C≡CR''')]	R' = R'' = Ph, R''' = CO_2Me R' = R'' = CO_2Me, R''' = Ph R' = R''' = Ph, R'' = CO_2Me R' = R''' = CO_2Me, R'' = Ph	*k*
	[$Co_2(CO)_8$] + 	X-ray	*l*
	$Na_2[PtCl_4]$ + 	X-ray	*m*
	[Ti(OBu-*t*)$_4$] + C_8H_8 + $(AlEt_3)_2$	X-ray	*n*
	[Cr(η-C_5H_5)$_2$] + $Na_2[C_8H_8]$	X-ray, ring-opened structure	*o*
	MCl_4 + $K_2[C_8H_8]$	X-ray (M = Mo or W)	*p*
	[$Mo(CO)_6$] + C_8H_8	X-ray, the metal atoms are bonded to the rings via adjacent η-allyl interactions, leaving an uncoordinated olefinic bond within each	*q*
	[[$Mo(CO)_3$(η-C_5H_5)]$_2$] + C_8H_8	X-ray, the complex isomerizes in polar solvents via H migration to yield 	*r*
	[Mo(diglyme)$(CO)_3$] or [$W(CO)_3(DMF)_3$] or [$Cr(CO)_3(CH_3CN)_3$] + [Co(η-C_5H_5)C_8H_8]	M = Mo (X-ray), Cr, or W	*s*

	[$Fe_2(CO)_9$] or [$Fe_3(CO)_{12}$] + 1,3,5-c-C_8H_{10}	X-ray, the structure is essentially the same as that of [$Ru_2(\eta$-$C_8H_8)(CO)_6$]	*t*
	[$M_2(CO)_9$] + c-C_8H_8	M = Fe or Ru(X-ray)	*u*
	[$M_2(CO)_6(\eta$-$C_8H_8)$]/Δ [$Fe(CO)_5$]/C_8H_8; [$Ru_3(CO)_{12}$]/C_8H_8	M = M′ = Fe or Ru, X-ray(Fe) M = Fe, M′ = Ru	*v*
	[$Fe_2(CO)_9$] + 1,3,5,7-c-$C_{12}H_{16}$	X-ray	*w*
	Li[$Fe(CO)_3(C_7H_7)$] + [{$Rh(CO)_2Cl$}$_2$]	X-ray, related complexes include the Mn and Re complexes [$Fe(CO)_3${C_7H_7}$M(CO)_3$]	*x*
[$Ln(\eta$-$C_8H_8)(THF)_2$][$Ln(\eta$-$C_8H)_2$]^z	Ln atoms + C_8H_8 at −196 °C; extract THF	M = La, Ce, Nd(X-ray), or Er; one of the η-$C_8H_8^{2-}$ rings of the anion is also η^2-bonded to the Nd atom of the cation	*y*

[a] Jeffery, J. C.; Mead, K. A.; Razay, H.; Stone, F. G. A.; Went, M. J.; Woodward, P. *J. Chem. Soc., Chem. Commun.* 1981, 867. [b] Finnimore, S. R.; Knox, S. A. R.; Taylor, G. E. *J. Chem. Soc., Chem. Commun.* **1980**, 411; *J. Chem. Soc., Dalton Trans.* 1982, 1783. [c] Churchill, M. R.; Rotella, F. J. *Inorg. Chem.* 1978, *17*, 2614. [d] Herrmann, W. A.; Plank, J.; Ziegler, M. L.; Weidenhammer, K. *Angew. Chem., Int. Ed. Engl.* 1978, *17*, 777. [e] Cotton, F. A.; Jamerson, J. D.; Stults, B. R. *Inorg. Chim. Acta.* 1976, *17*, 235. [f] Bright, D.; Mills, O. S. *J. Chem. Soc., Dalton Trans.* 1972, 2465. [g] Aumann, R.; Averbeck, H.; Krüger, C. *Chem. Ber.* 1975, *108*, 3336. [h] Baikie, P. E.; Mills, O. S. *J. Chem. Soc., Chem. Commun.* **1966**, 707. [i] Alper, H.; Chan, A. S. K. *J. Chem. Soc., Chem. Commun.* 1971, 1203. [j] Domingos, A. J. P.; Johnson, B. F. G.; Lewis, J.; Sheldrick, G. M. *J. Chem. Soc., Chem. Commun.* 1973, 912. [k] Yasufuku, K.; Yamazaki, H. *J. Organomet. Chem.* 1976, *121*, 405. [l] Hitchcock, P. B.; Mason, R. *J. Chem. Soc., Chem. Commun.* **1966**, 503. [m] Mason, R.; Robertson, G. B.; Whimp, P. O. *J. Chem. Soc. A* 1970, 535. [n] Dietrich, H. D.; Dierks, H. *Angew. Chem., Int. Ed. Engl.* 1966, *5*, 899. [o] Geibel, W.; Wilke, G.; Goddard, R.; Krüger, C.; Mynott, R. *J. Organomet. Chem.* 1978, *160*, 139. [p] Cotton, F. A.; Koch, S. A.; Schultz, A. J.; Williams, J. M. *Inorg. Chem.* 1978, *17*, 2093. [q] Connop, A. H.; Kennedy, F. G.; Knox, S. A. R.; Riding, G. H. *J. Chem. Soc., Chem. Commun.* 1980, 520. [r] Goddard, R.; Knox, S. A. R.; Stone, F. G. A.; Winter, M. J.; Woodward, P. *J. Chem. Soc., Chem. Commun.* 1976, 559. [s] Salzer, A.; Egolf, T.; Linowsky, L.; Petter, W. *J. Organomet. Chem.* 1981, *221*, 339. [t] Cotton, F. A.; Edwards, W. T. *J. Am. Chem. Soc.* 1969, *91*, 843. [u] Cotton, F. A.; Edwards, W. T. *J. Am. Chem. Soc.* 1968, *90*, 5412. [v] Fleischer, E. B.; Stone, A. L.; Dewar, R. B. K.; Wright, J. E.; Keller, C. E.; Pettit, R. *J. Am. Chem. Soc.* 1966, *88*, 3158. Abel, E. W.; Moorhouse, S. *Inorg. Nucl. Chem. Lett.* 1970, *6*, 621. [w] Cotton, F. A.; Takats, J. *J. Am. Chem. Soc.* 1968, *90*, 2031. [x] Bennett, M. J.; Pratt, J. L.; Simpson, K. A.; LiShingMan, L. K. K.; Takats, J. *J. Am. Chem. Soc.* 1976, *98*, 4810. [y] DeKock, C. W.; Ely, S. R.; Hopkins, T. E.; Brault, M. A. *Inorg. Chem.* 1978, *17*, 625. [z] Complexes contain cyclic anionic ligands bridging two metal atoms. [aa] Bristow, G. S.; Hitchcock, P. B.; Lappert, M. F.; Skelton, B. W., unpublished work. [ab] Hitchcock, P. B.; Lappert, M. F.; Skyropoulos, K., unpublished work.

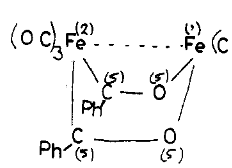


Figure 62. Schematic representation of the molecular structure of [Fe$_2${μ-C(Ph)O}$_2$(CO)$_6$].[171] Bond lengths (Å): FeFe', 2.568 (2); Fe(2)C(5), 1.945 (6); Fe(1)O(5), 1.967 (5); C(5)O(5), 1.262 (8). Bond angles (°): Fe(1)O(5)C(5), 104.5 (5); Fe(2)C(5)O(5), 114.6 (5); Fe(2)C(5)C(Ph), 131.1 (4); O(5)C(5)C(Ph), 114.3 (6).

change is 15.9 kcal mol^{-1}. At −45 °C the bridge methyls are identified by their coupling, J (^{89}Y–C^{1}H$_3$) = 5.0 Hz,[152] and J (^{89}Y–^{13}CH$_3$) = 12.2 Hz.[128] It is convenient that yttrium is naturally monoisotopic with nuclear spin $I = {}^1/_2$. Redetermination of bridge–terminal exchange activation energies for the series [YAl(μ-CH$_3$)$_2$(η-C$_5$H$_4$R)$_4$(CH$_3$)$_2$] led to the following ΔG^{*} values [kcal mol^{-1}, at the coalescence temperature (K) in parentheses]: R = H, 14.2 (287); R = Me, 13.8 (277); R = Et, 16.2 (325); R = Pr-i, 16.4 (329); R = Bu-t, 16.7 (335); and R = SiMe$_3$, 17.3 (345).[153]

The tetraethylaluminates [M'Al(μ-C$_2$H$_5$)$_2$(η-C$_5$H$_5$)$_2$(C$_2$H$_5$)$_2$] (M' = Sc, Y, or Ho) are significantly less thermally stable than their methyl homologues,[128] which are sublimable. The titanium compound, [TiAl(μ-CH$_3$)$_2$(η-C$_5$H$_5$)$_2$(CH$_3$)$_2$], g_{av} 1.977, is markedly less robust,[152] but is stabilized by addition of (AlMe$_3$)$_2$, probably because decomposition involves initial dissociation into the labile [{Ti(η-C$_5$H$_5$)$_2$(CH$_3$)}$_2$] and (AlMe$_3$)$_2$ (see eq 71).[128] The progressive increase in covalent character from left to right in the lanthanoid series is manifested in the tetramethylaluminates by the low solubility in hydrocarbons such as toluene of the lighter (Sm or Gd) rather than the heavier (Dy–Yb) complexes [MAl(μ-CH$_3$)$_2$(η-C$_5$H$_5$)$_2$(CH$_3$)$_2$].

The complex [Cr$_2$(μ-CH$_2$SiMe$_3$)$_2$(CH$_2$SiMe$_3$)$_2$(PMe$_3$)$_2$] has an interesting geometry (Figure 47).[125] The short CrCr distance is consistent with a quadruple bond, the two bridges are in a cis configuration and there is slight asymmetry in the bridge, probably because of a close bridge, α-H......Cr contact. An MO description in terms of d orbital overlap integrals concludes that the M≡M system is bent, with two cis electron-deficient bridges. Bridge-bonding in similar terms: two-electron three-center bonding was first introduced in the context of [{Cu(CH$_2$SiMe$_3$)}$_4$],[123] and the lanthanoid methyls[124] and tetramethylaluminates.[128] Simple MO calculations were carried out in the context of [Ni$_2$(μ-CH$_3$)$_2$(η-C$_3$H$_3$Me$_2$-1,3)$_2$].[121] The model chosen was again of 2-electron 3-center bridges and the qualitative conclusions were that for such compounds to be stable the acceptor orbitals on the metal must be well separated from any filled d orbitals; any departure from the strong σ-donor character of the $^{-}$CH$_3$ ligand to isoelectronic analogues such as NMe$_3$ (or strictly NH$_3$) is unlikely to give stable compounds. General discussions of electron-deficient bonding are found in ref 104, 154, 155, and 156.

B. Synthesis

The *protonation of a μ-CH$_2$ bridge* has already been mentioned, (eq 28[80] and 37);[41,75] in this fashion cationic μ-CH$_3$-Ru$_2$ complexes were obtained.

A *salt elimination* procedure is rather general and is exemplified in eq 63,[122] 64 (R = CH$_2$CMe$_3$, CH$_2$CMe$_2$Ph, or CH$_2$SiMe$_3$; MgR$_2$ has also been used),[126] 65,[76] and 66 (M = Sc,[128] Y,[152] Gd,[128] Dy, Ho, Er, Tm, or Yb or Ti;[152] Mg(AlMe$_4$)$_2$ was also employed).

$$\mathrm{CuI + Li(CH_2SiMe_3) \rightarrow {}^1/_4[\{Cu(CH_2SiMe_3)\}_4] + LiI} \quad (63)$$

$$\mathrm{MnCl_2 + 2Mg(R)Cl \rightarrow (1/\mathit{n})[(MnR_2)_{\mathit{n}}] + MgCl_2} \quad (64)$$

$$\mathrm{[Cr_2(O_2CMe)_4] + 2Mg(CH_2SiMe_3)_2 + 2PMe_3 \rightarrow [Cr(\mu\text{-}CH_2SiMe_3)_2(CH_2SiMe_3)_2(PMe_3)_2] + 2Mg(O_2CMe)_2} \quad (65)$$

$$\mathrm{{}^1/_2[\{M(\eta\text{-}C_5H_5)_2Cl\}_2] + Li[AlMe_4] \rightarrow [MAl(\mu\text{-}CH_3)_2(\eta\text{-}C_5H_5)_2(CH_3)_2] + LiCl} \quad (66)$$

Similar reactions have been used to obtain (i) Cr(CH$_2$Ar)$_2$ and [Mn$_2$(μ-CH$_2$Ar)$_2$(CH$_2$Ar)$_2$] (Ar = o-C$_6$H$_4$NMe$_2$) from 2Li(CH$_2$Ar) and CrCl$_2$ or MnI$_2$,[137] and (ii) CuAr',[143] AgAr',[146] CrAr'$_2$,[137] and MnAr'$_2$[137] (Ar' = o-C$_6$H$_4$CH$_2$NMe$_2$) and various other copper(I)[145] and silver(I)[146] aryls. A slightly more complicated variant is in eq 67[128] and is an interesting contrast with eq 66.

$$\mathrm{[\{Y(\eta\text{-}C_5H_5)_2Cl\}_2] + 2Li[InMe_4] \rightarrow [Y_2(\mu\text{-}CH_3)_2(\eta\text{-}C_5H_5)_4] + 2InMe_3 + 2LiCl} \quad (67)$$

A salt elimination route was also employed to obtain the bridging ketenide of eq 68 (M = Mn or Re),[137,157]

$$\mathrm{[M\{C(C_6H_4Me\text{-}\mathit{p})\}(\eta\text{-}C_5H_5)(CO)_2][BF_4] + [N(PPh_3)_2][Mn(CO)_5] \rightarrow [MMn\{\mu\text{-}C(C_6H_4Me\text{-}\mathit{p}){=}CO\}(\eta\text{-}C_5H_5)(CO)_6] + [N(PPh_3)_2][BF_4]} \quad (68)$$

although there is an accompanying CO transfer from one metal to another.

A *hydrocarbon elimination* pathway was employed to obtain a series of (μ-aryl)digold(I) cations and vinyl or ferrocenyl analogues [eq 69; R = Ph, p-tolyl, CH=CH$_2$, C$_5$H$_5$FeC$_5$H$_4$, C$_5$H$_5$FeC$_5$H$_3$X (X = Cl, OMe, or CH$_2$NMe)];[138] the salt [Au(PPh$_3$)][BF$_4$] was believed to be an intermediate.

$$\mathrm{2[Au(PPh_3)R] + H[BF_4] \rightarrow [Au_2(\mu\text{-}R)(PPh_3)_2][BF_4] + RH} \quad (69)$$

Thus, the complexes were also accessible by the following alternative salt elimination procedures: [Au(Cl)PPh$_3$] + Ag[BF$_4$] or [Au(PPh$_3$)R] + Z[BF$_4$] (Z = ferrocenyl, NO$_2$, or CH$_3$CO). Some of the complexes were also obtained by ligand exchange from [Au(Me)PPh$_3$)] and a diferrocenylmercury(II) or Bi(C$_6$H$_4$Me-p)$_3$ (see eq 77).

The tetramethylaluminates have provided a source of bridging methyls by the *nucleophilic bridge-splitting* reaction of eq 70 (M = Y, Ho, Er, Tm, or Yb).[124] The success of the procedure depends on the metal center being a stronger Lewis acid site than Al; thus the reaction is unsuitable for M = Sc (see eq 73).

$$\mathrm{2[M(\mu\text{-}CH_3)_2(\eta\text{-}C_5H_5)_2AlMe_2] + 2C_5H_5N(py) \rightarrow [M_2(\mu\text{-}CH_3)_2(\eta\text{-}C_5H_5)_4] + 2AlMe_3.py} \quad (70)$$

Lewis acid addition to a bridging methyldimetal complex may lead to a new bridged complex. The clearest sample is that of eq 71 (M = Y).[124] This is a promising method of stabilizing labile bridging methyls,

$$\mathrm{[M_2(\mu\text{-}CH_3)_2(\eta\text{-}C_5H_5)_4] + Al_2Me_6 \rightarrow 2[MAl(\mu\text{-}CH_3)_2(\eta\text{-}C_5H_5)_2(CH_3)_2]} \quad (71)$$

as of $\mathrm{Ti^{III}}$, and has been used for $[\mathrm{NiAl}(\mu\text{-CH}_3)_2(\eta\text{-C}_3\mathrm{H}_5)_2(\mathrm{CH}_3)_2]$,[120] and $[\mathrm{TiAl}(\eta\text{-C}_5\mathrm{H}_5)_2(\mathrm{CH}_3)_3\mathrm{Cl}]$ from $[\{\mathrm{Ti}(\eta\text{-C}_5\mathrm{H}_5)_2\mathrm{Cl}\}_2]$ and $(\mathrm{AlMe}_3)_2$,[128] a procedure which fails with the yttrium analogue (see eq 80).

Metathetical exchange reactions of the type shown in eq 72[153] may have some potential.

$$2[\mathrm{YAl}(\mu\text{-CH}_3)_2(\eta\text{-C}_5\mathrm{H}_4\mathrm{SiMe}_3)_2(\mathrm{CH}_3)_2] + \mathrm{Al}_2(\mathrm{C}_6\mathrm{H}_4\mathrm{Me}\text{-}p)_6 \rightarrow \mathrm{Al}_2\mathrm{Me}_4(\mathrm{C}_6\mathrm{H}_4\mathrm{Me}\text{-}p)_2 + [\mathrm{YAl}(\mu\text{-C}_6\mathrm{H}_4\mathrm{Me}\text{-}p)_2(\eta\text{-C}_5\mathrm{H}_4\mathrm{SiMe}_3)_2(\mathrm{CH}_3)_2] \quad (72)$$

C. Chemical Properties

Reactions already described in section IVB refer to *metathetical exchange* (eq 72),[153] and *nucleophilic bridge-splitting*. As for the latter, for a tetramethylaluminate as substrate, this may give rise to a homodimetallic di-μ-methyl complex as in the eq 70 or alternatively, as for a Sc complex, to $(\mathrm{AlMe}_3)_2$-elimination (eq 73).[124] Clearly, the relative Lewis acidities of a

$$2[\mathrm{Sc}(\mu\text{-CH}_3)_2(\eta\text{-C}_5\mathrm{H}_5)_2\mathrm{Al}(\mathrm{CH}_3)_2] + 2\mathrm{C}_5\mathrm{H}_5\mathrm{N} \rightarrow \underset{\text{LV}}{2[\mathrm{Sc}(\eta\text{-C}_5\mathrm{H}_5)_2(\mathrm{CH}_3)(\mathrm{py})]} + \mathrm{Al}_2\mathrm{Me}_6 \quad (73)$$

series of group III metal centers in complexes $[\mathrm{MAl}(\mu\text{-CH}_3)_2(\eta\text{-C}_5\mathrm{H}_5)_2(\mathrm{CH}_3)_2]$ increase in the sequence Y $\simeq$ Ln < Al < Sc. In this context it is noteworthy that whereas the Sc complex LV is isolable, the Y analogue, obtained as a solution species according to eq 74, dissociates into

$$[\mathrm{Y}_2(\mu\text{-CH}_3)_2(\eta\text{-C}_5\mathrm{H}_5)_4] + 2\mathrm{C}_5\mathrm{H}_5\mathrm{N} \rightleftharpoons 2[\mathrm{Y}(\eta\text{-C}_5\mathrm{H}_5)_2(\mathrm{CH}_3)(\mathrm{py})] \quad (74)$$

its factors upon removal of volatiles; a similar bridge-splitting reaction as that of eq 74 may be effected by use of other hard donors such as amines, THF, or triphenylphosphine oxide, but less readily with soft donors such as PPh_3 or PEt_3. Other examples of nucleophilic bridge-splitting relate to the reactions of $[(\mathrm{MnR}_2)_4]$ (R = $\mathrm{CH}_2\mathrm{CMe}_3$) with $\mathrm{Me}_2\mathrm{N}(\mathrm{CH}_2)_2\mathrm{NMe}_2$(TMEDA) or neopentyllithium to yield $[\mathrm{MnR}_2(\mathrm{TMEDA})]$ or $\mathrm{Li}_2[\mathrm{MnR}_4]$, respectively.[126] Alternatively, the nucleophile may act as a base and effect *deprotonation*, cf., $[\mathrm{Ru}_2(\mu\text{-CH}_2)_2(\mu\text{-CH}_3)(\mathrm{PMe}_3)_6]^+$ which with LiMe yields $[\mathrm{Ru}_2(\mu\text{-CH}_2)_3(\mathrm{PMe}_3)_6]$ (see eq 37).[41]

A further manifestation of *nucleophilic bridge-splitting* is shown in eq 75, in which the nucleophile (:Nu) is PPh_3, Cl^-, I^-, or morpholine.[138] Reactions of

$$[\mathrm{Au}_2(\mu\text{-C}_6\mathrm{H}_4\mathrm{Me}\text{-}p)(\mathrm{PPh}_3)_2]^+ + :\mathrm{Nu} \rightarrow [\mathrm{Au}(\mathrm{PPh}_3)(\mathrm{Nu})]^+ + [\mathrm{Au}(\mathrm{PPh}_3)(\mathrm{C}_6\mathrm{H}_4\mathrm{Me}\text{-}p)] \quad (75)$$

this type were extended (eq 76), whence the following donor strength series [relative to $\mathrm{Au}(\mathrm{PPh}_3)^+$] was derived $[\mathrm{Au}(\mathrm{Ph})(\mathrm{PH}_3)] < [\mathrm{Au}(\mathrm{C}_6\mathrm{H}_4\mathrm{Me}\text{-}p)(\mathrm{PPh}_3)] < \mathrm{O}(\mathrm{CH}_2\mathrm{CH}_2)_2\mathrm{NH} < [\mathrm{Fe}(\eta\text{-C}_5\mathrm{H}_5)\{\eta\text{-C}_5\mathrm{H}_3(1\text{-Cl})(1\text{-AuPPh}_3)\}] < [\mathrm{Fe}(\eta\text{-C}_5\mathrm{H}_5)\{\eta\text{-C}_5\mathrm{H}_3(1\text{-OMe})(2\text{-AuPPh}_3)\}] \approx [\mathrm{Fe}(\eta\text{-C}_5\mathrm{H}_5)(\eta\text{-C}_5\mathrm{H}_4\mathrm{Au}(\mathrm{PPh}_3)\}] < [\mathrm{Fe}(\eta\text{-C}_5\mathrm{H}_5)\{\eta\text{-C}_5\mathrm{H}_3(1\text{-CH}_2\mathrm{NMe}_2)(2\text{-AuPPh}_3)\}] < [\mathrm{Fe}(\eta\text{-C}_5\mathrm{H}_5)\{\eta\text{-C}_5\mathrm{H}_4\mathrm{SAu}(\mathrm{PPh}_3)\}] \approx \mathrm{PPh}_3 < \mathrm{Cl}^- < \mathrm{I}^-$.

$$[\mathrm{Au}(\mathrm{PPh}_3)\mathrm{Z}]^+ + \mathrm{Z}' \rightarrow [\mathrm{Au}(\mathrm{PPh}_3)\mathrm{Z}']^+ + \mathrm{Z} \quad (76)$$

Another example [cf. eq 72] of metathetical exchange is illustrated in eq 77.[138]

$$2[\mathrm{Au}_2(\mu\text{-C}_6\mathrm{H}_4\mathrm{Me}\text{-}p)(\mathrm{PPh}_3)_2]^+ + \mathrm{Hg}[\mathrm{C}_5\mathrm{H}_4\mathrm{Fe}(\mathrm{C}_5\mathrm{H}_5)]_2 \rightarrow 2[\mathrm{Au}_2\{\mu\text{-}(\mathrm{C}_5\mathrm{H}_4)\mathrm{Fe}(\eta\text{-C}_5\mathrm{H}_5)\}(\mathrm{PPh}_3)_2]^+ + \mathrm{Hg}(\mathrm{C}_6\mathrm{H}_4\mathrm{Me}\text{-}p)_2 \quad (77)$$

Equation 77 might alternatively be viewed as a *reaction with an electrophile* and a number of others (eq 78–80) are noteworthy.[124] Failure to isolate the mixed-bridge intermediate of eq 80 is probably due to the insolubility in solvent toluene of one of the ultimate products, LVI. Another example is the observation of rapid scrambling (by NMR) between $[\mathrm{Y}_2(\mu\text{-CH}_3)_2(\eta\text{-C}_5\mathrm{H}_4\mathrm{Me})_4]$ and $[\mathrm{Y}_2(\mu\text{-C}_4\mathrm{H}_9\text{-}n)_2(\eta\text{-C}_5\mathrm{H}_5)_4]$;[151] this is suggestive of a *dimer* $\rightleftharpoons$ *2 monomer equilibrium*, which would also neatly account for pathways of reactions according to eq 78–80.

$$[\mathrm{Y}_2(\mu\text{-CH}_3)_2(\eta\text{-C}_5\mathrm{H}_5)_4] + \mathrm{Al}_2(\mathrm{CH}_3)_2\mathrm{Cl}_4 \rightarrow 2[\mathrm{YAl}(\eta\text{-C}_5\mathrm{H}_5)_2(\mu\text{-Cl})_2(\mathrm{CH}_3)_2] \quad (78)$$

$$[\mathrm{Y}_2(\mu\text{-CH}_3)_2(\eta\text{-C}_5\mathrm{H}_5)_4] + \mathrm{Al}_2(\mathrm{CH}_3)_6 \rightarrow 2[\mathrm{YAl}(\mu\text{-CH}_3)_2(\eta\text{-C}_5\mathrm{H}_5)_2(\mathrm{CH}_3)_2] \quad (79)$$

$$[\mathrm{Y}_2(\mu\text{-CH}_3)_2(\eta\text{-C}_5\mathrm{H}_5)_4] + \mathrm{Al}_2(\mathrm{CH}_3)_4\mathrm{Cl}_2 \rightarrow \underset{\text{not isolated}}{2[\mathrm{YAl}(\mu\text{-CH}_3)(\eta\text{-C}_5\mathrm{H}_5)_2(\mu\text{-Cl})(\mathrm{CH}_3)_2]} \rightarrow \underset{\text{LVI}}{[\mathrm{Y}_2(\eta\text{-C}_5\mathrm{H}_5)_4(\mu\text{-Cl})_2]} + \mathrm{Al}_2(\mathrm{CH}_3)_6 \quad (80)$$

Yttrium or erbium complexes $[\mathrm{M}_2(\mu\text{-CH}_3)_2(\eta\text{-C}_5\mathrm{H}_4\mathrm{R})_4]$ (R = H, Me, or SiMe_3) are active homogeneous ethylene polymerization catalysts;[151] whereas the corresponding tetramethylaluminates or analogues $[\mathrm{M'Al}(\mu\text{-CH}_3)_2(\eta\text{-C}_5\mathrm{H}_4\mathrm{R})_2(\mathrm{CH}_3)_2]$ (M′ = Y, Er, Ho, or Yb) exhibit a threshold effect (e.g., they are inactive at 75 °C and 5 bar, but effective at >95 °C and 33 bar), which is lessened by the presence of air or Lewis base. It is possible that the active species in both cases is the dimetallic homonuclear complex, possibly as the monomer. Catalyst deactivation involves abstraction of hydrogen from a $\eta\text{-C}_5\mathrm{H}_4\mathrm{R}^-$ ligand, e.g., eq 81, which is

$$[\mathrm{Y}_2\{\mu\text{-CH}_2(\mathrm{CH}_2)_n\mathrm{Me}\}_2(\eta\text{-C}_5\mathrm{H}_4\mathrm{Me})_4] \rightarrow [\mathrm{Y}_2(\mu\text{-C}_5\mathrm{H}_3\mathrm{Me}\text{-}\eta,\sigma)_2(\eta\text{-C}_5\mathrm{H}_4\mathrm{Me})_2] + 2\mathrm{Me}(\mathrm{CH}_2)_n\mathrm{Me} \quad (81)$$

eliminated by use of the peralkylated ligand $\eta\text{-C}_5\mathrm{Me}_4\mathrm{Et}^-$. Another example of a bridging alkyl dimetallic complex in *catalysis* is $[\mathrm{Mn}(\mu\text{-CH}_2\mathrm{CMe}_2\mathrm{Ph})_2(\mathrm{CH}_2\mathrm{CMe}_2\mathrm{Ph})_2]$ in the cyclotrimerization of an acetylene $\mathrm{C}_2\mathrm{R}_2$ (R = Me or Ph).[126]

VI. (μ-Alkenyl)dimetal and Related Complexes, Including Metallacyclopentadienylmetal Complexes (Tables VIII and VIIIa)

As discussed in section I, space limitations make it impracticable to describe the chemistry of the title compounds. However Tables VIII and VIIIa provide a summary of the available complexes and some relevant data.

VII. (μ-Alkynyl)dimetal Complexes (Tables IX and IXa)

As discussed in section I, space limitations make it impracticable to describe the chemistry of the title compounds. However Tables IX and IXa provide a summary of the available complexes and some relevant data.

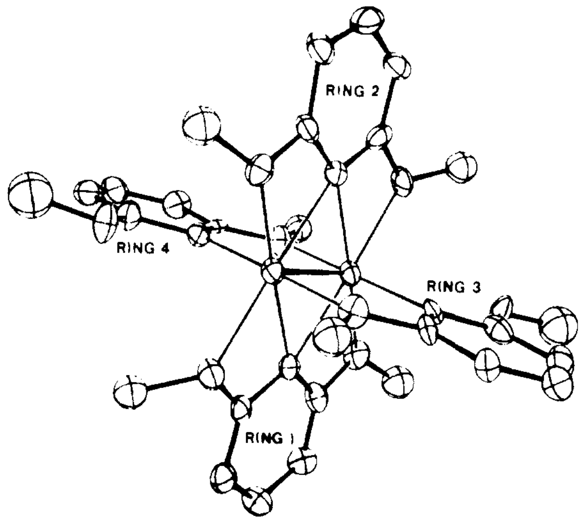


Figure 63. An ORTEP drawing of the molecule $[V_2\{\mu\text{-}C_6H_3\text{-}(OMe)_2\text{-}2,6\}_4]$. Reproduced, with permission, from: Cotton, F. A.; Millar, M. *J. Am. Chem. Soc.* 1977, *99*, 7886. The VV distance of 2.200 (2) Å is consistent with a triple bond. The molecule has C_{2h} symmetry, with rings 3 and 4 acting as bidentate and rings 1 and 2 as tridentate (2O's and 1C) ligands.

VIII. (μ-Allyl)dimetal Complexes (Tables X and Xa)

As discussed in section I, space limitations make it impracticable to describe the chemistry of the title compounds. However Tables X and Xa provide a summary of the available complexes and some relevant data.

IX. (μ-Acetylene)dimetal and Related Complexes (Table XI)

As discussed in section I, space limitations make it impracticable to describe the chemistry of the title compounds. However Table XI provides a summary of the available complexes and some relevant data.

X. μ-Hydrocarbyl-Main-group Metal-Transition-Metal Complexes (Tables XII and XIIa)

As discussed in section I, space limitations make it impracticable to describe the chemistry of the title compounds. However Tables XII and XIIa provide a summary of the available complexes and some relevant data.

XI. Miscellaneous μ-Hydrocarbyl- or μ-Hydrocarbon-Dimetal Complexes

Binuclear μ-hydrocarbyl or μ-hydrocarbon complexes which do not fit into any of the categories of Sections II–X are listed in Table XIII. As to discussion, we confine ourselves to just two categories of complex having monohapto connectivities to each of the metal atoms. In the first there is either a single carbon bridge with $\mu\text{-}CRR'^{2-}$ (Figures 54, 58, 59, and 60) or $\mu\text{-}C(\text{:}CRR')^{2-}$ (Figure 55), or a two-carbon bridge with $\mu\text{-}^{-}C(R){=}C(R')^{2-}$ (Figures 56 and 57); these classifications are gross oversimplifications, since inspection of Figures 54–61 reveals that each of the molecules in questions is zwitterionic. In the second class are more straightforward molecules exemplified by Figures 61–64, in which an alkyl ligand attached to one metal atom has a β- or γ-heteroatom (N or O) which binds either covalently (Figures 61 or 62) or coordinatively to the second metal atom.

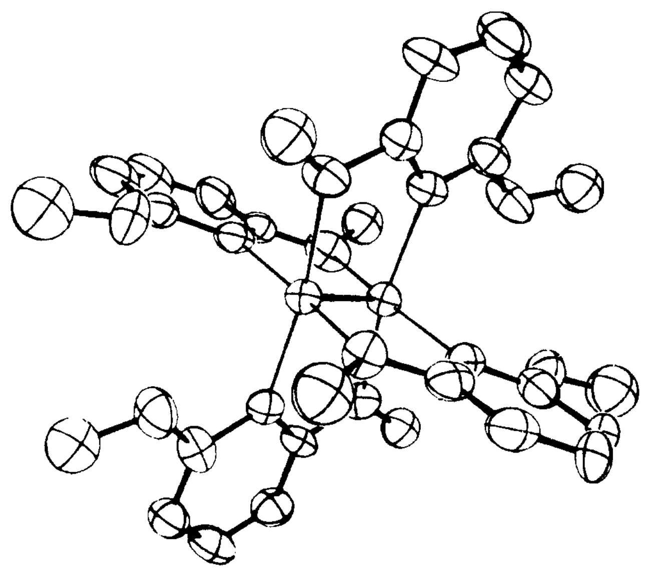
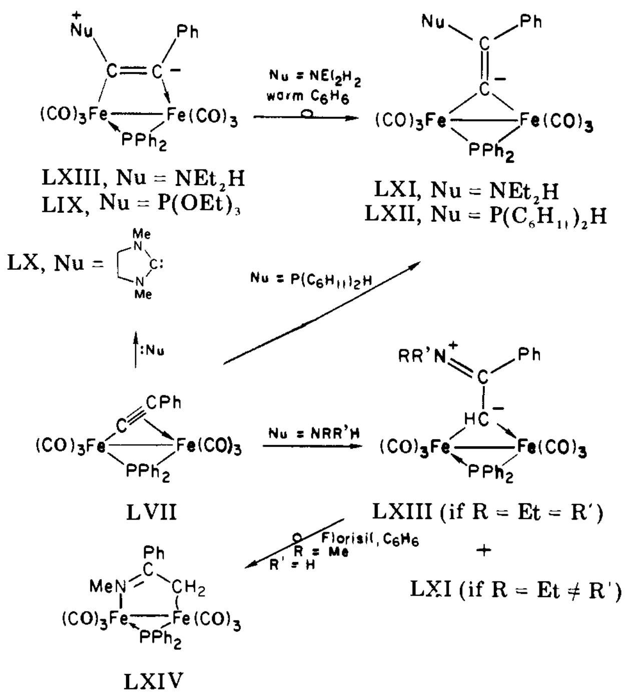
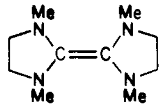


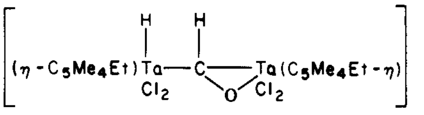
Figure 64. Schematic representation of the molecular structure of $[M\{\mu\text{-}O(Me)C_6H_3(OMe)\text{-}o\}_4]$ (M = Cr or Mo). Reproduced, with permission, from: Cotton, F. A.; Koch, S.; Millar, M. *J. Am. Chem. Soc.* 1977, *99*, 7372. The exceedingly short MM distances, 1.847 (1) (M = Cr) and 2.064 (1) Å (M = Mo), are consistent with quadruple bonds. The molecules have C_{2h} symmetry, with each ligand bidentate.

SCHEME I



The series of compounds of Figures 54 (LXIII), 55 (LXII), 56 (LIX), 57 (LX), and 61 (LXIV) is derived from the μ-(σ-,π-alkynyl)diiron compound LVII either by reaction of a C-, N-, or P-centered nucleophile or a subsequent isomerization, as illustrated in Scheme I.[158–162] Compounds LVIII and LIX may be described as ammonium or phosphonium betaines; the corresponding carbonium betaine LX is obtained by using the electron-rich olefin LXV as the carbenoid.[162]


LXV


LXVII

The tantalum complex of Figure 58 (LXVI) was obtained according to eq 82.[163] A bridging formyldi-

$$[\mathrm{Ta}(\eta\text{-}\mathrm{C_5Me_4Et})(\mathrm{CH_2CMe_3})\mathrm{Cl_2}] + \mathrm{H_2} \rightarrow \underset{\text{minor product (5\%)}}{[\mathrm{Ta_2}(\eta\text{-}\mathrm{C_5Me_4Et})_2\mathrm{Cl_5H}]} \xrightarrow[\text{(ii) PMe}_3]{\text{(i) CO}} \underset{\text{LXVI}}{[\mathrm{Ta_2}\{\mu\text{-}\mathrm{CH(PMe_3)}\}(\eta\text{-}\mathrm{C_5Me_4Et})_2\mathrm{Cl_4(H)}(\mu\text{-}\mathrm{O})]} \quad (82)$$

Ta-H by a ^1H signal at 10.0 δ.

The compound of Figure 59 was prepared as shown in eq 83,[60] and that of Figure 60 by the procedure of eq 84.[164]

$$[\mathrm{WRe}\{\mu\text{-}\mathrm{CPh}\}(\mathrm{CO})_9] + \mathrm{PMe_3} \rightarrow [\mathrm{WRe}\{\mu\text{-}\mathrm{CPh(PMe_3)}\}(\mu\text{-}\mathrm{CO})(\mathrm{CO})_8] \quad (83)$$

$$[\mathrm{Fe_3(CO)_{12}}] + (\mathrm{Me_3Sn})_2\mathrm{C{=}PPh_3} \rightarrow [\mathrm{Fe_2}\{\mu\text{-}\mathrm{C(CHO)PPh_2}\}(\mu\text{-}\mathrm{C_6H_4})(\mathrm{CO})_6] + \mathrm{CO} + [\mathrm{Fe(CO)_4(SnMe_3)_2}] \quad (84)$$

Treatment of pentacarbonyliron(0) according to eq 85 yielded the complex of Figure 61.[165]

$$[\mathrm{Fe(CO)_5}] \xrightarrow[\text{2.Ph}_3\text{CCl}]{\text{1.LiPh}} [\mathrm{Fe_2}\{\mu\text{-}\mathrm{C(Ph)O}\}_2(\mathrm{CO})_6] \quad (85)$$

(μ-o-Methoxyaryl)dimetal complexes of the type shown in Figures 63 and 64 were first reported in 1964 (the Cr compound);[166] a structure was proposed for a compound in 1976[142,168] and X-ray data appeared in 1977.[142,169] The V complex in Figure 63 is unusual in possessing a bridging aryl group coplanar with (rather than the more usual perpendicular to) the M-M bond.[144,171] Apart from these o,o′-dimethoxyphenyl complexes of V, Cr, and Mo, the related o-anisylmetal derivatives $[\mathrm{Mo_2}(\mu\text{-}\mathrm{C_6H_4OMe}\text{-}o)_4]$, $[\mathrm{Mo_2}(\mu\text{-}\mathrm{C_6H_4OMe}\text{-}o)_4(\mathrm{PMe_3})_2]$, and $[\mathrm{Re_2}(\mu\text{-}\mathrm{C_6H_4OMe})_6]$ have also been described.[170] They were prepared from $\mathrm{Mg(C_6H_4OMe}\text{-}o)_2$ and $[\mathrm{Mo_2}(\mu\text{-}\mathrm{O_2CMe})_4]$, in absence or presence of $\mathrm{PMe_3}$ or $[\mathrm{Re_2}(\mu\text{-}\mathrm{O_2CMe})_4\mathrm{Cl_2}]$. NMR spectra suggested similar types of structures to those of Figure 64, i.e., no μ-aryl bonding.

In Table XIII are found three examples of dimetallic complexes in which bridging involves a μ^2-bis(carbene), a bridging bis(carbyne).

XII. Organometallic Reactions Involving (μ-Hydrocarbyl)dimetal Intermediates

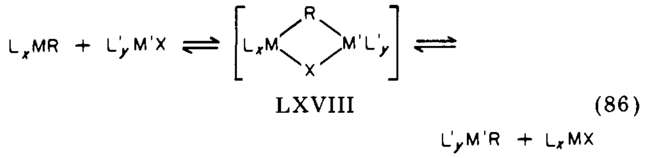
In the preceding sections of this Review we have been concerned with the chemistry of stable, discrete μ-hydrocarbyl- or μ-hydrocarbon–dimetal complexes. We now consider the part played by transient species. Our survey, of necessity selective, covers aspects of the role of bridged intermediates in stoichiometric reactions and in catalysis.

Some examples have already been encountered, e.g., μ-alkylidene intermediates in olefin metathesis (section III) and μ-alkyl species in polymerization (section V).

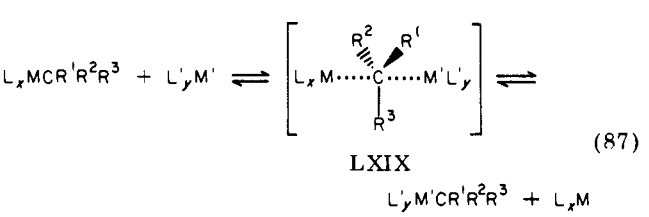
A. Hydrocarbyl Transfer between Metal Centers

Hydrocarbyl transfer between metals, both transition-metal–transition-metal and transition-metal–main-group metal represents the most widespread and general example of processes in which the reactive intermediates contain bridges. Examples include (a) R/halogen exchange as in the preparation of metal alkyls, (b) methyl-transfer reactions in natural systems mediated by methylcobalamin (as in the As and Hg cycles), and (c) catalyst activation in Ziegler–Natta systems (see section XIIC).

Two pathways can be identified. The first, and more general, involves pairwise exchange of groups between metals with formation of a (formally) electron-deficient bridge in LXVIII (eq 86). The second concerns transfer of a single hydrocarbyl entity (eq 87). In eq 86 X⁻ is either a halide (or another inorganic ion) or a hydrocarbyl group. The two cases are considered separately.



LXVIII (86)



LXIX (87)

The case where X = hydrocarbyl is the most straightforward and is exemplified by degenerate alkyl exchange as in: $[\mathrm{Co}(\eta\text{-}\mathrm{C_5H_5})\mathrm{Me_2(PR_3)}]$ and its $\mathrm{CD_3}$-labeled analogue,[172] cis-$[\mathrm{AuIMe_2(PPh_3)}]$ and $[\mathrm{AuMe(PPh_3)}]$,[173] $[\mathrm{Y_2}(\eta\text{-}\mathrm{C_5H_4R})_4\mathrm{R'_2}]$ and $[\mathrm{Y_2}(\eta\text{-}\mathrm{C_5H_4R})_4\mathrm{R''_2}]$,[151] $[\mathrm{YAl}(\mu\text{-}\mathrm{Me})_2(\eta\text{-}\mathrm{C_5H_4R})_2\mathrm{Me_2}]$ and $\mathrm{Al_2R'_6}$,[174] and $[\mathrm{U}(\eta\text{-}\mathrm{C_5H_5})_3\mathrm{R}]$ and $\mathrm{Al_2R'_6}$.[175] For certain early transition-metal complexes $\mathrm{ML_xR}$ the stable state is the dimer LXVIII (i.e., $L_xM = L_yM'$, and X = Me = R) for which there are several fully characterized complexes (e.g., Figure 45) with only transient existence of the monomeric entities, whereas for the majority of late transition metals the bridged structures represent an unstable intermediate or transition state for ligand transfer between stable mononuclear metal complexes.

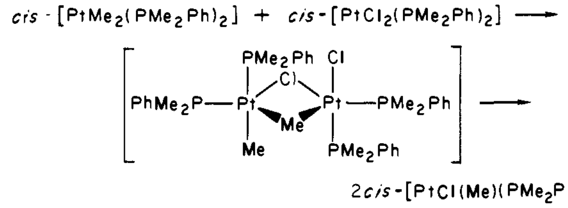
Alkyl exchanges between $[\mathrm{TiMe_4}]$ and $\mathrm{Al_2Me_6}$ or $\mathrm{Al_2(CD_3)_6}$ are known, and probably have direct relevance to mechanisms in Ziegler–Natta catalysts, but little is known of the transition state for exchange.[176] In these cases the possible formation of the ion pair $[\mathrm{TiMe_3}][\mathrm{AlMe_4}]$ complicates the picture.

R/halogen exchange provides the most general procedure for the synthesis of transition-metal alkyls and related hydrocarbyls [$L'_yM'R$ in eq 86, X = halogen]. The alkylating agent L_xMR is most usually LiR, a Grignard reagent, or an organoaluminum compound.[177] Such reactions may also give rise to (μ-hydrocarbyl)dimetal complexes (see sections V and X or alternatively, Table XII).

Mechanistic studies of R/halogen or $\mathrm{NO_3}$ exchange between transition metals provide the best examples. Methyl transfers between the metal centers $\mathrm{Pt^{II}}$, $\mathrm{Pd^{II}}$,

Au^I, and Au^{III},[178a] Pt^{II} and Pd^{II},[178b] and Au^I and Au^{III},[173] have all been interpreted in terms of transition states or intermediates of type LXVIII, e.g., eq 88. In the example of eq 88 the kinetic product *cis*-[PtCl(Me)(PMe$_2$Ph)$_2$] subsequently rearranges to the more stable trans isomer; the exchange is catalyzed by the μ-Cl$_2$-bridged complex [Pt$_2$Cl$_4$(PMe$_2$Ph)$_2$].[178a]

There is some evidence for the formation of stable (μ-R-μ-Cl)dimetal complexes of the type LXVIII (eq 86), as in [UAl(μ-Et)(μ-Cl)(η-C$_5$H$_5$)$_3$Et$_2$] {from [U(η-C$_5$H$_5$)$_3$Cl] and Al$_2$Et$_6$},[179] and [TiAl(μ-Me)(μ-Cl)(η-C$_5$H$_5$)$_2$Me$_2$].[152] We note too the existence of the related complex [TiAl(μ-CH$_2$)(μ-Cl)(η-C$_5$H$_5$)$_2$Me$_2$].[37]



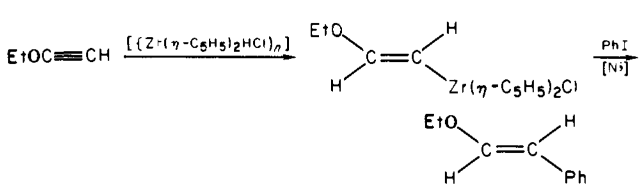
(88)

R/halogen exchange is also involved in transition-metal-mediated and -catalyzed cross-coupling reactions, a method of increasing versatility for the formation of carbon–carbon bonds (eq 89; R, R′ are hydrocarbyl groups, M is the metal of the alkylating agent, and M′ the catalyst).[180] Examples are (i) the nickel-catalyzed

$$RX + R'M \xrightarrow{[M']} RR' + MX \tag{89}$$

cross-coupling of an alkyl- or alkenyllithium compound or Grignard reagent with an aryl or alkenyl halide, and (ii) the nickel- or copper-promoted biaryl synthesis via the Ullmann reaction. Recent developments have extended the range of the metal M in the cross-coupling reaction to include boron, aluminum, and zirconium.[181]

The facility for alkyl transfer between metals enables the synthetic organic chemist to exploit sequentially the best features of a number of metal components, either as reagent or catalyst. In the zirconium–nickel system, for example, the stereospecific cis insertion of an acetylene into the Zr–H bond of [{Zr(η-C$_5$H$_5$)$_2$HCl}$_n$] to give the (*E*)-alkenylzirconocene chloride is coupled with the ability of nickel to effect catalytic coupling with an aryl halide, thereby providing a selective, high-yield synthesis of arylalkenes, e.g., eq 90.[181b]



(99%) (90)

The nickel-catalyzed coupling reaction is mechanistically the most thoroughly researched.[180] Of the several possibilities, the preferred pathway is shown in eq 91–93

$$Ni^IBr + ArBr \rightarrow ArNi^{III}Br_2 \tag{91}$$

$$ArNi^{III}Br_2 + RM \rightarrow ArNi^{III}RBr + MBr \tag{92}$$

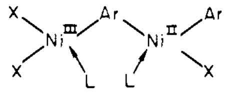
$$ArNi^{III}RBr \rightarrow Ni^IBr + ArR \tag{93}$$

where the hydrocarbyl-transfer step, eq 92, is presumed to proceed via a four-center transition state of type LXVIII.[182]

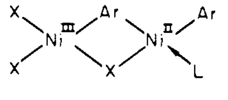
A similar sequence of events is also involved in the nickel-promoted biaryl synthesis.[183] Model studies have demonstrated the occurrence of an aryl-transfer reaction between two nickel species, eq 94, analogous to eq

$$ArNi^{III}X_2 + ArNi^{II}X \rightarrow Ni^{II}X_2 + Ar_2Ni^{III}X \tag{94}$$

92. Both mono- LXX and di- LXXI bridged intermediates were considered.



LXX



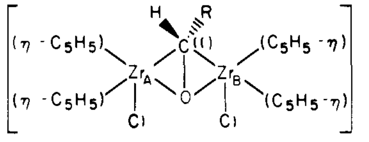
LXXI

The well-known propensity for organocopper or organocuprate complexes to form aggregates in solution (mainly tetra- or hexanuclear) with the formation of hydrocarbyl bridges suggests that bridged intermediates are implicated in syntheses involving such complexes.[180,184]

Single alkyl-transfer reactions, eq 87, play an important role in natural systems. Methyl migration from methylcobalamin to a mercury or arsenic substrate provides a major pathway in the biological Hg or As cycles. The extreme toxicity of HgMe$_2$ or methylmercuric complexes, coupling with the all-too-frequent occurrence of these metals as pollutants in aquatic environments, has provided a stimulus for mechanistic studies.[185]

B. Fluxional Processes

Bridged intermediates make a contribution to fluxional processes in di- or polynuclear metal hydrocarbyls, although a detailed discussion is outside our scope. Some recent illustrative examples for dinuclear species include (i) bridge–terminal exchange processes in [YAl(μ-R)$_2$(η-C$_5$H$_5$)$_2$R′$_2$] and related species, which show similarities to related exchange processes in Al$_2$R$_6$,[153] and (ii) intramolecular exchange of Zr$_A$ and Zr$_B$ with respect to their binding to either O or C of μ-$^-$O–$^-$CHR in [Zr$_2$(η-C$_5$H$_5$)$_4$Cl$_2$(μ-OCHR)]; this exchange which proceeds with inversion of configuration of C(1) and retention of configuration at Zr is consistent with the intermediate or transition state LXXII.[186]



LXXII

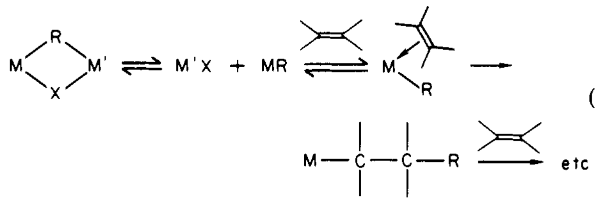
C. Olefin Polymerization

Hydrocarbyl bridges may be implicated in various reaction steps (identified below for Ziegler–Natta systems) in an active α-olefin polymerization catalyst; some of these steps are beneficial, others notably less so.

In *catalyst activation*, simple R/halogen exchange between the transition-metal salt and the cocatalyst generates a transition-metal alkyl that can initiate chain growth via sequential coordination and insertion of monomer. There is general agreement that chain growth takes place at a transition-metal–carbon (alkyl) bond and, in support of this, there are now several well-characterized complexes, e.g., [M$_2$(μ-Me)$_2$(η-C$_5$H$_5$)$_4$] (M = Y or a lanthanoid),[151] [Ni(OCPhCHPPh$_2$)Ph-

$(PPh_3)]$,[188] and $[Ni(\eta\text{-}C_3H_5)\{P(NSiMe_3)_2C_3H_5N(SiMe_3)_2\}]$,[189] containing metal–carbon bonds that form active catalysts in the absence of a cocatalyst.

Two, more controversial, roles are *direct participation in the chain propagating step* and *stabilization of active centers.* For the former, we refer to situations in which the active center contains the growing polymer chain bridging two, or perhaps more, metal atoms; insertion of olefin occurs with generation of a new bridged species. For the latter, we envisage a situation in which growing centers are stabilized via formation of bridged species (eq 95; R = growing polymer chain). If the

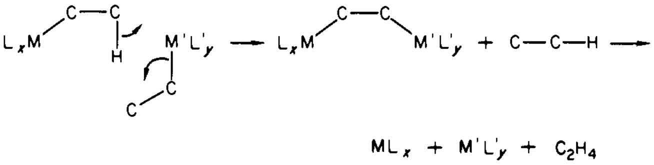


(95)

bridge is labile, it can break readily generating a vacant coordination site which is then available for binding and subsequent insertion of monomer. The formation of the bridged species can give enhanced catalyst stability by blocking hydrogen transfer via α- or β-elimination, processes requiring a free coordination position. These views are supported by (i) the improved stability of many active polymerization catalysts in the presence of excess cocatalyst, particularly alkylaluminium chlorides,[187] suggesting that stabilization is via μ-halogen-μ-alkyl bridging, (ii) the enhancement of stability observed on addition of excess Al_2Me_6 to $[TiAl(\mu\text{-}Me)_2(\eta\text{-}C_5H_5)_2Me_2]$;[152] and (iii) the formation of homogeneous catalysts for the polymerization of ethylene from the homonuclear methyl-bridged $[M_2(\mu\text{-}Me)_2(\eta\text{-}C_5H_5)_4]$ and, under slightly more forcing conditions, the heteronuclear $[MAl(\mu\text{-}Me)_2(\eta\text{-}C_5H_5)_2Me_2]$ (M = Y or a lanthanoid).[151] As for (iii), the former corresponds to a cocatalyst-free system while the latter incorporates $AlMe_3$ as the bound cocatalyst. There was no spectroscopic evidence for the presence of mononuclear species, either free $[M(\eta\text{-}C_5H_5)_2R]$ or its olefin complex, in active polymerizing solutions. This implies either that direct insertion takes place into the alkyl bridge or that the concentration of active species is small, with dissociation to monomer the rate-determining step.[151a]

The transfer of the growing polymer chain from transition metal to aluminum, presumably in a similar manner, is a common side reaction with polymerization catalysts that complicate active-site counting studies.

A well-documented *catalyst-aging process* (chain termination) is depicted in eq 96. For titanium-based

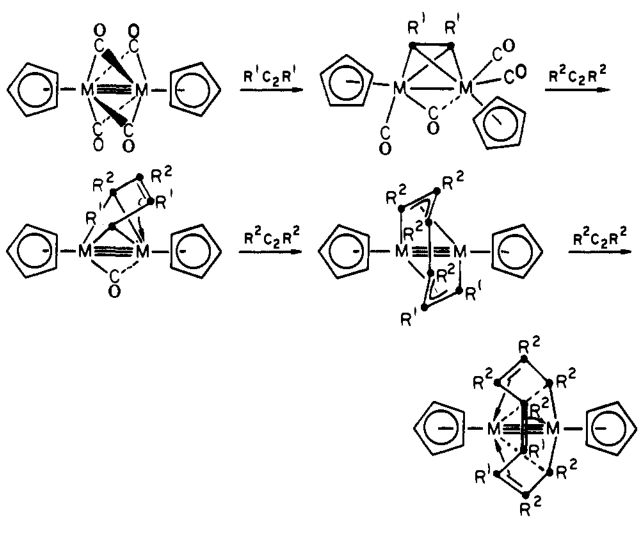


(96)

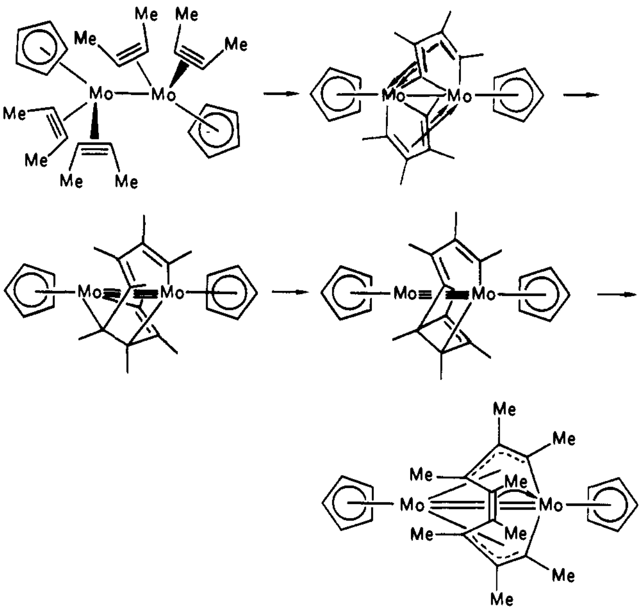
catalysts, operation of this pathway can lead to serious catalyst deactivation by formation of inactive Ti^{III} centers from active Ti^{IV}.[187a] Reaction occurs less rapidly with Zr and a well-characterized series of intermediates can be isolated (*cf.* section V).

With $[Y_2(\eta\text{-}C_5H_5)_4(\mu\text{-}Me)_2]$ a deactivation pathway has been identified which involves abstraction of a cyclopentadienyl hydrogen by the alkyl group with formation of alkane and the inactive $[Y_2(\eta\text{-}C_5H_5)_2(\mu\text{-}\eta^1,\eta^5\text{-}C_5H_4)_2]$. Complete substitution of the ring, as in C_5Me_4Et, precludes this path and gives long-lived catalysts.[151]

SCHEME II

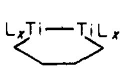


SCHEME III

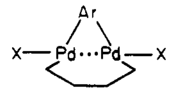


D. Oligomerization

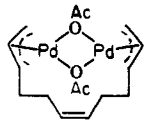
The structures LXXIII, LXXIV, and LXXV have been linked respectively with intermediates in the



LXXIII



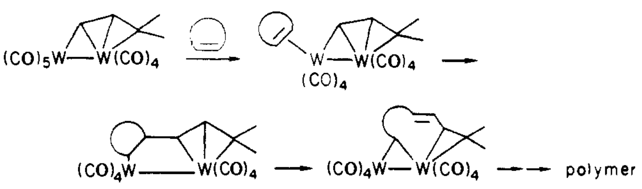
LXXIV



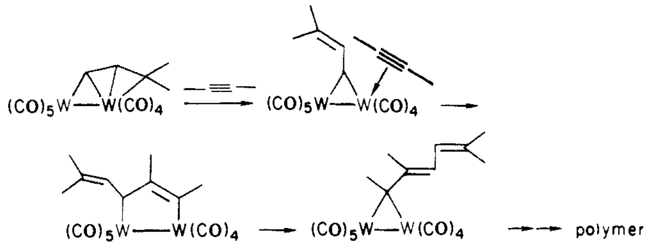
LXXV

disproportionation of ethylene to ethane and butadiene catalyzed by cyclopentadienyltitanium complexes,[190] palladium-catalyzed selective dimerization of ethylene to but-1-ene,[191] and palladium-catalyzed trimerization of butadiene to acyclic dodecatetraene isomers.[192] When dinuclear chromium and molybdenum complexes

SCHEME IV



SCHEME V



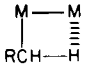
are used as models a series of reaction steps in the linking of acetylene molecules have been identified (Scheme II,[193] and III[194]) that may have relevance to acetylene polymerization and oligomerization to cyclooctatetraene. (See also ref 256, 266, and 267).

E. Olefin Metathesis

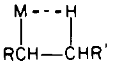
There now seems little doubt that the chain propagating entities in olefin metathesis are carbene–metal complexes and metallocyclobutanes.[195] Less certain are details of their structures. Recent reports have drawn attention to (μ-alkylidene)- and (μ-alkyl)dimetal species as active intermediates and have drawn attention to the similarities in mechanism for both olefin metathesis and alkyne polymerization.

Some novel (μ-alkylidene)ditungsten complexes (cf. section III) are active as catalysts for the metathetical ring-opening polymerization of cycloolefins (Scheme IV) and polymerization of alkynes (Scheme V).[196,197] Parallel chemistry is shown by (μ-alkylidene)diiron and -diruthenium complexes in their reactions with alkynes.[198]

The active species may also be heteronuclear with alkylidene bridges between a transition metal and a main-group metal. $[TiAl(\mu\text{-}CH_2)(\mu\text{-}Cl)(\eta\text{-}C_5H_5)_2(CH_3)_2]$ is unusual in forming a titanium-based catalyst.[38] It has been suggested that the propagating center in the catalyst $[WOCl_4]/SnMe_4$ has the structure $[Cl_3W(O)\text{-}CH_2SnMe_3]$.[199] As in polymerization, these proposals draw attention to one of the roles of the cocatalyst in stabilizing the active transition-metal center, via the formation of alkylidene or alkyl bridges. The formation of active centers in homogeneous catalysts, e.g., WCl_6/Al_2R_6, has been interpreted in terms of sequential R/halogen exchange and generation of the carbene–metal complex via α-elimination assisted by bridging between the transition-metal and the main-group-metal cocatalyst.[200] In this context, attention has been drawn to the ready pathway for α-elimination offered by di- and polynuclear aggregates. α-Elimination between two metals and β-elimination at a single metal site are formally analogous, compare LXXVI and LXXVII.[201]



LXXVI



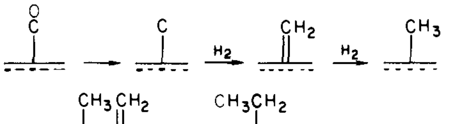
LXXVII

F. Metal Clusters and Relevance to Heterogeneous Catalysis

Our main concern has been with hydrocarbyl bridges in dinuclear metal complexes. In this, the last section, we touch briefly on the roles of hydrocarbyl bridges in tri- and polynuclear metal aggregates by way of reference to catalysis by metal clusters and heterogeneous catalysts.[202,203] Ensembles of metal atoms offer special opportunities for the stabilization of coordinatively unsaturated intermediates via bonding to two, three, or possibly more metal atoms. Thus we may expect to find chemistry not shown with mono- or even dinuclear metal complexes.

A priori there is no reason why involvement of polynuclear hydrocarbyl-bridged intermediates in catalysis is essential. Mechanistic studies of several of the now many homogeneous catalyzed industrial processes reveal no role for such species. There are, however, areas in which catalysis by discrete mononuclear complexes is unable to match that of heterogeneous catalysts. These include skeletal rearrangements and dehydrocyclizations of aliphatic hydrocarbons (which feature prominently in catalytic re-forming for the production of gasoline and aromatic hydrocarbons), and the conversion of synthesis gas (mixtures of carbon oxides and hydrogen) to hydrocarbons, collectively termed the Fischer–Tropsch Reaction.[204] For the former, it is possible to reconcile the disparity by virtue of the fact that the temperatures employed (ca. 500 °C) lie well above those considered as the typical range of stability for coordination complexes. The Fischer–Tropsch reaction is perhaps a good example of a process in which bridged-intermediates play key roles on the reaction pathway, a view that has received some support from very recent mechanistic studies.

Three separate and quite different mechanistic proposals have received the most consideration. There is as yet no consensus of agreement on which is the best description, and, indeed, it may well be that different mechanisms are operative with the same catalyst under different conditions. The first, suggested by Fischer and Tropsch in 1926,[205] outlined in eq 97 (bonding details omitted), involves metal-bound carbide, alkylidene (and possibly alkylidyne), and alkyl intermediates. A second mechanism, eq 98,[206] involves metal-bound hydroxycarbenes as the key species, while the



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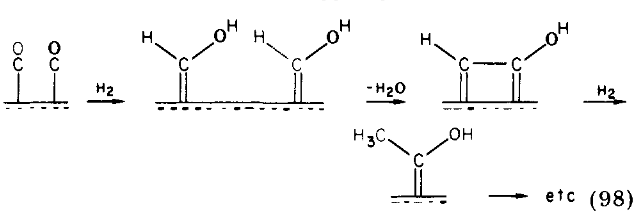

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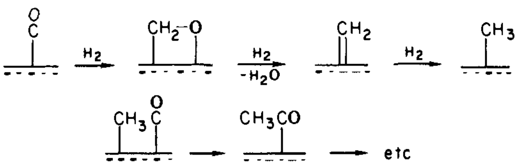
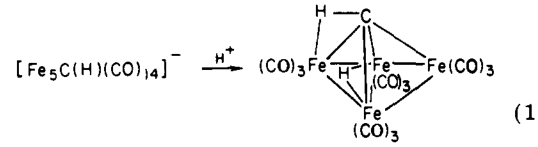


(99)

third, and most recent, eq 99,[207] refers to alkylidene-, alkyl-, and acylmetal species.

In the Fischer and Tropsch mechanism a multimetallic site is required for dissociative adsorption of carbon monoxide to give the initial surface-carbide species; and in all three mechanisms stabilization of, in particular, the alkylidene intermediates is provided via bonding to two or more metal atoms. Some recent observations are pertinent.

(i) The incorporation of a preformed surface-carbide layer on heterogeneous catalysts into the hydrocarbon products has been established by ^{13}C labeling.[208] Parallel studies with metal carbido clusters as models had, until recently, been much less useful.[209] The majority of carbide clusters are characterized in having the carbon atom totally encapsulated by metal atoms; in consequence the carbon is unreactive. The rarer examples which incorporate the carbon in a more exposed position at one of the metal faces have a better developed chemistry. The carbon in $[Fe_5C(H)(CO)_{14}]^-$ can be transformed via treatment with HCl to give a μ_4-alkylidyne, eq 100 an interesting feature is the Fe–H interaction (X-ray).[210] Removal, via oxidation with tropylium bromide, of one apex from $[Fe_6C(CO)_{16}]^{2-}$ gives an unstable face-centered Fe_5-carbide cluster that undergoes reaction with carbon monoxide and methanol at the carbide carbon to give a μ_4-CCOOMe group, eq 101; further reaction with hydrogen gives methyl acetate.[211]



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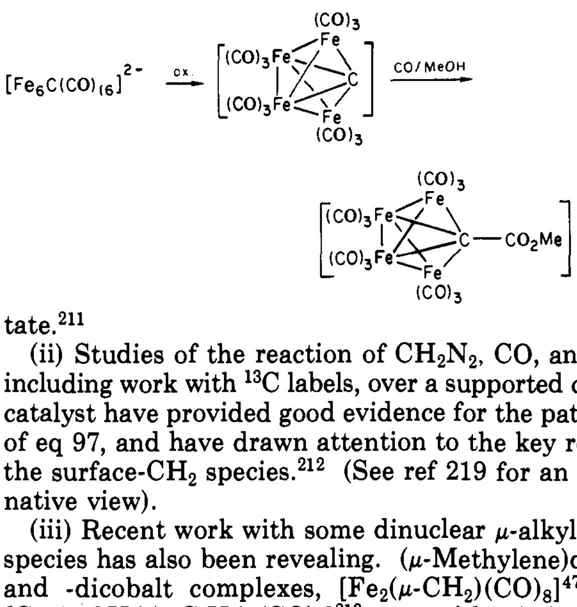
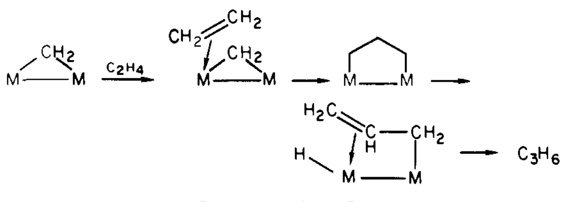


(101)

(ii) Studies of the reaction of CH_2N_2, CO, and H_2, including work with ^{13}C labels, over a supported cobalt catalyst have provided good evidence for the pathway of eq 97, and have drawn attention to the key role of the surface-CH_2 species.[212] (See ref 219 for an alternative view).

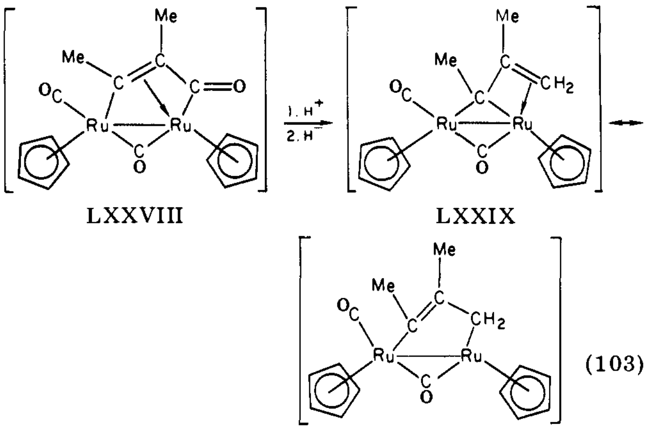
(iii) Recent work with some dinuclear μ-alkylidene species has also been revealing. (μ-Methylene)diiron and -dicobalt complexes, $[Fe_2(\mu\text{-}CH_2)(CO)_8]$[47] and $[Co_2(\mu\text{-}CH_2)(\eta\text{-}C_5H_5)_2(CO)_2]$[213] react with ethylene under mild conditions to give propylene as the major product. The most plausible pathway is via a μ-$(CH_2)_3$ intermediate (eq 102, ligands omitted for clarity).



(102)

In related studies of the decomposition of $[Zr(\eta\text{-}C_5H_5)_2(CH_2)PMePh_2]$ to CH_4, C_2H_4, and C_2H_6, spectroscopic evidence (^{13}C NMR) was obtained for a (μ-methylene)dizirconium intermediate.[214]

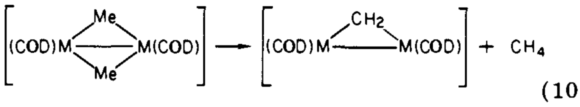
(iv) Sequential addition of H^+ (as $[HBF_4]$) and H^- (as $Na[BH_4]$) to the diruthenium complex LXXVIII has afforded the μ-alkylidene LXXIX and provides some support for a CO insertion/reduction pathway (eq 103).[215]



LXXVIII LXXIX

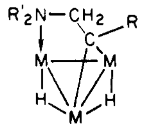
(103)

(v) The μ-CH_2-μ-H → μ-CH_3 tautomerism is well-established in the Os_3-cluster system (see XVI),[78] and in some dinuclear rhodium and iridium complexes there is an interesting conversion of (μ-CH_3) into μ-CH_2 + CH_4 (eq 104).[216]

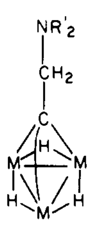


(104)

It is widely held that metal cluster complexes bear close resemblances to heterogeneous catalysts. In principle it should be possible to overcome the multisite nature, and hence lack of selectivity, of heterogeneous catalysts by the designed synthesis of appropriate cluster species.[202] The considerable promise of this approach has been slow to emerge; to date there are very few well-authenticated examples of catalysis by clusters.[203] One of these is the catalysis of H/D exchange in alkylamines by $[Ru_3(CO)_{12}]$, $[Rh_6(CO)_{16}]$, or a related group VIII metal cluster carbonyl.[217] The intermediacy of the μ_2-alkylidene- and μ_3-alkylidyne-cluster species LXXX and LXXXI was proposed to account for the strong preference for β-substitution in the products. Close parallels were also found in the substitution patterns with both the cluster species and palladium black providing a firm link between homogeneous clusters and heterogeneous metal catalysts.



LXXX



LXXXI

XIII. A Brief Survey of Recent Literature

A. 1981–mid 1982

Interest in the chemistry of μ-hydrocarbyl species has intensified since the completion (literature to end of

TABLE IVa. μ-Vicinal (1,n;n > 2) Alkylidenedimetal Complexes

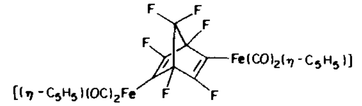
compound	preparation	comments	ref
$[V_2(\mu\text{-}C{\equiv}CC_6H_4C{\equiv}C\text{-}p)(\eta\text{-}Cp)_4]$	$[V(\eta\text{-}Cp)_2X] + LiC{\equiv}CC_6H_4C{\equiv}CLi\text{-}p$ ($X = Cl$ or Br)	$Cp = C_5H_5$ or C_5Me_4Et	221
$[V_2(\mu\text{-}C_6H_4\text{-}p)(\eta\text{-}Cp)_4]$	$[V(\eta\text{-}Cp)_2X] + LiC_6H_4Li\text{-}p$ ($X = Cl$ or Br)	$Cp = C_5H_5$, C_5H_4Me (X-ray) or C_5Me_4Et; 4 electrons per molecule remain unpaired	221
$[Mo_2(\mu\text{-}(CH_2)_4)(CO)_6(\eta\text{-}C_5H_5)_2]$	$[Mo(CO)_3(\eta\text{-}C_5H_5)]^- + I(CH_2)_4I$		222
	$[Fe(CO)_2(\eta\text{-}C_5H_5)]^- + C_7F_8$		223
$[Co_2(\mu\text{-}CH_2C_6H_4CH_2\text{-}o)(\eta\text{-}C_5H_5)_2(CO)_2]$	$Na[Co_2(\eta\text{-}C_5H_5)_2(\mu\text{-}CO)_2] + o\text{-}C_6H_4(CH_2Br)_2$		224a
$[Ni_2(\mu\text{-}CH_2C_6H_4CH_2)(PR_3)_2X_2]$	$Ni^0 + C_6H_4(CH_2X)_2$	1,2 isomer, $R = C_6H_{11}$, $X = Br$; 1,4 isomer, $R = Ph$, $X = Cl$	224b
$[Ni_2(\mu\text{-}C_{10}H_6(CH_2)_2\text{-}2,3)(PPh_3)_2Br_2]$	$Ni^0 + C_{10}H_6(CH_2Br)_2$		224b
$[Ni_2(\mu\text{-}C_6H_4\text{-}p)(PPh_3)_4Br_2]$	$[Ni(PPh_3)_2Br_2] + C_6H_4Li_2$		224b
$[Pd_2(\mu\text{-}C_6H_4\text{-}o)(\mu\text{-}dppm)_2I_2]$	$[Pd_2(dppm)_3] + C_6H_4I_2$		225
$[Pt(Cl)(PEt_3)(CH_2CH(CH_2NMe_2)CH(CH_2NMe_2)CH_2)Pt(Cl)(PEt_3)]$	$[Pt_2Cl_4(PEt_3)_2(\mu\text{-}C_4H_6)] + Me_2NH$	X-ray, analogues substituted at P and N also prepared	226
$[M_2(\mu\text{-}CH_2CH_2)(CO)_4(\eta\text{-}C_5H_5)_2L_2]$ or $[M(L_n)Re(\mu\text{-}CH_2CH_2)(CO)_5]$	e.g., $[M(CO)_2(L)(\eta^2\text{-}C_2H_4)(\eta\text{-}C_5H_5)]^+ + [M(CO)_2(L)(\eta\text{-}C_5H_5)]^-$	$M = Mo$ or W, $L = CO$; $M = W$, $L = PPh_3$ $M(L_n) = W(CO)_2(PPh_3)(\eta\text{-}C_5H_5)$ or $Re(CO)_5$	290

TABLE Va. μ-Geminal (1,1-) Alkylidenedimetal Complexes

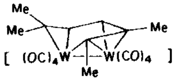
compound	preparation	comments	ref
$[ZrRu(\mu\text{-}CH_2)(\mu\text{-}Cl)Cl(PPh_3)_2(\eta\text{-}C_5H_5)_2]$	$[ZrMe_2(\eta\text{-}C_5H_5)_2] + [RuCl_2(PPh_3)_3]$		227
$[W_2(\mu\text{-}C{=}C{=}CR_2)(CO)_{10}]$	$[W(CO)_5({=}C{=}C{=}CR_2)]$ heat or $[W(CO)_6]$, $h\nu$	$R_2 = Ph_2$ or $C_6H_4C_6H_4\text{-}o,o'$; X-ray ($R = Ph$)	228
$[W_2(\mu\text{-}\eta^1,\eta^3\text{-}CMeCMe{=}CHCH{=}CMe_2)(CO)_9]$	$[W_2(\mu\text{-}\eta^1,\eta^3\text{-}CHCH{=}CMe_2)(CO)_9] + MeC{\equiv}CMe$	X-ray	229
	$[W_2(\mu\text{-}\eta^1,\eta^3\text{-}CHCH{=}CMe_2)(CO)_9] + MeC{\equiv}CMe$	X-ray	196
$[W(\mu\text{-}\eta^1,\eta^3\text{-}CHC_6H_4Me\text{-}p)(CO)_2(\eta\text{-}C_5H_5)ML_n][BF_4]$ (A)	$[W(\mu\text{-}CC_6H_4Me\text{-}p)(CO)_2(\eta\text{-}C_5H_5)ML_n] + H[BF_4]$	$ML_n = Co(CO)(\eta\text{-}C_5Me_5)$ or $Pt(PMe_3)_2$ (X-ray)	230
$[W(\mu\text{-}CHC_6H_4Me\text{-}p)(\mu\text{-}CO)(CO)(PMe_2R)(\eta\text{-}C_5H_5)\text{-}ML_n]BF_4$	(A) + PMe_2R	$R = Ph$, $ML_n = Co(CO)(\eta\text{-}C_5Me_5)$; $R = Me$, $ML_n = Pt(PMe_3)_2$	230
$[WCo(\mu\text{-}\eta^1,\eta^3\text{-}C(C_6H_4Me\text{-}p)CMe{=}CHMe)(\mu\text{-}CO)(CO)\text{-}(\eta\text{-}C_5H_5)(\eta\text{-}C_5Me_5)][BF_4]$	(A) + $MeC{\equiv}CMe$	X-ray	230
$[WPt(\mu\text{-}CHC_6H_4Me\text{-}p)(\mu\text{-}H)(CO)_2(PMe_3)_2(\eta\text{-}C_5H_5)]$	(A) + $KBH(CHMeEt)_3$	X-ray	230
$[MPt(\mu\text{-}C(OMe)C_6H_4R\text{-}p)(CO)_5(PR_3)_2]$	$[M(C(OMe)C_6H_4R\text{-}p)(CO)_5] + [Pt(cod)_2] + PR_3$	$M = Cr$, $R = Me$, $PR_3 = PMe_3$ or PMe_2Ph; $R = CF_3$, $PR_3 = PMe_3$. $M = W$, $R = Me$ or CF_3; $PR_3 = PMe_3$ or PMe_2Ph	231
$[MPt(\mu\text{-}C(OMe)C_6H_4Me\text{-}p)(CO)_4(PR_3)_3]$	$[MPt(\mu\text{-}C(OMe)C_6H_4R\text{-}p)(CO)_5(PR_3)_2] + PR_3$, $h\nu$	$M = Cr$, $PR_3 = PMe_3$ $M = W$, $PR_3 = PMe_3$ (X-ray) or PMe_2Ph	231
$[WPt(\mu\text{-}CPh_2)(CO)_4(PMe_3)_2L]$	$[W(CPh_2)(CO)_5] + [Pt(cod)_2] + PMe_3$	$L = CO$ or PMe_3	231
$[CrPt(\mu\text{-}COCH_2CH_2CH_2)(CO)_5(PMe_2Ph)_2]$	$[Cr(COCH_2CH_2CH_2)(CO)_5] + [Pt(cod)_2] + PMe_2Ph$		231

TABLE Va (*Continued*)

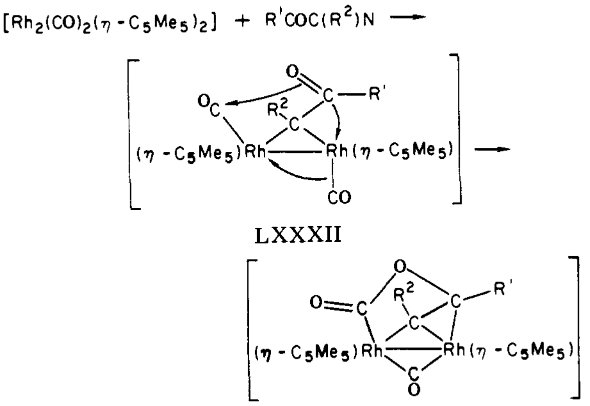
$[MnFe(\mu-C=CRR')(CO)_6(\eta-C_5H_5)]$	$[Mn(=C=CRR')(CO)_2(\eta-C_5H_5)] + [Fe_2(CO)_9]$	R,R' = H, COOMe (X-ray); CPh_2	232
$[Fe_2(\mu-CHR)(\mu-CO)(CO)_2(\eta-C_5H_5)_2]$	$[Fe_2(CO)_4(\eta-C_5H_5)_2] + Ph_3P=CHR$ or $[Fe(CO)_2(CH_2OCOMe)(\eta-C_5H_5)] + [Fe(CO)_2(\eta-C_5H_5)]^-$	R = H, Me or Pr; X-ray R = H (cis)	233, 234
$[Fe_2(\mu-CH_2)(\mu-CO)(\mu-dppm)(\eta-C_5H_5)_2]$	$[Fe_2(\mu-CH_2)(\mu-CO)(CO)_2(\eta-C_5H_5)_2]$ + dppm		235
$[Fe_2(\mu-CRR')(\mu-NO)_2(\eta-C_5H_5)_2]$	$[Fe_2(\mu-NO)_2(\eta-C_5H_5)_2] + RR'CN_2$	R,R' = Ph_2; $C_6H_4C_6H_4$-*o,o'*; CBr=CBrCBr; $C_6H_4COC_6H_4$-*o,o'*	236
$[Fe_2(\mu-CRR')(NO)_2(\eta-C_5H_5)_2]$	$[Fe_2(\mu-NO)_2(\eta-C_5H_5)_2] + RR'CN_2$	R,R' = H_2; H, Me; CH=CHCH=CH	236, 237
$[(OC)_3Fe(\mu-CHCH_2CH_2NCH_2CH_2)(\mu-CO)Fe(CO)_3]$	$[Fe_2(CO)_9] + CH_2=CHCH_2NCH_2CH_2$	via metal-induced, vinyl-ethylidene rearrangement	238
$[Fe_2(\mu-C)(TPP)_2]$	$[FeTPP] + CI_4$	TPP = 5,10,15,20-tetraphenylporphyrin (X-ray); first example of μ-carbidodimetal species; dialkylidene bonding, linear Fe=C=Fe	239
$[Fe_2(\mu-C=C(R)CH_2Ph)(\mu-CO)(CO)_2(\eta-C_5H_5)_2]$	$[Fe_2(CO)_2(\eta-C_5H_5)_2] + CHPhCHRCCl_2$, phase-transfer conditions	R = H or Ph (X-ray, cis isomer); reaction fails with $[Fe(CO)_2(\eta-C_5H_5)]^-$ in THF	272
$[Ru_2(\mu-CMe_2)(\mu-C=CH_2)(CO)_2(\eta-C_5H_5)_2]$	$[Ru_2(\mu-CMe)(\mu-CMe_2)(CO)_2(\eta-C_5H_5)_2][BF_4] + H_2O$		240
$[Ru_2(\mu-CHMe)(\mu-CMe_2)(CO)_2(\eta-C_5H_5)_2]$	$[Ru_2(\mu-CMe)(\mu-CMe_2)(CO)_2(\eta-C_5H_5)_2][BF_4] + Na[BH_4]$	X-ray; heat, 200 °C → $Me_2C=CHMe$	240
$[Ru_2(\mu-CR_2)(\mu-CO)(CO)_2(\eta-C_5H_5)_2]$	$[Ru_2(\mu-COCPhCPh)(\mu-CO)(CO)(\eta-C_5H_5)_2] + Ph_3P=CH_2$ (R = H) + Ph_2CN_2 (R = Ph) + $H(EtOOC)CN_2$ (R_2 = H, COOEt)	R = Ph readily decarbonylates to $(\mu-\eta^1,\eta^3-CPh_2)$ complex	241
$[Ru_2(\mu-\eta^1,\eta^3-CMeCRCH_2)(\mu-CO)(CO)(\eta-C_5H_5)_2]$	$[Ru_2(\mu-CMe)(\mu-CO)(CO)_2(\eta-C_5H_5)_2]^+ + RCH=CH_2$, $h\nu$ or $[Ru_2(\mu-CO)_2(CO)(C_2H_4)(\eta-C_5H_5)_2]$ + (i) LiMe, (ii) $H[BF_4]$, (iii) $Na[BH_4]$	R = H or Me (X-ray)	215
$[M_2(\mu-\eta^1,\eta^3-CRCRCHMe)(\mu-CO)(CO)(\eta-C_5H_5)_2]$	$[M_2(\mu-CHMe)(\mu-CO)(CO)_2(\eta-C_5H_5)_2] + RC\equiv CR$	M = Fe or Ru; R = H or COOMe X-ray (Figure 30) (M = Fe, R = COOMe)	198
$[Fe_2(\mu-CHCH=CHMe)(\mu-CO)(CO)_2(\eta-C_5H_5)_2]$	$[Fe_2(\mu-\eta^1,\eta^3-CHCHCHMe)(\mu-CO)(CO)(\eta-C_5H_5)_2]$ + CO (100 bar, 50 °C)	Heat or $h\nu$ causes loss of CO	198
$[Co_2(\mu-CH_2)(CO)_2(\eta-C_5Me_5)_2]$	$[Co_2(\mu-CO)_2(\eta-C_5Me_5)] + RHCN_2$		242
$[Co_2(\mu-CHMe)(\mu-CO)_2(\eta-C_5Me_5)_2]$			242
$[Co_2(\mu-CHR)(\mu-CO)(\eta-C_5Me_5)_2]$ (R = H or Me)			242
$[Co_2(\mu-CH_2)(\mu-CHMe)(\mu-CO)(\eta-C_5Me_5)_2]$	$[Co_2(\mu-CH_2)(\mu-CO)(\eta-C_5Me_5)_2] + MeCHN_2$		242
$[Co_2(\mu-CH_2)(\mu-SO_2)(\mu-CO)(\eta-C_5Me_5)_2]$	$[Co_2(\mu-CH_2)(\mu-CO)(\eta-C_5Me_5)_2] + SO_2$		242
$[Co_2(\mu-CH_2)(CO)_2(\eta-C_5H_4R)_2]$	$Na[Co_2(\mu-CO)_2(\eta-C_5H_4R)] + CH_2I_2$	R = H or Me, $(\eta-C_5H_5)(\eta-C_5H_4Me)$ species produced via disproportionation	213
$[CoRh(\mu-CH_2)(CO)_2(\eta-C_5H_5)_2]$	$[Co_2(\mu-CH_2)(CO)_2(\eta-C_5H_5)_2] + [Rh_2(CO)_4(\eta-C_5H_5)_2]$		213
$[Rh_2(\mu-CR_2)(CO)_2(\eta-C_5Me_5)_2]$	$[Rh_2(\mu-CO)_2(\eta-C_5Me_5)_2] + R_2CN_2$	$R_2 = (CO_2AlR'_2)_2$, $C_6H_4(CO)_2$-*o*; acyclic and nucleophilic carbonyl groups undergo cycloaddition to give μ-alkenyl complexes, cf. Table VIIIa	243
$[Hg\{Rh_2\{\mu-C(COOEt)\}(\mu-CO)_2(\eta-C_5Me_5)_2\}_2]$	$[Rh_2(\mu-CO)_2(\eta-C_5Me_5)_2] + [Hg(C(N_2)COOEt)_2]$	first heavy metal-substituted μ-alkylidene	244
$[Rh_2(\mu-CH_2)_2(Me)_2(\eta-C_5Me_5)_2]$	$[Rh(\eta-C_5Me_5)Cl_4]$ + MeLi (or Al_2Me_6)		245
$[Rh_2(\mu-CH_2)_2Cl_2(\eta-C_5Me_5)_2]$	$[Rh_2(\mu-CH_2)_2(Me)_2(\eta-C_5Me_5)_2]$ + HCl	$\mu-CH_2$ surprisingly unreactive, Cl/X exchange with NaX, X = Br, I, N_3, (X-ray), SCN (X-ray), OAc; or Al_2Et_6, X = Et	246
$[[Rh_2(C_8H_{14})_2(CO)_2Cl_2(\mu-C=C=O)_2]_x]$	$[Rh_2(C_8H_{14})_4Cl_2] + C_2O$	polymer with ketenide and chloro bridges	247
$[Rh_2(\mu-CRR')(\mu-CO)_2(\eta-C_5Me_5)_2]$	$[Rh_2(\mu-CO)_2(\eta-C_5Me_5)_2] + RR'CN_2$	R,R' = $C_6H_4C_6H_4$-*o,o'*, $C_6H_4COC_6H_4$-*o,o'*, CX=CXCX=CX (X=Cl, Br)	248
$[Rh_2(\mu-CRR')(\mu-CO)(\eta-C_5Me_5)_2]$	$[Rh_2(\mu-CO)_2(\eta-C_5Me_5)_2] + RR'CN_2$		

$[Rh_2(\mu\text{-}CRR')(CO)_2(\eta\text{-}C_5Me_5)_2]$	$[Rh_2(\mu\text{-}CO)_2(\eta\text{-}C_5Me_5)_2]$ + $RR'CN_2$	R,R' = H_2; H, Me; H, CF_3; H, Et; H, COOEt; H, C(COOEt)=NCN; $(COOMe)_2$; Ph_2; Ph, py; $C_6H_4(CO)_2$-o; CH=CHCH=CH	248
$[Rh_2(\mu\text{-}CH_2)(\mu\text{-}CPh_2)(\mu\text{-}CO)(\eta\text{-}C_5Me_5)_2]$	$[Rh_2(\mu\text{-}CPh_2)(\mu\text{-}CO)(\eta\text{-}C_5Me_5)_2]$ + CH_2N_2		248
$[Rh_2(\mu\text{-}C{=}CH_2)(CO)_2(\eta\text{-}C_9H_7)_2]$	$[Rh(CO)(C_2H_4)(\eta\text{-}C_9H_7)]$ + HC≡CH	C_9H_7 = indenyl; X-ray (trans)	249
$[Rh_2(\mu\text{-}CRR')(\mu\text{-}NO)(\eta\text{-}C_5Me_5)_2][BF_4]$	$[Rh_2(\mu\text{-}NO)(\mu\text{-}CO)(\eta\text{-}C_5Me_5)_2][BF_4]$ + $RR'CN_2$	R,R' = H_2; H, Me; H, Ph; Ph_2. (μ-CRR')(μ-NO)(μ-CO) intermediate not isolated—readily decarbonylates	250
$[Ir_2(\mu\text{-}CH_2)_2(cod)_2]$	$[Ir_2Cl_2(cod)_2]$ + MeLi	X-ray, unsymmetrical bridge	251
$[Pd_2(\mu\text{-}CHR)(\mu\text{-}dppm)_2X_2]$	$[Pd_2(dppm)_3]$ + $CHRX_2$	R = H or Me; X = Cl, Br, or I; + HBF_4, (μ-CH_2) → terminal Pd–Me; I displaced by pyridine or MeCN	225
$[Pt_2(\mu\text{-}CH_2)(\mu\text{-}dppm)_2X(L)][PF_6]$	$[Pt_2(\mu\text{-}dppm)H(L)][PF_6]$ + CH_2N_2	X = Me, L = CO or PMe_2Ph; X = Me or Cl, L = CH_2PPh_3	252
$[Au_2(\mu\text{-}CH_2)(\mu\text{-}CH_2PMe_2CH_2)_2X_2]$	$[Au_2(\mu\text{-}CH_2PMe_2CH_2)_2]$ + CH_2X_2	X = Cl (X-ray), Br, or I	253

1980) of sections I–X of our manuscript. A particular feature has been the rapid growth in publications dealing with μ-alkylidene (carbene) complexes (section III) which are widely considered to be models for μ-methylene and related dimetallic intermediates which may feature in Fischer–Tropsch catalysis.[218]

This section, added in August 1982, provides an account of additional material published to mid-1982. The text highlights these recent advances while a more comprehensive summary of new complexes is provided by way of supplementary tables (IVa–Xa, XIIa, and XIIIa). There is now a wealth of structural information on (μ-alkylidene)dimetal species; X-ray data are available for 17 new complexes (details in Table Va). Some recent results fully confirm earlier MO calculations on the alkylidene bridge; the detailed electron-density map from an X-ray analysis[282] and the He(I) photoelectron spectrum[283] of $[Mn_2(\mu\text{-}CH_2)(CO)_4(\eta\text{-}C_5H_5)_2]$ showed that high electron density is located in the region of the bridge carbon and not along the Mn–Mn vector.

The reactions of diazo compounds with unsaturated dimetal species continues to be a very popular and general route to (μ-alkylidene)dimetal complexes (cf. Table Va). In some cases reactions can take an unusual course. Treatment of $[Fe_2(\mu\text{-}NO)_2(\eta\text{-}C_5H_5)_2]$ or $[Rh_2(CO)_2(\eta\text{-}C_5Me_5)_2]$ with diazocyclopentadiene gave the μ-cyclopentadienylidene complexes, $[Fe_2(\mu\text{-}C_5H_4)(NO)_2(\eta\text{-}C_5H_5)_2]$ or $[Rh_2(\mu\text{-}C_5H_4)(CO)_2(\eta\text{-}C_5Me_5)_2]$, but with $[Mo_2(CO)_4(\eta\text{-}C_5H_5)_2]$ rearrangement and ligand loss gave the more common η^1,η^5-bonding mode of the C_5H_4 group in $[Mo_2(\mu\text{-}\eta^1,\eta^5\text{-}C_5H_4)(CO)_3(\eta\text{-}C_5H_5)_2]$.[237] In the reaction of $[Rh_2(CO)_2(\eta\text{-}C_5Me_5)_2]$ with a diazoalkane $R^1COC(R^2)N_2$ intramolecular cycloaddition via attack of the keto oxygen at CO afforded a series of μ-alkenyl complexes LXXXIII, (eq 105, R^1 = R^2 = Me, Ph, C_6H_4OMe-p, or COOEt; R^1 = Me, R^2 = Ph; X-ray data are available for R^1 = R^2 = Ph).[243] Only with nonnucleophilic keto groups [R^1 = R^2 = $COOAlR^3_2$, R^3 = alkyl], less electrophilic carbonyl groups (Co in place of Rh), or with cyclic diazo compounds [R^1, R^2 = $C_6H_4(CO)_2$-o] were the expected μ-alkylidene complexes LXXXII obtained. Another diazoalkane reaction, eq 106, R = C_6H_4Me-p), is of interest in part because it



LXXXII

LXXXIII (105)

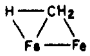
$$[Mo_2(\mu\text{-}CR_2)(CO)_4(\eta\text{-}C_5H_5)_2] + R_2CN_2 \rightarrow [(\eta\text{-}C_5H_5)(OC)_3MoMo(CR_2)(N_2CR_2)(\eta\text{-}C_5H_5)] \quad (106)$$

demonstrates a bridged-to-terminal alkylidene conversion.[289]

TABLE VIa. μ-Geminal (1,1-) Alkylidynedimetal Complexes

compound	preparation	comments	ref
$[MnPt(\mu\text{-}CSMe)(CO)_2(PMe_2Ph)_2(\eta\text{-}C_5H_5)][BF_4]$	$[MnPt(\mu\text{-}CS)(CO)_2(PMe_2Ph)_2(\eta\text{-}C_5H_5)] + [Me_3O][BF_4]$		254
$[Fe_2(\mu\text{-}CH)(\mu\text{-}CO)(CO)_2(\eta\text{-}C_5H_5)_2][PF_6]$	$[Fe_2(\mu\text{-}CH_2)(\mu\text{-}CO)(CO)_2(\eta\text{-}C_5H_5)_2] + [Ph_3C][PF_6]$		234
$[Ru_2(\mu\text{-}CMe)(\mu\text{-}CMe_2)(CO)_2(\eta\text{-}C_5H_5)_2][BF_4]$	$[Ru_2(\mu\text{-}CMe_2)(\mu\text{-}CO)(CO)_2(\eta\text{-}C_5H_5)_2]$ + (i) MeLi, (ii) $H[BF_4]$	mixed alkylidene-alkylidyne complex	240
$[(\eta\text{-}C_5H_5)(CO)_2M(\mu\text{-}CR)W(CO)_2(\eta\text{-}C_5H_5)_2]$	$[W(CR)(CO)_2(\eta\text{-}C_5H_5)] + M^0$	M = Ni, Pd, or Pt, R = C_6H_4Me-*p*, (X-ray, M = Ni, Pt)	255

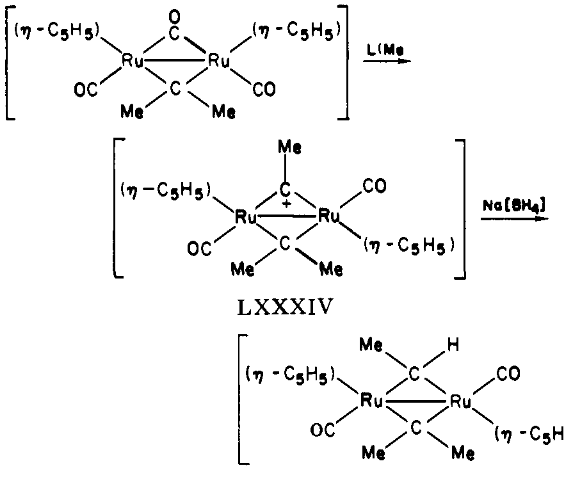
TABLE VIIa. μ-Alkyl or Aryl Electron-Deficient Dimetal Complexes

compound	preparation	comments	ref
$[Fe_2(\mu\text{-}Me)(\mu\text{-}CO)(\mu\text{-}dppm)_2(\eta\text{-}C_5H_5)_2][PF_6]$	$[Fe_2(\mu\text{-}CH_2)(\mu\text{-}CO)(\mu\text{-}dppm)_2(\eta\text{-}C_5H_5)_2] + H[PF_6]$	X-ray shows H–Fe interaction  (Figures 65)	235
$[Fe_2(\mu\text{-}Me)(\mu\ CO)(CO)_2(\eta\text{-}C_5H_5)_2]X$	$[Fe_2(\mu\text{-}CH_2)(\mu\text{-}CO)(CO)_2(\eta\text{-}C_5H_5)_2]$ + HX	X = CF_3SO_3 or BF_4, spectroscopic evidence for Fe-H interaction as above	234

Some new routes to μ-alkylidene complexes include: (a) *Alkylidene transfer from alkylidenephosphoranes* which succeeded with, e.g., $[Fe_2(CO)_4(\eta\text{-}C_5H_5)_2]$[233] and $[Ru_2(\mu\text{-}CPhCPhCO)(\mu\text{-}CO)(CO)(\eta\text{-}C_5H_5)_2]$[241] but failed with $[Mn(CO)_3(\eta\text{-}C_5H_5)]$.[233] The wide range of phosphorus ylides available suggests that this route is likely to receive wider attention. (b) A novel *double oxidative addition* of a dihaloalkane with a low-oxidation-state complex $[M_2L_n]$ (M = Pd, n = 3, L = dppm; or M = Au, n = 2, L = $CH_2PMe_2CH_2$) gave $[Pd_2(\mu\text{-}CHR)(\mu\text{-}L)_2X_2]$ (R = H or Me; X = Cl, Br, or I)[225] or $[Au_2(\mu\text{-}CH_2)(\mu\text{-}L)X_2]$ (X = Cl, Br, or I).[253] (c) Under conditions typical for *phase-transfer catalysis* the cyclopropanes $\overline{CCl_2CHPhCHR}$ (R = H or Ph) reacted smoothly with in situ generated $[Fe(CO)_2(\eta\text{-}C_5H_5)]^-$ to give the vinylidenediiron complexes $[Fe_2(\mu\text{-}C{=}CPhCH_2R)(\mu\text{-}CO)(CO)_2(\eta\text{-}C_5H_5)_2]$.[272] With preformed $Na[Fe(CO)_2(\eta\text{-}C_5H_5)]$ in THF the μ-alkylidene was not produced; instead the appropriate chloro(phenyl)cyclopropane was obtained.

An unusual oxidative addition reaction of CI_4 to [Fe(TPP)] has given the first structurally characterized (μ-carbido)dimetal complex $[\{Fe(TPP)\}_2C]$ (TPP = 5,10,15,20-tetraphenylporphyrin),[239] a species anticipated by MO calculations.[286] The short Fe–C distance (1.675 Å) and linear Fe_2C linkage is indicative of the predicted bis-μ-alkylidene bonding, i.e., Fe=C=Fe.

The high yield synthesis of the first heavy metal-substituted alkylidene, $Hg\{[Rh_2\{\mu\text{-}\overline{C(COOEt)}\}(\mu\text{-}CO)_2(\eta\text{-}C_5Me_5)_2]\}_2$, where the mercury is bonded to two bridging alkylidenes, is of interest as a potential starting material for the synthesis of hitherto inaccessible complexes.[244]

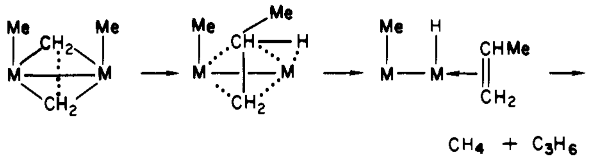


LXXXIV

LXXXV (107)

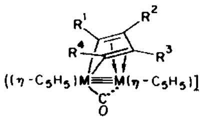
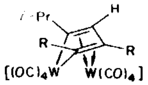
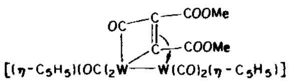
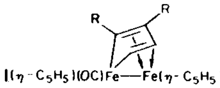
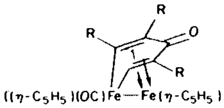
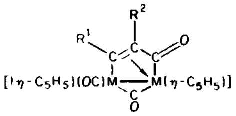
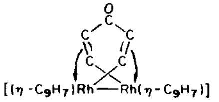
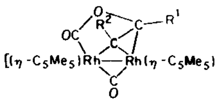
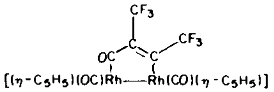
As information on singly bridging alkylidenes has consolidated, attention has turned increasingly to the synthesis and reactions of doubly bridged species, particularly those containing mixed alkylidenes, see, e.g., ref 240, 242, and 248. For example, the synthesis of the bis(μ-alkylidene)dimetal complex LXXXV proceeded *via* a novel isolable mixed (μ-alkylidene)(μ-alkylidyne)dimetal cation LXXXIV (eq 107).[240] LXXXV shows significant differences over its singly bridged counterparts in reactions with acetylene. For LXXXV both alkylidenes are expelled giving the (μ-acetylene)dimetal complex $[Ru_2(\mu\text{-}HCCH)(\mu\text{-}CO)(\eta\text{-}C_5H_5)_2]$, whereas $[Ru_2(\mu\text{-}CHMe)(\mu\text{-}CO)(CO)_2(\eta\text{-}C_5H_5)_2]$ gives an "insertion" product.[198] Heating to 200 °C also effects coupling of the two alkylidene groups to give $Me_2C{=}CHMe$ (70%).[240]

The bridging methylenes in $[Rh_2(\mu\text{-}CH_2)_2Me_2(\eta\text{-}C_5Me_5)_2]$, (LXXXVI), are exceptionally robust.[245,246] They remain intact during Me/Cl exchange with HCl to produce $[Rh_2(\mu\text{-}CH_2)_2Cl_2(\eta\text{-}C_5Me_5)_2]$ and this in turn undergoes further Cl/X exchange with NaX (X = Br, I, N_3, or SCN) or Cl/Et exchange with Al_2Et_6.[246] Pyrolysis of LXXXVI at 350 °C gave methane (48%), ethylene (20%), ethane (2%), and propylene (30%).[245a] Production of methane and propylene is thought to arise as shown in eq 108, a sequence which may closely resemble reaction pathways in Fischer–Tropsch catalysis. The more ready decomposition of the cis over the trans isomer presumably reflects a preferred arrangement of the methylenes and methyl groups in the transition state. The original low-yield synthesis of



(108)

TABLE VIIIa. (μ-Alkenyl)dimetal Complexes Including Metallocyclopentadienyl Complexes

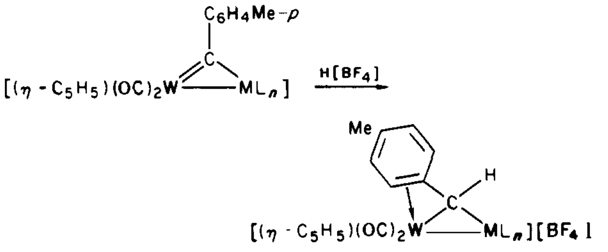
compound	preparation	comments	
 	$[Cr_2(CO)_4(\eta\text{-}C_5H_5)_2] + RC{\equiv}CR$	M = Cr, $R^1 = R^2 = R^3 = R^4$ = H, COOMe, or Ph (X-ray); $R^1 = R^3$ = Me or Ph, $R^2 = R^4$ = H; $R^1 = R^4$ = Ph, $R^2 = R^3$ = H, M = Mo, $R^1 = R^2 = R^3 = R^4$ = Ph  is an alternative (preferred) canonical structure	193, 256
	$[Mo_2(CO)_4(\eta\text{-}C_5H_5)_2(RC{\equiv}CR)] + RC{\equiv}CR$	M = Mo, R = Et	257
 	 , heat	R = Me (X-ray) or Et, no W–W bond	258
 	$[W_2(CO)_6(\eta\text{-}C_5H_5)_2]$ + $MeOOCC{\equiv}CCOOMe$, $h\nu$	X-ray	259
 	R = COOMe, $[Fe_2(\mu\text{-}\eta^1,\eta^3\text{-}CRCRCHMe)(\mu\text{-}CO)(CO)(\eta\text{-}C_5H_5)_2]$, heat; R = H, $[Fe_2(CO)_4(\eta\text{-}C_5H_5)_2] + HC{\equiv}CH$, $h\nu$	reaction byproduct (see below)	198 260
 	$[Fe_2(CO)_4(\eta\text{-}C_5H_5)_2] + RC{\equiv}CR$, $h\nu$	R = COOMe, reaction byproduct (see below)	260
 	$[M_2(CO)_4(\eta\text{-}C_5H_5)_2] + R^1C{\equiv}CR^2$, $h\nu$	M = Fe or Ru, $R^1 = R^2$ = H, Me, Ph; R^1 = H, R^2 = Me, Ph; R^1 = Me, R^2 = H, Ph; R^1 = Ph, R^2 = Me; M = Fe, $R^1 = R^2$ = COOMe, M = Ru, R = Ph, R^2 = H. (X-ray, M = Ru, $R^1 = R^2$ = Ph.)	260
$[Rh_2(\mu\text{-}CH{=}CH_2)(\mu\text{-}CO)(\eta\text{-}C_9H_7)_2][BF_4]$	$[Rh_2(\mu\text{-}C{=}CH_2)(CO)_2(\eta\text{-}C_9H_7)_2] + H[BF_4]$	C_9H_7 = indenyl	249
$[Rh_2(\mu\text{-}CMe{=}CH_2)(CO)_2(\eta\text{-}C_9H_7)_2][BF_4]$	$[Rh_2(CO)_2(\mu\text{-}H_2CCCH_2)(\eta\text{-}C_9H_7)_2]$ + $H[BF_4]$	X-ray	261
 	$[Rh_3(\mu\text{-}CO)_3(\eta\text{-}C_9H_7)_3] + HC{\equiv}CH$		249
 	$[Rh_2(\mu\text{-}CO)_2(\eta\text{-}C_5Me_5)_2] + RCOC(R^2)N_2$	R^1, R^2 = Ph_2 (X-ray); $(C_6H_4OMe\text{-}p)_2$; Me, Ph; Me_2; $(COOEt)_2$, intramolecular cycloaddition, requires nucleophilic keto group.	243
 	$[Rh_2(CO)_4Cl_2]$ + (i) $CF_3C{\equiv}CCF_3$, (ii) TlC_5H_5	X-ray; X-ray structure of the $\eta\text{-}C_5Me_5$ analogue shows a different bridging mode (cf. XCIV)	262

LXXXVI from [$Rh_2Cl_4(\eta\text{-}C_5Me_5)_2$] and Al_2Me_6, accomplished by the somewhat hazardous procedure of exposure to air at a defined point in the reaction sequence, is much improved if a hydrogen acceptor (acetone) is added to the heterobimetallic intermediate, [(η-C_5Me_5)$RhMe_2$(μ-Me)AlMeClL] (L = e.g., $AlMe_2Cl$).[245b]

Protonation of a singly bridging alkylidene to give a stable (μ-alkyl)dimetal cationic complex has now been demonstrated with both homonuclear, (eq 109, L_2 =

$$\underset{\text{LXXXVII}}{[\mathrm{Fe_2(\mu\text{-}CH_2)(\mu\text{-}CO)(\eta\text{-}C_5H_5)_2L_2}]} \xrightarrow{\mathrm{H^+}} \underset{\text{LXXXVIII}}{[\mathrm{Fe_2(\mu\text{-}Me)(\mu\text{-}CO)(\eta\text{-}C_5H_5)_2L_2}]^+} \quad (109)$$

$(CO)_2$[234] or μ-dppm[235]), and heteronuclear dimetal complexes (eq 110, ML_n = Co(CO)(η-C_5Me_5) or Pt(PMe_3)$_2$).[230] For the homonuclear diiron complex LXXXVIII (L = CO) NMR data were strongly supportive of a solution structure with an Fe–C–H interaction rather than the better known symmetrical bridge, as in L. Unlike [$Os_3(\mu\text{-}Me)(\mu\text{-}H)(CO)_{10}$], which also shows evidence of an Os–C–H interaction in solution but exists in the solid state exclusively as the methylene-bridged [$Os_3(\mu\text{-}CH_2)(\mu\text{-}H)_2(CO)_{10}$],[40] a single crystal X-ray study[235] of (LXXXVIII, L_2 = μ-dppm) (Figure 65) revealed that the asymmetric methyl bridge is retained in the solid state. The methyl is attached to one iron by an Fe–C σ-bond and to the other *via* an η^2-C–H interaction, cf. [$Fe_4(\mu\text{-}CH)(\mu\text{-}H)(CO)_{12}$][210] which has a similar Fe–C–H structure. It is thus a good representation of a possible intermediate along the pathway for α-elimination at a dimetal center or the reverse process, the formation of methyl groups from methylene and hydrido ligands. Hydride removal from LXXXVII (L = CO) with [Ph_3C][PF_6] provided [$Fe_2(\mu\text{-}CH)(\mu\text{-}CO)(CO)_2(\eta\text{-}C_5H_5)_2$][$PF_6$], the first example of the simplest μ-alkylidyne (μ-CH).[234] The alkylidyne carbon shows the lowest downfield shift in the ^{13}C NMR of any known diamagnetic complex (δ, 490.2 ppm).

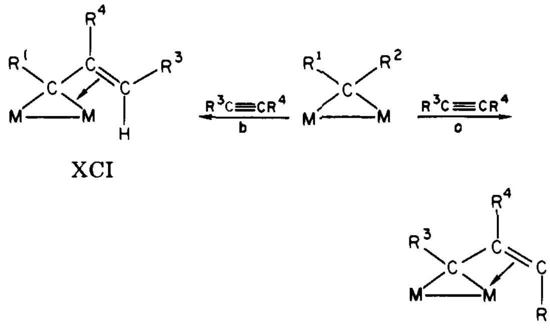


LXXXIX

(110)

Structural data (X-ray) are available for the heteronuclear complex LXXXIX [ML_n = Pt(PMe_3)$_2$], showing a not unprecedented μ-η^1,η^3-coordination of the alkylidene.[230] Whereas LXXXIX [ML_n = Co(CO)(η-C_5Me_5)] is readily deprotonated by K[BH(CHMeEt)$_3$], LXXXIX [ML_n = Pt(PMe_3)$_2$] gives a stable, neutral (μ-CHC_6H_4Me-*p*)(μ-H) complex which, unlike the cationic [$Rh_2(\mu\text{-}CH_2)(\mu\text{-}H)(CO)_2(\eta\text{-}C_5H_5)_2$]$^+$,[77,93] shows no tendency to isomerize to a μ-methyl species.

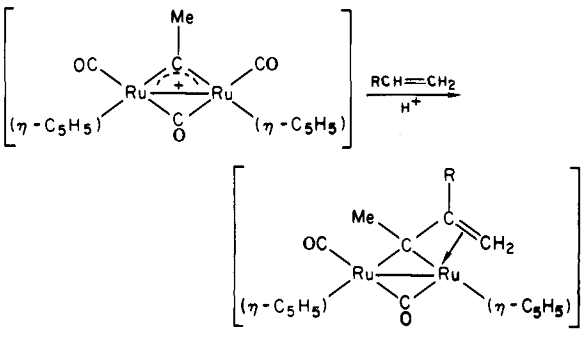
Some differences are beginning to emerge in the reactions of bridging alkylidenes and alkylidynes with alkenes or alkynes, steps of considerable importance in metathesis and ring-opening polymerization of olefins and in alkyne polymerization. Whereas a number of homonuclear μ-alkylidene complexes of W,[196,229,284] Fe,[198] and Ru[198] react readily with alkynes to afford the "products of insertion", XC, (eq 111, path a), the heteronuclear LXXXIX [ML_n = Co(CO)(η-C_5Me_5)] gives the "product of addition", [(η-C_5H_5)(OC)W{μ-η^1,η^3-C(C_6H_4Me-*p*)CMeCHMe}(μ-CO)Co(η-C_5Me_5)][BF_4] (XCI, eq 111, path b) with but-2-yne.[230] A (μ-alkylidyne)diruthenium complex also gives the "product of addition" in reactions with alkenes (eq 112, R = H or Me).[215]



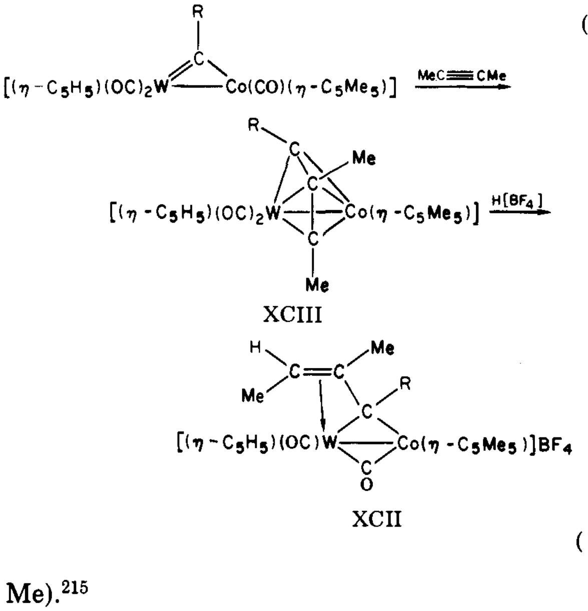
XCI

XC

(111)



(112)



XCIII

XCII

(113)

An alternative synthesis of a complex of type XCII involves the sequence of eq 113 (R = C_6H_4Me-*p*),[230] suggesting the possibility that an intermediate of the type XCIII is involved in both "insertion" and "addition" (eq 111), the precise course of the reaction depending on a delicate balance between simple rearrangement (insertion) and rearrangement with a 1,3-hydrogen transfer (addition).

Two (μ-alkenyl)dirhodium complexes [$Rh_2(\mu\text{-}CR{=}CH_2)(\mu\text{-}CO)(CO)(\eta\text{-}C_9H_7)_2$][$BF_4$], XCIV ($C_9H_7$ = inde-

TABLE IXa. (μ-Alkynyl)dimetal Complexes

compound	preparation	comments	ref
$[W_2(\mu\text{-}\eta^1,\eta^2\text{-}C{\equiv}CPh)(PhC{\equiv}CH)(CH)(CO)_4(\eta\text{-}C_5H_5)_2][BF_4]$	$[W(C{\equiv}CPh)(CO)_3(\eta\text{-}C_5H_5)]$ + $H[BF_4]$	X-ray	263
$[Fe_2(\mu\text{-}C{\equiv}CPh)(\mu\text{-}PPh_2)(CO)_4(CNBu\text{-}t)_2]$	$[Fe_2(\mu\text{-}C{\equiv}CPh)(\mu\text{-}PPh_2)(CO)_6]$ + t-BuNC	X-ray; monosubstitution product also obtained	281

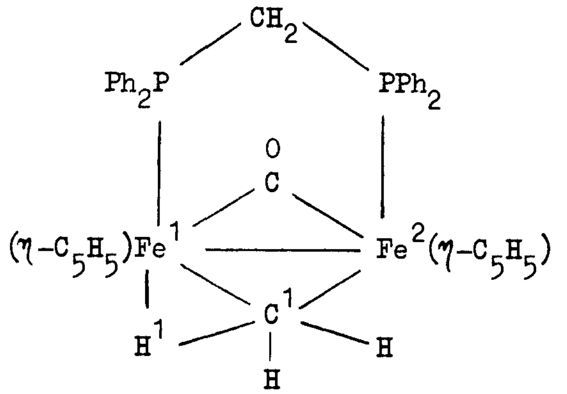
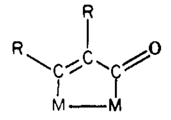


Figure 65. Schematic representation of the molecular structure (one of the two crystallographically independent cations) of $[Fe_2(\mu\text{-}Me)(\mu\text{-}CO)(\mu\text{-}dppm)\text{-}(\eta\text{-}C_5H_5)_2]^+$. Bond lengths: Fe–Fe, 2.544 (1); Fe(1)–C(1), 2.108 (3); Fe(2)–C(1), 2.008 (4); Fe(1)–H(1), 1.64 (4); C(1)–H(1), 1.06 (4) Å. Angles, Fe(1)–C(1)–Fe(2), 76.3 (1); Fe(1)–H(1)–C(1), 101 (3)°. All hydrogens were located.[235]

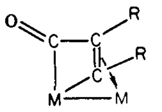
nyl), have been obtained by closely related reactions. Protonation of the bridged vinylidene complex $[Rh_2(\eta\text{-}C{=}CH_2)(CO)_2(\eta\text{-}C_9H_7)_2]$ gave XCIV (R = H) and not the alternative bridged alkylidyne (μ-CMe) as previously observed for Mn (eq 39)[91] and Ru (eq 38).[80,89] Protonation of the bridged allene–dimetal complex $[Rh_2(\mu\text{-}C_3H_4)(CO)_2(\eta\text{-}C_9H_7)_2]$ gave the bridged methylvinyl XCIV (R = Me);[261] deuteration showed exclusive addition to the terminal methylene group(s) thus excluding a pathway involving a bridging allyl species (cf. ref 285).

Cobalt readily exchanges bridging methylene and terminal cyclopentadienyl groups. The heteronuclear $[CoRh(\mu\text{-}CH_2)(CO)_2(\eta\text{-}C_5H_5)_2]$ and homonuclear $[Rh_2(\mu\text{-}CH_2)(CO)_2(\eta\text{-}C_5H_5)_2]$ were obtained by interaction of $[Co_2(\mu\text{-}CH_2)(CO)_2(\eta\text{-}C_5H_5)_2]$ and $[Rh_2(CO)_4(\eta\text{-}C_5H_5)_2]$,[213] while the Co^I and Co^{III} species $[Co(\eta\text{-}C_5H_5)(PPh_3)_2]$ and $[Co(\eta\text{-}C_5H_4Me)Me_2(PPh_3)]$ exchanged cyclopentadienyl groups, most plausibly *via* a symmetrically bridged intermediate of the type well-known with palladium,[287] (cf. ref 285). Bridging methylenes can be incorporated into oxygenated products in high yield;[288] $[Fe_2(\mu\text{-}CH_2)(CO)_8]$ reacted with alcohols (ROH) at 105 °C, or at 20 °C in the presence of phosphines, phosphites, or $AlBr_3$ to give alkyl acetates, $H\text{-}CH_2COOR$ (R = Me or Et).

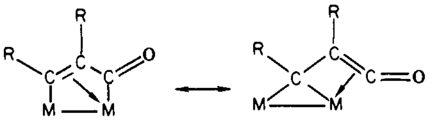
The importance of single crystal X-ray diffraction studies in the resolution of structural ambiguities with bridging ligands is shown with μ-C(R)C(R)CO, obtained from RC≡CR and CO and a possible intermediate in the metal-catalyzed carbonylation of alkynes. Isomeric forms XCV occur in $[Rh_2\{\mu\text{-}C(CF_3)C(CF_3)CO\}(CO)_2(\eta\text{-}C_5H_5)_2]$,[262] XCVI $[W_2\{\mu\text{-}C(COOMe)C(COOMe)CO\}(CO)_4(\eta\text{-}C_5H_5)_2]$,[259] and XCVII is found in $[Ru_2(\mu\text{-}CPhCPhCO)(\mu\text{-}CO)(CO)_2(\eta\text{-}C_5H_5)_2]$.[260] The lability of the μ-CPhCPhCO ligand has been exploited with the Ru complex which was found to be a very convenient starting material for the synthesis of other μ-hydrocarbyl, in particular μ-alkylidene, complexes.[241]



XCV



XCVI



XCVII

An interesting new synthetic approach to $\mu\text{-}^-CH_2CH_2^-$-bridged dimetallic complexes (section II) is by nucleophilic attack of a carbonylmetallate anion on a $\eta\text{-}C_2H_4$–metal cationic complex;[290] an example is shown in eq 114.

$$[W(\eta\text{-}C_2H_4)(CO)_3(\eta\text{-}C_5H_5)][BF_4] + Na[W(CO)_3(\eta\text{-}C_5H_5)] \rightarrow [\{W(CO)_3(\eta\text{-}C_5H_5)\}_2(\mu\text{-}CH_2CH_2)] + Na[BF_4] \quad (114)$$

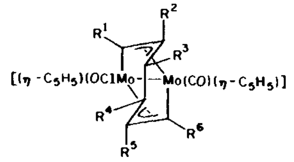
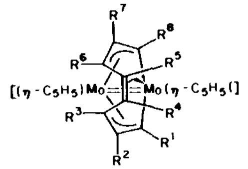
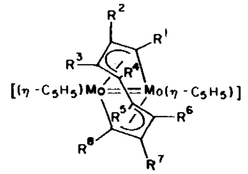
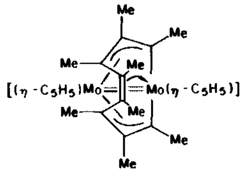
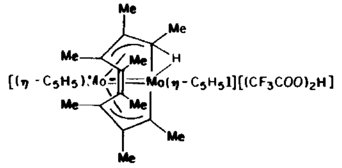
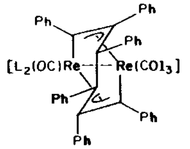
B. Mid 1982 to End of 1982 (Added in Proof)

Since this article was submitted for publication a number of relevant papers have appeared. This short addendum completes the literature coverage to the end of 1982.

The osmium complexes $[Os_2\{\mu\text{-}(CH_2)_n\}(CO)_8]$ (n = 1, 2, or 3) were prepared by reaction of $Na_2[Os_2(CO)_8]$ with the corresponding α,ω-disubstituted alkane.[292] The synthesis and structure of $[Pt_2(\mu\text{-}CH_2C_6H_4CH_2\text{-}o)(\mu\text{-}Ph_2PCH_2PPh_2)Me_4Br_2]$ have been reported,[293] and a further example of a bridging bis(carbene) ligand (see also Table XIII) in $[Ru_2(\mu\text{-}C{=}CHCCH_2CMe_2CH_2CCH)_2(\eta\text{-}C_5H_5)_2(PPh_3)_4][PF_6]_2$ has now been described.[294]

Numerous novel complexes containing a μ-geminal 1,1-alkylidene ligand have been reported: $[M_2(\mu\text{-}CHSiMe_2NSiMe_3)_2\{N(SiMe_3)_2\}_4]$ (M = Zr or Hf);[295] $[Mo_2(\mu\text{-}CH_2)(\mu\text{-}CH_2N_2)(\eta\text{-}C_5Me_5)_2(CO)_4]$;[296] $[N(PPh_3)_2][W_2(\mu\text{-}CHC_6H_4Me\text{-}p)(\eta\text{-}C_5H_5)(CO)_7]$;[297] $[WAu(\mu\text{-}CHC_6H_4Me\text{-}p)(\eta\text{-}C_5H_5)(CO)_2(PPh_3)]$;[297] $[FeMn(\mu\text{-}CH_2)(CO)_5(\mu\text{-}CO)(\eta\text{-}C_5H_5)]$ (two crystallographic forms identified);[298] $[FeCo\{\mu\text{-}C(SMe)_2\}(\eta\text{-}CO)(CO)_4]$;[299] $[Rh_2(\mu,\mu\text{-}CHCMe_2CHCO)(\eta\text{-}C_5Me_5)_2(\mu\text{-}CO)]$;[300] $[Rh_2(\mu\text{-}CH_2)(\mu\text{-}CF_3C{\equiv}CCF_3)(Ph_2PCH_2PPh_2)_2Cl_2]$;[301] and $[M_2\{\mu\text{-}CCH_2(CH_2)_3CH_2\}(\eta\text{-}C_5Me_5)_2(\mu\text{-}CO)_2]$, the first example of a saturated carbocyclic alkylidene bridge (M = Co or Rh).[302] Reaction of sulfur dioxide with $[Rh_2(\mu\text{-}CH_2)(\eta\text{-}C_5Me_5)_2(\mu\text{-}CO)_2]$ leads to insertion and ring expansion affording a $\mu\text{-}CH_2SO_2$ bridged structure;[303] similarly diphenylacetylene inserts into the iridium–methylene-bridged complex to yield $[Ir_2(\mu\text{-}CPhCPh{=}CH_2)(\mu\text{-}CH_2)(\eta\text{-}C_8H_{12})_2]$.[304] The cyclooctadiene ligand in $[WPt(\mu\text{-}C(OMe)C_6H_4Me\text{-}p)(CO)_5(\eta\text{-}C_8H_{12})]$ is dis-

TABLE Xa. μ-Allyl, μ-Cyclopentadienyl, and Related Dimetal Complexes

compound	preparation	comments	ref
$[Ti_2(\mu\text{-}\eta^1,\eta^5\text{-}C_5Me_4CH_2)(\mu\text{-}O)_2(\eta\text{-}C_5Me_5)_2]$	$[Ti(\eta\text{-}C_5Me_5)_2] + N_2O$	X-ray; first structurally characterized μ-$C_5Me_4CH_2$ complex	264
$[(\mu_3\text{-}N_2)\{Ti_2(\eta^5,\eta^5\text{-}C_{10}H_8)(\eta\text{-}C_5H_5)_2\}\text{-}\{Ti_2(\eta^1,\eta^5\text{-}C_5H_4)(\eta\text{-}C_5H_5)_3\}$	$[Ti_2(\mu\text{-}\eta^1,\eta^5\text{-}C_5H_4)(\eta\text{-}C_5H_5)_3] + N_2$	X-ray	265
	$[Mo_2(CO)_4(RC\equiv CR)(\eta\text{-}C_5H_5)_2] + R'C\equiv CR'$	$R^1 = R^2 = R^5 = R^6 =$ COOMe, $R^3 = R^4 =$ H, COOMe, or $SiMe_3$; $R^3 = R^4 = R^5 = R^6 =$ COOMe, $R^1 = R^2 =$ H or $SiMe_3$; $R^1 = R^2 =$ H, $R^3 = R^4 = R^5 = R^6 =$ Ph	193, 256
	$[Mo_2(CO)_4(RC\equiv CR)(\eta\text{-}C_5H_5)_2] + R'C\equiv CR'$	several complexes; X-ray, $R^1 = R^2 = R^3 = R^4 = R^7 = R^8 =$ COOMe; $R^5 = R^6 =$ H	193, 256, 266, 267
	$[Mo_2(CO)_4(RC\equiv CR)(\eta\text{-}C_5H_5)_2] + RC\equiv CR$	R = COOMe, X-ray	256, 266
	$[Mo(NCMe)(MeC\equiv CMe)(\eta\text{-}C_5H_5)][BF_4] + Na[Fe(CO)_2(\eta\text{-}C_5H_5)]$	X-ray	194
	product above + CF_3COOH	X-ray	194
$[Mo_2(\mu\text{-}\eta^1,\eta^5\text{-}C_5H_4)(CO)_3(\eta\text{-}C_5H_5)_2]$	$[Mo_2(CO)_6(\eta\text{-}C_5H_5)_2] + C_5H_4N_2$; $[Mo_2(OAc)_4] + NaC_5H_5$, CO	X-ray	237, 268
$[Mo_2(\mu\text{-}\eta^1,\eta^5\text{-}C_5H_4)(H)(\eta\text{-}C_5H_5)_3]$	$[Mo_2(OAc)_4] + NaC_5H_5$, PPh_3	X-ray	268
$[WIr(\mu\text{-}\eta^1,\eta^5\text{-}C_5H_4)(\mu\text{-}H)_2(H)L(\eta\text{-}C_5H_5)]$	$[WH_2(\eta\text{-}C_5H_5)_2] + [IrH_2L_2(EtOH)_2][PF_6]$	L = e.g., PEt_3, PPh_3, rare example of μ-η^1,η^5-C_5H_4 with bridging hydrides and with late transition metal	269
	$[Re_2(CO)_{10}]$ + (i) $PhC\equiv CPh$, (ii) L	X-ray, L = p-$MeC_6H_4SO_2CH_2NC$	270

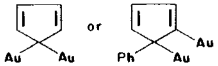
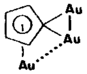
$[Ru_2(\mu\text{-}\eta^1,\eta^3\text{-}C_3H_4)(CO)_4(\eta\text{-}C_5H_5)_2]$	$[Ru_2(\mu\text{-}CPhCPhCO)(\mu\text{-}CO)(CO)(\eta\text{-}C_5H_5)_2] + C_3H_4$		241
$[(\eta\text{-}C_5H_5)(OC)Ru(\mu\text{-}CO)_2Ru(CO)\text{-}(\mu\text{-}\eta^1,\eta^5\text{-}C_5H_4)Ru(CO)_2(\eta\text{-}C_5H_5)]$	$[Ru_2(CO)_4(\eta\text{-}C_5H_5)_2] + PhC{\equiv}CPh$	minor product	260
$[Au_2(\mu\text{-}C_5Ph_4)(PPh_3)_2]$	$[(AuPPh_3)_3O][BF_4]$ + (i) $Ph_4C_5H_2$, (ii) NaH	bonding? 	271
$[Au\{\eta^5\text{-}(Au_2(\mu\text{-}C_5Ph_4)(PPh_3)_2\}(PPh_3)][BF_4]$	$[Au(C_5Ph_4H)PPh_3] + [AuPPh_3][BF_4]$	X-ray, skeleton 	271

TABLE XIIa. μ-Hydrocarbyl- Main-Group Metal-Transition-Metal Complexes

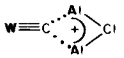
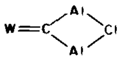
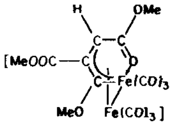
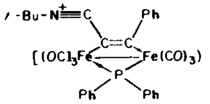
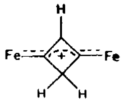
compound	preparation	comments	ref
$[ZrAl(\mu\text{-}CHCH_2R)(\mu\text{-}Cl)R'_2(\eta\text{-}C_5H_5)_2]$ $[ZrAl(\mu\text{-}\eta^2\text{-}CH_2CHR)(\mu\text{-}Cl)R'_2(\eta\text{-}C_5H_5)_2]$	$[Zr(CH{=}CHR)Cl(\eta\text{-}C_5H_5)_2] + HAlR'_2$ or $[ZrH(Cl)(\eta\text{-}C_5H_5)_2] + AlR'_2(CH{=}CHR)$	R = Me, Bu, or Bu-*t*; R′ = Me or Bu-*i*; ratio of products depends on steric bulk of R. μ-Cl replacable by a range of nucleophiles including $CH_2Bu\text{-}t$. $[TiAl(\mu\text{-}CHEt)(\mu\text{-}Cl)(Pr\text{-}i)_2(\eta\text{-}C_5H_5)_2]$ also prepared.	273
$[MAl(\mu\text{-}C{=}CMeR)(Me)_2(Cl)(\eta\text{-}C_5H_5)_2]$	$[TiCl_2(\eta\text{-}C_5H_5)_2]$ or $[ZrMeCl(\eta\text{-}C_5H_5)_2] + RC{\equiv}CAlMe_2$	M = Ti or Zr; R = Pr or pentyl, useful as alkenylidene and alkenyl transfer agents	274
$[W(CAl_2Me_4Cl)(Me)(PMe_3)_2(C_2H_4)]$	$[WAl(\mu\text{-}CH)(\mu\text{-}Me)Cl_2(Me)(PMe_3)_3] + Al_2Me_6, C_2H_4$	bonding descriptions  preferred over 	275
$[RhAl(\mu\text{-}Me)Me_3(Cl)(L)(\eta\text{-}C_5Me_5)]$	$[Rh_2(\mu\text{-}Cl)_2Cl_2(\eta\text{-}C_5Me_5)_2] + Al_2Me_6$	L = e.g., $AlMe_2Cl$; + $Me_2CO \rightarrow [Rh_2(\mu\text{-}CH_2)_2Me_2(\eta\text{-}C_5Me_5)_2]$	245b

TABLE XIIIa. Miscellaneous μ-Hydrocarbyl- or μ-Hydrocarbon-Dimetal Complexes

compound	preparation	comments	ref
$[Ta_2(\mu\text{-}\eta^2\text{-}CHO)(\mu\text{-}H)Cl_4(\eta\text{-}C_5Me_4Et)_2]$	$[Ta(CH_2Bu\text{-}t)_2Cl_2(\eta\text{-}C_5Me_4Et)]$ + (i) H_2, (ii) CO	X-ray, side-on bonded formyl	276
$[M_2(\mu\text{-}\eta^2\text{-}MeCO)(CO)_4(\eta\text{-}C_5H_5)_2]$	$[MMe(CO)_3(\eta\text{-}C_5H_5)] + [M(CO)_3(\eta\text{-}C_5H_5)][PF_6]$	M = Mo or W (impure), side-on bonded acetyl	277
$[MPt(\mu\text{-}C(C_6H_4Me\text{-}p)L)(PR_3)_2(\mu\text{-}CO)(CO)(\eta\text{-}C_5H_5)]^{n+}$	$[MPt(\mu\text{-}CC_6H_4Me\text{-}p)(CO)_2(PR_3)_2(\mu\text{-}C_5H_5)] + L$	M = Mn or Re; *n* = 1, L = PR'_3; *n* = 0, L = $SC_6H_4Me\text{-}p$	278
$[WRe(\mu\text{-}C(Ar)PMe_3)(\mu\text{-}CO(CO)_7(PMe_3)]$	$[WRe(CAr)(CO)_9] + PMe_3$	Ar = Ph or $C_6H_4Me\text{-}p$ (X-ray); further CO substitution by PMe_3 at elevated temperature	279
	$[Fe(\eta^3\text{-}C(OMe)C(COOMe)CHCOOMe)(CO)_3] + [Fe_2(CO)_9]$	X-ray	280
	$[Fe_2(\mu\text{-}C{\equiv}CPh)(\mu\text{-}PPh_2)(CO)_6] + t\text{-}BuNC$	X-ray; *i*-$PrNH_2$ adds to N≡C	281
$[Fe_2(\mu\text{-}C_4H_3)(CO)_2(L)(\eta\text{-}C_5H_5)_2][BF_4]$	$[Fe(C{=}CH_2)(CO)(L)(\eta\text{-}C_5H_5)][BF_4]$ in THF	L = PPh_3 or $P(C_6H_{11})_3$ bonding 	291

placed by phosphines or diphosphines; in contrast, reaction with CO or CNBu-*t* (L) affords the cluster complex $[Pt_3\{\mu\text{-}C(OMe)C_6H_4Me\text{-}p\}_3L_3]$.[305]

The cationic methylidyne complex $[Fe_2(\mu\text{-}CH)(\eta\text{-}CH)(\eta\text{-}C_5H_5)_2(\mu\text{-}CO)(CO)_2][PF_6]$ has been prepared by hydride abstraction from the methylene-bridged complex using $[Ph_3C][PF_6]$.[306] Alkenes insert into the C–H bond of the bridging methylidyne to yield a variety of alkylidene-bridged complexes whereas reaction with CO affords the acylium complex $[Fe_2(\mu\text{-}CHO)(\eta\text{-}C_5H_5)_2(\mu\text{-}CO)(CO)_2][PF_6]$.[307]

The alkenyl-bridged compound $[Mo_2(\mu\text{-}CH{=}CHPh)(\eta\text{-}C_5H_5)_2(O)(CO)(\mu\text{-}PPh_2)]$ is obtained as a byproduct from the reaction of $Ph_3P{=}CH_2$ with $[Mo_2(\eta\text{-}C_5H_5)_2(CO)_4]$ and has been characterized by X-ray analysis.[308] Passing $[Ru(\eta\text{-}C_5H_5)(\eta\text{-}C_3H_5)(CO)]$ down a deactivated silica gel column provides easy access to $[Ru_2(\mu\text{-}CHCH{=}CH_2)(\eta\text{-}C_5H_5)_2(CO)(\mu\text{-}CO)]$;[309] complexes of this type were previously prepared by the reaction of a μ-alkylidene species with an alkene. A simple preparation of alkenyl-bridged rhenium complexes has been reported; the UV irradiation of $[Re_2(CO)_{10}]$ in the presence of a terminal alkene results in the formation of $[Re_2(\mu\text{-}CH{=}CHR)(\mu\text{-}H)(CO)_8]$ (R = H, Me, Et, or $n\text{-}C_4H_7$).[310]

Reaction of $[Ru_2(\mu\text{-}C_2Ph_2)(\eta\text{-}C_5H_5)_2(\mu\text{-}CO)]$ with diazomethane leads to the incorporation of two methylene units: one bridging the two metal atoms, and the second reacting with the alkyne to yield $[Ru_2(\mu\text{-}CH_2)(\mu\text{-}CPhCPh{=}CH_2)(\eta\text{-}C_5H_5)_2(CO)]$, which upon heating isomerizes to afford $[Ru_2(\mu\text{-}CPhCPhCHCMe)(\eta\text{-}C_5H_5)_2(\mu\text{-}CO)(CO)]$ via C–C bond formation.[311]

Both $[Pd_2(\mu\text{-}C_5H_5)_2(PPr\text{-}i_3)_2]$ and $[Pd_2(\mu\text{-}C_5H_5)(\mu\text{-}C_3H_4)(PPr\text{-}i_3)_2]$ react with a carboxylic acid or a thiol by displacement of a cyclopentadienyl ligand to yield $[Pd_2(\mu\text{-}C_5H_5)(\mu\text{-}OCOR)(PPr\text{-}i_3)_2]$ and $[Pd_2(\mu\text{-}C_3H_4)(\mu\text{-}OCOR)(PPr\text{-}i_3)_2]$, respectively or the corresponding μ-SR analogues.[312] Further reaction of the Pd_2–carboxylato-bridged complex with $Na[M(\eta\text{-}C_5H_5)(CO)_3]$ (M = Cr, Mo, or W) gives the cluster complex $[Pd_2(\mu\text{-}L)(PPr\text{-}i_3)_2(\mu\text{-}CO)_3M(\eta\text{-}C_5H_5)]$ (L = C_5H_5 or C_3H_4).

The reaction of (cyclobutadiene)tricarbonyliron with $[M(\eta\text{-}C_5H_5)(CO)_2]$ gives the ferrametallocene $[\{\eta\text{-}Fe(CH)_3CH(CO)_3\}M(\eta\text{-}C_5H_5)]$ [M = Co or Rh (X-ray)]: the analogous benzoferrametallocenes were prepared from benzocyclobutadienetricarbonyliron (M = Co, X-ray).[313]

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