The Chemistry of Transition-metal Carbene Complexes and their Role as Reaction Intermediates

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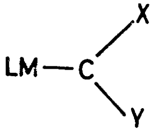
1 Introduction

The title compounds have the formula (1). They were discovered during the past decade,[1] although the Chugaev salts, first prepared in 1915,[2] were recently[3,4] recognized to contain carbene complexes (*e.g.* see Figure 1).[3] Nevertheless there have now been more than 200 publications and the topic is one of the fastest growth areas in organometallic chemistry (30 papers in 1971). Initially, interest centred on synthesis and structures, but subsequently much was also learned of the chemistry of the co-ordinated carbene ligands, and of other reactions of carbene complexes. These themes continue to be elaborated, but a further development is the identification of transition-metal carbene complexes as reactive intermediates in various (organic) syntheses.



(1)

We may therefore consider two main approaches to the study of transition-metal carbene complexes. One is to examine stable compounds; the other is to investigate those transition-metal systems in which carbene complexes are intermediates, including transition-metal-catalysed organic reactions. The former aspect has been comprehensively reviewed[5] (and accounts of the contributions from E. O. Fischer's laboratory are available[6,7]) and we now lay more emphasis on the second topic.

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2 Stable Transition-metal Carbene Complexes

A. Survey of Compounds and their Classification.—Carbene complexes are now known for many of the later transition metals. Metal electron configurations range from d^3 to d^{10}, with d^5 and d^9 as yet unrepresented, oxidation states from 0 to + 4, and co-ordination numbers from 2 to 7 [taking (π-C_5H_5) as providing a single co-ordination position]; the corresponding configurations around the metal include linear, square planar, tetrahedral, trigonal bipyramidal, and octahedral. These data are summarized in Table 1 and typical examples are shown in Table 2. Systematic (I.U.P.A.C.) nomenclature for these compounds uses the suffix -ylidene, the ligand being regarded as neutral with respect to the metal oxidation state; thus $(OC)_5Cr—C(OMe)Me$ is called pentacarbonyl-(1-methoxyethylidene)chromium(0), but trivially is methoxy(methyl)carbene-pentacarbonylchromium(0).

The majority of *carbene complexes* are neutral, mononuclear, and have a single co-ordinated carbene. However, cationic species are known, as are a number of di- and tri-nuclear derivatives. To date no anionic carbene complexes have been reported, although the acyl-metallates $(LM—COR)^-$ are intermediates in a number of syntheses [see Section 2C(i)]. Oligocarbene complexes LM(carbene)$_n$ (n = 1—4) have been prepared (*e.g.* the mercury compound in Table 2) and also complexes with a chelating dicarbene ligand (*e.g.* Figure 1).[3]

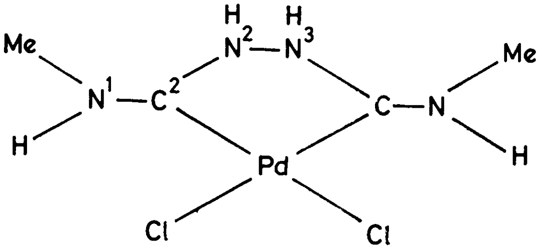


Figure 1 *Approximately square-planar around* Pd (C_{2v}): Pd—C = 1.86 Å, C-1—N-1 = 1.45 Å, N-2—N-3, C-1—N-2 = 1.38 Å, *and* Pd—Cl = 2.38 Å (*see ref.* 3)

The majority of *carbene ligands* are terminal and unidentate (*e.g.* Figures 7 and 10) although a few bridging examples (Figures 2—4)[8,9,12] are reported. In this review a metal carbene complex, whether terminal or bridging, is defined as a species having the ligand CXY with an approximately sp^2-hybridized C_{carb}, attached to the metal without a formal $C_{carb}—X$ or $C_{carb}—Y$ multiple bond. Consequently, compounds such as those shown in Figures 4, 5, and 9 are not classified as carbene complexes, whereas Figure 3 represents a bridging carbene (sp^2-C_{carb}). Generally the co-ordinated ligands (CXY) are 'tertiary', neither X nor Y being hydrogen atoms, but there are some examples[13,13a] of secondary carbenes. Stable methylene complexes are unknown at present. *trans-cis* Isomerism, arising

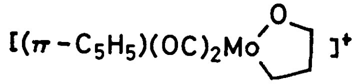
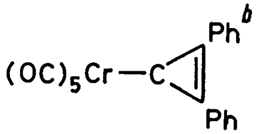
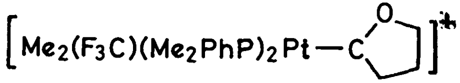
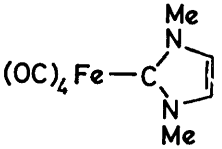
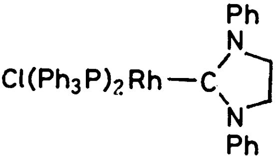
Table 1 *The occurrence of carbene complexes*[a]

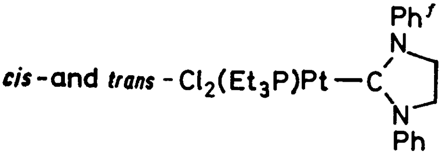
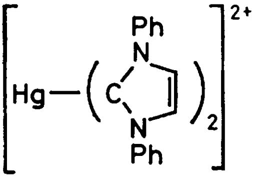
d^3	d^4	d^6	d^7	d^8	d^{10}
		Cr^0(6, n; 4, n^c)	Mn^0(6, n, d)	Fe^0(5, n; 6, n, d, br; 7, n, t, br)	Ni^0(4, n, t)
		Mn^I(4, n)		Co^I(4, n;[d] 5, n)	
		Fe^{II}(4, n;[b] 4, n^c)			
Nb^{II}(5, n, d, br)	Mo^{II}(5, n, or c^1)	Mo^0(6, n; 4, n^c)		Rh^I(4, n)	
		Ru^{II}(4, c^1)			
		W^0(6, n; 4, n^c)			
		Re^I(4, n)		Pd^{II}(4, n or c^1)	Au^I(2, n)
		Ir^{III}(6, n)		Pt^{II}(4, n or c^1, c^2)	Hg^{II}(2, c^2)
		Pt^{IV}(6, n, c^1)			

[a] Numbers in parentheses indicate metal co-ordination number [(π-C_5H_5) taken as occupying a single site], and abbreviations are: n, neutral; c^1, cationic (+ 1); c^2, cationic (+ 2); d, dinuclear; t, trinuclear; br, bridging carbene. [b] This refers to $Fe(CO)(NO)_2CXY$. [c] This refers to (π-C_5H_5)M(CO)(NO)CXY. [d] This refers to $Co(CO)_2(NO)CXY$.

Note: oligocarbene complexes, LM(carbene)$_n$, are known as follows: $n = 2$, M = Cr^0, W^0, Fe^{II}, Rh^I, Pd^{II}, Pt^{II}, and Hg^{II}; $n = 3$, M = Ir^I, Rh^I, Ni^{II}, and Pt^{II}; $n = 4$, M = Pt.

Table 2 *Typical carbene complexes*

Complex	*Ref.*
$(Me_3SiCH_2)_4Nb_2(CSiMe_3)_2$[a]	6
	21
	17
$(\pi\text{-}C_5H_5)(OC)_2Mn—C(OMe)Me$	22
$[(\pi\text{-}C_5H_5)(OC)(Ph_3P)Fe—C(OEt)Me]^+$	23
$[(\pi\text{-}C_5H_5)(OC)_2(R_3P)Mo—C(OEt)Me]^+$	23
cis-$(OC)_4(Ph_3P)Mo—C(OMe)Me$	24
$[(\pi\text{-}C_5H_5)(OC)(R_3P)Ru—C(OEt)Me]^+$	23
$I_3(OC)\overline{Rh—C(Ph)N(Me)C(Ph){:}N}Me$[c]	9, 25
$(OC)_5W—C(NHMe)Me$	16
$(\pi\text{-}C_5H_5)(OC)_2Re—C(OMe)Me$	26
$Cl_3(Ph_3P)_2Ir—C(H)NMe_2$	13
	27
$Cl_4\overline{Pt — C(NMeH)NHNHC}(NMeH)$	28
$(OC)_9Mn_2—C(OMe)Ph$	29
	30
$[(OC)_3Fe—C(:O)Ph]_2$[d]	11
$(OC)_4\overline{Fe—(OC)_3Fe(H)(CNMe_2)Fe}(CO)_3$	11*a*
$(OC)_2(ON)Co—C(Et)NMe_2$	31
$Ph_3Sn(OC)_3Co—C(OEt)Ph$	32
	33
$Cl_2(PhNC)Pd—C(NHPh)OMe$	34
$Cl_2\overline{Pd—C(NMeH)NHNHC}(NMeH)$[e]	3

Complex	*Ref.*
	13, 14
trans-$[\mathrm{Me(Me_3As)_2Pt{-}C(OMe)Me}]^{+}\mathrm{PF_6}^{-}$	35
trans-$[\mathrm{(EtNC)(PMe_2Ph)_2Pt{-}C(SCH_2Ph)NHEt}]^{2+}$	36
$[\mathrm{(OC)Ni{-}C(OMe)Ph}]_3$	37
$\mathrm{ClAu{-}C(OMe)C_6H_4Me}$-*p*	38
	39

[a] Figure 2. [b] Figure 10. [c] Figure 6. [d] Figure 3. [e] Figure 1. [f] Figures 7 and 8.

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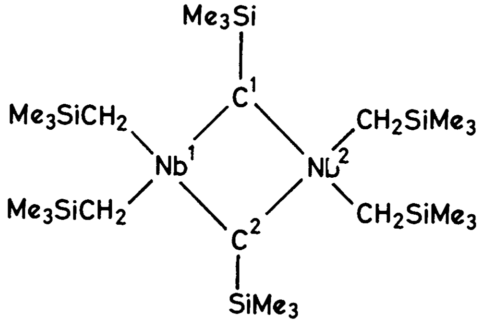
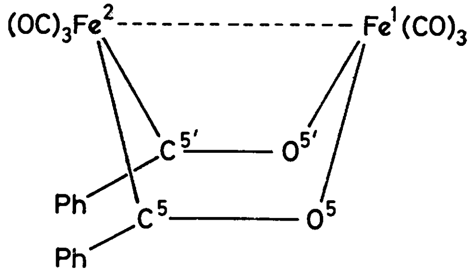


Figure 2 Nb-1—C-1 = 1.995 Å, Nb-2—C-1 = 1.954 Å, *and* Nb-1—Nb-2 = 2.897 Å; $\widehat{\text{C-1Nb-1C-2}}$ = 85.6°, $\widehat{\text{Nb-1C-1Nb-2}}$ = 94.4°, $\widehat{\text{Nb-1C-1Si}}$ = 119.8°, *and* $\widehat{\text{Nb-2 C-1 Si}}$ = 142.4° (Nb-1 *and* Nb-2 *and* C-1 *and* C-2 *are related by a centre of symmetry inside the ring*)[10]



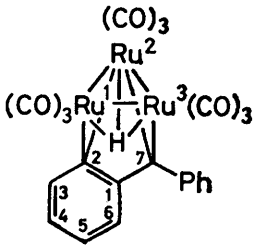


Figure 3 *Both metals have a distorted octahedral environment and lie in a crystallographic mirror plane:* Fe-2—C-5 = Fe-2—C-5′ = 1.945 Å, C-5—O-5 = 1.262 Å, Fe-1—O-5 = Fe-1—O-5′ = 1.967 Å, *and* Fe-1—Fe-2 = 2.568 Å; $\widehat{\text{Fe-2 C-5 O-5}}$ = 114°, $\widehat{\text{C-2 Fe-2 C-5}}$ = 8.41° (*see ref.* 11)

Figure 4 Ru-1, Ru-2, Ru-3, *and* C-1 *to* C-7 *all coplanar, with* Ph *ring perpendicular to this plane, ring* 1—6 *shows marked bond-length alternation*: Ru-3—C-7 = 2.09 Å (*see ref.* 12)

from alternative arrangements of ligands around a central metal, is established for square-planar Pd^{II} and Pt^{II} (*e.g.* Figures 7 and 8)[14,15] and geometrical isomerism due to alternative arrangements within the carbene ligand is known for Cr^0, Mo^0, W^0, and Pt^{II} [*e.g.* (2) and (3)].[16]

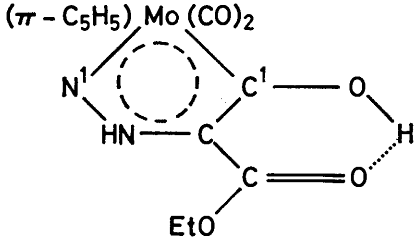


Figure 5 Mo—C-1 = 2.08 Å *and* Mo—N-1 = 2.11 Å (*see ref.* 8)

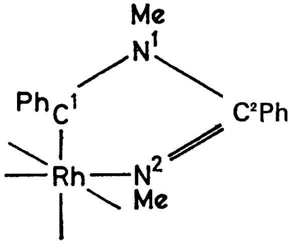


Figure 6 *Approximate octahedral environment around* Rh: Rh—C-1 = 1.97 Å, Rh—N-2 = 2.05 Å, C-1—N-1 = 1.33 Å, N-1—C-2 = 1.43 Å, *and* C-2—N-2 = 1.30 Å (*see ref.* 9)

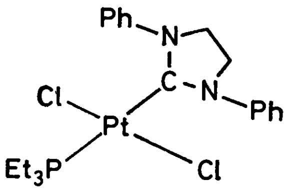


Figure 7 *Square-planar environment around* Pt: Pt—C = 2.020 Å, Pt—Cl = 2.311 Å, Pt—P = 2.291 Å, C_{carb}—N = 1.348 Å, *and* N—Ph = 1.403 Å (*see refs.* 14 *and* 15)

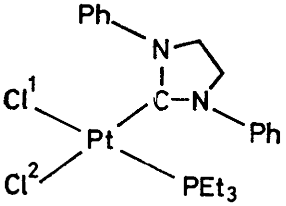


Figure 8 *Square-planar environment around* Pt: Pt—C = 2.009 Å, Pt—Cl-1 = 2.362 Å, Pt—Cl-2 = 2.381 Å, Pt—P = 2.234 Å, C_{carb}—N = 1.327 Å, N—Ph = 1.395 Å (*see ref.* 15)

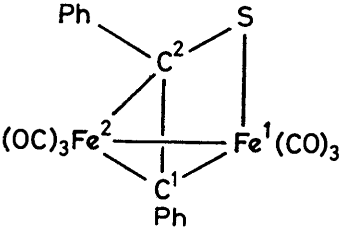


Figure 9 Fe-1—C-1 = 2.089 Å, Fe-2—C-1 = 1.969 Å, Fe-2—C-2 = 2.069 Å, Fe-1—S = 2.243 Å, *and* Fe-1—Fe-2 = 2.533 Å (*see ref.* 19)

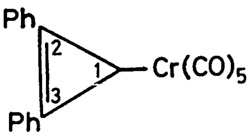
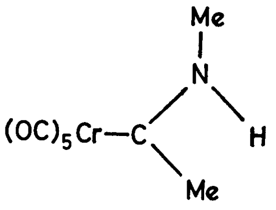
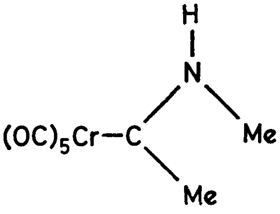


Figure 10 *Approximate octahedral environment around* Cr: Cr—C-1 = 2.05 Å, C-2 *or* C-3—Ph = 1.45 Å, Cr—CO = 1.88—1.92 Å, *and* C-2—C-3 = 1.35 Å (*see ref.* 17)

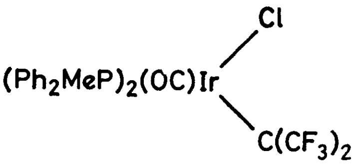


(2)



(3)

All the authenticated stable carbene complexes so far described (more than 300 compounds) have X and/or Y capable of conjugating with the electrophilic C_{carb} and, except for three compounds with the ligand 2,3-diphenylcyclopropene (*e.g.* Figure 10),[17] have X and/or Y as an oxy-, thio-, seleno-, or amino-substituent; ligands are listed in Table 3. Hence, existing complexes may be said to originate from nucleophilic carbenes.[18] A single electrophilic carbene structure (4) remains to be verified;[20] an alternative structure, $(Ph_2MeP)_2(OC)IrCCl(CF_3)_2$, is possible.



(4)

Cationic[35,74] and anionic carbene complexes may alternatively be regarded as metallo-carbonium ions or -carbanions. For example, in the compound formulated as *trans*-$[Me(Me_3As)_2Pt—C(OMe)Me]^+PF_6^-$ in Table 2, the positive charge may be largely localized on either Pt or C_{carb}. The carbonium ion symbolism has been useful for rationalizing some of the reactions of such complexes.[35] A mercury dicationic compound (see Table 2) may more reasonably be formulated[74] as shown.

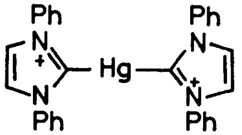
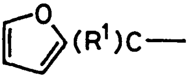
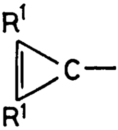
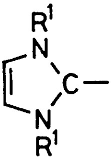
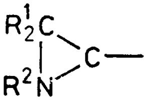
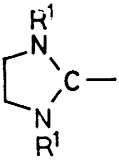
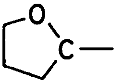
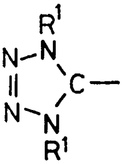
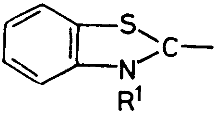
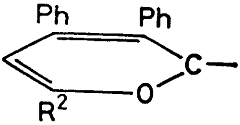


Table 3 *Carbene ligands**

(i) *Acyclic carbenes*

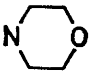
Non-chelated	*Footnote*	*Bidentate or chelated*	*Footnote*
$R^1(R^2O)C$—	*a*	—$O(R^1)C$—	*m*
$R^1R^2N(R^3O)C$—	*b*	—$CNMe_2$—	*n*
$R^1R^2C{:}N(R^3O)C$—	*c*	—$C(MeNH)NR^1\cdot(MeNH)C$—	*o*
$R^1(R^2S)C$—	*d*	—$C(MeNH)\cdot NR^1\cdot NH(MeNH)C$—	*p*
$R^1(R^2Se)C$—	*e*	—$NR^1C(R^2)NHR^1(R^2)C$—	*q*
$R^1(H_2N)C$—	*f*	—$CH\cdot NMe\cdot CH_2\cdot NMe\cdot CH$—	*r*
$R^1(R^2NH)C$—	*g*		
$R^1(R^2{}_2N)C$—	*h*		
$R^1NH(R^2NH)C$—	*i*		
$R^1{}_2N(R^2NH)C$—	*j*		
$R^1(R^2R^3C{:}N)C$—	*k*		
	*l*		

(ii) *Cyclic carbenes*

Carbene	*Footnote*	*Carbene*	*Footnote*
	*s*		*w*
	*t*		*x*
	*u*		*y*
	*v*		*z*

References occur on next page

* Footnotes show the identity of groups R^1, R^2, and R^3 excepting that simple alkyl and aryl groups [Me, Et, Pr, Bu, and (*o*, *m*, *p*)-$C_6H_4 \cdot X$ (X = H, Me, OMe, NMe_2, F, Cl, Br, or CF_3)] are not listed separately in the footnotes, but are denoted by the symbol R; fu =  (X = O, S, or NR).

[a] R;[22,23,26] $R^1 = C_6F_5$,[40] C_6Cl_5,[41] $PhCH_2$,[42] $PhC{\vdots}C$,[43] $CH_2{:}CH$,[44] 1-naphthyl,[45] ferrocenyl,[41] fu,[44,46] or CH_2SiMe_3;[46] R^2 = H,[23,26] fu,[44,46] $SiMe_3$,[47] Li,[48,49] or CpTiCl. [b] R.[31,50–52] [c] R.[53] [d] R;[54,55] R^1 = fu[43,45] or $SiMe_3$.[56] [e] R.[6] [f] R;[54,57] R^1 = fu.[44,46] [g] R;[54,58,59] $R^1 = CH_2{:}(MeO)C$, Me(O:)C, or $Me(MeO)_2C$.[60,62] [h] R;[58,59,63] R^1 = H. [i] R.[13,34,50,65,66] [j] R.[67] [k] R.[68] [l] $R^1 = N_3$, C_4H_8N, or MeO(O:)C.[46] [m] R.[11,48] [n] See ref. 11*a*. [o] R.[69] [p] R^1 = H or $C(:O)NH_2$.[4] [q] R.[25] [r] See ref. 13*a*. [s] R.[70] [t] R^1 = Ph(MeO); $R^2 = C_6H_{11}$.[60,62] [u] See refs. 21, 27, and 71. [v] R.[15] [w] R.[20,39] [x] R.[14,15,33]. [y] R.[72] [z] R^2 = OR, NHEt, Ph, or  .[73]

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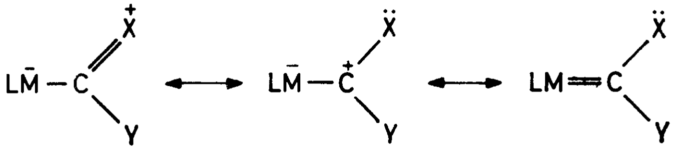
B. Structure and Bonding.—It has been noted (see Section 2A) that stable metal carbene complexes are derived from nucleophilic carbenes and that C_{carb} is highly electrophilic. This results in multiple bonding with the heteroatoms (X or Y) of the ligand [see (5a)] and not in $(d\text{–}p)\pi$ (back bonding) with the metal. As a ligand,[6] we can therefore describe the co-ordinated carbene as a strong σ-donor, but a weak π-acceptor. In this context the polarity clearly differentiates it from the 'ylide' (*e.g.*, $R_3\overset{+}{P}\text{—}\overset{-}{C}H_2$), structure.

The conclusion that (5a) and (5b) are the principal canonical forms implies (i) the absence of a bond order significantly greater than unity in $M\text{—}C_{carb}$, (ii) the considerable multiple bond character in $C_{carb}\text{—}X$, (iii) the electrophilic character of C_{carb}, (iv) the analogy between $C_{carb}\text{—}OR$ or $C_{carb}\text{—}NR^1R^2$ and $C_{acyl}\text{—}OR$ or $C_{acyl}\text{—}NR^1R^2$, rather than $C_{alkyl}\text{—}OR$ or $C_{alkyl}\text{—}NR^1R^2$ organic compounds, and (v) an electronic effect of the carbene ligand on M.


(5a) (5b) (5c)

The clearest evidence for (i), (ii), and (iv) is crystallographic. *X*-Ray results are now available for more than fifteen compounds. The first such study was on a chromium complex (Figure 11);[75] some other data are summarized in Figures 1—9.

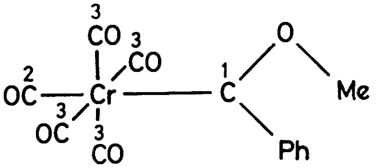


Figure 11 *Essentially octahedral environment for* Cr; Ph at 90° *to plane of* $sp^2\text{-}C_{carb}$ Cr—C-1 = 2.04 Å, C-1—O = 1.33 Å, O—Me = 1.46 Å, C-1—Ph = 1.47 Å, Cr—C-2 = 1.87 Å, *and* Cr—C-3 = 1.86—1.91 Å; $\widehat{\text{Cr C-1 O}}$ = 134°, $\widehat{\text{Cr C Ph}}$ = 122°, $\widehat{\text{O C-1 Ph}}$ = 104°, *and* $\widehat{\text{C-1 O Me}}$ = 121° (*see ref.* 75)

It is manifest that $l(M\text{—}C_{carb})$ (l denotes bond length) is not particularly short: *e.g.*, from Figure 11 note that $l(Cr\text{—}C_{carb}) > l(Cr\text{—}CO)$; and from Figures 7 and

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8 $l(\mathrm{Pt{-}C}) \approx l(\mathrm{Pt{-}C}_{sp^3})$ in *trans*-$[\mathrm{Cl(Ph_2MeP)_2Pt{-}CH_2SiMe_3}]$ (2.079 Å).[76] On the other hand, $l(\mathrm{C_{carb}{-}X})$ is significantly shorter than expected for a single bond: *e.g.* from Figure 11 note that $l(\mathrm{C_{carb}{-}O})$ is shorter even than the $\mathrm{C_{acyl}}$—OR bond in an ester such as $\mathrm{MeCO_2Et}$ (1.36 Å) and from Figures 7 and 8 that $l(\mathrm{C_{carb}{-}N})$ is shorter than in an amide such as MeCONHPh (1.35 Å).[77]

Supporting testimony for (i) is chemical. Thus, there are scarcely any reactions of carbene complexes which suggest $\mathrm{M{=}C_{carb}}$ double-bond character (see Section 2C), but insertion reactions with PhSeH or $\mathrm{C_6H_{11}NC}$ may conveniently, although not inevitably, be interpreted as proceeding *via* such a structure.

Nuclear magnetic resonance studies of rotation about $\mathrm{C_{carb}{-}NR^1R^2}$ or $\mathrm{C_{carb}{-}OR}$ bonds show that the energy barriers are considerable and indeed higher than in carboxylic acid amides or esters, thus providing further demonstration of (ii) and (iv). In $\mathrm{(OC)_5Cr{-}C(OMe)C_6H_4{\cdot}OMe}$-*o*, -*m*, or -*p*, $\Delta G^\ddagger = 13.2$, 11.9, or < 8 kcal mol^{-1}, respectively, and in $\mathrm{(OC)_5Cr{-}C(OMe)C_6H_4{\cdot}CF_3}$-*o*, -*m*, or -*p* is 13.5, 12.1, or 12.3 kcal mol^{-1}, respectively:[45,78] these trends support the view that the high barrier is due to CO bond multiplicity rather than inversion at oxygen. In $\mathrm{(OC)_5Cr{-}C(OEt)Me}$, $\mathrm{(OC)_5Cr{-}C(NMe_2)Me}$, $\mathrm{(OC)_5Cr{-}C(OEt)NMe_2}$, and $\mathrm{(OC)_4Fe{-}C(NDMe)_2}$, $\Delta G^\ddagger$ values are 13.6 (about CO), > 25 (about CN), 20.8 (about CN; < 8 about CO), and 16.6 (about CN) kcal mol^{-1}, respectively.[6] Such data show that barriers to rotation are greater about CN than about CO (and hence probably that $\ddot{\mathrm{N}}\overset{\curvearrowright}{-}\mathrm{C_{carb}}$ occurs to a greater extent than $\ddot{\mathrm{O}}\overset{\curvearrowright}{-}\mathrm{C_{carb}}$) and that when both the groups X and Y are capable of π-bonding with $\mathrm{C_{carb}}$, CX and CY bond multiplicities are lower than is the case when only X or Y has this capacity.

Consistent with (ii), (iii), and (iv) are the reactions of the co-ordinated carbene ligand. These have been most clearly demonstrated for alkoxycarbenechromium(0) compounds (see Figure 13). Nucleophilic substitution reactions at $\mathrm{C_{carb}}$ and electrophilic substitution at the contiguous carbon in $\mathrm{LM{-}C_{carb}(OMe)CH_2R}$ are particularly significant.

Also relevant to (iii) and (iv) are some n.m.r. data. ^{13}C chemical shifts, $\delta(^{13}\mathrm{C})$, which promise to provide a useful diagnostic tool for metal carbene complexes, show that $\mathrm{C_{carb}}$ is substantially deshielded. Values of $\delta(^{13}\mathrm{C})$ (in p.p.m., relative to $\mathrm{Me_4Si}$ in $\mathrm{CDCl_3}$) for various complexes are: $\mathrm{(OC)_5Cr{-}C(OMe)Me}$, 362.3;[79] $\mathrm{(OC)_5Cr{-}C(OMe)Ph}$, 354.5;[80] $\mathrm{(OC)_5Cr{-}C(NHMe)Me}$, 284.8;[80] $\mathrm{(OC)_5Cr{-}C(NMe_2)Ph}$, 277.5;[79] $\mathrm{(OC)_5W{-}C(OMe)Ph}$, 322.8;[80] $\mathrm{(OC)_5W{-}C(OMe)Me}$, 332.9;[81] $\mathrm{(OC)_5W{-}C(SMe)Me}$, 332.5;[81] *cis*-$\mathrm{(OC)_4Cr{-}[C(NMeCH_2)_2]_2}$, 141.0;[82] $\mathrm{(OC)_4Fe{-}C(NMeCH_2)_2}$, 213.0;[82] *trans*-$[\mathrm{Cl_2(Bu^n_3P)Pt{-}C(NMeCH_2)_2}]$, 178.0;[82]

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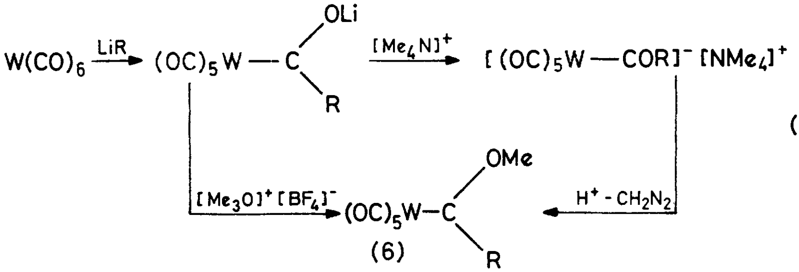
cis-$[Cl_2(Bu^n_3P)Pt—C(NMeCH_2)_2]$, 196.5;[82] and *trans*-$[Cl(Et_3P)_2Pt—C(NMeCH_2)]^+ BF_4^-$, 191.[82] The values are similar to those found for carbonium ions: *e.g.*, $\delta(^{13}C)$ of Me_3C^+ is 273 p.p.m. to lower field than in Me_3CCl.[83] Of eighteen organometallic compounds reported in ref. 79, C_{carb} in $(OC)_5Cr—C(OMe)Me$ has by far the lowest $\delta(^{13}C)$, although C_{acyl} in $(\pi\text{-}C_5H_5)(OC)_2FeCOMe$ is not far removed. For a range of secondary carbene complexes having the $H(Me_2N)C—$ ligand, $\delta(^1H)$ for $C_{carb}H$ is at $\tau = -1.2$ to $+0.9$.[13] Other more peripheral data (from electric dipole moments, vibrational force constants, ionization potentials, electronic spectra, and other aspects of ^1H n.m.r. spectra) have been used to discuss the electronic nature of the carbene ligands.[6]

The *trans* influence (defined as the tendency of a ligand to weaken the bond *trans* to itself)[84] of several carbene ligands in Pt^{II} complexes is similar to that of a tertiary phosphine.[15,50] This may be illustrated by the l(Pt—Cl) and l(Pt—P) data of Figures 7 and 8. Supporting evidence comes from ν(Pt—Cl) and $J(^{195}Pt\text{-}^{31}P)$ of such compounds,[15,50] and $J(^{195}Pt\text{-}^1H)$ in *trans*-$\{PtMe(Y)L_2\}^+PF_6^-$; Y is the *trans* ligand, including $R(R^1O)C—$, and L is a tertiary phosphine or arsine.[35]

C. Synthesis and Reactions.—Transition-metal carbene complexes have been obtained from three classes of precursors, (i)—(iii) in Figure 12.

(i) *Syntheses from Metal–Carbon Compounds.* The metal carbonyl route is illustrated in equation (1). The tungsten compounds (6; R = Me or Ph) were the



(1)

first stable transition-metal complexes to be prepared; methylation then involved diazomethane.[1] The synthesis was improved by using oxonium salts,[60] and was extended to other transition metals (Cr, Mo, Mn, Fe, Ru, and Re)[10,22,24,26,29,48] and other ligands (Table 3). Grignard reagents have been employed, but they are less reactive than the lithium compounds.[42]

Neutral acyl compounds may likewise be converted into carbene complexes [equations (2)[23,85] and (3)[52]], and such intermediates, (7) and (8), are probably formed in reactions (4)[21] and (5).[72]

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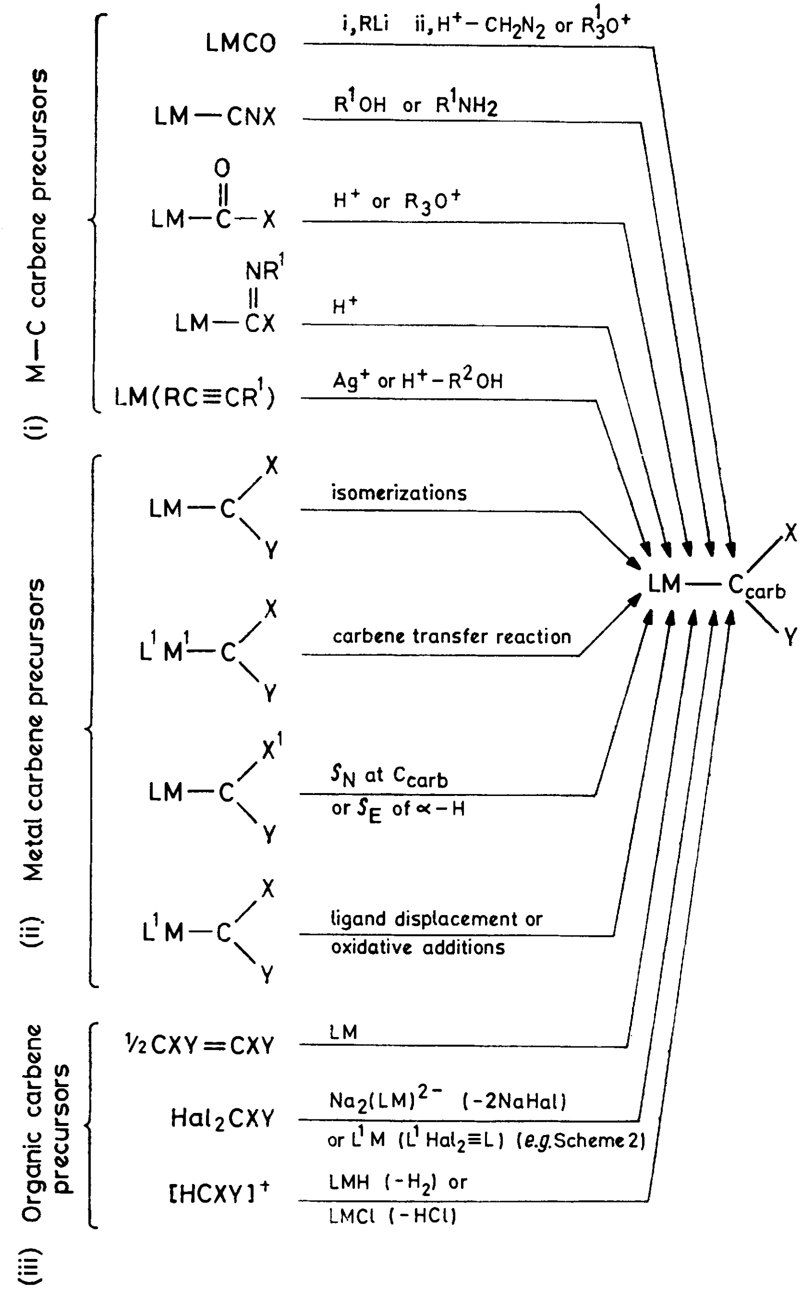
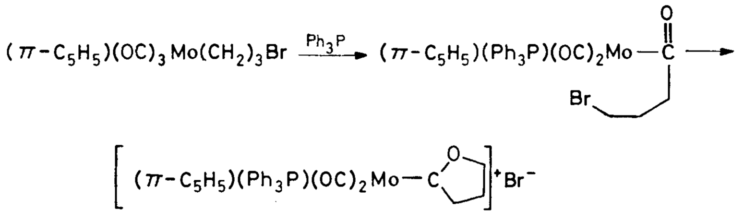
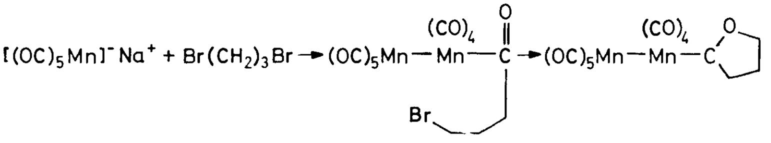


Figure 12 *Principal synthetic routes to transition-metal carbene complexes*

$$(\pi\text{-}C_5H_5)(OC)_2Fe\text{—}COMe + HCl \rightarrow [(\pi\text{-}C_5H_5)(OC)_2Fe\text{—}C(OH)Me]^+Cl^- \qquad (2)$$

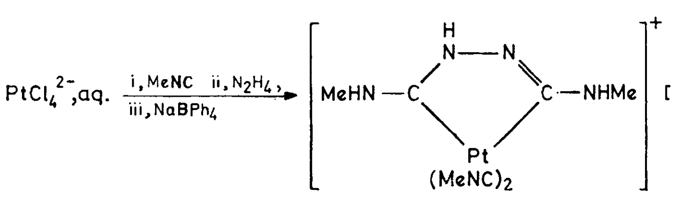
$$Hg(CONR^1R^2)_2 + 2[Me_3O]^+[BF_4]^- \rightarrow [Hg\{C(OMe)NR^1R^2\}_2]^{2+}[BF_4]_2^- \qquad (3)$$


(4)


(5)

Co-ordinated isonitriles react with alcohols, primary amines, and sodium borohydride[13a] to yield carbene complexes.[3,4,34,50,65,66,86,87] The first example is shown in equation (6);[50] others refer to Pd^{II}, Pt^{II}, Hg^{II}, and Fe^{II}. Isonitrile complexes of Cr^0 and Mo^0 as well as $PdI_2(Bu^tNC)_2$ (in contrast to the corresponding chloride[87]) were unreactive.[88] The preparation of Chugaev salts is of this class,[2-4,86] as illustrated for (9) in equation (7).[4] The chelating anionic (monocarbene ligand in (9) is clearly related to the neutral bidentate (dicarbene) ligand of Figure 1.

$$cis\text{-}Cl_2(Et_3P)Pt\text{—}CNPh + EtOH \rightarrow cis\text{-}Cl_2(Et_3P)Pt\text{—}C(OEt)NHPh \qquad (6)$$


(7)

(9)

Neutral imidoyl compounds may also be converted into carbene com-

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[86] A. Burke, A. L. Balch, and J. H. Enemark, *J. Amer. Chem. Soc.*, 1970, **92,** 2555.
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plexes,[25, 89, 90] as shown in equation (8).[89] The formation of cationic $\mathrm{Pt^{II}}$ complexes from acetylenes [equation (9)] is critically dependent on the nature of the acetylene, ligands Q, and solvent, and on the reaction conditions.[27,35,89,91]

$$\textit{trans}\text{-}\mathrm{I(Ph_3P)_2Pt{-}C({:}NMe)Ph} \xrightarrow{\mathrm{[NH_4]^+[PF_6]^-}} \textit{trans}\text{-}\mathrm{[I(Ph_3P)_2Pt{-}C(NHMe)Ph]^+(PF_6)^-} \qquad (8)$$

$$\textit{trans}\text{-}\mathrm{ClQ_2MePt} + \mathrm{R^1C{\equiv}CR^2} \xrightarrow[\mathrm{ii,\ MeOH}]{\mathrm{i,\ Ag^+[PF_6]^-}} \textit{trans}\text{-}\mathrm{[MeQ_2Pt{-}C(OMe)CHR^1R^2]^+[PF_6]^-} \qquad (9)$$

(ii) *Syntheses from Metal–Carbene precursors.* Reactions of the co-ordinated carbene ligand have been most widely studied for methoxycarbenechromium(0) complexes, and are shown, with other reactions of such compounds, in Figure 13. Some of these (also found for Mo, W, and Mn) illustrate the analogy mentioned earlier between alkoxycarbenes and carboxylic esters, namely the rections with ammonia, primary and secondary amines, ketimines, and thiols [equation (10)]. It is noteworthy that not all protic compounds behave similarly [see Figure 13 and Section 2C(iv)]. Both the stereochemistry[16,105] and the kinetics[59,106] of the aminolysis reaction have been studied. The latter revealed that the reaction proceeds by initial protonation at OMe, [equation (10)], followed by co-ordination of a nucleophile and finally reaction of $\mathrm{R_2NH}$ [= HA in equation (10)]. Deprotonation affords $\mathrm{LM{-}C(NR_2)R^1}$. In paraffinic solvents $\mathrm{R_2NH}$ is capable of acting both as proton donor and acceptor. Clearly $\mathrm{C_{carb}}$ is an electrophilic centre; this is further demonstrated by the protonic character of the α-hydrogens

$$\mathrm{(OC)_5Cr{-}C(OMe)R + HA \rightarrow MeOH + (OC)_5Cr{-}C(A)R} \qquad (10)$$

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[90] D. F. Christian, G. R. Clark, W. R. Roper, J. M. Waters, and K. R. Whittle, *J.C.S. Chem. Comm.*, 1972, 458.

[91] M. H. Chisholm and H. C. Clark, *Inorg. Chem.*, 1971, **10**, 2557.

[92] P. E. Baikie, E. O. Fischer, and O. S. Mills, *Chem. Comm.*, 1967, 1199.

[93] E. O. Fischer and R. Aumann, *Chem. Ber.*, 1968, **101**, 963; *Angew. Chem. Internat. Edn.*, 1967, **6**, 181.

[94] E. O. Fischer and V. Kiener, *Angew. Chem. Internat. Edn.*, 1967, **6**, 961.

[95] E. O. Fischer and A. Maasböl, *J. Organometallic Chem.*, 1968, **12**, P15.

[96] E. O. Fischer, E. Louis, W. Bathelt, E. Moser, and J. Müller, *J. Organometallic Chem.*, 1968, **14**, P9.

[97] H. Werner and H. Rascher, *Inorg. Chim. Acta*, 1968, **2**, 181; *Helv. Chim. Acta*, 1968, **51**, 1765.

[98] E. O. Fischer and L. Knauss, *Chem. Ber.*, 1969, **102**, 223.

[99] C. G. Kreiter, *Angew. Chem. Internat. Edn.*, 1968, **7**, 390.

[100] L. Knauss and E. O. Fischer, *J. Organometallic Chem.*, 1971, **31**, C71.

[101] J. A. Connor and P. D. Rose, *J. Organometallic Chem.*, 1970, **24**, C45.

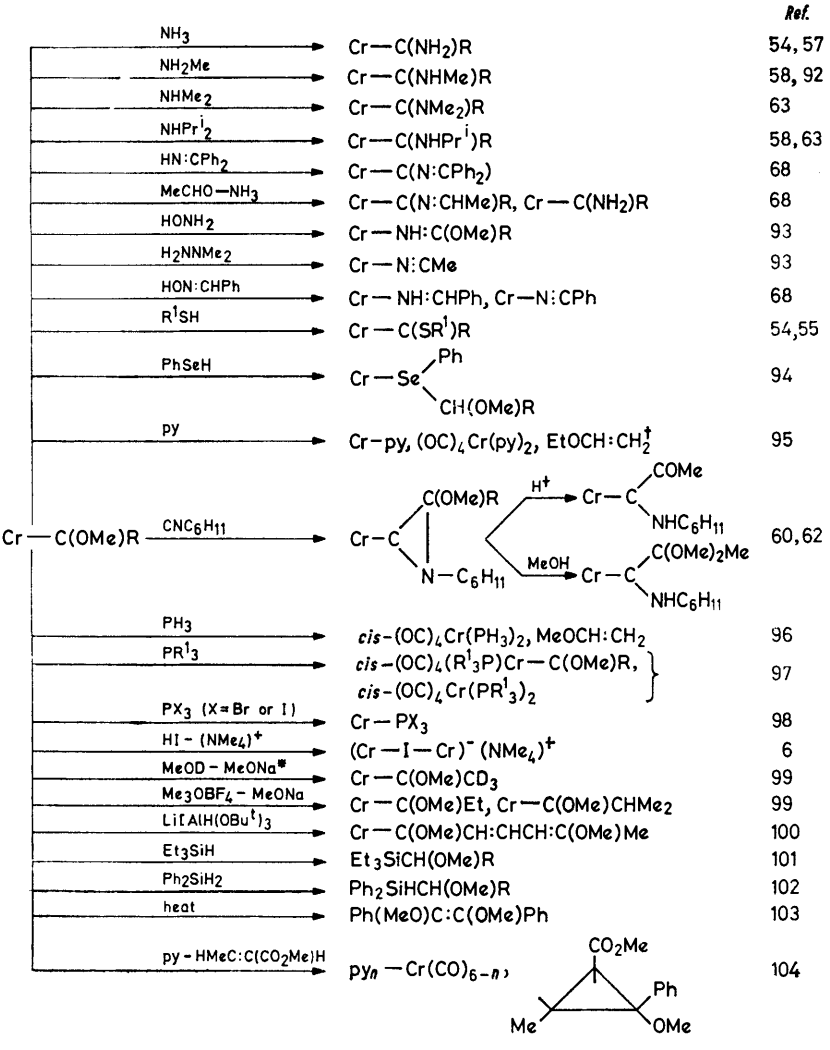
[102] E. O. Fischer and K. H. Dötz, *J. Organometallic Chem.*, 1972, **36**, C4.

[103] E. O. Fischer, B. Heckl, K. H. Dötz, J. Müller, and H. Werner, *J. Organometallic Chem.*, 1969, **16**, P29.

[104] E. O. Fischer and K. H. Dötz, *Chem. Ber.*, 1970, **103**, 1273.

[105] E. Moser and E. O. Fischer, *J, Organometallic Chem.*, 1968, **15**, 147.

[106] H. Werner, E. O. Fischer, B. Heckl, and C. G. Kreiter, *J. Organometallic Chem.*, 1971, **28**, 367.

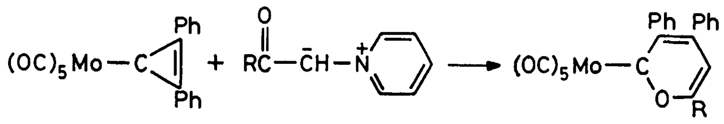


*In catalytic amount. †Refers to $(OC)_5Cr—C(OEt)Me$

Figure 13 *Reactions of alkoxycarbenechromium*(0) *complexes* Cr—C(OMe)R (R = Me or Ph), *such as* $(OC)_5Cr—C(OMe)Me$

in $(OC)_5Cr—C(OMe)CH_3$, as shown by the facile conversion (OMe^-–MeOD) into $(OC)_5Cr—C(OMe)CD_3$ or $(OC)_5Cr—C(OMe)CH_nMe_{3-n}$ (n = 1 or 2).[99] An interesting reaction of a co-ordinated carbene is shown in equation (11).[73]

Displacement reactions of either neutral or anionic ligands from transition-



(11)

metal carbene complexes may provide a method of synthesis of further carbene complexes. This is demonstrated by equation (12),[13] and has also been used in Cr^0 (*e.g.* Figure 13), Mo^0, W^0, Rh^I, Pd^{II}, and Pt^{II} (*e.g.* Figure 14) chemistry.

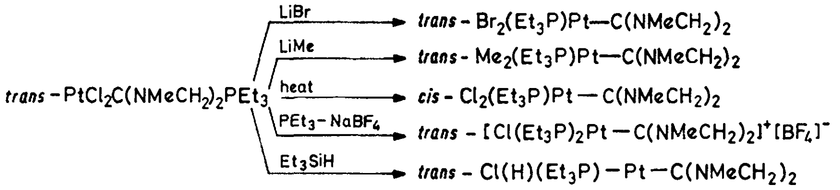
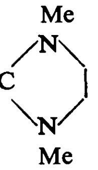


Figure 14 *Reactions*[110] *of* trans-$Cl_2(Et_3P)Pt$—C



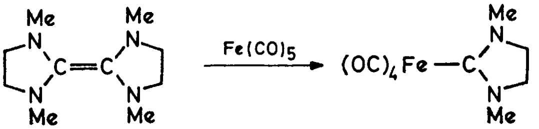
Additionally, for Rh^I compounds, it has been possible to displace one carbene ligand by another [*e.g.* equation (13)].[33] Nucleophiles may, however, react in other ways [*e.g.* Figure 13; for $C_6H_{11}NC$ see also Section 2C(iv)]. Some Pt^{II} carbene complexes are converted into Pt^{IV} derivatives by reaction with chlorine.[28]

$$Cl_3(Ph_3P)_2Rh\text{—}C(NMe_2)H \xrightarrow{Et_3P} Cl_3(Et_3P)_2Rh\text{—}C(NMe_2)H \qquad (12)$$

$$Cl(Ph_3P)_2Rh\text{—}C[N(Ph)CH_2]_2 \xrightarrow{\{C[N(C_6H_4\cdot Me\text{-}p)CH_2]_2\}_2} Cl(Ph_3P)_2Rh\text{—}C[N(C_6H_4\cdot Me\text{-}p)CH_2]_2 \qquad (13)$$

Two examples of carbene ligand transfer from one metal to another one are known[37,107] [*e.g.* equation (14)].[37] It is possible that this proceeds *via* an electron-rich olefin by analogy with reaction (15).[56]

$$(\pi\text{-}C_5H_5)(ON)(OC)Mo\text{—}C(OMe)Ph \xrightarrow[h\nu]{Fe(CO)_5} (OC)_4Fe\text{—}C(OMe)Ph \qquad (14)$$



(15)

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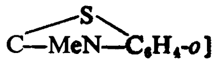
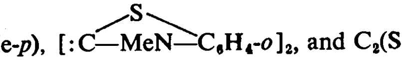
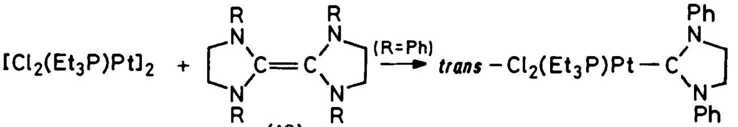
[107] K. Öfele and M. Herberhold, *Angew. Chem. Internat. Edn.*, 1970, **9**, 739.

Square-planar d^8 complexes *trans*-$Hal_2QM—CXY$ rearrange thermally to give the thermodynamically more stable *cis*-isomers [M = Pd or Pt; Hal = Cl or Br; Q = R_3P or R_3As; CXY = $C(NPhCH_2)_2$, $C(NMeCH_2)_2$, or  $\overset{S}{\overbrace{C—MeN—C_6H_4\text{-}o}}$] ($Pd^{II}$ reacts more readily than Pt^{II}).[15]

(iii) *Syntheses from Organic Carbene Precursors.* Electron-rich olefins, such as (10), are good nucleophiles[108] and have exceptionally low first ionization potentials (*ca.* 6 eV).[109] They react with certain transition-metal substrates which are responsive to nucleophilic attack to furnish carbene complexes. The first example of this reaction is shown in equation (16) (R = Ph).[14] Other carbene complexes to have been made by this procedure are complexes of Cr^0,[56] Fe^0,[56] Rh^I,[33,56] Pd^{II},[15,110] and Pt^{II},[14,15,110] and include dicarbene complexes [from $Rh_2Cl_2(CO)_4$ or $Cr(CO)_6$];[56] olefins to have been employed are $[:CN(R)CH_2]_2$ (R = Me, Ph, or $C_6H_4\cdot Me$-*p*),  $[:\overset{S}{\overbrace{C—MeN—C_6H_4\text{-}o}}]_2$, and $C_2(SMe)_4$.

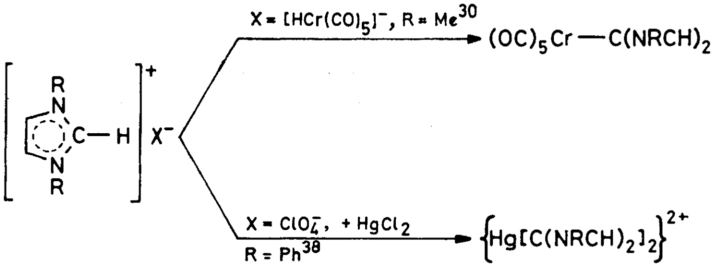


(10)

(16)

Imidazolium salts have been used (Scheme 1) to obtain complexes of Cr^0, Fe^0, and Hg^{2+}.[30,38,72]

Electron-rich *gem*-dichlorides, in which the C—Cl bonds have appreciable ionic



Scheme 1

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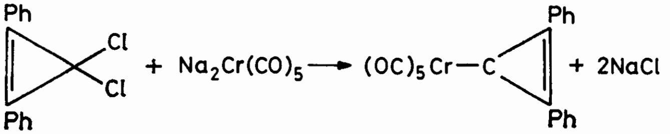
[108] R. W. Hoffmann, *Angew. Chem. Internat. Edn.*, 1968, **7**, 754; N. Wiberg, *ibid.*, p. 766.

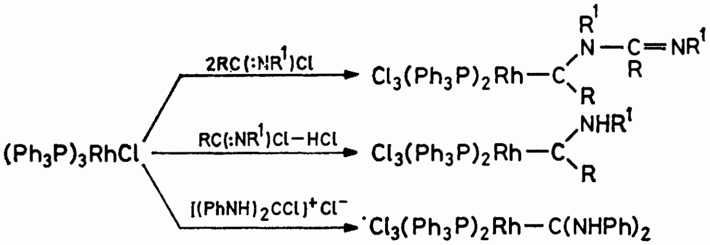
[109] B. Çetinkaya, G. H. King, S. S. Krishnamurthy, M. F. Lappert, and J. B. Pedley, *Chem. Comm.*, 1971, 1370.

[110] B. Çetinkaya, E. Cetinkaya, and M. F. Lappert, *J.C.S. Dalton*, in the press.

character, combine with dianions, as shown in equation (17), the earliest example of such a reaction;[30] other reports relate to Me_2NCHCl_2 and either $Na_2Cr(CO)_5$


(17)

or $Na_2Fe(CO)_4$.[13] Such dichlorides have also been used with co-ordinately unsaturated low-oxidation-state substrates (Rh^I, Ir^I, or Pt^{II} complexes[13] or Pd metal[70]). This procedure gives carbene complexes by a three-fragment oxidative-addition process, a sequence first postulated in order to account for the reaction products from imidoyl chlorides and Rh^I complexes (*e.g.* Scheme 2). $[Me_2NCHCl]^+Cl^-$,[13] $[(PhNH)_2CCl]^+Cl^-$ (Scheme 2),[13] and 2,3-diphenyl-1,1-dichlorocyclopropene have been used.[70]

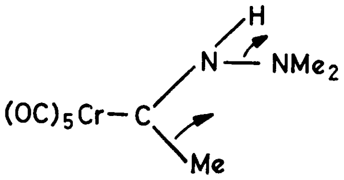


Scheme 2

Three-membered-ring compounds L$\overline{\mathrm{M—C(X)S}}$ [*e.g.* $(\pi\text{-}C_5H_5)(OC)_2$-$\overline{\mathrm{Mo—C(NMe_2)S}}$ and $(Et_3P)Cl\overline{\mathrm{Pt—C(SMe)S}}$] are known for X = SMe[56] and NMe_2.[64]

(iv) *Other Reactions.* The reactions of transition-metal complexes may be divided into those in which (*a*) another carbene complex is formed [see Section 2C(ii)], (*b*) the carbene ligand is transformed, but its constituents remain within the co-ordination sphere of the metal, and (*c*) the carbene ligand is displaced. Illustrations are provided in Figures 13 and 14.

A number of protic compounds do not behave according to equation (10). These include $HONH_2$, HONHPh, H_2NNMe_2, PhSeH (Figure 13), and HN_3 {on $[Me_4N]^+[(OC)_5Cr—C(O^-)CH_2SiMe_3]$ to give $(OC)_5Cr—NCMe$}.[45] All these reagents afford metal–nitrogen co-ordination compounds: the formation of isonitrile complexes may involve an initial methoxy displacement as shown in equation (10) and subsequent rearrangement [*e.g.* (11)]. The reactions with PhSeH and $C_6H_{11}NC$ are essentially insertions into the Cr—C_{carb} bond (Figure



(11)

13). There is a single example of conversion of a co-ordinated carbene into a substituted methyl complex [equation (18)].[23] A related reaction is the reversible conversion of $Cl_2(Ph_3P)Pd—C(OMe)NHPh$ with base into the imidoyl complex $[Cl(Ph_3P)PdC(OMe)(:NPh)]_2$.[111]

$$[(\pi\text{-}C_5H_5)(Ph_3P)(OC)Fe—C(OEt)Me]^+ \xrightarrow{NaBH_4\text{-}EtOH} (\pi\text{-}C_5H_5)(Ph_3P)(OC)Fe—CH(OEt)Me \qquad (18)$$

From Figure 13 it is evident that the carbene ligand may be displaced from chromium by a suitable nucleophile such as pyridine or a phosphine. Similar, but less extensive, results are available for complexes of Mo^0, W^0, Rh^I, and Hg^{II}: an example is in equation (19).[112] Especially noteworthy are those reactions in

$$Hg[C(NPhCH)_2]_2^{2+} + H_2S \rightarrow HgS + 2[HC(NPhCH)_2]^+ \qquad (19)$$

which the carbene ligand is trapped, by dimerization, rearrangement [*e.g.* $Me(MeO)C: \rightarrow MeOCH{=}CH_2$], or a trapping agent. Because stable metal carbene complexes are derived from nucleophilic carbenes, olefins such as cyclohexene are not particularly good reagents for this purpose, and hence the use of compounds such as $\alpha\beta$-unsaturated esters.[104] Silanes and related hydrides are particularly effective: the carbene inserts into the M—H bond[101,102] (but see Figure 14).

3 Metal Carbenes as Reaction Intermediates or Transition States.

Several reactions are known for which metal carbene complexes have been postulated as intermediates or transition states. This section describes such reactions, some of which are synthetically important.

Figure 15 summarizes details of organic and transition-metal reactants and products for the types of reactions outlined in Sections 3A—E, and Scheme 3 gives a particular example for Section 3D.

The evidence in favour of intermediate carbene complexes in the reactions shown in Figure 15 is not equally strong in all cases. Thus, whereas the metal-catalysed decomposition of diazoalkanes (Section A) and the alkylation of carbonylmetallates (Section B) leaves little room for doubt concerning such

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[111] B. Crociani and T. Boschi, *J. Organometallic Chem.*, 1970, **29**, C1.
[112] H. W. Wanzlick and H. J. Schönherr, *Angew. Chem. Internat. Edn.*, 1968, **7**, 141.

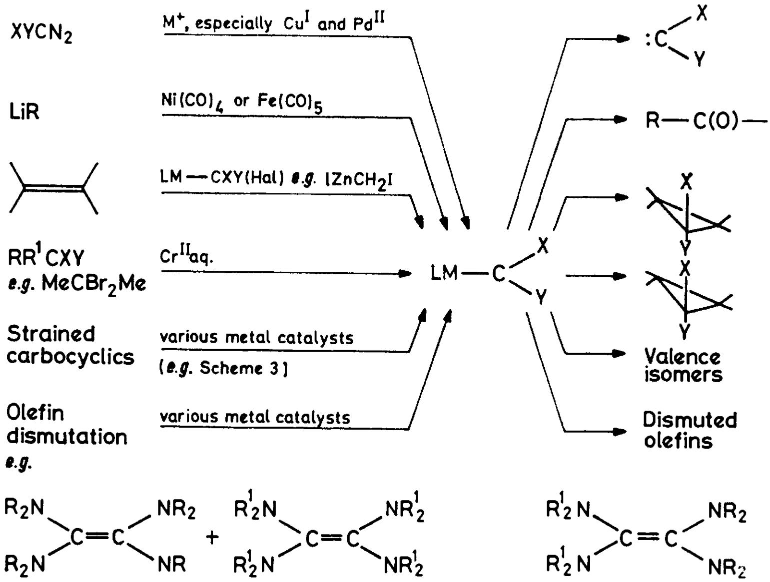
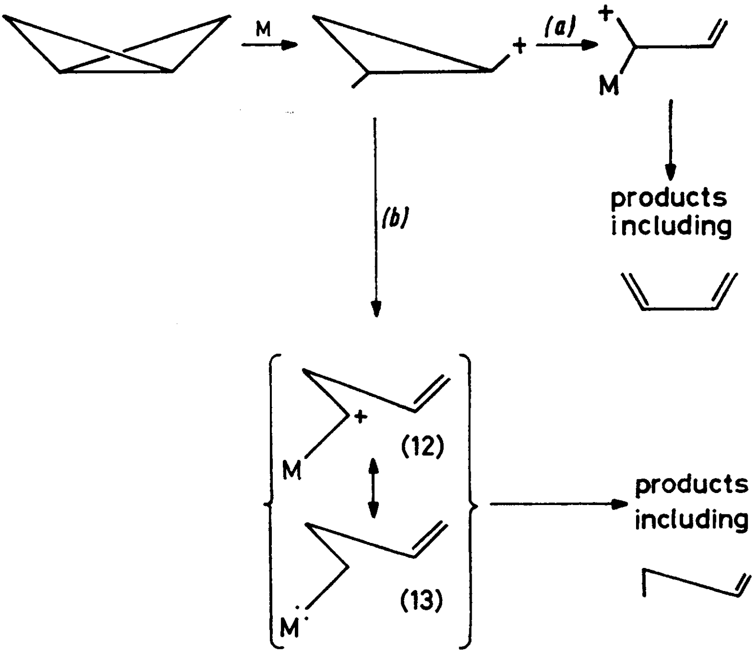


Figure 15 *Reactions proceeding* via *carbene–metal complexes*



Scheme 3

intermediates, the role of the metal in the cyclopropanation reactions (Section C) is rather different. As to Section D, many strained-carbocyclic rearrangements certainly do not involve complexed carbenes, although there is a wealth of circumstantial evidence in favour of such a mechanism in other cases. In terms of Scheme 3 we are here concerned only with reactions proceeding *via* species analogous to [(12)↔(13)] (path *b*) *i.e.* carbene complexes or metallocarbonium ions, and not *via* metal-substituted carbonium ions, (path *a*) in which the metal is at a site remote from the carbon with greatest positive charge.

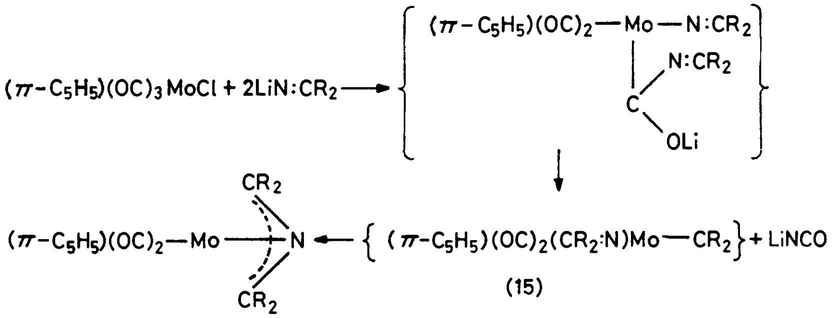
Finally, attention is drawn to some reactions which proceed through unstable carbene species but are not of general synthetic utility and are not outlined in Figure 15. These include [braces { } denoting those which have not been isolated] $\{(\pi\text{-C}_5\text{H}_5)(\text{OC})_2\text{Fe—CH}_2^+\}$ (see Section C), $\{(\pi\text{-C}_5\text{H}_5)(\text{OC})_3\text{Mo—CH}_2^-\}$, and $\{(\pi\text{-C}_5\text{H}_5)(\text{OC})_3[(\text{C}_6\text{H}_4\cdot\text{Me-}p)_2\text{CN}]\text{Mo—C}(\text{C}_6\text{H}_4\cdot\text{Me-}p)_2\}$, which are detailed here.

The reaction of $(\pi\text{-C}_5\text{H}_5)(\text{OC})_3\text{MoNa}$ with $\text{ClCH}_2\text{SiMe}_3$ surprisingly afforded $(\pi\text{-C}_5\text{H}_5)(\text{OC})_3\text{Mo—Me}$, and not the expected silylmethyl derivative.[113] Deuterium labelling studies exclude the possibility of Me migration (from SiMe_3). The reaction proceeds *via* the silyl derivative, as in equation (20), but subsequent

$$(\pi\text{-C}_5\text{H}_5)(\text{OC})_3\text{Mo—CH}_2\text{SiMe}_3 \xrightarrow[\text{room temperature}]{(\pi\text{-C}_5\text{H}_5)(\text{OC})_3\text{Mo}^-\text{Na}^+\text{–THF}}$$

$$\underset{(14)}{\{(\pi\text{-C}_5\text{H}_5)(\text{OC})_3\text{Mo—CH}_2^-\text{Na}^+\}} \rightarrow (\pi\text{-C}_5\text{H}_5)(\text{OC})_3\text{Mo–CH}_3 \qquad (20)$$

attack by $(\pi\text{-C}_5\text{H}_5)(\text{OC})_3\text{Mo}^-$ gives rise to (14); this is presumably because (i) anchimeric assistance by the cyclopentadienyltricarbonylmolybdenum group facilities CH_2—Si bond cleavage (unusual at room temperature) and (ii) the negative charge in (14) is substantially delocalized. A metallocarbene intermediate (15) has been proposed in the reaction between $(\pi\text{-C}_5\text{H}_5)(\text{OC})_3\text{MoCl}$ and $\text{LiN:C}(\text{C}_6\text{H}_4\cdot\text{Me-}p)_2$ (Scheme 4).[114] An intermediate of this type is entirely



R = Ph or *p*-tolyl

Scheme 4

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[113] M. R. Collier, B. M. Kingston, and M. F. Lappert, *Chem. Comm.*, 1970, 1498.
[114] H. R. Keable and M. Kilner, *J.C.S. Dalton*, 1972, 153.

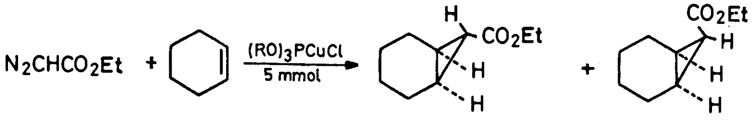
possible; the reaction of a lithium ketimide with co-ordinated carbonyl has been shown to afford carbene complexes [equation (21)],[53] but here the subequent reaction is not possible.

$$\mathrm{(OC)_6Cr} \xrightarrow[\text{ii, }[\mathrm{Et_3O}]^+[\mathrm{BF_4}]^-]{\text{i, }\mathrm{LiNCPh_2}} \mathrm{(OC)_5Cr{-}C(OEt)NCPh_2} \qquad (21)$$

A. Metal-catalysed Carbene Generation from Diazoalkanes.—The influence of metals in reactions of diazo-compounds $XYCN_2$ has been known for many years,[115] particular attention having been paid to catalytic decomposition by copper derivatives. The reactions afford nitrogen, and in many cases the products are those to be expected from the intermediacy of free carbenes. The reactions with metal and metalloid derivatives have been reviewed;[116] only those believed to involve carbene–metal species are considered here.

As well as transition-metal carbene complexes (LM—CXY), other proposed intermediates include $LM(CXYN_2)$ and $LM(CXYN_2CXY)$ (LM = catalyst). A few stable compounds having such compositions have been isolated,[115] but this does not necessarily imply that they play a role in the catalysed reaction path. Examples of these are (i) $(\pi\text{-}C_5H_5)(OC)_2W{-}N{:}N{-}CH_2SiMe_3$ from $(\pi\text{-}C_5H_5)(OC)_3WH$ and Me_3SiCHN_2[117] and (ii) *cis*-$(Ph_3P)_2Pt[(CF_3)_2C{:}N{\cdot}N{:}C(CF_3)_2]$ from $(Ph_3P)_3Pt$ and $(CF_3)_2CN_2$.[14]

Differences in the reactions undergone by the :CXY groups led to the proposal that complexed carbenes were true reaction intermediates,[118] rather than the free carbenes. This proposal has been examined in detail for reaction (22),[119]



(22)

(16) *(exo)* (17) *(endo)*

which is homogeneous. It has been observed that, in reactions of this type, the ratios of *exo*/*endo* products are very different from the photochemical and metal-initiated reactions.[120] Since the photochemical mechanism clearly cannot involve metal, these differences were taken as evidence for the intermediacy of copper–carbene complexes. Moser[119] found that the *thermal* reaction affords products, the *exo*/*endo* ratios of which lie closer to those of the metal-modified reactions, implying that these ratios are not sufficient evidence of LM—CXY intermediates. Better evidence for such intermediates has now been obtained by a study of the

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[115] A. Loose, *J. prakt. Chem.*, 1909, **79**, 507.

[116] M. F. Lappert and J. S. Poland, *Adv. Organometallic Chem.*, 1970, **9**, 397.

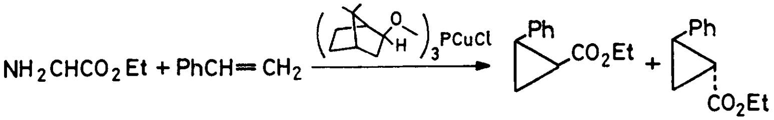
[117] M. F. Lappert and J. S. Poland, *Chem. Comm.*, 1969, 1061.

[118] P. Yates, *J. Amer. Chem. Soc.*, 1952, **74**, 5376.

[119] W. R. Moser, *J. Amer. Chem. Soc.*, 1969, **91**, 1135, 1141.

[120] P. S. Skell and R. M. Etter, *Chem. and Ind.*, 1958, 624.

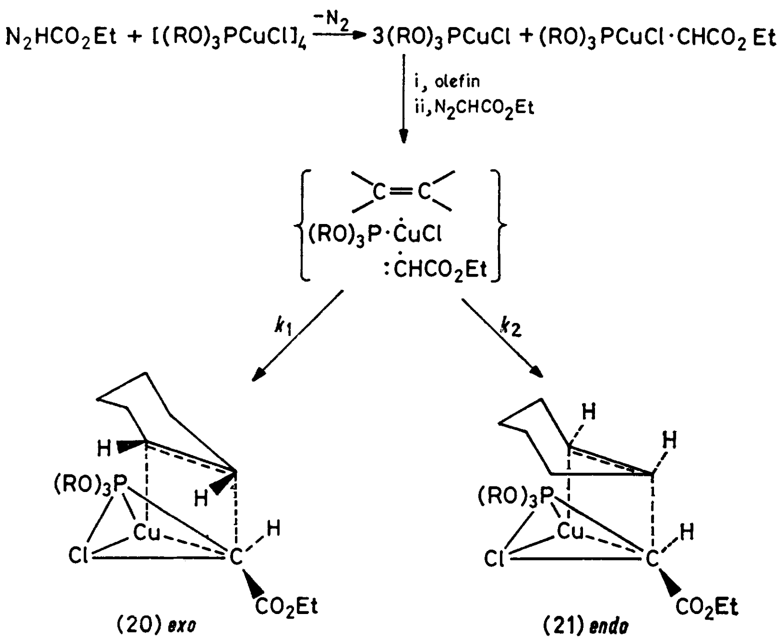
results of changing electronic or steric effects of substituents on the metal catalyst.[119] In summary, it was found that increasing the size of the phosphite [in $(RO)_3PCuCl$] favours formation of the *endo*-isomer (16), additionally electron-withdrawing groups favour a higher proportion of the *endo*-product (17). Additionally, use of the optically active (–)-tribornyl phosphitecopper(I) chloride gave two optically active cyclopropanes with optical yields of 3.2% (18) and 2.6% (19) [equation (23)].



(18) (19)

(23)

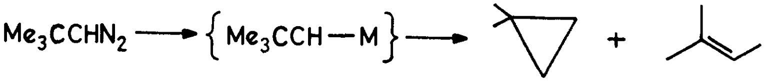
From the results, including an Arrhenius treatment of the reaction studied at various temperatures, it was concluded (i) that the final transition state (20 or 21) leading to products involves olefin, metal, and the carboxymethylene, (ii) that the transition state is asymmetric, and (iii) that any intermediate leading to it decomposes unimolecularly to products. A mechanism incorporating these factors has been proposed,[119] and is shown in Scheme 5.



Scheme 5

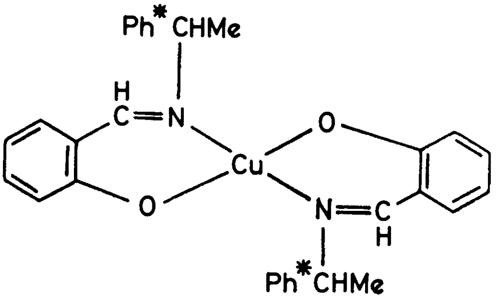
The effect of electronegative ligands (favouring formation of the *endo*-product) has been rationalized in terms of increased steric hindrance in (20) leaving (21) relatively unaffected. The dissociation of the copper phosphite is based on kinetic data.[121] Finally, probably the best evidence for copper–carbene complexes as intermediates is the induction of asymmetry at the cyclopropanes, and the *linear* correlation of *exo*/*endo* ratios with normal (Hammett) σ-constants of substituents in the aromatic ring using triaryl phosphite–copper complexes. Good correlations of this type are not common in catalytic reactions.

In a study[122] comparing thermal, photolytic, and metal-initiated decomposition of diazoalkanes with copper or silver salts, both olefins and cyclopropanes were formed [equation (24)] and evidence for metal carbene intermediates emerged.



(24)

Asymmetric induction in cyclopropanes similar to that using norbornyl phosphite complexes has been demonstrated using an optically active chelate (22) of copper (Scheme 6).[123] In this case the optical yields were rather higher



(22)

(~ 6%) than with tribornyl phosphitecopper chloride, as one might have predicted with an asymmetric centre closer to the metal. In this case the reaction was inhibited by addition of co-ordinating bases such as pyridine. Scheme 6 also shows asymmetric induction with an oxetan.[123]

Another chelate, acetylacetonatocopper(II), has been examined with benzoyldiazomethane.[124,125] Here, metal complexation was believed to account for

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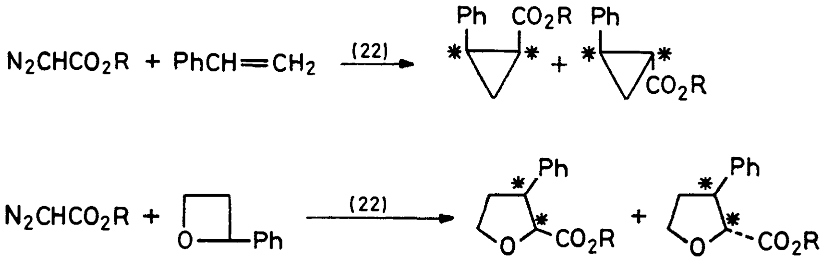
[121] A. G. Witenberg, I. A. D'yakorov, and A. Zindel, *Zhur. org. Khim.*, 1966, **2**, 1532.

[122] W. Kirmse and K. Horn, *Chem. Ber.*, 1967, **100**, 2698.

[123] H. Nozaki, S. Moriuti, H. Takaya, and R. Noyori, *Tetrahedron Letters*, 1966, 5239.

[124] M. Takebayashi, T. Ibata, H. Kohara, and Bu Hong Kim, *Bull. Chem. Soc. Japan*, 1967, **40**, 2392.

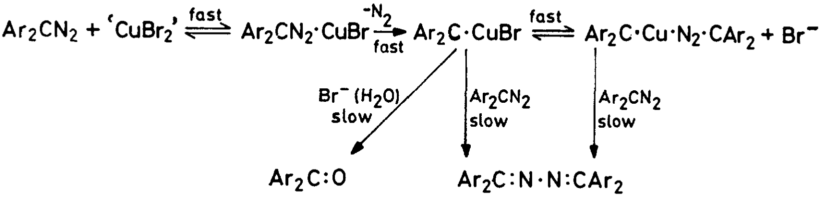
[125] M. Takebayashi, T. Ibata, H. Kohara, and K. Ueda, *Bull. Chem. Soc. Japan*, 1969, **42**, 2938.



Scheme 6

reduced carbene reactivity. A number of copper salts catalysed a cycloheptatriene synthesis from aromatic systems.[126,127] In one study,[128] with Cu, Hg, or Co catalysts, a mercury intermediate[129] was isolated and its subsequent reaction demonstrated.

Reactions catalysed by zinc halides, especially ZnI_2, are of particular interest because of the possible similarity between intermediate species in this and in the Simmons–Smith reaction (see Section 3C). Kinetic studies with Ph_2CN_2 show that two intermediates are involved, the first of which may be a carbene complex. In subsequent reactions, ZnI_2 differs from the chloride and bromide.[130,131] Decomposition of the same diazo-compound and analogues by $CuBr_2$ in acetonitrile yields the diaryl ketone and ketazine. Kinetic studies point to the reaction pathway of Scheme 7, which shows only the essential metal ligands. The



Scheme 7

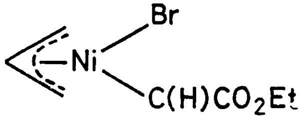
kinetic evidence, including spectroscopic, indicates the intermediate formation of Cu^{II}–carbene complexes, but the diazoalkane complex is inferred from stopped-flow data on the initial phase of the reaction.[131]

[126] E. Müller and H. Fricke, *Annalen*, 1963, **661**, 38.
[127] E. Müller, H. Kessler, H. Fricke, and W. Kiedaisch, *Annalen*, 1964, **675**, 63.
[128] T. Saegusa, Y. Ito, T. Shimizu, and S. Kobayashi, *Bull. Chem. Soc. Japan*, 1969, **42**, 3535.
[129] A. N. Nesmeyanov and G. S. Powch, *Ber.*, 1934, 67, 971.
[130] D. Bethell and K. C. Brown, *Chem. Comm.*, 1967, 1266; *J. C. S. Perkin II*, 1972, 895.
[131] D. Bethell and M. Eeeles, personal communication.

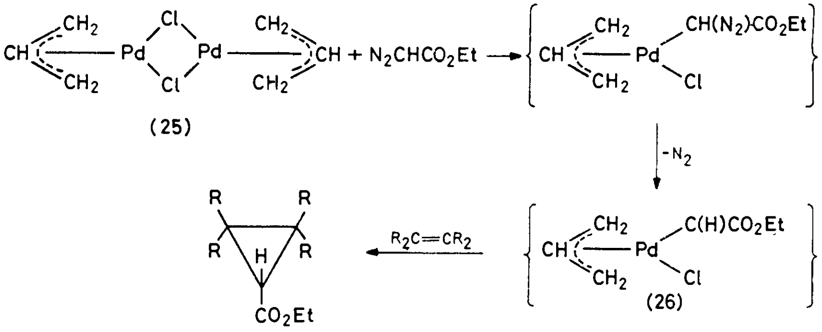
By contrast with the above catalytic decompositions, ethyl diazoacetate *reacts* with the organic ligand of bromo-π-allylnickel(I), affording butadiene derivatives, mainly isomers of (23).[132] A possible reaction scheme involves the carbene intermediate (24). It is proposed that the carbene then inserts into the adjacent Ni—C bond (*cf.* carbon monoxide) to form, *e.g.*, (23). Decomposition of ethyl diazoacetate by an allylpalladium complex (25) has also been examined;[133] here reaction with co-ordinated allyl was not observed. The proposed mechanism (Scheme 8) involves the carbene species (26), an analogue of (24). In this study, comparison between (25) and copper salts as catalysts was made. Thus for reactions of N_2CHCO_2Et with but-2-yne, (25) is an effective catalyst at 0—10°C, whereas copper derivatives required temperatures of 65—120°C, and curiously, whereas the former afforded mainly diethyl fumarate in the dimerization reaction, diethyl maleate was the major product in the latter case. In another comparative study, catalytic decomposition of the unusually stable diazotetrachlorocyclopentadiene by (25) in acetylenes (as solvents) was examined.[134] When carried out in tolan or 3-hexyne at 75—82°C using copper or copper sulphate, the spiro[2,4]-heptatrienes (27; R = Me or Ph) were obtained. However, with the palladium

$CH_2{=}CH{—}CH{=}C(H)CO_2Et$

(23)



(24)



Scheme 8

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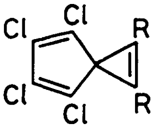
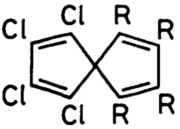
[132] I. Moritani, Y. Yamamoto, and H. Konishi, *Chem. Comm.*, 1969, 1457.
[133] R. K. Armstrong, *J. Org. Chem.*, 1966, **31**, 618.
[134] E. T. McBee, G. W. Calundann, and T. Hodgins, *J. Org. Chem.*, 1966, **31**, 4260.

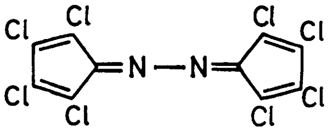
complex at 10—20 °C, low yields of the adducts with two acetylene molecules (28; R = Me or Ph), but no cyclopropane derivatives, were isolated, together with 50—60 % of the azine (29) (not detected with copper catalysts). The proposed mechanism for the Pd-catalysed system (Scheme 9) involves both a carbene complex (31) and a butadiene complex (30); the latter is postulated to account for the unique feature, namely lack of reaction with solvent acetylene.



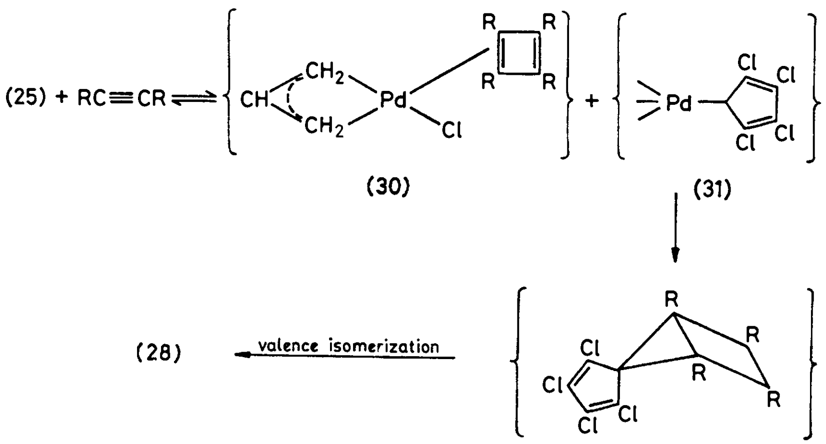
(27)



(28)



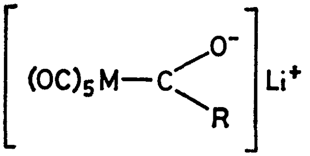
(29)



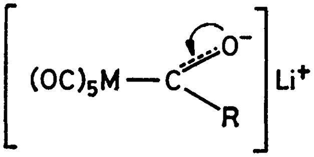
Scheme 9

[The decomposition of CH$_2$N$_2$ by Ni(CO)$_4$ is described in the following section, and the use of diazoalkanes in mechanistic studies relevant to carbocyclic rearrangements is described in Section 3D.]

B. Synthesis of Organic Carbonyl Compounds using Metal Carbonyls.—In the syntheses of the Group VIA-metal carbene complexes first used by Fischer and co-workers,[6,7] acylmetallates (32) are intermediates. These may be regarded as anionic carbene complexes, and such a view has been widely accepted. However, the contribution of forms such as (33) cannot be ignored (see Table 3 and ref. 49). In a number of reactions intermediate carbonylmetallates react with organic reagents forming alkyl- or aryl-(carbene) complexes (OC)$_n$M—C(OR)Ph which decompose to products: in this section both ions and neutral species are regarded, formally, as carbenes.

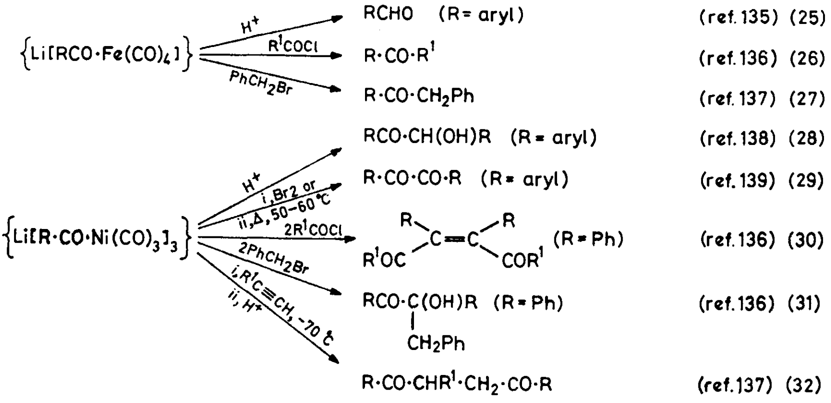


(32)



(33)

As we have seen, the acylmetallates derived from RLi and a Group VIA-metal hexacarbonyl are stable complexes which require rather good alkylating agents [*e.g.* CH_2 then H^+, or $(Et_3O)^+BF_4^-$] for conversion into neutral carbenes. By contrast the carbonyls $Fe(CO)_5$ and $Ni(CO)_4$ are more reactive to organolithium reagents (the latter reacts exothermically at − 70 °C), forming rather unstable salts, sensitive to air and moisture. They are, however, useful intermediates in organic syntheses by virtue of their reactions with olefins, alkyl halides, and other organic substances. Such syntheses are exemplified in equations (25)—(34).



$$Ph_2C{=}CH{-}CHPhLi + M(CO)_6 \rightarrow \{Li[(OC)_5M{-}C(O)CHPh{\cdot}CH{=}CPh_2]\} \xrightarrow{H^+} PhCH(CHO)CH{=}CPh_2 \qquad \text{(ref. 140)} \quad (33)$$

(M = Group VIA metal; routes to unsaturated aldehydes are relatively uncommon)

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[135] M. Ryang, I. Rhee, and S. Tsutsumi, *Bull. Chem. Soc. Japan*, 1965, **38**, 330.

[136] Y. Sawa, M. Ryang, and S. Tsutsumi, unpublished work cited in ref. 7; *Tetrahedron Letters*, 1969, 5189.

[137] Y. Sawa, I. Hashimoto, M. Ryang, and S. Tsutsumi, *J. Org. Chem.*, 1968, **33**, 2159.

[138] Y. Sawa, M. Ryang, and S. Tsutsumi, *J. Org. Chem.*, 1970, **35**, 4183.

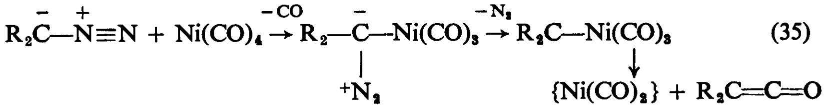
[139] M. Ryang, S. K. Myeong, Y. Sawa, and S. Tsutsumi, *J. Organometallic Chem.*, 1966, **5**, 305.

[140] E. O. Fischer and A. Maasböl, G. P. 1214233/1966.

$$\mathrm{LiNMe_2 + Ni(CO)_4 \rightarrow \{LiN(Me_2)CO{\cdot}Ni(CO)_3\} \xrightarrow{HgCl_2} Me_2NCO{\cdot}CO{\cdot}NMe_2 + Hg + 2LiCl} \qquad \text{(ref. 141)} \quad (34)$$

The intermediate salts of Fe and Ni are too reactive to permit structural studies. They are believed to be mono- and di-nuclear respectively; thus, products from the coupling of two organic groups are formed from the nickel derivatives. The proposed mechanism[137] for an acyloin and stilbenediol diester are shown in Scheme 10; the use of this route for direct addition of acyl groups to conjugated enones has been described.[142]

The reaction of diphenyldiazomethane with $Ni(CO)_4$ is extremely vigorous. Catalytic amounts of the carbonyl afford mainly benzophenone azine together with nitrogen, ethylene, and small quantities of other nitrogen-containing compounds.[143] With excess nickel, carbonylation takes place. The proposed mechanism, equation (35), involves a metal–carbene intermediate. Reaction of CO with free carbene is not known.



$$\mathrm{R_2\overset{-}{C}{-}\overset{+}{N}{\equiv}N + Ni(CO)_4 \xrightarrow{-CO} R_2{-}\underset{+N_2}{\overset{-}{C}}{-}Ni(CO)_3 \xrightarrow{-N_2} R_2C{-}Ni(CO)_3 \rightarrow \{Ni(CO)_2\} + R_2C{=}C{=}O} \qquad (35)$$

Formation of ketazine may well involve the carbene intermediate (and R_2CN_2), a view in harmony with the dependence on the concentration of metal carbonyl.

C. Carbene Transfer Reactions, Especially to Olefins.—A number of 'CXY' transfer reactions (in which the carbene is derived from a diazo-compound) have been described in Section A; others are detailed here, including the synthetically important dihalogenocarbene reactions.

Unusually mild conditions (dilute HCl, room temperature) are required for the cleavage of the ether linkage in (34), shown in equation (36).[144] Similar behaviour is typical of acetals where hydrolysis is favoured by C=O double-bond forma-

$$\underset{(34)}{(\pi\text{-}C_5H_5)(OC)_2Fe{-}CH_2OCH_3} \underset{\mathrm{MeOH\text{-}NaOH}}{\overset{\mathrm{HCl}}{\rightleftharpoons}} \underset{(35)}{(\pi\text{-}C_5H_5)(OC)_2Fe{-}CH_2Cl} \qquad (36)$$

tion. An attractive hypothesis[144] is that reaction (36) is facilitated by carbene formation (stabilization, 'double-bond' formation with Fe). Support for this view has been obtained by reaction of (35) with $AgBF_4$: AgCl may be filtered off, after which the filtrate reacts with cyclohexene affording norcarane, presumably

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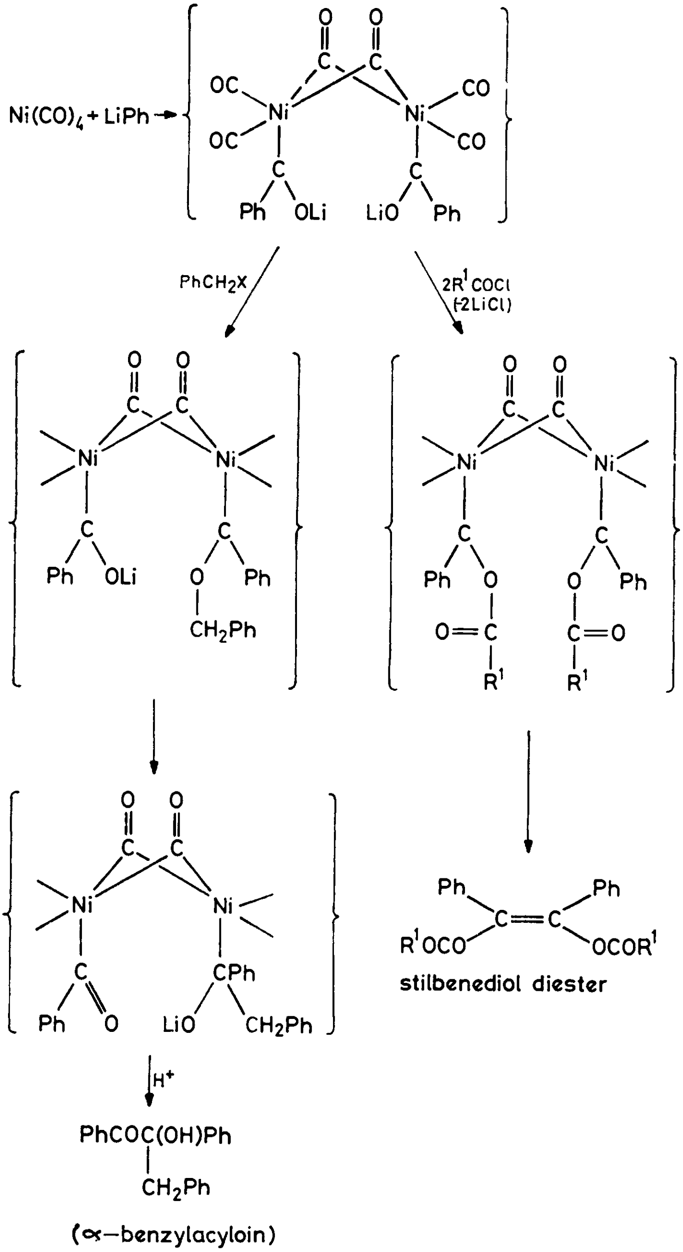
[141] S. K. Myeong, Y. Sawa, M. Ryang, and S. Tsutsumi, *Bull. Chem. Soc. Japan*, 1965, **38**, 330.
[142] E. J. Corey and L. S. Hegedus, *J. Amer. Chem. Soc.*, 1969, **91**, 4926.
[143] C. Rüchardt and G. N. Schrauzer, *Chem. Ber.*, 1960, **93**, 1840.
[144] M. L. H. Green, M. Ishaq, and R. N. Whiteley, *J. Chem. Soc.* (*A*), 1967, 1508.

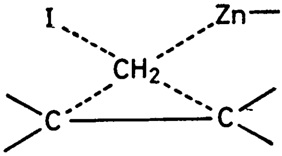


PhCOC(OH)Ph
CH$_2$Ph
(α—benzylacyloin)

Scheme 10

from the intermediate $\{[(\pi\text{-}C_5H_5)(OC)_2FeCH_2]^+BF_4^-\}$ (36).[145] Without the separation step norcarane yields of 46% were obtained, and using *cis*- and *trans*-but-2-enes trapping was stereospecific. The compounds isolated in the absence of traps were $(\pi\text{-}C_5H_5)(OC)_2FeCH_3$ and $[(\pi\text{-}C_5H_5)(OC)_2Fe(CH_2{=}CH_2)]^+$, both of which are clearly plausible products from further reaction of (36). Trapping experiments were positive also in the reaction of $(\pi\text{-}C_5H_5)(OC)_3MoCH_2OMe$ with acids and in similar but much slower reactions with Re and Mn methoxymethyl species.[145]

Since the discovery of reactive dihalogenocarbenes from haloforms[146,147] and from the Simmons–Smith reagent $IZnCH_2I$,[148,149] there has been much interest in carbene transfer reactions. A number of studies have suggested a transition state (37) involving methylene and metal, but the species does not come within our definition of a carbene complex (see refs. 146—157). The subject has been authoritatively reviewed.[152]

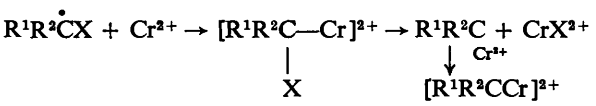


(37)

The reduction of *gem*-dihalides by chromium(II) sulphate has been shown to proceed *via* chromium-carbene intermediates.[158] Kinetic data, products, and reactivity sequences support a reduction involving carbenes derived from an initially formed α-halogenomethyl radical:

$$R^1R^2CX_2 + Cr^{2+} \rightarrow [R^1R^2C(X)\cdots X\cdots Cr^{2+}] \rightarrow R^1R^2\dot{C}X + CrX^{2+} \qquad (37)$$

followed by



$$R^1R^2\dot{C}X + Cr^{2+} \rightarrow [R^1R^2\underset{\substack{|\\ X}}{C}\text{—}Cr]^{2+} \rightarrow \underset{\substack{\downarrow\, Cr^{2+}\\ [R^1R^2CCr]^{2+}\\ (38)}}{R^1R^2C} + CrX^{2+} \qquad (38)$$

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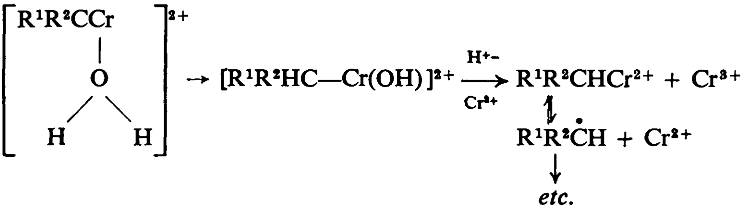
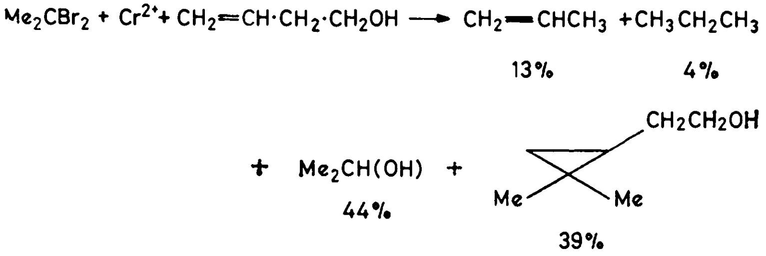
[145] P. W. Jolly and R. Pettit, *J. Amer. Chem. Soc.*, 1966, **88**, 5044.
[146] W. von E. Doering and A. K. Hoffmann, *J. Amer. Chem. Soc.*, 1954, **76**, 6162.
[147] G. Köbrich, H. Büttner, and E. Wagner, *Angew. Chem. Internat. Edn.*, 1970, **9**, 169.
[148] E. P. Blanchard and H. E. Simmons, *J. Amer. Chem. Soc.*, 1964, **86**, 1337.
[149] H. E. Simmons, E. P. Blanchard, and R. D. Smith, *J. Amer. Chem. Soc.*, 1964, **86**, 1347.
[150] T. L. Gilchrist and C. W. Rees, 'Carbenes, Nitrenes, and Arynes', Nelson, London, 1969.
[151] G. L. Closs and R. A. Moss, *J. Amer. Chem. Soc.*, 1964, **86**, 4042.
[152] D. Seyferth, *Accounts Chem. Res.*, 1972, **5**, 65.
[153] D. Seyferth and J. M. Burlitch, *J. Amer. Chem. Soc.*, 1964, **86**, 2730.
[154] W. von E. Doering and W. A. Henderson, *J. Amer. Chem. Soc.*, 1958, **80**, 5274.
[155] D. Seyferth, J. Y.-P. Mui, and J. M. Burlitch, *J. Amer. Chem. Soc.*, 1967, **89**, 4953.
[156] D. Seyferth, M. E. Gordon, and K. V. Darragh, *J. Organometallic Chem.*, 1968, **14**, 43.
[157] D. Seyferth, J. Y.-P. Mui, and R. Damrauer, *J. Amer. Chem. Soc.*, 1968, **90**, 6182.
[158] C. E. Castro and W. C. Kray, *J. Amer. Chem. Soc.*, 1966, **88**, 4447.

Reduction takes place by proton transfer:



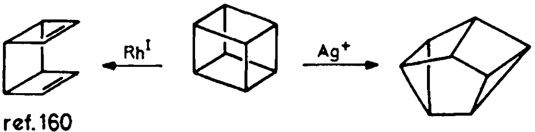
$$\left[\begin{array}{c} R^1R^2CCr \\ | \\ O \\ H \quad H \end{array}\right]^{2+} \rightarrow [R^1R^2HC{-}Cr(OH)]^{2+} \xrightarrow[Cr^{2+}]{H^+-} \begin{array}{c} R^1R^2CHCr^{2+} + Cr^{3+} \\ \updownarrow \\ R^1R^2\dot{C}H + Cr^{2+} \\ \downarrow \\ etc. \end{array} \qquad (39)$$

Carbenes have been trapped in this reaction; with 3-butenol and Me_2CBr_2 the cyclopropyl product was obtained in 39% yield [equation (40)]. These results indicate a carbene of rather reduced reactivity, presumably species (38).



(40)

D. Valence Isomerizations of Strained-ring Carbocyclic Compounds.—(i) *Nature of the Reaction.* A number of remarkable σ-bond rearrangements in highly strained ring compounds are catalysed by transition-metal ions or their complexes. Examples are shown in the equations (41)—(47); the bonds specified are those cleaved.

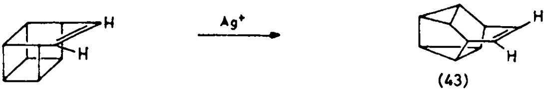


(41)

ref.160

ref.159

(39) (40) (41)



(ref. 161) (42)

(42)

(43)

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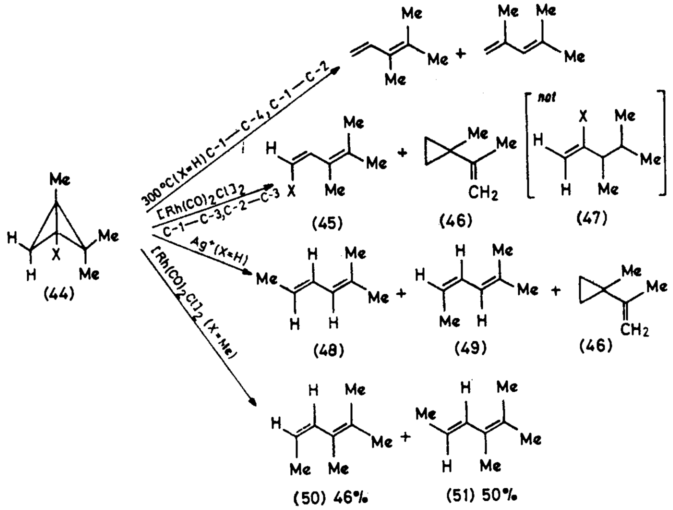
[159] L. Cassar, P. E. Eaton, and J. Halpern, *J. Amer. Chem. Soc.*, 1970, **92**, 6366.
[160] L. Cassar, P. E. Eaton, and J. Halpern, *J. Amer. Chem. Soc.*, 1970, **92**, 3515.
[161] L. A. Paquette and J. C. Stowell, *J. Amer. Chem. Soc.*, 1971, **93**, 2459.

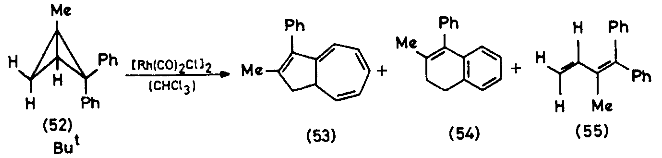


(ref.162) (43a)

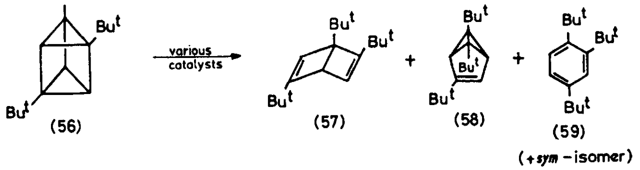
(ref.163) (43b)

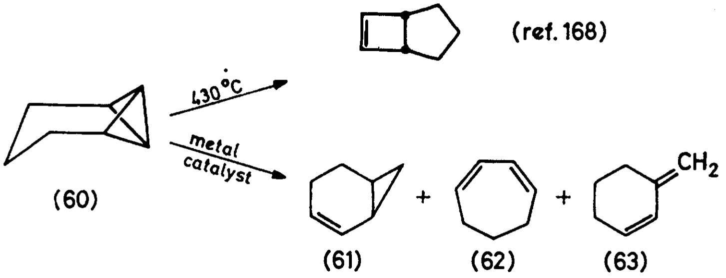
(ref.164) (43c)

(ref.165) (43d)



(ref.166) (44)





(ref.168) (46a)

(refs. 165,169) (46b)

[162] G. L. Closs and P. E. Pfeffer, *J. Amer. Chem. Soc.*, 1968, **90**, 2452.

[163] P. G. Gassmann and F. J. Williams, *J. Amer. Chem. Soc.*, 1970, **92**, 7631.

[164] M. Sakai and S. Masamune, *J. Amer. Chem. Soc.*, 1971, **93**, 4610.

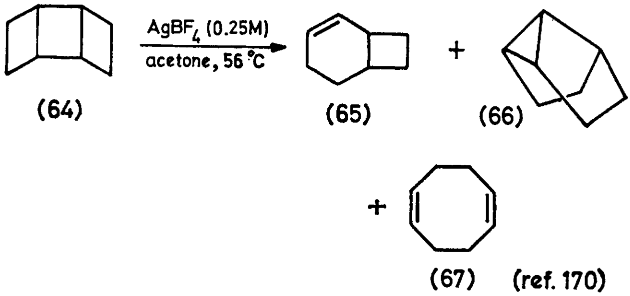
[165] P. G. Gassmann, T. J. Atkins, and F. J. Williams, *J. Amer. Chem. Soc.*, 1971, **93**, 1812; P. G. Gassmann and T. J. Atkins, *ibid.*, p. 4597; but see also B. S. Solomon, C. Steel, and A. Weller, *Chem. Comm.*, 1969, 927; ref. 181.

[166] P. G. Gassmann and T. Nakai, *J. Amer. Chem. Soc.*, 1971, **93**, 5897.

[167] K. L. Kaiser, R. F. Childs, and P. M. Maitlis, *J. Amer. Chem. Soc.*, 1971, **93**, 1270.

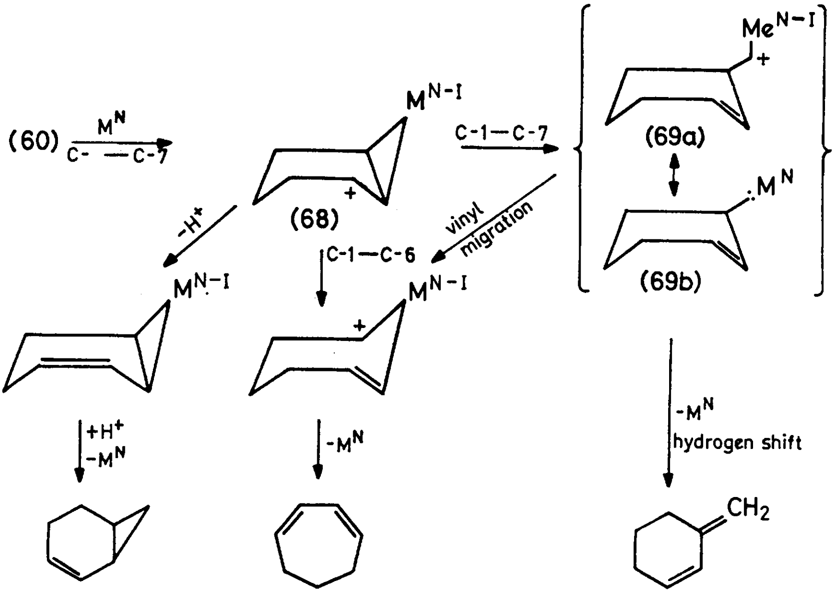
[168] K. B. Wibert and G. Szeimies, *Tetrahedron Letters*, 1968, 1235.

[169] L. A. Paquette, G. R. Allen, and R. P. Henzel, *J. Amer. Chem. Soc.*, 1970, **92**, 7002; see also L. A. Paquette, R. P. Henzel, and S. E. Wilson, *ibid.*, 1971, **93**, 2335.



(47)

Particular attention has been given to Ag^I, Rh^I, and Pd^{II} catalysts, among others, and in some cases simple Lewis acids are effective. The Ag^I catalyses have been reviewed.[171] The driving force for these reactions is the relief of the high ring strain initially present,[171,172] and the role of the transition metal is tc provide a low-activation-energy pathway which is otherwise inaccessible, owing to the constraints of orbital symmetry.[173,174] Attention is drawn to the hybrid (69) shown in Scheme 11 with both the carbene (69b) and metallo-carbonium ion



Scheme 11

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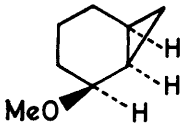
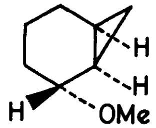
[170] J. Wristers, L. Brenner, and R. Pettit, *J. Amer. Chem. Soc.*, 1970, **92**, 7499.
[171] L. A. Paquette, *Accounts Chem. Res.*, 1971, **4**, 280.
[172] K. B. Wiberg, *Adv. Alicyclic Chem.*, 1968, **2**, 185.
[173] M. G. Evans, *Trans. Faraday Soc.*, 1939, **35**, 824.
[174] R. B. Woodward and R. Hoffmann, *Angew. Chem. Internat. Edn.*, 1969, **8**, 781.

(69a) contributors. Further evidence for (68) and (69) comes from trapping experiments with nucleophiles (see below). The derivatives (70) and (71) were produced



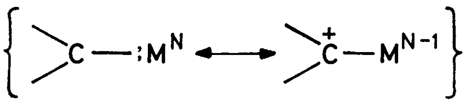
(70)



(71)

when the $[Rh(CO)_2Cl]_2$ catalysis of (60) was conducted in methanol, and significantly in the same ratio when sulphuric acid was used in place of the metal catalyst.[176] These experiments support both the stepwise nature of the reaction and the intermediacy of carbonium ions, but do not provide conclusive evidence for (69); some related systems have been rationalized in terms of the parallel with conventional carbonium ion chemistry.[177] A similar charge-transfer (cation radical) intermediate has been proposed for the prismane rearrangement [equation (45)].[167] We may contrast conditions of the thermal (unchanged 3 h, 150 °C; 86% recovery after gas-phase pyrolyses 1 s, 500 °C) and catalysed (quantitative conversion, < 3 min, 40 °C) reactions analogous to equation (42) for the (saturated) bis(methylcarboxylate) of compound (42). Kinetic factors are presumably also responsible for the contrasting behaviour of (64) with $AgBF_4$, the *anti*-isomer being inert under the same conditions [equation (47)]. Finally we note the synthetic utility of some reactions: equation (44) shows a novel route to azulenes,[166] and the first preparations of semibullvalene were based on a bishomocubyl rearrangement.[175]

(ii) *Mechanisms.* A large amount of evidence supports the existence of carbene intermediates or 'metallo-carbonium ions' in many of these reactions, having the structural feature shown. The evidence includes (*a*) satisfactory product identification, (*b*) kinetic data, (*c*) labelling experiments, (*d*) trapping experiments both internally and with additives, and (*e*) studies with model systems.



Point (*a*) is illustrated with reference to equation (46b); the thermal reaction (46a) follows a different course (and, probably, a different mechanism). The product ratios are dependent on the catalyst employed, of which there are many (including Rh, Pd, Cu, Ag, Zn, and Hg derivatives) having the common feature

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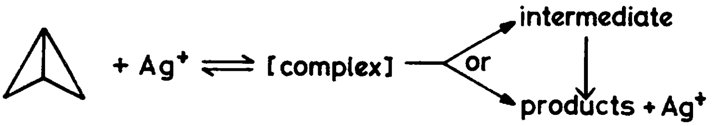
[175] L. A. Paquette, *J. Amer. Chem. Soc.*, 1970, **92**, 5765; R. Askami, *Tetrahedron Letters*, 1970, 3349; L. Cassar, P. E. Eaton, and J. Halpern, *J. Amer. Chem. Soc.*, 1970, **92**, 6367.

[176] M. Sakai, H. H. Westburg, H. Yamaguchi, and S. Masamune, *J. Amer. Chem. Soc.*, 1971, **93**, 4611.

[177] J. E. Byrd, L. Cassar, P. E. Eaton, and J. Halpern, *Chem. Comm.*, 1971, 40.

of Lewis acidity. A common intermediate (68) has been proposed, which can account easily for the observed products of Scheme 11.

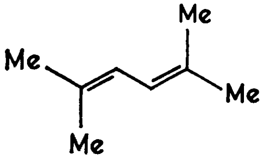
Kinetic data (*b*) relating to bicyclobutane systems [especially equation (46)] have shown that the reactions are not concerted processes and that the derived rate law[169] is consistent with the following mechanism:



(48)

Kinetic studies with cubane systems[178] and a norbornene derivative[179] also establish stepwise pathways.

Point (*c*) is illustrated by reference to equation (43). Different bonds are cleaved in the thermal reaction[162] (43a) from those in catalysed pathways[163,164] (43b and c); the ambiguity (C-1—C-3 and C-2—C-3 or C-1—C-4 and C-2—C-3) in pathway (43b) was resolved by a labelling study [X = D; (43b)]. The C-1—C-3 cleavage was also rigorously established for the Ag^+-initiated rearrangements[180] of *exo,exo*- and *endo,endo*-1,4-dimethylbicyclo[1,1,0]butanes which are, respectively, largely and highly stereospecific. The methylated analogue (44; X = Me) gives an almost statistical distribution of products [equation (43)], but the isomeric 2,2,4,4-tetramethyl derivative, which has no 2- or 4-hydrogen atom available for migration after the skeletal change, afforded (72) only.[165] This might imply a new bond-breaking sequence, but a more attractive explanation is that



(72)

the unchanged sequence leads to (73) [*cf.* (69)], which subsequently undergoes a vinyl migration. Studies on migratory aptitudes to carbenoid centres show an order H > vinyl > methyl.[181] Further support for (73) is provided by the low-temperature decomposition of (74) catalysed by the same Rh^I species, which affords (72) as the only volatile product.[165]

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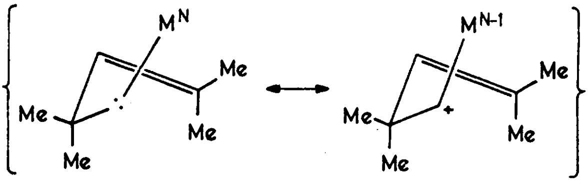
[178] L. Cassar, P. E. Eaton, and J. Halpern, *J. Amer. Chem. Soc.*, 1970, **92**, 3515, 6366.

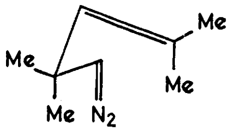
[179] T. J. Katz and S. A. Cerefice, *J. Amer. Chem. Soc.*, 1969, **91**, 6520.

[180] M. Sakai, H. Yamaguchi, H. H. Westburg, and S. Masamune, *J. Amer. Chem. Soc.*, 1971, **93**, 1043.

[181] H. Shechter, personal communication quoted in ref. 182; see also D. M. Lemal and K. S. Shim, *Tetrahedron Letters*, 1964, 323; G. L. Closs and R. B. Larabee, *ibid.*, 1965, 287.

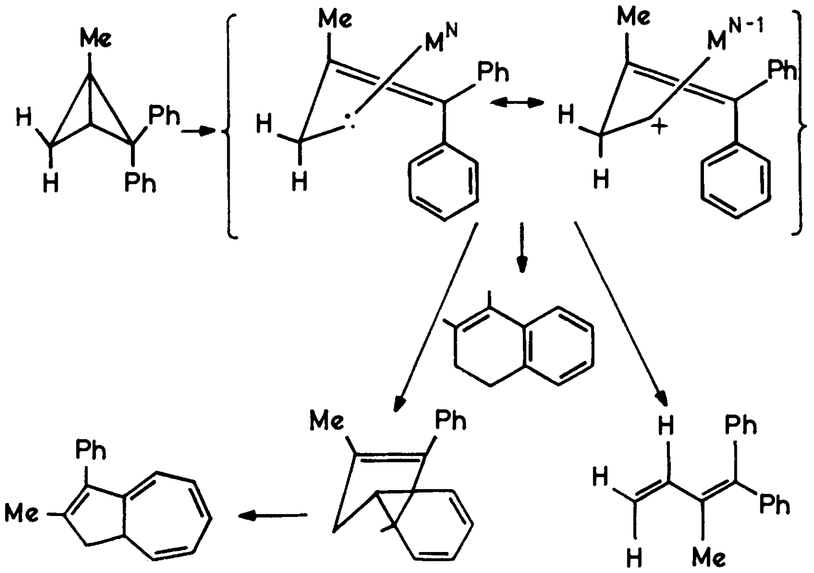


(73)



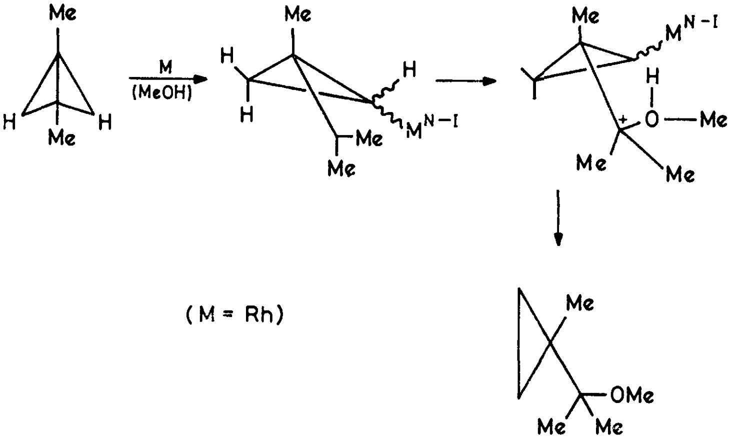
(74)

Trapping reactions (*d*) have been widely used in other systems as evidence for intermediate carbene species. Particularly interesting in this context is the internal benzene into norcaradiene conversion, a typical carbene reaction, believed to take place in the rearrangement of (52) [equation (44)]. The proposed reaction scheme is presented in Scheme 12.[171]



Scheme 12

A (carbonium ion) precursor to the metal carbene complex has been detected in the 1,2,2-trimethylbicyclo[1,1,0]butane system by intermolecular trapping with methanol.[166] These experiments confirm the stepwise nature of the process, and establish that C-2—C-3 bond rupture precedes C-1—C-3 scission in the reaction (see labelling experiments above), as shown in Scheme 13. The methoxy-derivative was obtained at a rate (97%, 1 min, 25 °C) comparable to that of the

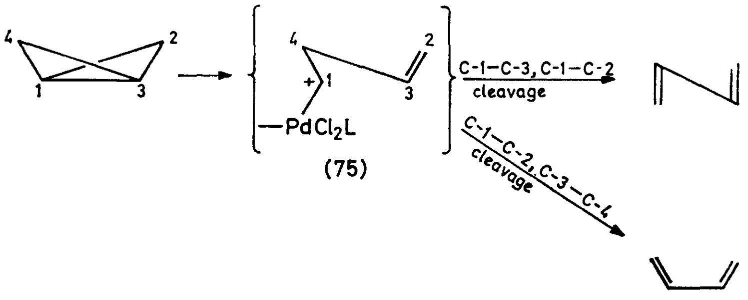


Scheme 13

rearrangement. Acid catalysis was eliminated (control experiments) but the possibility that methanol solvent promotes a different mechanism from that in chloroform, although improbable and without experimental foundation, could not be ruled out.[166]

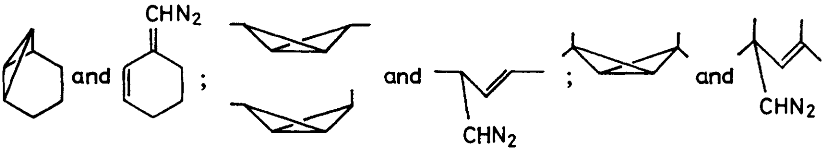
Synthesis of the proposed carbene intermediates in these reactions from model compounds and a study of their subsequent reactions have tended to confirm the proposals for some systems only. It is known that the metal-catalysed decomposition of diazo-compounds proceeds *via* carbene complexes (see Section 3A) and this reaction has been used to provide the required intermediates. [One example, (74), has been mentioned above.]

In the palladium-catalysed rearrangements of bicyclobutanes, two bond-breaking pathways are known, as shown in Scheme 14; the intermediate (75)



Scheme 14

corresponds to (73) in the Rh^{I}-catalysed reactions. The percentage distribution of products is very sensitive both to the catalyst and to substituents in the substrate. Diazo-compounds were synthesized, such that their decomposition would lead to corresponding carbonium ion analogues of the general intermediate (75).[164] Bicyclobutanes with the appropriate diazo-models are shown below.



For the palladium-catalysed [$(\text{PhCN})_2\text{PdCl}_2$] reactions of the bicyclobutanes the product distribution was similar or identical to that obtained with the relevant model, strongly supporting a carbene (metallo-carbonium ion) intermediate. However, the silver-catalysed decompositions led to entirely different ratios.[176] It seems here that an initial C-1—C-2 heterolysis is followed by a cyclopropyl- to allyl-carbinyl rearrangement and loss of metal ion.[174] Evidence for this using traps has been presented above.

In conclusion, we may consider for which systems and metals carbene–metal complexes may be intermediates. There is clear evidence for these both from trapping experiments (especially internal insertion into benzene[166]) and from suitable models for several bicyclobutane rearrangements catalysed by both rhodium[165] and palladium.[164] For the Ag^+ catalyses, evidence for metallo-carbenes is no more than circumstantial, although two aspects have been clearly established: (i) the stepwise nature involving different bonds in the carbon framework from the thermal reactions and (ii) the involvement of carbonium ions, possibly metal-containing but conceivably at a site remote from greatest positive charge.

E. Olefin Dismutation (or Metathesis).—The reaction is illustrated in equation (49), in which X and/or Y are H, alkyl, or some other univalent atom or group. Catalysis may be heterogeneous, the catalyst comprising a 'promoter', a metal oxide (*e.g.* MoO_3) and a 'supporter', an oxide or phosphate (*e.g.* Al_2O_3). We are concerned principally with homogeneous systems: catalysts include WCl_6–$2\text{Bu}^{\text{n}}\text{Li}$, [$(\text{Ph}_3\text{P})_2\text{Cl}_2$-$\text{W(NO)}_2$]–($\text{Me}_3\text{Al}_2\text{Cl}_3$), and $(\text{Ph}_3\text{P})_3\text{RhCl}$ (for electron-rich olefins). Reviews are available,[182–184] but these do not consider the role of metal–carbene complexes. There is increasing evidence for the participation of such

[182] G. C. Bailey, *Catalysis Rev.*, 1969, **3**, 37; M. L. Khidekel', A. D. Shebaldova, and I. V. Kalechits, *Russ. Chem. Rev.*, 1971, **40**, 669; S. Yoshitomi, *Sekiyu Gakkai Shi*, 1970, **13**, 92; C. Inoue and K. Hirota, *Yuki Gosei Kagaku Kyokai Shi*, 1970, **28**, 744; J. Tsuji, *Kagaku No Ryoiki Zokan*, 1970, **89**, 169.

[183] F. D. Mango and J. H. Schachtschneider, in 'Transition Metals in Homogeneous Catalysis', ed. G. N. Schrauzer, Marcel Dekker, New York, 1971, 223.

[184] N. Calderon, *Accounts Chem. Res.*, 1972, **5**, 127; N. Calderon, E. A. Ofstead, J. P. Ward, W. A. Judy, and K. W. Scott, *J. Amer. Chem. Soc.*, 1968, **90**, 4133.

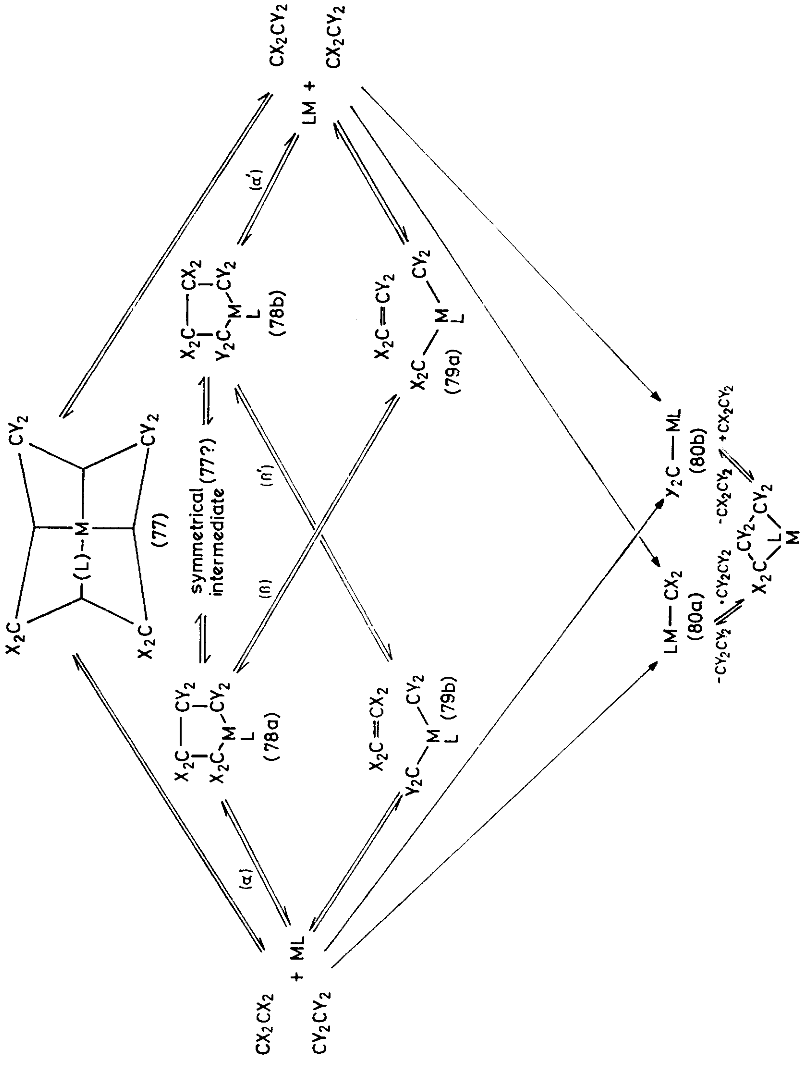


Figure 16 *Possible organometallic species in olefin dismutation*

species in the reaction, as discussed below and summarized schematically in Figure 16, in which LM represents the transition metal with ancillary ligands. Support for a metal–carbene intermediate comes from kinetic data on the heterogeneous Co–Mo catalysis of (*a*) CH_2N_2 decomposition into N_2 and C_2H_4 and (*b*) the dismutation of C_3H_6 into C_2H_4 and $CH_3CH{:}CHCH_3$;[185] the rates for (*a*) and (*b*) are similar and, as discussed in Section 3A, (*a*) very probably involves a metal–CH_2 species.

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[185] J. J. Rooney and P. P. O'Neill, *J.C.S. Chem. Comm.*, 1972, 104.

$$2CX_2{:}CY_2 \rightleftharpoons CX_2{:}CX_2 + CY_2{:}CY_2 \qquad (49)$$

It will be convenient to classify organometallic species according to the number of active M—C sites: the 4-C systems are (76),[184] (77),[186] and (78);[187] the 3-C is (81);[33] the 2-C is (79);[33] and the 1-C is (80).[33]

A four-carbon–metal species is consistent with the results of labelling experiments[188,189] and product characterization,[182–184] as exemplified by equation (50). However, in several systems products are formed which are not so readily explained (*e.g.* see refs. 189 and 190). For instance, the dismutation of oct-1-ene, catalysed by WCl_6–$EtAlCl_2$, affords not only the expected ethylene and $Me(CH_2)_5CH{:}CH(CH_2)_5Me$ but also olefins having odd numbers of carbon atoms (C_7—C_{15}), especially at high catalyst concentration.[191] It is well known that transition-metal complexes often cause the isomerization of olefins, and this affords a possible rationalization of the results [*e.g.* equation (51)]; however, the possibility of a carbene intermediate has been considered,[191] presumably of type (80).

$$2CH_3{-}CH{=}{}^{14}CH_2 \rightleftharpoons {}^{14}CH_2{=}{}^{14}CH_2 + CH_3{-}CH{=}CH{-}CH_3 \qquad (50)$$

$$\begin{array}{lcl} CH_2{=}CH(CH_2)_5CH_3 & \rightleftharpoons & C_2H_4 + CH_3(CH_2)_5CH{=}CH(CH_2)_5CH_3 \\ \quad\upharpoonleft\downharpoonright & & \qquad\qquad\qquad\qquad (51) \\ CH_3CH{=}CH(CH_2)_4CH_3 & \rightleftharpoons & CH_2{=}CH(CH_2)_4CH_3 \\ & & \quad + CH_3(CH_2)_5CH{=}CHCH_3 \end{array}$$

A quasi-cyclobutane intermediate, (76), was first suggested for heterogeneous systems,[192] but now appears unlikely[186] because (i) cyclobutanes are not detected in dismutation experiments and (ii) dismutation catalysts do not transform cyclobutanes into olefins. These experiments were taken to imply that a so-called 'tetramethylene complex' (77) was involved.[186] In (77), the four CX_2 or CY_2 fragments, formed by simultaneous scission of both σ- and π-bonds of C_2X_4 and C_2Y_4, are co-ordinated to M by the overlap scheme of Figure 17, each carbon utilizing hybrid orbitals approximating to sp^3. Thus, (77) is not a metal carbene complex, as defined in Section 2A (sp^2-C being required).

Further evidence for a four-carbon–metal species, and especially (77), comes from experiments on dismutation of non-4-ene by the d^6 complex (π-MePh)-$W(CO)_3$.[186] In order to form such a species, taking each of CX_2 or CY_2 as a two-electron donor to the metal, it is necessary that both toluene and at least one CO ligand be displaced from the metal, unless the metal is to exceed its complement of 18 valence electrons. No dismutation occurred when carbon monoxide loss was prevented, and inhibition was noted when excess of toluene was present.

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[186] G. S. Lewandos and R. Pettit, *J. Amer. Chem. Soc.*, 1971, **93**, 7087.

[187] R. H. Grubbs and T. K. Brunck, *J. Amer. Chem. Soc.*, 1972, **94**, 2538.

[188] J. C. Mol, J. A. Moulijn, and C. Boelhouwer, *Chem. Comm.*, 1968, 633.

[189] A. Clark and C. Cook, *J. Catalysis*, 1969, **15**, 420; G. V. Isagulyants and L. F. Rar, *Bull. Acad. Sci. U.S.S.R.*, 1969, 1258.

[190] F. F. Woody, M. J. Lewis, and G. B. Wills, *J. Catalysis*, 1969, **14**, 389.

[191] K. Hummel and W. Ast, *Naturwiss.*, 1970, **57**, 245.

[192] R. L. Banks and G. C. Bailey, *Ind. and Eng. Chem.* (*Proc. Res. and Development*), 1964, **3**, 170; C. P. C. Bradshaw, E. J. Howman, and L. Turner, *J. Catalysis*, 1967, **7**, 269.

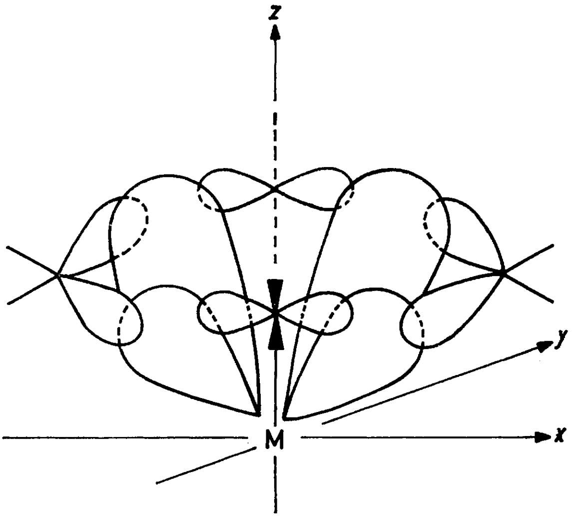
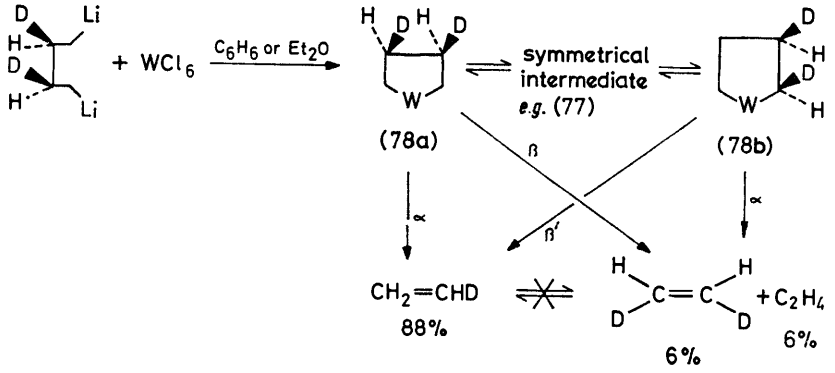


Figure 17 *Orbital overlap for a 'tetramethylene complex'* (77)

The four-carbon metallocyclic species (78) was suggested for systems such as those catalysed by WCl_6–$2Bu^nLi$ (see ref. 193), as a consequence of the experiments on (i) *meso*-1,4-dilithio[2,3-$^2H_2$]butane, illustrated in Scheme 15,[187] and (ii) the *dl*-compound which gave $CH_2{=}CHD$ (88%), *trans*-$CHD{=}CHD$ (6%), and C_2H_4 (6%).



Scheme 15

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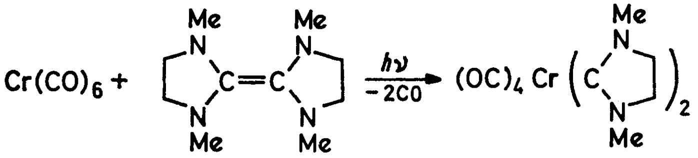
[193] J. Wang and H. R. Menapace, *J. Org. Chem.*, 1968, **33**, 3794.

The metallocycles were not isolated, but as a class such compounds are known. Their interconversion requires a symmetrical transition state or intermediate, *e.g.* (77), although a [1,3] shift has also been considered.[183] The pathways α and α' (for the minor product) were suggested.[187] However, the possibility of steps β and β', *via* two-carbon fragments (79), is now proposed. This allows for alternative competing pathways, such as α and β. Additionally, it provides a plausible route to the origin of the metallocycles in Figure 16.

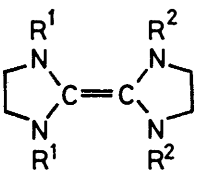
$$\mathrm{LM} + \text{olefin} \rightleftharpoons \pi\text{-complex (82)} \rightleftharpoons (79) \underset{-\,\text{olefin}}{\overset{\text{olefin}}{\rightleftharpoons}} (78)$$

The dicarbene (79) may form *via* a π-olefin complex (82); these are, of course, well-known. As described in Section 2C(iii), electron-rich olefins yield one-carbon complexes (80), probably *via* (82) and a free carbene. However, it is also possible to isolate a dicarbene complex (79) [equation (52)].[56] It may be significant that Group VIA hexacarbonyls are considered to be active dismutation catalysts only if a mechanism exists which provides for the loss of two or more CO ligands (*e.g.* by irradiation[194]).



(52)

Recently a three-carbon metallocyclic species (81) has been suggested, and definitive evidence for a one-carbon species (80) (a metal–carbene complex) has been presented in the homogeneously catalysed dismutation of the electron-rich olefins (83).[83] A mixture of (83a) and (83b) at 140 °C in xylene for 2 h in the presence of a rhodium(I) complex $L(Ph_3P)_2RhCl$ ($L = Ph_3P$ or CO) underwent a dismutation reaction to produce (83c) in yields approaching the statistical (50%).



(83a) $R^1 = R^2 = Ph$
(83b) $R^1 = R^2 = p\text{-tol}$
$\Big\} = CX_2CX_2$ or CY_2CY_2

(83c) $R^1 = Ph$
$R^2 = p\text{-tol}$
$\Big\} = CX_2CY_2$

The suggested mechanism is shown in the lower part of Figure 16. The evidence rests on: (i) the isolation of the monocarbene complexes of type (80a),

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[194] E. S. Davie, D. A. Whan, and C. Kemball, *J. Catalysis*, 1972, **24**, 272.

$L(Ph_3P)Rh(CX_2)Cl$, from the reaction of C_2X_4 with $L(Ph_3P)_2RhCl$ under dismutation conditions; (ii) the demonstration that compounds (80) also catalyse the dismutation; and (iii) the conversion (80a) $\xrightarrow{(83b)}$ (80b) for L = Ph_3P. Additionally, (iv) the oxidative addition step seems plausible because other oxidative addition reactions of Rh^I carbene complexes can be demonstrated,[195] whereas (v), the carbene complex $(Et_3P)Cl_2Pt—C[N(Ph)CH_2]_2$, which is known to be unreactive with regard to oxidative addition, is not a dismutation catalyst under the conditions employed. The possibility of a metal–dicarbene complex (79) in this system is not ruled out (see above). Such a compound has been isolated by reaction of an olefin of type (83) with $[Rh(CO)_2Cl]_2$.[56]

At present, whether the dismutation of simple alkenes is related to that of electron-rich olefins remains an open question.

4 Addendum

Although selective in nature, this section brings the literature coverage up to the end of 1972. The existence of transient anions derived by proton abstraction from co-ordinated carbenes[99] has been confirmed by generation at low temperature and affords useful syntheses.[196] The intramolecular cyclization reaction[71] has been extended to cationic and neutral compounds having 2-heteroatom substituents.[197] Reactions of nucleophiles with the electrophilic C_{carb} of :C(OMe)Ph bound to a Group VI metal have been studied: the secondary phosphine $HPMe_2$ co-ordinates through phosphorus to C_{carb} affording a substituted ylide structure,[198] but phosphonium ylides cleave the carbene and afford a route to vinyl ethers.[199] Two developments in syntheses of carbene complexes from neutral precursors are noteworthy. *viz.* a general synthesis, particularly of oligocarbene derivatives using electron-rich olefins,[200] and diphenylcarbene complexes of rhodium prepared from Ph_2CN_2 or $Ph_2C{=}C{=}O$, which are among the very few co-ordinated carbenes not stabilized by a hetero-substituent on C_{carb}.[201] For recent developments in the mechanism of metal-catalysed rearrangements of strained-ring compounds see references 202 and 203.

We thank Dr. D. Bethell for unpublished data and the S.R.C. for their support.

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[195] D. J. Cardin, M. J. Doyle, and M. F. Lappert, to be published.

[196] C. P. Casey, R. A. Boggs, and R. L. Anderson, *J. Amer. Chem. Soc.*, 1972, **94**, 8947.

[197] M. Green, J. R. Moss, I. W. Nowell, and F. G. A. Stone, *J.C.S. Chem. Comm.*, 1972, 1339.

[198] F. R. Kreissl, C. G. Kreiter, and E. O. Fischer, *Angew. Chem. Internat. Edn.*, 1972, **11**, 643.

[199] C. P. Casey and T. J. Burkhardt, *J. Amer. Chem. Soc.*, 1972, **94**, 6543.

[200] B. Çetinkaya, P. Dixneuf, and M. F. Lappert, *J.C.S. Chem. Comm.*, 1973, in the press.

[201] P. Hong, N. Nishii, K. Sonogashira, and N. Hagihara, *J.C.S. Chem. Comm.*, 1972, 993.

[202] L. A. Paquette, R. P. Henzel, and J. E. Wilson, *J. Amer. Chem. Soc.*, 1972, **94**, 7780 and references therein.

[203] P. G. Gassman and T. J. Atkins, *J. Amer. Chem. Soc.*, 1972, **94**, 7.