Metal σ-Hydrocarbyls, MR$_n$. Stoichiometry, Structures, Stabilities, and Thermal Decomposition Pathways[†]

PETER J. DAVIDSON, MICHAEL F. LAPPERT,* and RONALD PEARCE

School of Molecular Sciences, University of Sussex, Brighton BN1 9QJ, England

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I. Introduction and General Considerations

The purpose of this article is to assess metal σ-hydrocarbyls from the standpoint primarily of the range of known compounds and their stability. We shall deal with homo- and heteroleptic compounds. In this context definitions are as follows: a homoleptic metal σ-hydrocarbyl is a species of the formula (MR$_n$)$_x$, in which M is an element other than H, C, O, Na, K, Rb, Cs, Ca, Sr, Ba, chalcogen, halogen, or rare gas (the alkali and alkaline earth metals are excluded, because their organometallic complexes are ionic), and R is generally a monohapto hydrocarbyl group, including an alkyl, aralkyl, alkenyl, alkynyl, or aryl group, or a substituted derivative thereof; "stability" is clearly a relative term and refers to thermal robustness under vacuum or in an anhydrous, anaerobic, inert atmosphere. The adjective "homoleptic" is preferred to "binary", which is appropriate only for (MX$_n$)$_y$ in which X represents a single atom. [For such compounds the term "isoleptic" has been used in the same context (*Inorg. Syn.*, **13**, 73 (1970)). We prefer to reserve it to describe the relationship *between two or more compounds;* e.g., each of the following *pairs* is isoleptic: (i) SiMe$_4$ and TiMe$_4$ and (ii) Me$_3$SiCl and Me$_3$TiCl. Compounds i are homoleptic and ii are heteroleptic. We thank Drs. J. G. Stamper and R. A. Jackson for pointing out these distinctions.[1]] The species (MX$_n$X'$_m$)$_y$ is termed heteroleptic.[1]

[†] Reprints not available from authors.

Attention will focus on neutral complexes, but reference will also be made to anions and cations, radical anions, and metal-centered free radicals, R$_n$M·. The last-named are discussed because it is illogical to consider paramagnetic transition metal alkyls such as CrR'$_3$ and not a species such as R'$_3$Sn· [R' = (Me$_3$Si)$_2$CH]. We shall consider homoleptic metal σ-hydrocarbyls with reference to stoichiometry, structure, and bonding; and all hydrocarbyls from the standpoint of stability and thermal decomposition pathways (section III). We aim to provide a comprehensive survey including publications up to November 1974 (and in section V, up to November 1975), but for main group element homoleptic complexes there will be a considerable element of selection and primary references discussed in a review of 1967[2] will not all be referred to again. Other reviews[1-7] will also be used occasionally in place of primary data; we have recently provided an account of homoleptic metal alkyls in the context of our researches in this area;[1] more general surveys are also available.[8-10]

Progress in the chemistry of metal σ-hydrocarbyls may be considered in three phases. The first starts with Frankland's discovery[11] in 1849 of ZnEt$_2$ and continues until about 1960. In this period homoleptic metal σ-hydrocarbyls were described for most of the main group (but none of the transition) elements, albeit only in the higher oxidation states for elements such as Hg, Tl, Sn, or Pb; the present position for neutral and ionic complexes of these elements, summarized in Table I, was already largely then established.[2] Unsuccessful attempts to prepare simple transition metal derivatives led to the generalization that they are much less stable than their main group element analogues[3] and that transition metal–carbon bonds are weak, a view supported by calculations.[12] The existence of numerous radicals such as MeHg· or Me$_2$P· was inferred from kinetics, e.g., thermolysis or photolysis of HgMe$_2$ or PMe$_3$.[4,5]

The second phase corresponds roughly to the next decade and marks significant progress in the transition metal chemistry of the σ-hydrocarbyl ligand[6] and the characterization, particularly by ESR, of several metal-centered radicals especially of group 4 elements Si, Ge, Sn, Pb.[13] Homoleptic transition metal compounds were unusual and the known compounds were highly unstable; e.g., TiMe$_4$ decomposed at low temperature,[14] but numerous stable complexes having "stabilizing ligands", e.g.,[15] cis-[PtMe$_2$(PEt$_3$)$_2$], were prepared. Many of these "stabilizing ligands" were potential π acceptors, such as CO, PR$_3$, or η^5-C$_5$H$_5^-$. A general theory of transition metal σ-hydrocarbyl stability emphasized ground-state electronic effects.[6,15] It was proposed that the initial step in the decomposition of a metal σ-hydrocarbyl is the promotion of an electron from the highest filled orbital to a vacant

σ^*-antibonding orbital. Thus, stability was favored by increasing the energy difference between these orbitals, which in turn was encouraged by strong σ-donor ligands which stabilize bonding orbitals and destabilize the σ^*-orbital whereas π-acceptor ligands lower the energy of d orbitals of the metal by π-bond formation. This analysis provided satisfactory rationalization of other data: e.g., (i) that metal σ-hydrocarbyls were (then) predominantly found for complexes in which the metal was in a low oxidation state; (ii) that for an isostructural series of transition metal alkyls stability was believed to increase from left to right along a transition metal series and from top to bottom down the series, i.e., stability is maximized in a heavy late transition metal such as Pt; and (iii) that for hydrocarbyls, stability decreased in the sequence o-aryl > Ph > alkyl. (Many of the results which emerged from the third phase provide contradictory data to such propositions,[1] and the role of "stabilizing" ligands such as CO, PR$_3$, or η^5-C$_5$H$_5^-$ is seen as depending on their firm occupation of coordination sites.)

The third phase, much concerned with transition metal complexes, dates from the independent suggestion from two groups[16,17] that such metal–carbon bonds are not inherently weak and that complexes can be made kinetically stable by choice of suitable ligands. The β-elimination pathway is an important decomposition route (vide infra), and ligands such as Me$_3$SiCH$_2^-$, Me$_3$CCH$_2^-$, or PhCH$_2^-$, which have no β-hydrogen atoms, often lead to stable complexes.[1,8,9] Several other ligands have since been used to generate stable neutral or ionic homoleptic transition metal complexes [Tables II and III: although not comprehensive, these are intended to show *representative* complexes which are reasonably stable at ca. 0 °C (e.g., TiMe$_4$ is not included), and which have been characterized, omitting minor variations on the same theme; e.g., Me$_3$CCH$_2^-$ is listed, but not PhMe$_2$CCH$_2^-$ or Ph$_3$CCH$_2^-$. A complete list of "neopentyl-type" complexes, including the ligands Me$_3$SiCH$_2^-$, (Me$_3$Si)$_2$CH$^-$, Me$_3$CCH$_2^-$, Me$_3$SnCH$_2^-$, o-MeOC$_6$H$_4$SiMe$_2$CH$_2^-$, Me$_2$PhSiCH$_2^-$, MePh$_2$SiCH$_2^-$, Me$_2$PhCCH$_2^-$, and Ph$_3$CCH$_2^-$, has appeared elsewhere.[1]] Ligands which have been used as a source of stable homoleptic transition metal σ-hydrocarbyls may be divided into the five classes, 1–5 of Table IV (for details, see Tables II and III). The stability of the complexes is largely attributable to the high activation energy for decomposition, which is a consequence of the absence of β- or α-H on the ligand and/or steric crowding around the central metal which thus has no readily available vacant coordination site. Some of the ligands are bidentate (class 5, Table IV), and this offers chelating possibilities, in principle, of two differing types I or II; e.g.,

$$Me_2P\diagdown \text{CH}_2 \diagup \text{CH}_2 \quad (-)^{18} \quad or \quad o\text{-MeOC}_6H_4SiMe_2CH_2^- {}^{19}$$
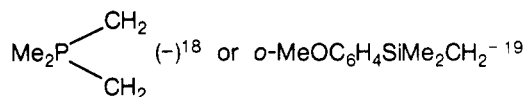
Ligands such as Me$_3$SiCH$_2^-$ must not be regarded intrinsically as "stabilizing". In practice, they often provide kinetic stability for a complex, in part by virtue of steric hindrance to access to the central metal atom of the complex. However, they can in principle decrease stability by steric acceleration; for example, the compound [(Ph$_3$P)$_3$RhCH$_2$SiMe$_3$] is less stable than [(Ph$_3$P)$_3$RhMe], presumably because elimination leading to III is encouraged by the bulkier ligand.[20] Similarly, many bulky phosphines cause enhanced tendency for such
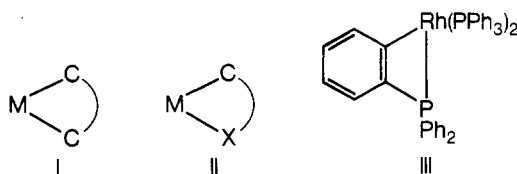

TABLE I. Representative Stable Homoleptic Main Group Element σ-Hydrocarbyls[a]

	Group 1[2]		Group 2[2,50]		Group 3[2,37,91]		Group 4[2,92]		Group 5[2,93]	
	Neutral	Ionic	Neutral	Ionic	Neutral	Ionic	Neutral	Ionic	Neutral	Ionic
	$(LiR)_n$ E.g., Bu^n, $n=6$ Bu^t $n=4$ (benzene soln)		$(BeR_2)_n$ Me, $n=1$ (vapor) $n=\infty$ (solid) Bu^t, $n=1$ Pr^i, Bu^n, Bu^i, $n=2$	$[BeEt_3]^-$ $[BePh_3]^-$	BR_3	$[BAr_3]^{\cdot-}$ $[BAr_3]^{2-}$ $[BR_4]^-$	$M[CH(SiMe_3)_2]_2$ M = Ge,[25] Sn[26] (dimeric as solid[25]), Pb[26] $(MR_2)_n$ M = Si, Ge, Sn $n=4,5,6$	$[MR_3]^-$ M = Si,[96] Ge, Sn, Pb	$(MR)_n$ M = P, $n=4,5,6$ M = As, $n=5$ (Me), $n=6$ (Ph) $(MR_2)_2$ M = P, As, Sb	$[MPh_4]^+$ M = P, As, Sb, Bi $[M(o\text{-}C_6H_4C_6H_4\text{-}o)_2]^+$ M = P, As $[SbMe_3]^{2+}$
			$(MgR_2)_n$ n-pentyl,[94] Bu,[95] $n=2$ Me, Et, $n=\infty$ ZnR_2	$[BeMe_4]^{2-}$ $[Be(C\equiv CPh)_4]^{2-}$ $[MgPh_3]^-$	$(AlR_3)_n$ E.g., Me, $n=2$ Pr^i, Me$_3$CCH$_2$, $n=1$ $(GaR_3)_n$ $n=1$; but for Vi, $n=2$	$[AlR_4]^-$ $[GaMe_3]^{2-}$	$M[CH(SiMe_3)_2]_3$ M = Ge,[23] Sn[28] $R(MR_2)_nR$		MR_3 M = P, As, Sb, Bi MR_5 M = P, As, Sb, Bi R = Ph	$[MR_2]^-$ M = P, As, Sb
			CdR_2	$[GaMe_3]^{2-}$	$(InR_3)_n$ $n=1$; but for Me, $n=1$ (solution) $n=4$ (solid) $(TlR_3)_n$ $n=1$; but for Me, $n=1$ (solution) $n=4$ (solid)	$[InR_4]^{-142}$ $[TlR_4]^-$	MR_4		MR_3 M = As, R = Me[9a] M = Sb, R = Me	$[BiPh_2]^-$ $[SbPh_6]^-$ $[M(o\text{-}C_6H_4\cdot C_6H_4\text{-}o)_3]^-$ M = P, As
			HgR_2 (R = H, Ph)	$[CdPh_3]^-$ $[Cd(C\equiv CR)_4]^{2-}$		$[Tl(C\equiv CR)_4]^-$				

[a] R = alkyl or aryl, unless specified below the compound concerned; Ar = aryl; Vi = vinyl.

TABLE II. Stable Neutral Homoleptic Transition Metal Alkyls[a]

Group 3	Group 4	Group 5	Group 6	Group 7	Group 8	Group 1
ScR_3 o-MeOC$_6$H$_4$SiMe$_2$CH$_2$, Ph,[97] PhC≡C[97] YR_3 (Me$_3$Si)$_2$CH,[76] Ph[97] *Lanthanides* YbR_3 (Me$_3$Si)$_2$CH76b EuR_2 R'C≡C[98] *Actinides* ThR_4 PhCH$_2$[99]	$(TiR_2)_n$ PhCH$_2$[100] Ph[101] $(TiR_3)_n$ (Me$_3$Si)$_2$CH (n = 1),[76] (NC)$_3$C,[102] C(Cl)=NMe[273] TiR_4 Me$_3$SiCH$_2$,[16] Me$_3$CCH$_2$,[90] norbornyl,[75] PhCH$_2$,[103] Ph,[104] 1-adamantyl,[105] Me$_3$SnCH$_2$,[252] C(Cl)=NMe[273] ZrR_4 Me$_3$SiCH$_2$,[16] Me$_3$CCH$_2$,[90] norbornyl,[75] PhCH$_2$,[103] Me$_3$SnCH$_2$,[252] CCl=NMe$_2$[273] HfR_4 Me$_3$SiCH$_2$,[16] Me$_3$CCH$_2$,[90] norbornyl,[75] PhCH$_2$,[106] C(Cl) = NMe[273]	$(VR_3)_n$ (Me$_3$Si)$_2$CH (n = 1),[76] (NC)$_3$C[102] VR_4 Me$_3$SiCH$_2$,[17] norbornyl,[75] PhCH$_2$[274] NbR_4 C$_6$F$_5$[107] TaR_5 Me[38]	CrR_2 o-MeOC$_6$H$_4$[108] Cr_2R_4 Me$_2$P(CH$_2$)$_2$[109] CrR_3 (Me$_3$Si)$_2$CH,[76] trimethyl- norbornyl,[75] Me$_2$P(CH$_2$)$_2$,[73] o-CH$_2$PPh$_2$C$_6$H$_4$,[73] o-R$_2$NCH$_2$C$_6$H$_4$[6] CrR_4 Me$_3$SiCH$_2$,[17] Me$_3$CCH$_2$,[79] But,[110] norbornyl[75] Mo_2R_4 Me$_2$P(CH$_2$)$_2$[109,275] Mo_2R_6 Me$_3$SiCH$_2$[17,61] Me$_3$CCH$_2$[111] W_2R_6 Me$_3$SiCH$_2$[17,61] WR_4 PhCH$_2$[112] WR_5 C$_6$F$_5$[107] WR_6 Me[39,276]	MnR_2 Me$_3$SiCH$_2$,[277] Me$_3$CCH$_2$[277] MnR_4 norbornyl[75] 2,2,3- ReR_6 Me[40,276]	FeR o-C$_6$H$_4$CH$_2$NMeCH$_2$- CH$_2$NMeC$_6$H$_4$-o[113] FeR_4 norbornyl[75] CoR_3 o-R'$_2$NCH$_2$- C$_6$H$_4$[114] CoR_4 norbornyl[75] NiR_2 o-Ph$_2$PC$_6$H$_4$CH$_2$,[115] Ph$_3$C,[116] 2,4,6-Me$_3$C$_6$H$_2$[278] Ni_2R_4 Me$_2$P(CH$_2$)$_2$ [66a,74b,d] (2 isomers) PdR_2 o-Ph$_2$PC$_6$H$_4$CH$_2$,[115] o-R'$_2$NCH$_2$C$_6$H$_4$[117] PtR_2 o-R'$_2$PC$_6$H$_4$- CH$_2$,[115,118] o-R'$_2$NCH$_2$C$_6$H$_4$,[117] o-allylC$_6$H$_4$[119] $(Pt_2R_6)_n$ Me[6]	$(CuR)_n$ Me$_3$SiCH$_2$ (n = 4),[31,45] RR'P(CH$_2$)$_2$ (n = 2; RR' = Me$_2$, Ph$_2$, or MePh),[74a,c] Me$_2$As(CH$_2$)$_2$ (n = 2),[281] o-, m-, p-MeC$_6$H$_4$,[120] C$_6$F$_5$(n = 4),[121] m-CF$_3$C$_6$H$_4$ (n = 8),[122] o-R'$_2$NCH$_2$C$_6$H$_4$ (n = 4),[123,279,280] MeC≡C,[124] PhC≡C,[124] ButC≡C (n = 8),[125] NCCH$_2$,[126] o-R'$_2$NCH$_2$C$_6$H$_4$Ċ=NR'',[127] Ph$_2$PCHPPh$_2$ (n = 3)[64] $(AgR)_n$ RR'P(CH$_2$)$_2$ (n = 2; RR' = Me$_2$, Ph$_2$, or Me, Ph),[74a,c] Me$_2$As(CH$_2$)$_2$ (n = 2),[281] Ph,[128] o-R'$_2$NCH$_2$C$_6$H$_4$,[129] PhCH=CH,[130] trans- F$_3$CCF=CCF$_3$,[131] C(OR')=NR''[132] $(AuR)_n$ Me$_2$P(CH$_2$)$_2$ (n = 2),[18] ButC≡C,[133] PhC≡C,[133] C(OR')=NR'' (n = 3),[134] 2-pyridyl (n = 3)[135]

[a] R', R'' = an alkyl group.

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TABLE III. Stable Ionic Homoleptic Transition Metal Alkyls[a]

Group 3	Group 4	Group 5	Group 6	Group 7	Group 8	Group 1
Lanthanides $[LaR_4]^-$ Ph[97] $[PrR_4]^-$ Ph[97] $[LuR_4]^-$ 2,6-Me₂C₆H₃[136] *Actinides* $[UR_6]^{2-}$ Me₃SiCH₂,[277] o-Me₂NCH₂C₆H₄[277]	$[TiR_2]^-$ o-C₆H₄OC₆H₄-o[317] $[TiR_5]^-$ Me[137] $[ZrR_6]^{2-}$ Me[41]	$[VR_3]^{3-}$ o-C₆H₄OC₆H₄-o[317] $[VR_6]^{4-}$ Ph[6] $[NbR_6]^{4-}$ Ph[318] $[NbR_7]^{3-}$ Ph[138] $[TaR_6]^-$ Ph[282]	$[Cr_2R_4]^{4-}$ -(CH₂)₄-[6,69] $[CrR_3]^{3-}$ -(CH₂)₄-[4 or 5] $[CrR_3]^{3-}$ o-C₆H₄OC₆H₄-o[317] $[CrR_3]^{2-}$ -(CH₂)₄-[5] $[Cr_2R_6]^{2-}$ Ph[6] $[CrR_4]^{2-}$ Ph[139], Me[6] $[CrR_4]^-$ Me₃SiCH₂,[17] Me₃CCH₂[79] Ph[320] $[Cr_2R_8]^{4-}$ Me[140] $[CrR_5]^{2-}$ Ph[141] $[CrR_6]^{3-}$ Me,[6,70] Ph[6] $[Mo_2R_8]^{4-}$ Me[72] $[MoR_6]^{3-}$ Ph[143] $[WR_5]^-$ C₆F₅[107] $[WR_6]^{2-}$ Ph[6] $[WR_8]^{2-}$ Me[276]	$[MnR_2]^{2-}$ o-C₆H₄OC₆H₄-o[317] $[MnR_2]^-$ o-C₆H₄OC₆H₄-o[317] $[MnR_3]^-$ Me[144] $[MnR_4]^{2-}$ HC≡C;[145] MeC≡C,[145] PhC≡C[145] Me[276]	$[FeR_2]^{2-}$ o-C₆H₄OC₆H₄-o[317] $[FeR_4]^{2-}$ Me[146] $[FeR_6]^{2-}$ HC≡C,[147] MeC≡C,[147] PhC≡C[147] $[CoR_2]^{2-}$ o-C₆H₄OC₆H₄-o[317] $[CoR_3]^{3-}$ o-C₆H₄OC₆H₄-o[317] $[CoR_4]^{2-}$ Me,[276] Me₃SiCH₂[276] $[CoR_6]^{4-}$ HC≡C,[148] MeC≡C[148] $[NiR_2]^{2-}$ o-C₆H₄OC₆H₄-o[317] $[NiR_4]^{2-}$ Ph,[283] Me[283] $[PtR_6]^{2-}$ Me[321]	$[CuR_2]^-$ o-R₂'NCH₂C₆H₄,[149] m-MeC₆H₄,[120] MeC≡C,[150] PhC≡C[150] $[CuR_3]^{2-}$ HC≡C,[150] MeC≡C,[150] PhC≡C[150] $[CuR_2]^+$ Me₃PCH,[74c] Me₃P(Me₃Si)CH,[74c] Ph₃PCHR'(R' = H, Me, or Pr^i)[284] $[AgR_2]^-$ o-R'₂NCH₂C₆H₄,[151] C₆F₅,[152] HC≡C,[153] MeC≡C,[153] PhC≡C[153] $[AgR_2]^+$ Ph₃PCHR'(R' = H, Me, or Pr^i)[284] $[AuR_2]^-$ HC≡C,[154] PhC≡C,[154] o-Me₂NCH₂C₆H₄,[285] $[AuR_4]^-$ Me[286] $[AuR_2]^+$ Me₃P(Me₃Si)CH,[18] Me₃PCH₂[18,287,288]

[a] R' = an alkyl group. The entries in this table are not intended to infer the presence of discrete $[MR_x]^{n-}$ ions. It is likely that many involve alkyl bridging between the transition metal and the metal "cation"; cf. Li₃CrMe₆·3dioxane.
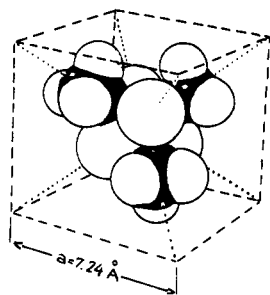
Figure 1. The crystal and molecular structure of (LiMe)₄:[158] Li ⋯ Li, 2.56 Å; Li–C, 2.27 Å; Me ⋯ Me, 3.68 Å.

Figure 2. The crystal and molecular structure of (AlMe₃)₂:[42] Al ⋯ Al, 2.606 Å; Al–C(1), 2.125 Å; Al–C(2), 1.956 Å; ∠C(2)–Al–C(3), 123.2°; ∠Al–C(1)–Al', 75.7°.

ortho metalation.[21] [Other factors which have influenced our choice of ligands such as Me₃SiCH₂⁻, Me₃CCH₂⁻, or (Me₃Si)₂CH⁻ include good hydrocarbon solubility, simple ¹H NMR or ESR spectra, and analogy with (Me₃Si)₂N⁻ [1] (a review on these and related ligands is available[306]) which is isoelectronic with (Me₃Si)₂CH⁻ and often yields stable metal amides of low coordination number (especially 3).[22-24] In this connection, stable amidometal-centered radicals [(Me₃Si)₂N]₃M· (s¹ complexes)[23] and the s² complexes [(Me₃Si)₂N]₂M'[24] have been prepared (M = Ge or Sn; M' = M or Pb).]

The same concepts must be valid for main group element derivatives: a contribution has been the isolation of the stable yellow germanium(II),[25] red tin(II),[26] and purple lead(II),[26] dialkyls MR'₂ [R' = (Me₃Si)₂CH] which are monomeric in solution (C₆H₆ or c-C₆H₁₂) although SnR'₂ is dimeric in the solid (section II); by contrast, attempts to prepare the less bulky MR₂ (R = Me₃CCH₂) yield M₂R₆.[27]

As kinetic stability is proposed as the underlying factor, it is appropriate to identify decomposition pathways (see section III). We hope to show that main group and transition element homoleptic σ-hydrocarbyls are qualitatively similar, with quantitative differences relating to the greater readiness of transition metals to (i) expand their coordination sphere and/or (ii) afford lower energy d-orbital participation in transition states.

This third phase has also been marked by the identification of relatively stable metal-centered radicals RₙM·, especially of Si, Ge, and Sn.[23,28] Notable among these is R'₃Sn·,[28] which shows no sign of decomposition after 750 h in benzene at 20 °C in the dark. This, like related group 4 radicals (Me₃Si)₃C· and (Me₃C)₃C·, which decay by first-order processes,[29] is kinetically stable; it is too sterically crowded to dimerize, and the low Sn–H bond strength provides no inducement for H-abstraction from solvent. R'₃Ge· is similarly stable at 20°.[23] Early ideas of radical stability concentrated on ground-state thermodynamic, rather than kinetic, effects. This picture is changing: for example, for Ph₃C· there is now less emphasis on electron delocalization than on difficulty of dimerization, first highlighted by the proof[30] that the dimer is IV and not hexaphenylethane.

IV
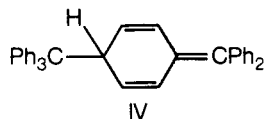
The continuing study of metal σ-hydrocarbyls is relevant to various fields of endeavour. Such complexes feature as synthetic reagents (e.g., Grignard reagents or LiR), raw materials (e.g., Me₂SiCl₂ in silicones, or PbEt₄ in the petroleum industry), catalytic intermediates (e.g., alkyls of Ti in Ziegler–Natta polymerization), or in one case (vitamin B₁₂ coenzyme) of an essential biological material. A knowledge of their chemistry and especially of their structure, stability, and the making and breaking of M–C bonds is vital. New bonding situations are being discovered, e.g., single alkyl bridges in (Cu-
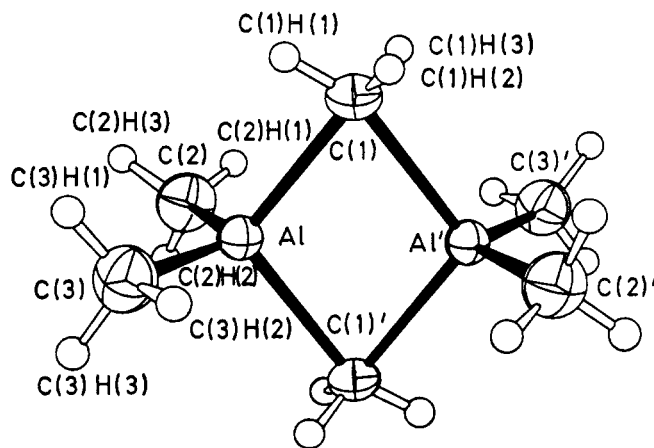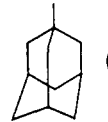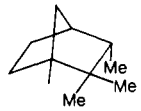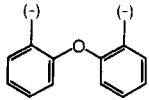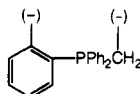
CH₂SiMe₃)₄,[31] and new areas of chemistry opened up, e.g., the polymerization of α-olefins by Al₂O₃- or SiO₂-supported zirconium(IV) alkyls[32] or the coordination chemistry of heavy atom group IV donors such as Šn[CH(SiMe₃)₂]₂.[26,33,307]

II. Structure, Bonding, and Some Ground-State Properties

From Tables I–III it is evident that homoleptic σ-hydrocarbylmetal complexes may be neutral or ionic. Cationic complexes are rare (except, possibly in mass spectrometry, and for Cuᴵ or Auᴵ, see Table III); for example, siliconium ions, the analogues of carbonium ions, are unknown (but see ref 308), although solvated species such as [R₃Si(bpy)]⁺[34] or [R₂B(py)₂]⁺[35] are accessible. For coordinatively unsaturated anions, electron delocalization may be important; e.g., Ar₃Si⁻ but not R₃Si⁻ ions are readily obtained;[36] this may also be relevant for the radical anions [Ar₃B]·⁻.[37] The instability of cationic species may be due to a facile irreversible decomposition pathway via a carbonium ion and/or to a bimolecular mechanism of decomposition which requires nucleophilic attack at the metal center. (On the other hand, hydrocarbyl metal groups exert a powerful stabilizing influence on neighboring carbenium ions, which has been discussed in terms of σ–π conjugation.[309]) Conversely, anionic complexes are often stable. The stoichiometry of stable homoleptic complexes varies from (MR)ₘ (Li, Cu) to MR₆; TaMe₅,[38] WMe₆,[39] ReMe₆,[40] ZrMe₆²⁻,[41] and CrMe₆³⁻[6] are noteworthy (class 3, Table IV) and illustrate the principle that even with small ligands the occupancy of a large number of coordination sites (coordination saturation) enhances stability.

The σ-hydrocarbyl group (e.g., R) is usually a terminal ligand (V), bonding to the metal via a two-electron–two-center bond. However, it may be bridging, as in the electron-deficient main group element compounds. For the lithium derivatives, an alkyl group bridges three metal atoms (VI), as in (LiMe)₄ (Figure 1),[2] and the bonding may be described in terms of two-electron–four-center orbitals. For Be, Mg, and Al derivatives, two σ-hydrocarbyl groups bridge a pair of metal atoms (VII) (cf. Figures 2[42] and 3[43]). The phenyl bridge in (AlPh₃)₂ (Figure 3) or (AlMe₂Ph)₂[43] has a structure similar to that of a Wheland intermediate in electrophilic aromatic substitution; for an Os₃ cluster, bridging of two Os atoms by a single Ph group has been established.[44] The recently discovered[45] (CuCH₂SiMe₃)₄ has a single alkyl bridge (VIII) for each pair of metal atoms (Figure 4),[31] and it is to be expected that other examples of bridged σ-hydrocarbyls will be found elsewhere in transition metal chemistry [2 R groups (e.g., R = Me or Et) have been found to bridge a pair of group 3B metal

TABLE IV. Classification of Ligands Found in Stable Homoleptic Transition Metal σ-Hydrocarbyls[a]

Characteristic features	Ligand type	Examples
1. A bulky alkyl ligand free from β-hydrogen atoms	(a) "Neopentyl-type" $(R_3M')_m CH_{3-m}^-$ (m = 1, 2, or 3)	(a) Generally favoring metal 4-coordination: $Me_3SiCH_2^-$, $Me_3CCH_2^-$, $Me_3SnCH_2^-$, $Me_2PhSiCH_2^-$, $MePh_2SiCH_2^-$, $Me_2PhCCH_2^-$, $Ph_3CCH_2^-$, $[Me_3PCH_2$, $Me_3PC(SiMe_3)H]$
		(b) Generally favoring metal 3-coordination: $(Me_3Si)_2CH^-$
	(b) Another substituted alkyl	$PhCH_2^-$ $NCCH_2^-$
2. A bulky ligand free from α-hydrogen atoms	(a) A bridge-head cycloalkyl	(a) Generally favoring metal 4-coordination: (1-norbornyl)$^-$ (1-adamantyl)$^-$ (b) Favoring metal 3-coordination: (2,2,3-trimethyl-1-norbornyl)$^-$
	(b) A t-alkyl	$Bu^t{}^-$ Me^-
3. A simple alkyl ligand (a) Metal in high co-ordinate environment (b) Miscellaneous[c]		$(NC)_3C^-$ $C_nF_{2n+1}^-{}^{[b]}$ $n\text{-}C_6H_{13}^-{}^{[c]}$
4. An aryl, alkenyl, or alkynyl[d] ligand		Ph^-, $C_6F_5^-$, $R'N{=}C(OR')^-$, $CF_3CF{=}C(CF_3)^-$, $PhCH{=}CH^-$, $HC{\equiv}C^-$, $PhC{\equiv}C^-$
5. A chelating σ-hydrocarbyl ligand		$o\text{-}MeOC_6H_4SiMe_2CH_2^-$ $RR'P(CH_2)_2^-$ (RR' = Me_2, Ph_2, or MePh) $o\text{-}Ph_2PC_6H_4CH_2^-$ $(CH_2)_{4 \text{ or } 5}{}^{2-}$ $o\text{-}R_2NCH_2C_6H_4^-$

[a] For details of complexes, see Tables II and III. [b] These are incompletely characterized, in the context of Cu^I.[155] [c] There is a claim for an incompletely characterized di-n-hexyldimercury(I).[156] [d] These are often explosive.

atoms in $\{(\eta\text{-}C_5H_5)_2MR\}_2$ (M = Y, Yb, Er, Ho, or Dy)[315] and in $(\eta\text{-}C_5H_5)_2MR_2AlR_2$ (M = Sc, Y, Yb, Er, Ho, Dy, Gd, or Ti)[310]. It is surprising that in this formally d^{10} Cu complex the four metal atoms are coplanar; bonding may involve linear (CCuC) coordination at Cu with metal–metal bonding relatively unimportant. In the solid state, $InMe_3$[46] and $TlMe_3$[47] are effectively tetrameric with a bridging situation as in VIII but unsymmetrical, M–C—M (cf.[47] Figure 5). A multicenter molecular orbital scheme may be used to describe the bonding in all these electron-deficient compounds (e.g., ref 48).
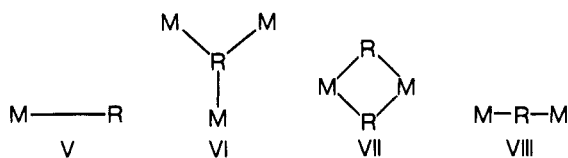
Steric effects often influence the state of molecular aggregation. This has been examined in some detail for alkyllithiums in C_6H_6 or C_6H_{12} by cryoscopy;[49] the compounds are hexameric unless branching occurs at α or β carbon when a tetramer (but no smaller aggregate) is favored. Dimethylberyllium is a polymer with Be atoms in a tetrahedral environment, but the hot vapor is largely monomeric;[50] the diethyl homologue is dimeric in C_6H_6 or C_6H_{12} by cryoscopy; $BeBu^t{}_2$ is a monomer at ambient temperature in the vapor, and many diarylberylliums are dimeric in C_6H_6.[51] Dimethylmagnesium has a polymeric structure similar to the Be analogue in the crystal,[52] and the more hindered $MgPr^i{}_2$ is a dimer in the vapor. Tris(trimethylsilylmethyl)alane is a mixture of monomer and dimer in benzene, by cryoscopy.[53] The possibility of chelation (II) by an ω-alkenyl ligand in the corresponding alane is strongly indicated by ^1H NMR and cryoscopic molecular weight measurements;[54] thus, whereas $\{Al\text{-}[(CH_2)_3CH_3]_3\}_2$ is a dimer, the unsaturated analogue $\{Al\text{-}[(CH_2)_2CH{=}CH_2]_3\}$ is monomeric and probably has structure IX. Compounds $Tl(Hal)R_2$ are polymers, unless R is a bulky group such as Me_3SiCH_2, when they exist as dimers in solution with di-μ-halide bridges.[55] Electron diffraction[56] and vibrational spectroscopy[57] have shown that the group 3 tri-
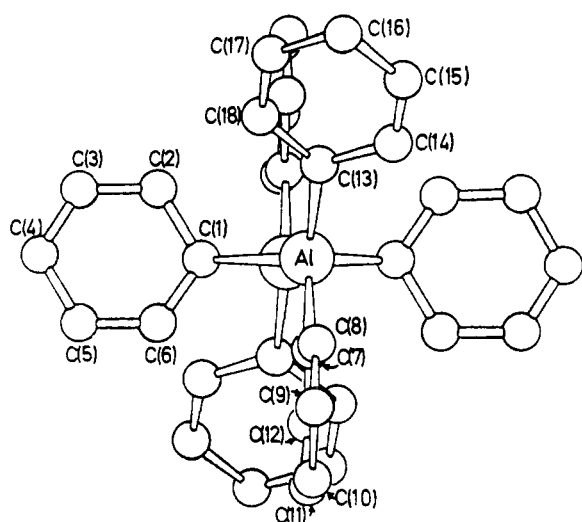
Figure 3. The crystal and molecular structure of $(AlPh_3)_2$:[43] Al ⋯ Al, 2.702 Å; Al–C(1), 2.184 Å; Al–C(7), 1.960 Å; ∠C(1)–Al–C(1′), 103.5°; ∠C(1)–Al–C(7), 108.4°; ∠C(1)–Al–C(13), 111.5°; Al–C(1)–Al′, 76.5°.

Figure 5. The crystal and molecular structure of $(TlMe_3)_4$:[47] Tl–C(1), 2.30 Å; Tl–C(1′), 3.16 Å; Tl–C(2), 2.22 Å; Tl ⋯ Tl, 5.46 Å; ∠Tl(1)–C(1)–Tl(2), 180°; ∠Tl(1)–C(3)–Tl(3), 170°; ∠C(1)–Tl–C(2), 131°; ∠C(2)–Tl–C(3), 110°; ∠C(1)–Tl–C(3), 118°.

Figure 4. The crystal and molecular structure of $(CuCH_2SiMe_3)_4$:[31] Cu–Cu, 2.417 Å; Cu–C (mean), 2.02 Å; ∠C–Cu–C, 164°; $Cu_4C_4Si_2$ coplanar; centrosymmetric.

IX
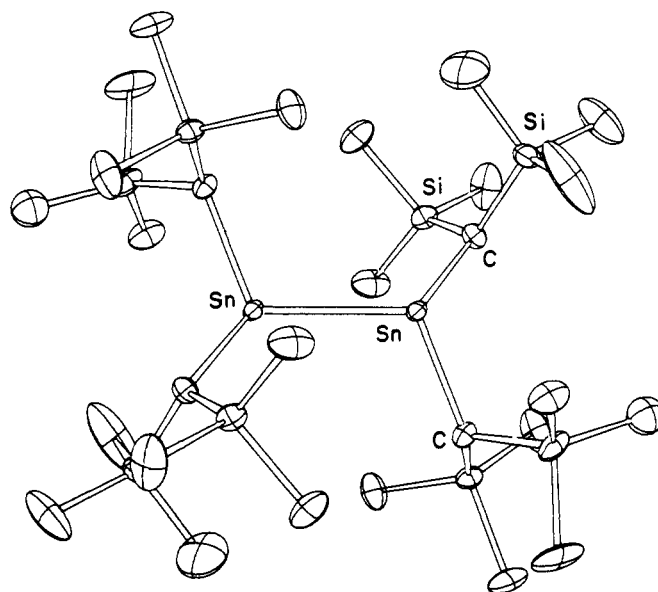
Figure 6. The crystal and molecular structure of $\{Sn[CH(SiMe_3)_2]_2\}_2$ (ref. 25): Sn–Sn, 2.76 Å; Sn–C, 2.17 Å; ∠Sn–Sn–C (mean), 115°; ∠C–Sn–C, 112°.

methyls, other than the dimeric Al_2Me_6 (a monomer of D_{3h} symmetry also exists[58]), are monomeric (D_{3h}) in the vapor phase. He(I) photoelectron spectroscopy shows that the $(AlMe_3)_2$ dimeric vapor dissociates into the monomer upon heating, with orbital ionization potentials (and hence structures) similar to those of the other monomers MMe_3;[59] cryoscopic measurements[60] and vibrational data[57] suggest that $TlMe_3$ is monomeric also in solution in benzene. The new dialkyls of Ge^{II},[25] Sn^{II},[26] and Pb^{II} [26] MR'_2 [R′ = $(Me_3Si)_2CH$] are also monomeric by cryoscopy in benzene or cyclohexane. However, in the crystalline state the tin compound is a dimer $R'_2Sn–SnR'_2$ (Figure 6[25]), with bond angles at Sn intermediate between sp^2 and sp^3 hybridization at the metal and a Sn–Sn bond length similar to that found in $(SnPh_3)_2$ and

slightly shorter than in tetrahedral metallic tin. The compound is diamagnetic in the solid, and the Sn–Sn bond may therefore have double bond character, possibly by d_π–d_π rather than p_π–p_π overlap to be consistent with the long bond. That the Sn–Sn bond is weak is shown also by chemical behavior; e.g., SnR'_2 reacts readily with $[Cr(CO)_6]$ to afford $[R'_2Sn–Cr(CO)_5]$,[26] in which x-ray analysis shows the tin to be trigonal with C_2SnCr coplanar and bond angles at Sn corresponding to sp^2 hybridization at tin.[33] However, this is a solution experiment, and SnR'_2 is a monomer in solution.

For the neutral complexes listed in Table II, the only others for which x-ray structural parameters are available are shown in Figures 7,[61] 8,[62] 9,[63] 10,[64] 11,[65] 12,[66] and 13;[66a] a closely related Nb compound (Figure 14)[67] is not strictly within our terms of reference (but is relevant to section III), having a bridging carbene ligand;[68] neither are the formally anionic chromium complexes which have alkyl bridges (VII) between Li and Cr (e.g., Figure 15[69] and ref 70); cf., $LiBMe_4$.[71] The
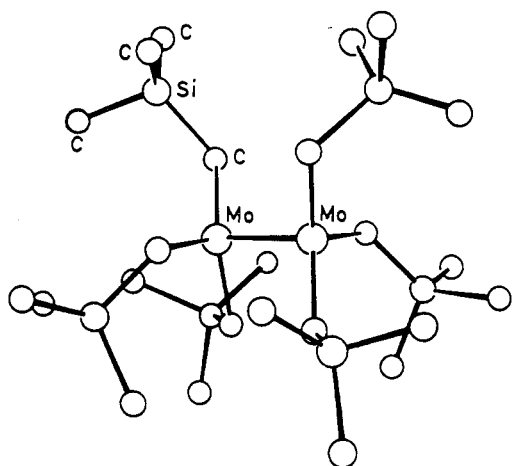
Figure 7. The crystal and molecular structure of [Mo(CH₂SiMe₃)₃]₂ (ref. 61): Mo-Mo, 2.167 Å; Mo-CH₂, 2.131 Å; ∠Mo-Mo-CH₂, 100.6°; ∠Mo-CH₂-Si, 121.1°.
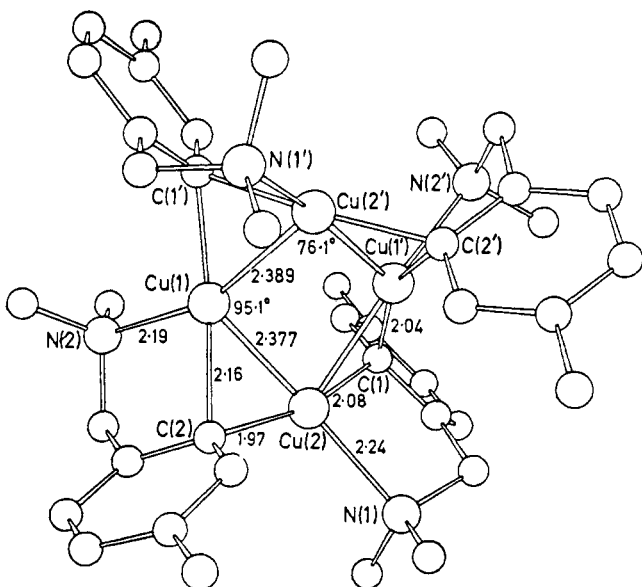
Figure 8. The crystal and molecular structure of (CuC₆H₄CH₂NMe₂-o)₄:[62] Cu-Cu, 2.38 Å; Cu-C (mean), 2.1 Å; Cu-N, 2.19 Å; ∠Cu(2)-Cu(1)-Cu(2'), 95.1°; ∠Cu(1)-Cu(2')-Cu(1'), 76.1°.
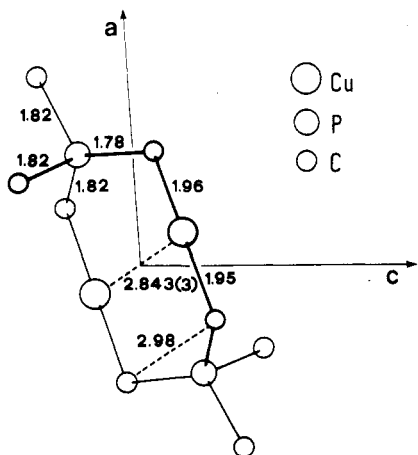
Figure 9. The crystal and molecular structure of [Cu(CH₂)₂PMe₂]₂:[63] Cu-C, 1.96 Å; P-CH₂, 1.78 Å; P-CH₃, 1.82 Å; Cu···Cu, 2.843 Å; ∠C-Cu-C, 175.8°; ∠CH₃-P-CH₃, 103.0°; ∠CH₂-P-CH₂, 112.1°; ∠Cu-C-P (mean), 108.4°.
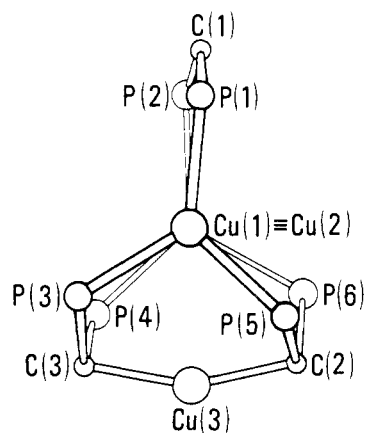
Figure 10. The crystal and molecular structure of (CuPh₂PCHPPh₂)₃.[64]
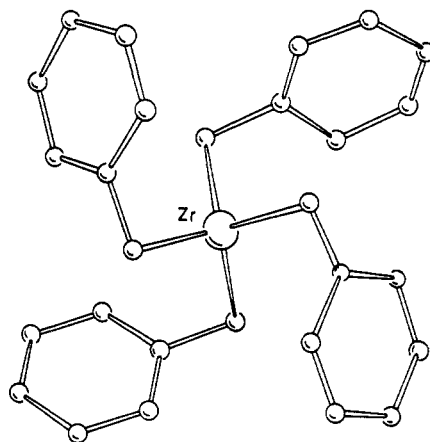
Figure 11. The crystal and molecular structure of Zr(CH₂Ph)₄:[65] Zr-C (mean), 2.27 Å; ∠C-Zr-C (mean), 95°.
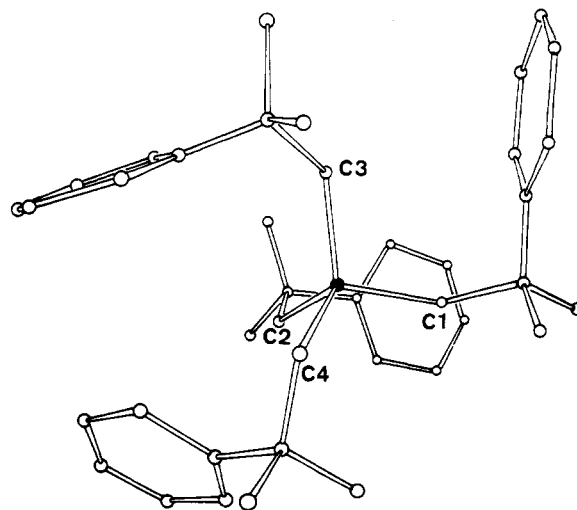
Figure 12. The crystal and molecular structure of Cr(CH₂CMe₂Ph)₄ (ref. 66): Cr-C, 2.05 Å; ∠Cr-C-C (mean), 123.5°.

very short Mo-Mo distances in Mo₂(CH₂SiMe₃)₆ (Figure 7)[61] and Li₄[Mo₂Me₈]·4C₄H₈O (Figure 16)[72] have been attributed to a quadruple bond, and the large SiCH₂Mo angle in the former is probably caused by steric repulsion. Zr(CH₂Ph)₄ and Hf(CH₂Ph)₄ have a distorted tetrahedral structure in the crystal (Figure 11), with MCPh angles of ca. 90°.[65] Ti(CH₂Ph)₄ is similar but ∠TiCPh averages 103°, whereas Sn(CH₂Ph)₄ is perfectly tetrahedral.[65] It is possible that in the d⁰ systems there is interaction between the metal and the π electrons.
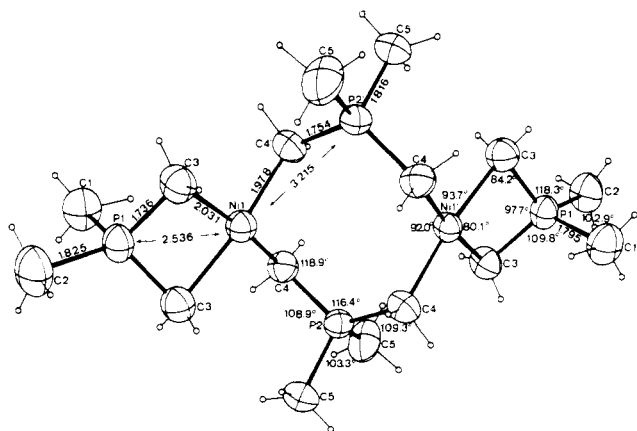
Figure 13. The crystal and molecular structure of $Ni_2[(CH_2)_2PMe_2]_4$ (ref. 66a): Ni(1)–C(3′), 2.031 Å; Ni(1)–C(4′), 1.978 Å; C(3′)–P(1), 1.736 Å; P(1)–C(2), 1.825 Å; C(4′)–P(2′), 1.754 Å; P(2′)–C(5‴), 1.816 Å; bonds at nickel essentially square planar.
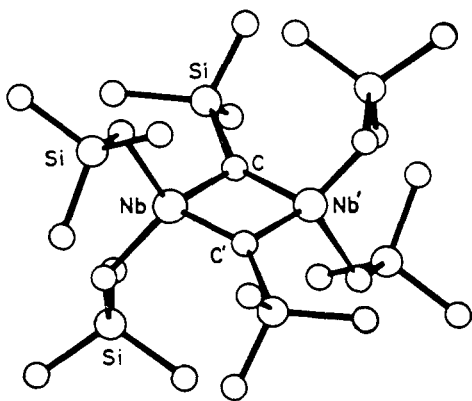
Figure 14. The crystal and molecular structure of (Me₃Si-CH₂)₂NbCSiMe₃Nb(CH₂SiMe₃)₂CSiMe₃:[67] Nb–C (mean), 1.974 Å; Nb–CH₂ (mean), 2.160 Å; ∠C–Nb–C, 85.6°; ∠Nb–C–Nb, 94.4°; Nb ⋯ Nb, 2.897 Å; ∠Nb–C–Si, 119.8°; ∠Nb′–C–Si, 142.4°.

The coinage metal complexes with a phosphonium ylide ligand have been formulated as X (M = Cu, Ag, or Au); the

X
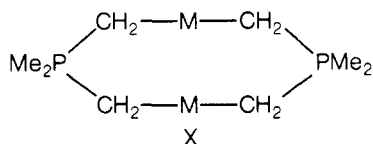
same bidentate ligand R⁻ has been found in CrR_3[73] and Ni_2-R_4[66a, 74b, 74d] $[M(CH_2PMe_3)_2]^+Cl^-$ and $\{Au[CH(SiMe_3)P-Me_3]_2\}^+Cl^-$ (M = Cu,[74a,c] Ag,[74a,c] or Au[18]) (see also Figure 9), and complexes related to X $\{M_2[(CH_2)_2PMePh]_2\}$ and $\{M_2[(CH_2)_2PPh_2]_2\}$ have been prepared.[74c] Ni_2R_4 has been obtained in two isomeric forms;[74d] one of these is believed to have four equivalent –CH₂–PMe₂–CH₂– bridges, and the other is shown in Figure 13.[66a] In Cr(CH₂CMe₂Ph)₄, the CrCC angles (Figure 12) are significantly greater than the tetrahedral angle, with consequential dense packing of alkyl and aryl groups.[66] The only lanthanide homoleptic hydrocarbyl for which structural data are available is shown in Figure 17.[136]

From Tables I–III it is noted that the coordination number 4 is common, and coordination numbers greater than 5 are rare. Because of the bulk of "neopentyl-type" and some other σ-hydrocarbyl ligands, it is not surprising that metal coordination number in these cases is affected primarily by the nature of the ligand rather than oxidation state or electronic configuration of the metal,[1] e.g., MNor₄ (M = Ti, V, Cr, Mn, Fe, Co, Zr, Hf; Nor = 1-norbornyl)[75] and M(CH₂SiMe₃)₄ (M = Ge, Sn, Pb, Ti, Zr, Hf, V, Cr, or Cr⁻),[1] but variations on
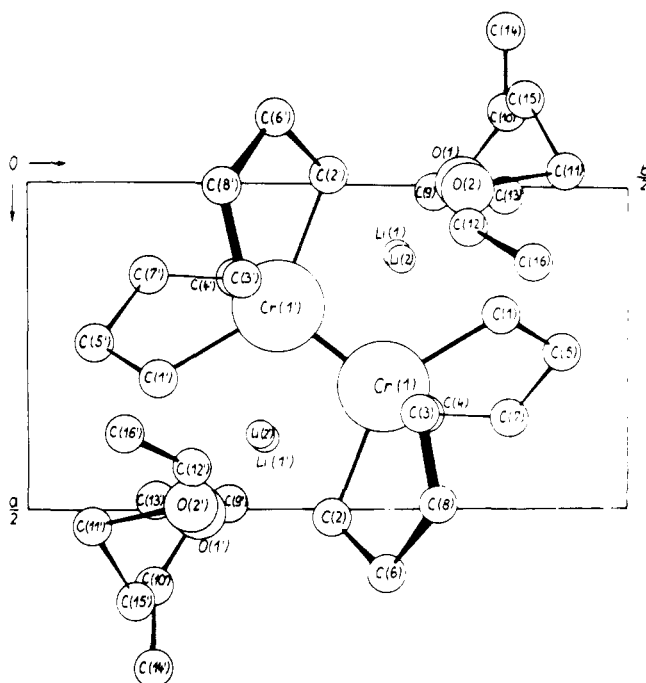
Figure 15. The crystal and molecular structure of $Li_4Cr_2(C_4H_8)_4\cdot$ 2THF:[69] Cr–Cr, 1.975 Å; Li–Cr, 2.54 Å; Li–CH₂ (mean), 2.47 Å; Li–O, 1.98 Å; ∠Cr(1′)–Cr(1)–C(1), 111.2°; Cr(1′)–Cr(1)–C(2), 109.1°; ∠Cr(1′)–Cr(1)–C(3), 107.3°; Cr(1′)–Cr(1)–C(4), 108.7°.
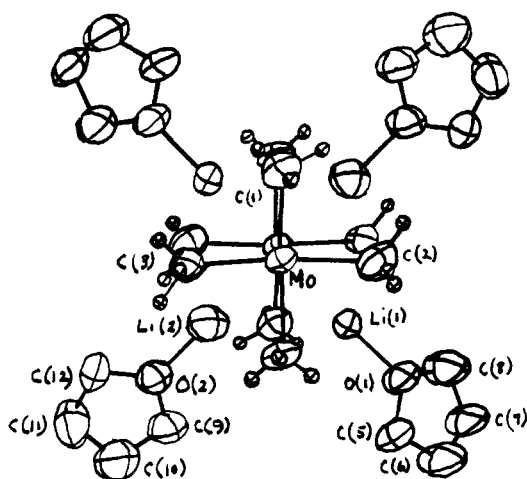
Figure 16. The crystal and molecular structure of $Li_4(Mo_2Me_8)\cdot$ 4THF:[72] Mo–Mo, 2.148 Å; Mo–C (mean), 2.29 Å; ∠Mo–Mo–C (mean), 105.8°. (The corresponding Cr compound has short Li ⋯ Cr contacts, and has been described as having a CrCr quadruple bond.[140])
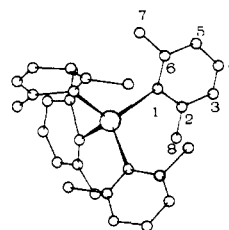
Figure 17. The crystal and molecular structure of $Lu(C_6H_3Me_2)_4^-$:[136] Lu–C (mean), 2.45 Å; ∠C–Lu–C (mean), 110°.

these themes lead to lower coordination number or oxidation state, e.g., $[M(CH_2SiMe_3)_3]_2$ (M = Mo or W),[1] CrNor′₃ (Nor′ = 2,2,3-trimethyl-1-norbornyl),[75] MR′₃ [M = Si,[23] Ge,[23] Sn,[28] Y,[76] Yb,[76b] Ti,[76] V,[76] or Cr;[76] R′ = (Me₃Si)₂CH],[1] or MR′₂ (M = Ge, Sn, or Pb).[1,25] It is interesting that the skeletal geome-

TABLE V. Some M–X Thermochemical Bond Energy
Terms: Trends for (a) X = C, N, O, or Cl; and (b) M =
Ge, Sn, Ti, Zr, or Hf

Bond	Ref compound	Bond energy term $(\bar{E}, \text{kcal mol}^{-1})^a$	Ref
Ge–C	GeMe$_4$	59	85
Ge–C	GeEt$_4$	57	85
Ge–N	Me$_3$Ge–NMe$_2$	55	157
Ge–O	Me$_3$Ge–OEt	79	157
Ge–Cl	Me$_3$Ge–Cl	81	85
Sn–C	SnMe$_4$	52	85
Sn–C	SnEt$_4$	46	85
Sn–N	Me$_3$Sn–NMe$_2$	41	157
Sn–O	Me$_3$Sn–OEt	66	157
Sn–Cl	Me$_3$Sn–Cl	75	85
Ti–C	Ti(CH$_2$CMe$_3$)$_4$	44	86
Ti–C	Ti(CH$_2$SiMe$_3$)$_4$	64	86
Ti–C	Ti(CH$_2$Ph)$_4$	63	86
Ti–N	Ti(NMe$_2$)$_4$	79	86
Ti–O	Ti(OPr^i)$_4$	112	86
Ti–Cl	TiCl$_4$	103	85
Zr–C	Zr(CH$_2$CMe$_3$)$_4$	54	86
Zr–C	Zr(CH$_2$SiMe$_3$)$_4$	75	86
Zr–C	Zr(CH$_2$Ph)$_4$	74	86
Zr–N	Zr(NMe$_2$)$_4$	91	86
Zr–O	Zr(OPr^i)$_4$	136	86
Zr–Cl	ZrCl$_4$	117	85
Hf–C	Hf(CH$_2$CMe$_3$)$_4$	58	86
Hf–N	Hf(NEt$_2$)$_4$	95	86
Hf–O	Hf(OPr^i)$_4$	137	86
Hf–Cl	HfCl$_4$	119	85

^{a} An alternative way of describing bond strengths is in terms of the mean bond dissociation energy $\bar{D}$(M–X) when, e.g., $\bar{D}$(Ti–C$_{\text{neopentyl}}$) = 50 and $\bar{D}$ (Ti–C$_{\text{benzyl}}$) = 54 kcal mol^{-1}; the difference between the neopentyl and benzyl systems is disguised in the $\bar{D}$ procedure by the considerably greater stability of PhCH$_2$ compared with Me$_3$CCH$_2$.

try for the MR$_5$ species approximates to D_{3h} for M = P or As, but C_{4v} for M = Sb;[2] for MR$_6$ or MR$_4$ it is octahedral or tetrahedral, respectively. Coordination number 3 is associated with a skeletal D_{3h} arrangement (e.g., in BMe$_3$ and probably CrR$'_3$) or C_{3v} (e.g., in PMe$_3$). Two-coordination leads to a linear (e.g., HgMe$_2$) or bent (C_{2v}) configuration. The latter may be present in SnR$'_2$ in solution or vapor; it appears from its diamagnetism in solution at ambient temperature to exist there as a singlet rather than triplet.[26] SbMe$_5$ has long been known,[2] but AsMe$_5$ has only recently been prepared.[96a] Attempts to obtain PMe$_5$ have provided the reactive ylide Me$_3$PCH$_2$, the transition metal chemistry of which has been exploited.[18,74] There has been some discussion of short formally nonbonding H···M contacts, as in M'–C–H···M, exemplified for cyclohexyllithium[76a] and LiBeMe$_4$.[71]

The very high values for metal (^{29}Si, ^{73}Ge, ^{117}Sn, and ^{119}Sn) hyperfine coupling constants (ESR) indicate that the group 4 metal-centered radicals R$'_3$M· [R$'$ = (Me$_3$Si)$_2$CH] are pyramidal.[23,28] For a metal-centered three-coordinate radical A$_3$M· there is a trend toward planarity which is a function of electronegativity difference between M and A and thus alkyl radicals are flat; in the isoelectronic series Me$_3$Al·$^-$, Me$_3$Si·, and Me$_3$P·$^+$ radicals become flatter across the periodic table,[77] and in the series (Me$_3$Si)$_{3-n}$Me$_n$Si· as the Me groups are replaced by the less electronegative Me$_3$Si there is a trend towards planarity.[78]

The isolation of paramagnetic homoleptic transition metal compounds (Table II) is noteworthy, because such species were until recently essentially unknown even with "stabilizing" ligands.[6] Magnetic and ESR data are available,[1] especially for the Cr^{IV} complexes.[17,79,80] Electronic configurations of stable neutral homoleptic σ-hydrocarbyls now range from a rare gas core (Y^{III}, Yb^{III}, Ti^{IV}, Zr^{IV}, Hf^{IV}, Ta^V, W^{VI}, and

light main group element ions), to s^1 (Si^{III}, Ge^{III}, Sn^{III}), s^2 (Ge^{II}, Sn^{II}, Pb^{II}), d^1 (Ti^{III}, V^{IV}, Re^{VI}), d^2 (Ti^{II}, V^{III}, Cr^{IV}, and W^{IV}), d^3 (Cr^{III}, Mo^{III}, W^{III}, Mn^{IV}), d^4 (Cr^{II}, Fe^{IV}), d^5 (Co^{IV}), d^6 (Fe^{II}, Co^{III}), d^8 (Ni^{II}, Pd^{II}, Pt^{II}), and d^{10} (Cu^I, Ag^I, Au^I, and heavy main group metal ions) (see Tables I–III). The stabilization of high and unusual metal oxidation states by σ-hydrocarbyl ligands is noted; FeNor$_4$ is the first example not only of a stable homoleptic Fe σ-hydrocarbyl, but also of a low-spin Fe^{IV} complex.[75] Of the three-coordinate complexes, the d^3 situation seems especially favorable. Symmetry arguments have been discussed for hypothetical MMe$_6$ complexes to explain that whereas $(t_{2g})^3$ and $(t_{2g})^6$ complexes are inert to substitution and dissociation, $(t_{2g})^1$ complexes are substitution labile, but dissociatively inert.[81] This treatment, in terms of configuration interaction among d^n states along the reaction coordinates for homolysis, has been critically analyzed.[82]

The He(I) photoelectron spectra of several compounds of formula MR$_4$ (M = Si, Ge, Sn, Ti, Zr, Hf, or Cr; R = Me$_3$SiCH$_2$ or Me$_3$CCH$_2$) have been measured;[83] the spectra have been assigned in terms of a localized bond model assuming a tetrahedral MC$_4$ framework. The highest occupied molecular orbital lies in the range 8–9 eV (except for the d electrons of Cr which are at 7.25 eV) and is assigned to σ(M–C). For transition metal group 4 alkyls this orbital is insensitive to the nature of the central metal, but for the main group 4 alkyls there is a monotonic decrease in first ionization potential due to decrease in electronegativity as the atomic number increases. Small inductive effects of the ligands account for the different ionization potentials of Me$_3$SiCH$_2$ compounds compared with Me$_3$CCH$_2$ analogues. Broadening is observed for the first band of Zr and Hf neopentyls which may be due to a distortion of the MC$_4$ framework to D_{2d}. In summary, occupied σ-M–C molecular orbitals for the d^0 and d^{10} complexes show only minor differences in energy levels. In keeping with the good donor properties of the compounds M[CH(SiMe$_3$)$_2$]$_2$ (M = Ge, Sn, or Pb),[33,307] the first ionization potentials are low (7.75, 7.42, or 7.25 eV, respectively), and comparable to the energy of the metal np orbitals, and were attributed to electrons in metal lone-pair orbitals.[311]

In the series trans-[Pt(R)Cl(PMe$_2$Ph)$_2$] x-ray and spectroscopic results show that the trans influence of R$^-$ has little sensitivity to substituent or hybridization effects (R = Me$_3$SiCH$_2$, CH$_2$=CH, or PhC≡C, compared with R = Me).[84]

From much data on standard heats of formation of homoleptic compounds of the main group elements,[85] it is clear that M–C bond strengths are not especially low and comparable often with, for example, M–N or M–O bond strengths (Table V). General trends are that M–C mean thermochemical bond energy terms, $\bar{E}$, within a group fall with increasing mass of M, and for a given M in the order Ph > Me > Et. Hence conjugative and hyperconjugative effects may have a small role, as has been most extensively discussed for B.[37] Similar comparative data are now becoming available for transition metal σ-hydrocarbyls and reveal basically the same pattern,[86] except that $\bar{E}$ increases with increasing mass of M within a group.[86] It is surprising that the M–C$_{(CH_2CMe_3)}$ bond is considerably weaker than the M–C$_{(CH_2SiMe_3)}$, and this must be due to a substantial steric effect; it will be interesting to know whether this effect is paralleled by M–C bond lengths. Calorimetric data are more meaningful for homoleptic than heteroleptic complexes because of the need for minimal subsidiary thermochemical parameters for the former case. Thus, it has been shown that alcoholysis with excess of i-C$_3$H$_7$OH of MCl$_4$, M(NMe$_2$)$_4$, or MR$_4$ (R = Me$_3$SiCH$_2$, Me$_3$CCH$_2$, or PhCH$_2$; M = Ti, Zr, or Hf) to yield M(OC$_3$H$_7$-i)$_4$ is rapid and quantitative, and hence suitable for use in calorimetry.[86] In this way standard heats of formation have been obtained and bond energy terms derived. Data in Table V therefore provide a comparison of M–X bond strengths for corresponding ele-

ments of an A with a B subgroup. Results are also available for a small number of heteroleptic metal alkyls; for example, D(Me–Mn) in MnMe(CO)$_5$ = 27.9 or 30.9 kcal mol^{-1} = $\frac{1}{2}D$(Mn–Mn) in Mn$_2$(CO)$_{10}$ + 18.5 kcal mol^{-1}, and D(Me–Re) in ReMe(CO)$_5$ = 53.2 ± 2.5 kcal mol^{-1} = $\frac{1}{2}D$(Re–Re) in Re$_2$(CO)$_{10}$ + 30.8 kcal mol^{-1};[87] and E(Pt–C) = ~27.6 kcal mol^{-1} in [Pt^{IV}(CH$_2$)$_3$Cl$_2$].[88]

Thermochemical data are also available for the radicals Me$_3$M·, mainly by using appearance potential (mass spectra) results.[89] There is no significant gain in delocalization energy for Me$_3$M· relative to Me$_4$M, in contrast to Me$_3$C· relative to Me$_4$C.[89a] Ph$_3$Si· is destabilized with respect to Me$_3$Si· by ca. 14.1 kcal mol^{-1} (contrast Ph$_3$C· vis-à-vis Me$_3$C·).[89b]

Infrared and Raman spectra for MR$_4$ (M = Sn, Ti, Zr, Hf, V, or Cr; R = Me$_3$SiCH$_2$)[1,90] show that the MC$_4$ asymmetric stretching mode falls in the range 470–530 cm^{-1}, which suggests that the MC$_4$ asymmetric stretching force constant, and hence MC bond strength, is largely independent of the electronic structure.

III. Decomposition Pathways of Metal σ-Hydrocarbyls

A. Introduction

Thermal decomposition of metal σ-hydrocarbyls often affords a complex mixture of products. Although it is not always possible to ascertain all the product-forming reactions, it is important, for an analysis of the comparative stability of these complexes, to establish rate-determining decomposition pathways and to assess their relative importance within various combinations of metal and ligand. Our first objective is to identify these pathways. We are concerned with pathways in thermal decomposition and not with stability towards oxidation, hydrolysis, etc. Because there are limited data on homoleptic complexes, we make reference to heteroleptic complexes also and reject inferences on stability that have in the past, often wrongly, been made from the inability to prepare a particular complex within a series. Available results are sometimes contradictory, the effect of impurities in determining the contributions of the various pathways possibly being overlooked (cf. ref 159 and 160). Much early information derives from random observations made in the context of describing the chemistry of a series of complexes, and it is only recently that efforts have been made to study the problem of decomposition systematically. This is largely due to the realization that transition metal–carbon bonds are not inherently weak (e.g., data of Table V) and that it is necessary to explain the relative *lability* of certain transition metal complexes rather than the relative *stability* of others.

Metal–carbon bond-breaking may formally be uni- or bimolecular. A unimolecular process involves either (a) migration of a substituent from the σ-hydrocarbyl group to the metal (α-, β-, γ-elimination) or (b) M–C homolysis. The pathways of higher molecularity result in disproportionation or formation of clusters (referred to below as bimolecular eliminations), or may require the participation of a reactive donor site (attack at a coordinated ligand).

Decomposition pathways for metal-centered radicals will not be discussed further; the principles are qualitatively those applicable to organic radicals, but disproportionation routes to metalloolefins are unfavorable, and atom-abstraction reactions (e.g., of H or Hal) are influenced by bond strengths (of M–H or M–Hal).

Some of the discussion on mechanism that follows is conjectural, often being based on qualitative rather than quantitative information. Clearly, more extensive kinetic studies are required. We identify the following eight pathways (sections III.B to III.I) as contributing to the decomposition of metal σ-hydrocarbyls.

B. β-Elimination

Many authors, when discussing the stability of transition metal alkyls, have laid great stress on the β-elimination pathway in decomposition and by so doing have, possibly erroneously, given the impression that this predominates. In fact, it is but one of a number of pathways, generally being preferred for complexes with simple alkyls containing a β-hydrogen (e.g., Et, Pr^n, Pr^i, or Bu^i). The impression is founded on the contrast between the main group metals for which such simple homoleptic alkyls are well known, whereas in the transition series stable complexes are very often only obtained by the use of a more restricted series of hydrocarbyl groups (Table IV).

β-Elimination may be represented by the general eq 1. For

$$LM—X—Y—Z \rightleftharpoons LMZ + X=Y \qquad (1)$$

simple alkyls (X = Y = a saturated C atom; Z = H) this requires migration of a β-hydrogen from carbon to the metal (M) probably in a concerted manner (XI), with formation of an
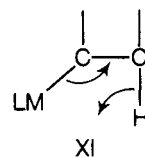
alkene. In the transition series the olefin may remain within the coordination sphere of the metal, as in the ethylnickel complex in eq 2.[161]

Ni(η^3-allyl)(Et)PPh$_3$ $\rightleftharpoons$

Ni(η^3-allyl)(H)(C$_2$H$_4$)PPh$_3$ $\rightleftharpoons$ Ni(η^3-allyl)(H)PPh$_3$ + C$_2$H$_4$
XIIa   XIIb

$$C_3H_6 + Ni + PPh_3 \qquad (2)$$
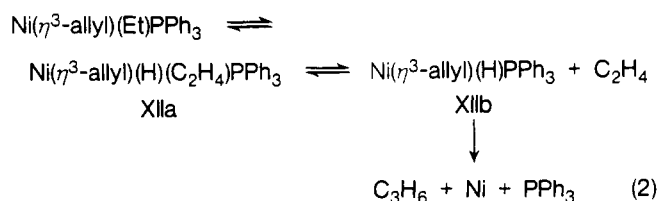
Other general examples of β-elimination are in eq 3,[162] 4,[163] and 5.[164]

$$[PtBu_2(PPh_3)_2] \underset{}{\overset{-PPh_3}{\rightleftharpoons}} [Pt(H)Bu(C_4H_8)PPh_3] \longrightarrow$$

$$n\text{-}C_4H_8 + n\text{-}C_4H_{10} + [Pt(PPh_3)_2] \qquad (3)$$

$$[CuCH_2CD_2C_2H_5(PBu_3)] \longrightarrow$$

$$CuD(PBu_3) + CH_2 = CDCH_2CH_3 \qquad (4)$$

$$LiEt \longrightarrow C_2H_4 + LiH \qquad (5)$$
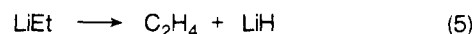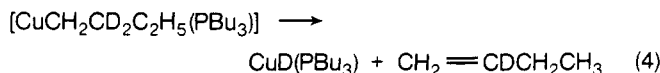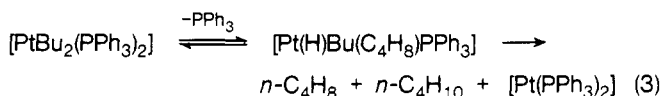
β-Elimination is reversible, and indeed both metal–carbon bond-making and bond-breaking by this route are important in syntheses; e.g., bond-making in olefin or acetylene hydrogenation, hydroformylation, hydroboration, hydrosilylation, or isomerization; and bond-breaking in isomerization or as a chain termination pathway in olefin polymerization or oligomerization.[6] This reversibility is elegantly demonstrated by the example of eq 2, a feature being the isolation of the intermediates XIIa and XIIb. Isomerization of the alkyl group of a metal alkyl by this route is illustrated in eq 6[91] and 7[165] and

$$=AlCHMeCH_2CH_3 \longrightarrow =AlH +$$

$$CH_2=CHCH_2CH_3 \rightleftharpoons =AlCH_2CH_2CH_2CH_3 \qquad (6)$$

$$AuMe_2Bu^i(PPh_3) \longrightarrow AuMe_2Bu^i(PPh_3). \qquad (7)$$
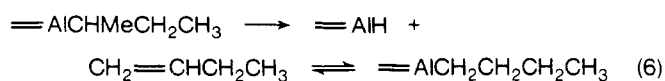
in the attempts to prepare BBu$^t_3$ which gave either BBu^{t}Bu$^i_2$, or, on heating, BBu$^i_3$.[37] Similar steric control to give on heating the least hindered borane is the basis for internal to terminal olefin conversion via hydroboration (for Zr, see also ref 322).

Deuterium labeling has been used effectively to assign the steric course of the reaction, i.e., that it is the β-hydrogen that is transferred. Examples are in the systems of eq 3 and 4 and with a number of alkylchromiums[166] prepared in situ and several alkylnickel species.[161,167] In some cases an interpretation of the results may be complicated by the ready reversibility of the reaction, where a series of elimination and readdition sequences (i.e., isomerization) effectively leads to scrambling of the label between the α and β positions. An illustration is in the decomposition of the ethylplatinum complex in eq 8.[168]

$$trans\text{-}[Pt(CD_2CH_3)Br(PEt_3)_2] \longrightarrow$$

$$trans\text{-}[Pt(H)Br(PEt_3)_2] + trans\text{-}[Pt(D)Br(PEt_3)_2] \quad (8)$$
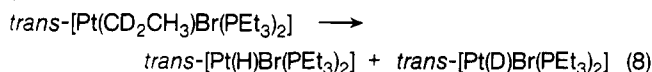
The kinetic isotope effect for β-hydrogen elimination from the alkyliridium(I) complexes $Ir(CH_2CHXC_6H_{13}\text{-}n)CO(PPh_3)_2$ (X = H or D) has been found to be $k_H/k_D = 2.28 \pm 0$ 20;[169] where β-H elimination is rate determining, and there are no complications of H/D scrambling. This has been interpreted in terms of a transition state in which C–Ir and H–Ir bond formation are both important. Comparison may be made with a value of $k_H/k_D = 3.7$ (at 25 °C) for the decomposition of $Al(CH_2CDMe_2)_3$,[170] interpreted in terms of the transition state XI.

In the general eq 1, Z is not restricted to H; e.g., in eq 9[91] Z = alkyl and in eq 10[171] Z = halogen, while β-elimination

$$=AlCH_2CMe_3 \rightleftharpoons =AlMe + CH_2=CMe_2 \quad (9)$$

$$\equiv SiCH_2CH_2Cl \longrightarrow \equiv SiCl + CH_2=CH_2 \quad (10)$$
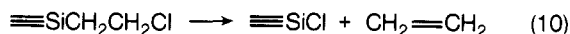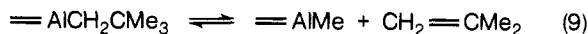
also provides a pathway for the decomposition of metal alkoxides to metal hydrides (X = O, Z = H),[172] and is postulated to play a role in the homogeneous oxidation of amines by Mo complexes.[173] For the transition metals there are as yet no substantiated examples of alkyl migration as in eq 9.

β-Elimination is favored when LMZ and X=Y are stable species. Thus, it is not particularly important for Ag,[159] for which there are no reported hydrides, or with ligands containing β-group 4 metals (e.g., as in CH_2SiMe_3).[90] In the latter case metalloolefin would be produced. This has been advanced as an argument to account for the relative stability of silylmethyl complexes, but may not in fact be relevant.[1] Thus neopentyl derivatives are of similar stability, and reluctance to undergo alkyl migration may therefore be an important factor. Pyrolysis studies show that Ti, Zr, or Hf alkyls MR_4 (R = Me_3SiCH_2, Me_3CCH_2, or Me_3SnCH_2) do not decompose by this route, bimolecular or reductive elimination being preferred (see below). A further argument would be to compare the stability of Bu^i and CH_2SiMe_2H complexes; detailed studies have not been undertaken, but the formation of $RhH(PPh_3)_4$ from $RhCl(PPh_3)_3$ and HMe_2SiCH_2MgCl[20] and of $Fe(\eta^5\text{-}C_5H_5)SiMe_3(CO)_2$ from $Fe(\eta^5\text{-}C_5H_5)(CO)_2^-$ and HMe_2SiCH_2Cl[174] indicates that β-elimination may well have a role even with alkyls having a β-silicon atom. In the same context, we draw attention to the isomerization of $Fe(\eta^5\text{-}C_5H_5)(SiR_2CH_2Cl)(CO)_2$ to $Fe(\eta^5\text{-}C_5H_5)(CH_2SiR_2Cl)(CO)_2$.[175]

Certain constraints within the transition state must be recognized which determine the relative rates of reaction and the products therefrom. It has been observed that migration of H is preferred to alkyl and it is generally true that formation of 1-alkene rather than 2-alkene predominates, although subsequent isomerization of 1- to 2-alkene may complicate the analysis. In the decomposition of (supposedly) monomeric complexes, some alkyls of Cr^{III}, conformational preferences favor elimination of trans- rather than cis-2-alkene,[166] whereas, within a metal cluster, the tetramer of sec-butyllithium, steric constraints favor the formation of the less stable cis-but-2-ene.[164] In the decomposition of a series of vinyliridium(I) complexes, $Ir(CR^1=CR^2R^3)CO(PPh_3)_2$ (R^1, R^2, R^3 = H

or Me) there are contributions to the elimination of both cis-β-vinyl-H (i) and β-allyl-H (ii), the former predominating, but none from elimination of trans-β-vinyl-H (iii), or γ-allyl-H (iv);

i   ii   iii   iv
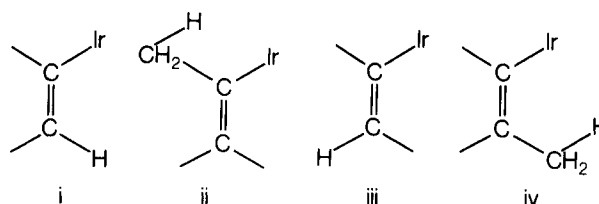
both pathways precluded for a concerted elimination mechanism. The preferred elimination of cis-β-vinyl- over β-allyl-H may reflect relative product stabilities (hydridoacetylene over hydridoallene).[176] A vacant coordination site is required at the metal center and is often more accessible for transition metal complexes, for which the process is accordingly of lower activation energy (note, for example, the considerable differences in stability of main group and transition metal ethyls, and the dominance of higher valence state main group metal alkyls; ease of catenation is another relevant factor and may account for the low kinetic stability of lower valent main group metal hydrocarbyls). Some idea of these differences in activation energy has been obtained from a study of ethylene oligomerization by soluble titanium-based Ziegler catalysts which gave an activation energy for chain transfer of 6.7 kcal mol^{-1} (note, however, that this low value and the very low A factor lead the authors to propose a six-center transition state involving a molecule of coordinated ethylene). This is considerably less than the typical values for aluminum alkyls of 20–30 kcal mol^{-1}.[177] In this context it is important to realize that if the metal is effectively coordinatively saturated, ligand dissociation may be required for reaction. For example, isomerization of $AuBu^tMe_2(PPh_3)$[165] and elimination from $PtBu_2(PPh_3)_2$[162] take place only after initial loss of a coordinated PPh_3. A suitable transition state geometry is required; i.e., the dihedral angle of the M–C–C–H moiety should approach zero. Thus, it is possible to inhibit thermal decomposition by the use of (a) bulky hydrocarbyl and/or supporting ligands; (b) chelating alkyls, when the dihedral angle is $\geqslant 90°$; or (c) chelating supporting ligands, when ligand loss and rearrangement within the coordination sphere are hindered. Examples are to be found (a) in $CrBu^t_4$ where the "cog-wheel" effect of the Bu^t groups effectively prevents close approach of Cr and β-H;[110] (b) the complexes

$$Pt\begin{array}{c}CH_2\\ \\CH_2\end{array}(CH_2)_n(PPh_3)_2 \quad (n = 2 \text{ or } 3)$$
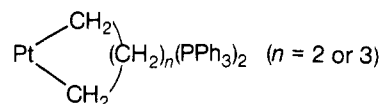
which are considerably more stable than $PtBu_2(PPh_3)_2$,[178] although surprisingly the α-methyl homologue 1 is of similar stability to 2 and (c) 3 which is more stable than $PtBu_2(PPh_3)_2$,[178] and the chelated 4, which is considerably more stable than the analogue $TiC_6H_4Me\text{-}o\text{-}(\eta^5\text{-}C_5H_5)_2$, whereas the unchelated $VC_6H_4CH_2NMe_2\text{-}o\text{-}(\eta^5\text{-}C_5H_5)_2$ is of similar stability to $VC_6H_4Me\text{-}o\text{-}(\eta^5\text{-}C_5H_5)_2$.[179] A further good example of (a) is the comparison between the thermally stable $Zr(\eta^5\text{-}C_5H_5)_2[CH(SiMe_3)_2]Bu^n$ and the labile $Zr(\eta^5\text{-}C_5H_5)_2Bu^n_2$.[76b]

There are conflicting reports on the influence of the electron demand of the metal center on the reaction in relation to oxidation state and/or electronic influence of other ligands, the reaction being related in some respects to a nucleophilic attack at the metal. Thus, from polymerization studies with titanium-based Ziegler catalysts it was concluded that the increased electron demand by the metal favored β-elimination,[180] whereas with the nickel complexes $Ni(\eta^3\text{-}allyl)(Et)L$

1

2

3

4

marked acceptor character in the ligand L inhibited reaction.[161] For the complexes

$$\overline{Pt(CH_2)_3X_2L_2} \quad (X = Cl\ or\ Br,\ L = e.g.,\ py)$$

β-elimination leading to propene is favored by ligands L of low trans influence, whereas the reverse holds for the competing process of reductive elimination leading to cyclopropane (section III.E).[88] Increase in oxidation state appears to favor reaction; cf. PtI(Me)Et$_2$(PMe$_2$Ph)$_2$ which decomposes at ca. 30°, whereas cis-PtEt$_2$(PMe$_2$Ph)$_2$ is stable at 100°.[181]

The above discussion has centered on alkyls. β-Elimination has also been proposed for the decomposition of metal aryls,[10] where evidence for formation of a coordinated benzyne was provided,[182] e.g., eq 11, and confirmed by deuterium-labeling experiments.[183]

$$TiPh_2(\eta^5\text{-}C_5H_5)_2 \longrightarrow PhH + \left[Ti \bigcirc (\eta^5\text{-}C_5H_5)_2 \right] \quad (11)$$

Finally, we mention here reactions of the type shown in eq 12,[184] which may be regarded as an intramolecular β-elimination.

(12)

C. γ- and Higher Elimination

In principle this is similar to β-elimination; examples are in eq 13[91] and 14.[92a]

(13)

$$Et_2MeSi(CH_2)_3Cl \longrightarrow Et_2MeSiCl + \overline{CH_2CH_2CH_2} \quad (14)$$

D. α-Elimination

This process is represented by eq 15 and involves migration of a substituent from the α carbon to the metal with formation of a carbenic fragment which may remain coordinated to the metal. It is well established for main group metals

$$LMCRR'R'' \longrightarrow LMR + CR'R'' \quad (15)$$

where it is of synthetic utility; compounds of e.g., Li, Sn, Zn, or Hg with R = alkoxy or halogen, can act as carbene transfer reagents, although in most cases free carbenes are not involved.[185] An example is shown in eq 16.[186]

$$Ph_3SiCPh(OMe)_2 \xrightarrow{heat} Ph_3SiOMe + [PhCOMe] \quad (16)$$

α-Elimination is generally less well established than β-elimination throughout the periodic table, but may be favored in certain competitive situations, e.g., eq 17.[187] In these cases, the relative contributions from α- and β-elimination are sensitive to changes in substituents; for example, from recent studies in the series RCH(OSiMe$_3$)CCl$_2$Li it appears that the contribution from β-elimination is clearly related to the ease of access to suitable conformers for concerted LiOSiMe$_3$ elimination. Where these are relatively inaccessible, α-elimination predominates.[188]

$$Cl_3SiCF_2CFCl_2 \xrightarrow{heat}$$

$$Cl_3SiF + \underset{\beta\text{-elimination}}{CF_2\!=\!\!CCl_2\ (7\%)} + \underset{\alpha\text{-elimination}}{CFCl\!=\!\!CFCl\ (80\%)} \quad (17)$$

Such decompositions are less well documented for transition metal σ-hydrocarbyls, being best substantiated for methyls. Examples come from decomposition of methylchromium(III) species prepared in situ, where deuterium labeling has helped establish the pathway;[166,189,190] the decomposition of FeMe$_2$(Ph$_2$PCH$_2$CH$_2$PPh$_2$);[191] and in the fragmentation of a nickel alkyl, Ni(Br)CH$_2$COOEt(PPh$_3$)$_2$, as a minor pathway.[192]

More recently, evidence comes from the reactions of W(η^5-C$_5$H$_5$)$_2$Me(C$_2$H$_4$)$^+$ or W(η^5-C$_5$H$_5$)$_2$CD$_3$(C$_2$H$_4$)$^+$ with PMe$_2$Ph to give respectively inter alia W(η^5-C$_5$H$_5$)$_2$H(CH$_2$PMe$_2$Ph)$^+$ and W(η^5-C$_5$H$_5$)$_2$D(CD$_2$PMe$_2$Ph)$^+$.[193] Results were rationalized by proposing an equilibrium between a 16-electron methyl complex and an 18-electron hydridomethylene species, formed via α-elimination after loss of coordinated C$_2$H$_4$, which were trapped by the added PMe$_2$Ph (Scheme I). This example illustrates an important

SCHEME I

point. In this article we are concerned with thermal decomposition and not with reactions of metal hydrocarbyls with added reagents and have generally excluded examples of the latter. We include this example since the authors propose reasonably that the phosphine acts to trap the methyl and hydridomethylene species and does not act to initiate their formation. On the other hand, we have excluded from consideration under β-elimination (section III.B) reactions of, e.g., B(CH$_2$SiMe$_2$OSiMe$_3$)$_3$ which under suitable conditions yields the elusive Me$_2$Si=CH$_2$ (trapped as Me$_3$SiOEt via reaction with EtOH); suitable conditions require the presence of a nucleophile, EtO$^-$, proceeding via

the complex being stable thermally to ca. 100°.[194]

α-Elimination has been proposed in decompositions of a number of higher alkyls of Cr^{III} prepared in situ,[166] but here evidence is less compelling since in the product olefin, eq 18, deuterium transfer may also arise via a β-elimination–readdition sequence as outlined earlier (section III.B) (cf. ref 162). The formation of Ta(CH$_2$CMe$_3$)$_3$(CHCMe$_3$) from TaCl$_5$–

$$CrCH_2CD_2\text{---}R(L) \longrightarrow$$

$$CrH(L) + [:CHCD_2\text{---}R] \longrightarrow DHC = CD\text{---}R \quad (18)$$

LiCH$_2$CMe$_3$ has been interpreted as an α-elimination from Ta(CH$_2$CMe$_3$)$_5$ (see section III.H).[195] Differential thermal analysis results on AsMe$_5$ thermolysis at 100–122 °C have been interpreted as involving two decomposition pathways (Table VII), one of which involves formation of AsMe$_3$(CH$_2$) + CH$_4$.[96a]

It may also have a role in (i) reactions of phosphorus ylides with transition metal species, e.g., eq 19;[196] (ii) in the three-

$$Ni(COD)_2 + Me_3PCH_2 \longrightarrow Ni(PMe_3)_4 + (CH_2)_n + (COD) \quad (19)$$

fragment oxidative addition reaction, e.g., eq 20;[197a] and (iii) in the decompositions of the α-halohydrocarbyl complexes
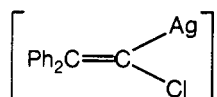
$$[RhCl(CO)_2]_2 + (Me_2NCHCl)Cl \longrightarrow \{Rh[CH(Cl)NMe_2]Cl_2(CO)_2\}$$

$$\downarrow \quad (20)$$

$$RhCl_3(CO)_2CHNMe_2$$
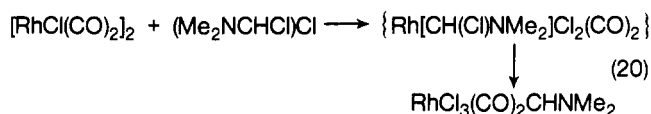
Fe(η^5-C$_5$H$_5$)CH$_2$Cl(CO)$_2$,[198] IrCH$_2$Cl(CO)(PPh$_3$)$_2$[199] (to give the corresponding M–Cl compound, and a transfer of CH$_2$ to another substrate or production of a mixture of hydrocarbons), and a halovinylsilver complex[200]

$$\left[Ph_2C = C \begin{array}{c} Ag \\ \\ Cl \end{array} \right]$$

(to give Ph$_2$C=C=C=CPh$_2$ in ca. 40% yield); and (iv) in reactions of 1-chloro-2,2-dicyanovinyl complexes, e.g., W(η^5-C$_5$H$_5$)C(Cl)=C(CN)$_2$(CO)$_2$.[201]

Finally, it should be pointed out that decomposition of metal acyls, as in eq 21, is formally an α-elimination. It has been suggested that the stability of Ni(COPh)Cl-[P(O-bornan-2-yl)$_3$]$_2$ is due to steric inhibition of the process of eq 21.[202]

$$LM\overset{\overset{O}{\|}}{C}\text{---}R \longrightarrow LM \begin{array}{c} CO \\ \\ R \end{array} \quad (21)$$
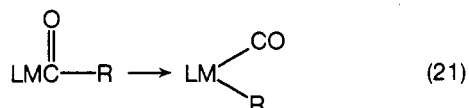
E. Reductive Elimination

This pathway, the reverse of oxidative addition, provides a route for the cleavage of M–C bonds and is especially important for the late transition metals. It is naturally confined to those metals having stable oxidation states differing by two. The process is shown schematically in eq 22; both the coordination number and the oxidation state of the metal are reduced by two.

$$LM \begin{array}{c} X \\ \\ Y \end{array} \longrightarrow LM + X\text{---}Y \quad (22)$$
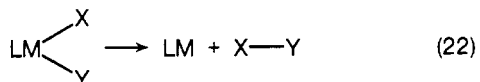
Eliminations, generally cis, of C–C or C–H combinations provide the main examples, but fragmentations of other combinations are possible. It plays a role in several organic syntheses where transition metal species are involved in the formation of C–C bonds, e.g., using complexes of Rh[203] or Ni[204] (see Scheme II). [The opposite reaction, the activation of saturated hydrocarbons, is of considerable importance. Examples, apart from enzyme-controlled systems, are mainly confined to the labile [W(C$_5$H$_5$)$_2$][205] or H/D exchange reactions with Nb(η^5-C$_5$H$_5$)$_2$H.[206] In this context the preparation of Ni(CPh$_3$)$_2$ from the triphenylmethyl dimer is noteworthy.[116]] Some examples of reductive elimination are given in eq 23,[2] 24,[101,207,208] 25,[209] and 26.[210] Equation 22 reveals nothing of the details of the pathway. Two alternative mechanisms for reductive elimination have been put forward: (i) concerted

SCHEME II

$$L_2 = \text{e.g., } 2Et_3P, \alpha,\alpha'\text{-bpy}$$
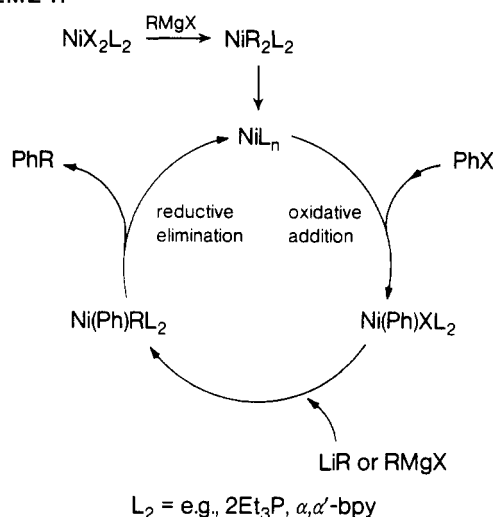
intramolecular cis elimination, or (ii) initial M–C homolysis. Illustrations are to be found respectively in (i) the process of eq 26, and with D-labeled analogues,[210] and (ii) the detection

$$SbPh_5 \longrightarrow SbPh_3 + Ph_2 \quad (23)$$

$$MPh_4 \longrightarrow [MPh_2(OEt_2)_n]_m + Ph_2 \quad (24)$$

$$(M = Ti, Zr, or V)$$

$$AuMe_3(PPh_3) \longrightarrow AuMe(PPh_3) + C_2H_6 \quad (25)$$

$$PtMe_3I(PPhMe_2)_2 \longrightarrow PtMeI(PPhMe_2)_2 + C_2H_6 \quad (26)$$
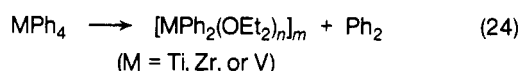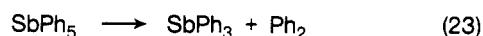
of the radical RCH(COOEt)CH(COOEt)Ṅ(O)Bu^t in the reaction of PtR$_2$L$_2$ (L = α,α'-bpy or 1,10-phen) with diethyl fumarate in the presence of Bu^{t}NO.[211] In the related nickel system the intermediate olefin complex may be isolated in a number of cases, as in eq 27,[212] and it is reasonable to assume that homolysis takes place subsequently.

$$NiR_2L_2 + \text{olefin} \longrightarrow NiR_2(\text{olefin})L_2 \longrightarrow Ni(\text{olefin})L_2 + R_2$$

$$(L_2 = \alpha,\alpha'\text{-bpy}) \quad (27)$$
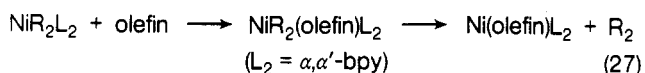
Where the stereochemistry at the α carbon is maintained throughout the elimination, the homolytic pathway may be ruled out. For example, the process of eq 28 proceeds with retention of stereochemistry at the double bond.[213] Here, as

$$(28)$$
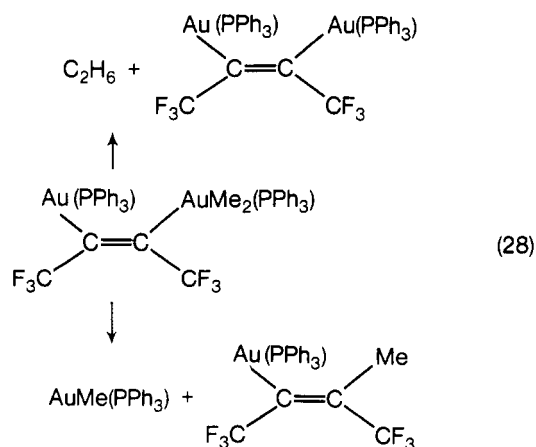
elsewhere, where competing pathways are available, the relative importance of each is influenced by changing the ligands at the metal.

In contrast to α- and β-elimination, a vacant coordination position is not a prerequisite for reaction, although there is evidence that in some six-coordinate Pt^{IV} [181] and square-pla-

nar Au^{III} [165] complexes neutral ligand predissociation takes place prior to reductive elimination and is rate determining. Thus, in cis- or trans-$AuMe_2R(PPh_3)$ a common trigonal intermediate formed via loss of PPh_3 is proposed in the processes of reductive elimination and hydrocarbyl group (R) isomerization. Loss of neutral ligand may in fact be a more general feature of the decomposition pathways of complexes of this type than has been supposed; cf. the decomposition of $PtBu_2(PPh_3)_2$ where β-elimination takes place only after loss of one PPh_3.[162] This proposition offers a contributory explanation of the increased stability of complexes containing chelating neutral ligands.

Reductive elimination is facilitated by increasing occupation of the coordination sphere, increasing orbital occupation (the two preceding points may be related), and the formation of cationic species. Thus bulky hydrocarbyl groups or supporting ligands may act either (a) directly, by accelerating loss of cis hydrocarbyls, or (b) indirectly, by facilitating loss of a neutral ligand and/or by promoting metalation of a coordinated ligand to give a hydrido hydrocarbyl from which reductive elimination is rapid. Examples are in (a) the decompositions of $AuMe_3(PR_3)$[214] and $AuMe_2(PR_3)_2^+$ [215] where increasing the size of R leads to more ready elimination of C_2H_6 and (b) the decompositions of $RhR(PPh_3)_3$ (R = Me, Me_3CCH_2, or Me_3SiCH_2) where increasing the size of R facilitates metalation with subsequent alkane (RH) loss to give $RhPPh_2C_6H_4$-o-$(PPh_3)_2$[20] (III) (see section I).

Reductive elimination involves a lowering of the orbital occupation at the metal by two units; thus if the occupation is higher than "normal", elimination will be favored (cf. ref 10b). This "normal" value varies across the transition series; for the late transition metals, it is 18 for the Fe, Ru, Os triad, whereas it decreases to 14 on reaching Cu, Ag, Au. This is illustrated by the decomposition of $NiEt_2bpy$ (eq 27); the activation energy for decomposition is 65.5 kcal mol^{-1} which reduces to ca. 15.5 kcal mol^{-1} upon complexation of an olefin.[212] A good example of these effects is to be found in the use of the so-called "accelerator" ligands (CO or PR_3) which favor reductive elimination over β-elimination in oligomerizations involving organonickel species.[216]

Cationic species are not particularly well known and have been extensively studied only for Pt^{IV}, where they appear less stable to reductive elimination than their neutral counterparts, and generally are more labile in other ways, e.g., to isomerization.[217]

Other ligands attached to the metal can exert an electronic influence on reductive elimination which will be particularly important where competing eliminations are possible (cf. eq 28). For $Pt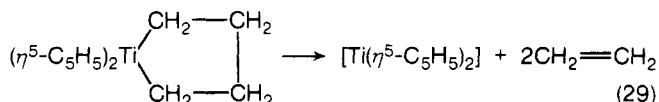Me_3I(PPhMe_2)_2$ and D-labeled analogues (cf. eq 26) methyl groups trans to PR_3 are eliminated more readily than those trans to I^-,[210] while in the series fac-$PtMe_3L_3^+$ elimination is especially favored when the two groups to be eliminated are trans to ligands of high trans-influence and where they are chemically nonequivalent.[217] For the complexes $Pt(CH_2)_3X_2L_2$, ligands L of high trans influence favor reductive elimination to afford cyclopropane (section III.B).[88]

An elimination of a different kind that we prefer to include in this category is shown in eq 29.[218] Here, orbital occupa-
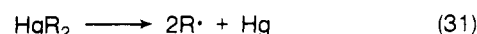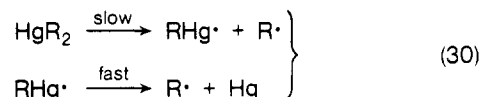
$$(\eta^5\text{-}C_5H_5)_2Ti\underset{CH_2\text{---}CH_2}{\overset{CH_2\text{---}CH_2}{\diagup\diagdown}} \longrightarrow [Ti(\eta^5\text{-}C_5H_5)_2] + 2CH_2{=}CH_2 \quad (29)$$

tion and the number of coordinated ligands are both reduced by two; the process does not involve β-elimination {cf. decomposition of $Pt(CH_2)_4(PPh_3)_2$ to $[Pt(PPh_3)_2]$ and butene}[178] or other recognized pathways. The reaction may be relevant to metathesis of olefins; earlier results with a similar system, the in situ reaction between WCl_6 and $Li(CH_2)_4Li$ and D-sub-

stituted compounds, had shown that (i) elimination proceeds as shown in eq 29 from the proposed metalo cyclic intermediate $[W(CH_2)_4Cl_4]$, and also (ii) there is some concomitant isomerization of the carbon skeleton.[219]

F. Homolysis

Among the clearest examples of homoleptic σ-hydrocarbyls which undergo thermal decomposition by a pathway requiring homolysis of the M-C bond are Hg^{II} complexes.[7] Two classes of decomposition are recognized: stepwise (class I, eq 30) or concerted (class II, eq 31).

$$\left. \begin{array}{l} HgR_2 \xrightarrow{\text{slow}} RHg\cdot + R\cdot \\ \\ RHg\cdot \xrightarrow{\text{fast}} R\cdot + Hg \end{array} \right\} \quad (30)$$

$$HgR_2 \longrightarrow 2R\cdot + Hg \quad (31)$$

Decomposition often gives a complex mixture of products, the composition of which is dependent on reaction conditions. In the absence of solvent, secondary reactions of the radicals with the metal alkyl probably occur; e.g., $HgMe_2$ with Me· gives $MeHgCH_2$·, which can enter into further reactions. For mechanistic purposes, studies may be simplified by use of a gas-phase flow system using an excess of a radical scavenger (e.g., toluene or cyclopentane) and a low partial pressure of the alkyl. Homolysis also occurs in the decomposition of the homoleptic alkyls of Zn, Cd, Si, Ge, Sn, and Pb, and methyls of Ga, In, Tl, As, Sb, and Bi.[7] Although for the higher alkyls of B and Al β-elimination is implicated, for methyls both radical (unimolecular)[7] and nonradical (bimolecular)[91,220] pathways have been described. It is to be expected that the former will predominate in the gas phase at low partial pressure, while the latter will predominate in the pure condensed phase and especially under pressure.

In the transition series, homolysis is uncommon; i.e., it is usually a route of higher activation energy than alternative processes. Homolysis has been proposed in much speculative discussion of decomposition pathways, but where more detailed studies have been made it has often been shown to be of relatively little importance.

Evidence implicating this pathway as a major contributor in the decomposition of transition metal σ-hydrocarbyls comes from studies of $MnCH_2Ph(CO)_5$,[221] $Pt(\eta^5\text{-}C_5H_5)Me_3$,[222] $Ni(\eta^5\text{-}C_5H_5)(Me)PR_3$,[223] $Pt(I)Me_3(\alpha,\alpha'\text{-}bpy)$,[210] $Pt(\eta^3\text{-}allyl)Me_2\text{-}Br(PMe_2Ph)_2$,[181] $CuCH_2CMe_2Ph(PBu_3)$,[224] $(CuCH_2SiMe_3)_4$,[45] and $(AgCH_2SiMe_3)_n$.[225] It has been postulated to play a minor role in organotitanium decompositions (a bimolecular process predominating),[226] and for $Zr(CH_2Ph)_4$ both radical[227] and nonradical[103,228] mechanisms have been suggested. Typically, pointers to the absence of this pathway fall into six categories: (i) where stereochemistry is maintained at the α-carbon of the hydrocarbyl ligand in the organic product, cis- and trans-alkenyls being the most studied;[213,229a,230] (ii) where methylcyclopentane is not found as a product in decomposition of 5-hexenyl compounds, cyclization of 5-hexenyl radical being more rapid than H-abstraction from donor solvents;[163,231] (iii) where disproportionation:combination ratios differ markedly from the norm for radical reactions;[159,232] (iv) where reaction is unchanged on addition of an effective radical transfer agent (e.g., cumene, decalin) or inhibitor;[159,232-234] (v) where either a label (D) is not incorporated into the products in decompositions in the presence of a labeled transfer agent, usually the solvent, or where similarly H is not incorporated into the products from labeled hydrocarbyl groups using unlabeled solvents (cf. ref 183, 226, 235, and 236); (vi) where CIDNP effects are not observed in the NMR spectra of solutions during decomposition (see also ref 323).[230]

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The pathway has been discussed for alkyls of the transition metals: surprisingly, it was predicted to be relatively unimportant at the end of the series, but more significant for early metal derivatives.[10c] This view was based on the expectation that d-orbital involvement in transition metal systems ($\sigma \rightarrow$ d or d $\rightarrow \sigma^*$ promotion) would lead to a lower activation energy for homolysis than in the corresponding main group systems. Another paper relegates homolysis to minor significance even for the early transition metal σ-hydrocarbyls.[235] On the other hand, photochemical reactions are expected to give radical products; cf. ref 10b and the photolyses of $MMe_2(\eta^5\text{-}C_5H_5)_2$ (M = Ti, Zr, or Hf[237a]) or some organo Co complexes.[237b] Irradiation of $MnCH_2Ph(CO)_5$ in presence of the spin-trap nitrosodurene has led to the ESR identification of the nitroxides derived from both $PhCH_2\cdot$ and $\dot{M}n(CO)_5$;[238] coenzyme B_{12} or ethylcobalamin upon photolysis in an aqueous medium in presence of Bu^tNO gave $R(Bu^t)N\dot{O}$ (R = 5'-deoxyadenosyl or Et).[312] M–C homolysis has been reviewed in the context of free-radical organometallic chemistry.[313]

M–C homolysis for transition metals formally involves oxidation of the ligand ($R^- \rightarrow R\cdot$) with corresponding decrease in the oxidation state of the metal. Hence, additional ligands will inhibit homolysis by their σ-donor rather than by their π-acceptor capacity, because the tendency for metal reduction is inhibited by increase of electron density at the metal. The norbornyl group, in common with other strained bridgehead systems, forms a relatively stable anion but a less stable radical (or cation),[239] and this may contribute to the remarkable stability of the tetranorbornyls[75] and tetra(1-adamantyl)titanium.[105] We draw attention here to the ferrocenylmethyl ligand ($\eta^5\text{-}C_5H_5Fe\text{-}\eta^5\text{-}C_5H_4CH_2$-) which differs from the above ligands in forming a very stable cation.[240] The stability of complexes with this ligand does not yet appear to have been investigated.[241]

Several authors, while excluding a *free* radical process, have suggested a bound-radical mechanism, in which the formed radical remains within the coordination sphere of the metal or cluster, or within the solvent cage, and there undergoes reaction (e.g., dimerization or hydrogen abstraction) (see e.g., ref 166 and 242). As mentioned below (see section IV.I) distinctions between this and other concerted pathways may become semantic, and in the limit they are indistinguishable.

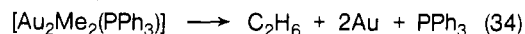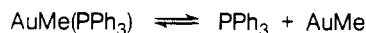## G. Binuclear Elimination (with Concomitant Change in Metal Oxidation State)

This has been suggested as a pathway in the decomposition of a number of transition metal σ-hydrocarbyls where reduction of the metal takes place and where significant participation by free radical intermediates has been ruled out. Complexes involved include the alkyls of Ti^{IV},[235] Cr^{III},[166] Mn^{II},[231] Fe^{III},[243] Cu^{I},[229,233] Ag^{I},[159,244,245] and Au^{I}.[232] The alkyl group can be eliminated as its dimer or disproportionation products (if the group contains a β-hydrogen). Alternatively, a mixture is obtained, the relative proportions of which depend on the alkyl group, the metal, and, to some extent, on the solvent.[246] For example, dimers are formed almost exclusively with Ag^{I} whereas only disproportionation products arise from Mn^{II} complexes; for Au^{I} species, there is a transition from dimerization to disproportionation on passing from n- to sec- and tert-alkyl groups.

Requirements are that the cleavage of M–C bonds and the formation of C–C or C–H bonds are synchronous and take place within a dimer or higher aggregate without participation of radical intermediates or transfer of H to the metal. Where dimers are produced and with complexes $(MR)_n$ (e.g., M = Ag) the pathway is established, but where disproportionation products arise there is some dispute as to the relative contri-

butions of bimolecular and β-elimination. The alternative mechanism involves β-elimination, eq 32, followed by protonolysis, eq 33, where both steps are important in determining the overall product distribution (see ref 233 for a discussion of this point). These steps have been independently demonstrated for Cu^{I},[163,232] and are implicated in the decomposition of $Ir(CO)C_8H_{17}\text{-}n\text{-}(PPh_3)_2$.[169,247]

$$MCH_2CH_2R \longrightarrow RCH=CH_2 + MH \qquad (32)$$

$$MH + MCH_2CH_2R \longrightarrow RH + 2M \qquad (33)$$
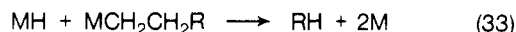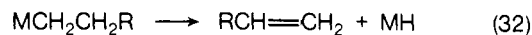
Further data on this pathway come from studies of the decomposition of $AuMe(PPh_3)$,[232] $(CuC_6H_4CF_3\text{-}m)_8$,[122] $Cu_6R_2(C_6H_4CH_2NMe_2\text{-}o)_4$,[245] and $AgBu(PBu_3)$.[159] For $AuMe(PPh_3)$, loss of PPh_3 is rate limiting, suggesting the pathway of eq 34 involving the reactive fragment AuMe combining with further $AuMe(PPh_3)$ to give a dimeric species, possibly the solvated aurate $[AuPPh_3]^+[AuMe_2]^-$. Such rate-limiting loss of coordinated ligand to give a reactive fragment which may combine with other species for elimination is also in accord with observations on complexes prepared in situ:

$$AuMe(PPh_3) \rightleftharpoons PPh_3 + AuMe$$

$$AuMe + AuMe(PPh_3) \longrightarrow$$

$$[Au_2Me_2(PPh_3)] \longrightarrow C_2H_6 + 2Au + PPh_3 \qquad (34)$$

Their decomposition is retarded by more strongly coordinating solvents.[229c,233] Higher aggregates may also be involved. For Cu, homoleptic clusters have been isolated (cf. ref 45 and 122), and for $(CuC_6H_4CF_3\text{-}m)_8$ elimination of biaryl with production of a new Cu_8 cluster has been observed.

$$(CuC_6H_4CF_3\text{-}m)_8 \longrightarrow (m\text{-}C_6H_4CF_3)_2 + Cu_8(C_6H_4CF_3\text{-}m)_6 \quad (35)$$
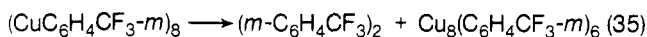
Similar elimination takes place in decompositions of the related heteroleptic complexes $Cu_6R_2(C_6H_4CH_2NMe_2\text{-}o)_4$ (R = C≡CPh or C≡CC_6H_4Me-p); the production of $o\text{-}Me_2NCH_2C_6H_4R$ as the sole organic product indicates the intramolecularity of the reaction.

Decomposition of $AgBu(PBu_3)$ is unaffected by the presence of radical species, e.g., Bu^t_2NO over a range of concentrations, thus eliminating significant contributions from radical pathways.[159]

Recent results show too that intermolecular alkyl transfer reactions between, e.g., alkylchromium cations, proceed via a bimolecular, rather than by a homolytic pathway, as had previously been assumed.[248]

Another type of disproportionation, involving changes in oxidation state of the metal rather than changes in the ligand, has recently been observed for a photolytic decomposition of a main group metal(II) alkyl, which may prove applicable for the preparation of other metal-centered radicals, eq 36 [R = $(Me_3Si)_2CH$];[28] similar reactions have been demonstrated for GeR_2,[25] and $R_3Ge\cdot$ and $R_3Si\cdot$ have been prepared by related photochemical procedures.[23]

$$2SnR_2 \longrightarrow R_3Sn\cdot + [RSn] \qquad (36)$$
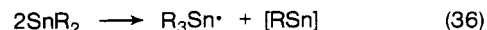
H. Binuclear Elimination (without Concomitant Change in Metal Oxidation State)

Reactions of this type, which do not involve free radicals, are characterized primarily by the nature of the decomposition products: alkane (from metal alkyls) and a solid containing linkages of the types $(LM)_2C=$, $(LM)_3C$-, or $(LM)_4C$. They are best documented for the methyls of metals at the left of the transition series (especially Ti) and those of a number of main group metals, e.g., eq 37[2] and 38.[220]

In the transition series tetramethyltitanium has been studied in most detail. Decomposition affords methane (approxi-

$$BeMe_2 \xrightarrow[-CH_4]{} (CH_2Be)_n \longrightarrow (Be_2C)_n \qquad (37)$$

$$BMe_3 \xrightarrow[-CH_4]{} (MeB)_6(CH)_4 \qquad (38)$$
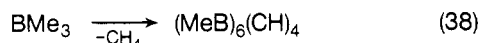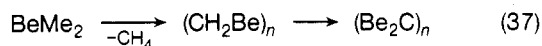
mately 3 mol/mol of $TiMe_4$) and a black diamagnetic solid, which upon hydrolysis gives mainly methane with traces of higher hydrocarbons.[226,249] Labeling studies (D and ^{13}C) have shown that the hydrogens of the methane and the carbon in the black solid are derived from the tetramethyltitanium and that the solid contains linkages of the types TiMe, Ti_2CH_2, Ti_3CH, and Ti_4C.[226,250,251] The reaction is autocatalytic, and catalysis by reduced transition metal species has been demonstrated.[249]

Decomposition of the tetrabenzyls,[103] -neopentyls,[90] and -silylmethyls[16,90] of Ti and Zr gives similar products, the most striking difference being in the thermal stabilities; $TiMe_4$ decomposes below 0°, whereas the others decompose in the range 60–130 °C. We propose that a possible transition state for the decomposition is as in eq 39, which accounts for the observed differences in thermal stability: R = Ph, Me_3C,

$$LMCH_2R \longrightarrow \begin{array}{c} LM{-\!\!\!-}CHR{-\!\!\!-}H \\ | \qquad | \\ LM{-\!\!\!\!-\!\!\!-}CH_2R \end{array} \longrightarrow (LM)_2CHR + RCH_3 \qquad (39)$$

$Me_3Si \gg H$. Others have argued that reaction proceeds via the 1,2-elimination of eq 40.[226] Further studies in systems where complicating autocatalysis does not occur, are needed to establish the details of the pathway.

$$TiMe_4 \longrightarrow [Me_2Ti{=}CH_2] + CH_4 \qquad (40)$$

Surprisingly, the complexes $M(CH_2SnMe_3)_4$ (M = Ti, Zr, or Hf) are less stable than their Me_3SiCH_2 or Me_3CCH_2 analogues, and appear to decompose by reductive elimination, $(Me_3SnCH_2)_2$ being isolated in good yield.[1,252]

We note that the complex $(Me_3SiCH_2)_2\overline{NbCSiMe_3Nb}$-$(CH_2SiMe_3)_2CSiMe_3$, obtained from $NbCl_5$ and Me_3-$SiCH_2MgCl$,[111] may be regarded as an intermediate in the decomposition of the hypothetical $Nb(CH_2SiMe_3)_5$ by loss of 4 mol of Me_4Si. Similarly, $AsMe_3(CH_2)$[96a] and $Ta(CH_2C$-$Me_3)_3(CHCMe_3)$ (XIII) (obtained from $TaCl_5$ and $LiCH_2CMe_3$)[195] may be regarded as the decomposition products of $AsMe_5$ and the hypothetical $Ta(CH_2CMe_3)_5$, respectively (section IV.D). Deuterium labeling studies lead to the following reaction sequence being proposed (Scheme III).[195]

SCHEME III

$$Ta(CH_2CMe_3)_3Cl_2 \xrightarrow{k_1} \text{an intermediate} \xrightarrow{k_2}$$

$$Ta(CH_2CMe_3)_5 \xrightarrow{k_3} \underset{\text{XIII}}{Ta(CH_2CMe_3)_3(CHCMe_3)}$$

$$(k_3 \geqslant k_2 > k_1)$$

However, it seems to us that an alternative mechanism might involve $Ta(CH_2CMe_3)_4Cl$ which with LiR provides metalation of an α-H to afford $[Ta(CH_2CMe_3)_3(\overline{CHCMe_3})Cl]Li^+$ which loses LiCl to give the product. Metalation of an alkyl group rather than chloride abs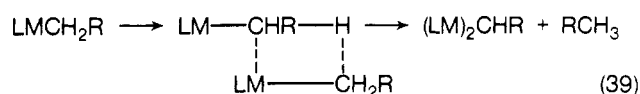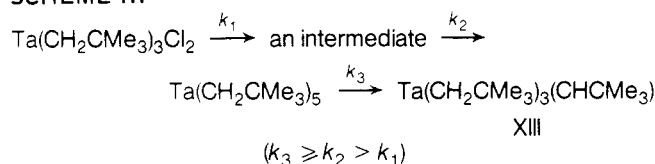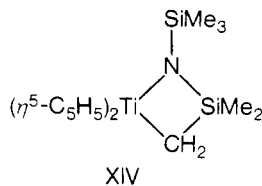traction might well be favored for steric reasons. Evidence for this view comes from a related example of γ-metalation. Thus $Ti(\eta^5-C_5H_5)_2Cl_2$ and LiN-$(SiMe_3)_2$ yield XIV.[254] Further examples of a similar reaction

XIV

pathway as that shown for compound XIII have led to analogs of which the stable $Ta(\eta^5-C_5H_5)_2$ $(Me)(CH_2)$ is the most interesting;[253] its structure has been confirmed by x-ray analysis.[314]

This bimolecular pathway will apply only to those metals which form stable carbides (methanides rather than acetylides) (but clearly relative thermodynamic stabilities are significant, e.g., carbide vs. a carbosilane). A particularly striking comparison may be made between the main group and transition metal methyls $SiMe_4$ and $TiMe_4$ in the similarity of the decomposition products and the dissimilarity of their thermal stabilities. $SiMe_4$ gives a range of stable carbosilanes in which the linkage Si–C–Si is the dominant feature;[92a,255,256] whereas $SiMe_4$ is stable to ca. 500°, $TiMe_4$ decomposes below 0°. While the detailed decomposition pathways may differ (decomposition of $SiMe_4$ may occur via Si–C and C–H homolysis), this may reflect the ease with which the transition metal is able to expand its coordination sphere and utilize energetically accessible d orbitals.

Binuclear elimination is also probably implicated in the decomposition of Al_2Ph_6,[91] but the transition metal phenyls MPh_4 (M = Ti, Zr, or V) afford isolable metal(II) species presumably by a reductive process.[101,207,208]

I. Attack at Coordinated Ligands

We include here reactions, both inter- and intramolecular, involving bond-making and bond-breaking occurring at a coordinated ligand as well as at the metal center, along with a number of reactions that do not readily fit into the previously discussed pathways.

Decompositions, involving attack at a coordinated neutral ligand, generally the solvent, are important for both the main group and transition metals. A vacant coordination position is required and so, for the former, examples come from derivatives of group 1 to 3 metals. There is less restriction in transition metals where the coordination sphere is readily expanded. With ethers, reaction of the ethereal β-hydrogen is implicated, a good example of this pathway being provided by the detailed study, using D labeling, of the reactions of organolithium reagents with diethyl ether, eq 41.[257]
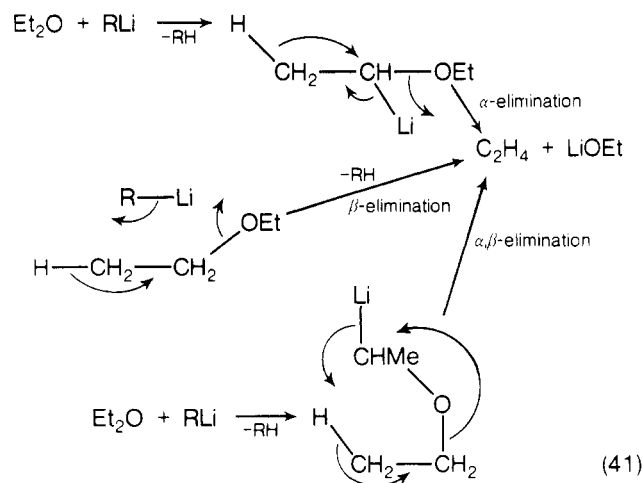
In the transition series it is generally a pathway of relatively high activation energy, occurring when other reactions are suppressed. Examples are found in the decompositions of alkyls of Ti,[235] Mn,[231] Fe,[243] Cr,[166] and U.[230] Reaction may be precluded by use of ethers without β-hydrogens, e.g., Ph_2O.[235] Other reactions that fall in this category are shown in eq 42,[258] 43,[234] 44,[103] 45,[91] and 46.[259] These involve attack at a coordinated anionic ligand, which may be a hydrocarbyl group.

Two recently established pathways for complexes contain-

$$TiMe_2(\eta^5\text{-}C_5Me_5)_2 \longrightarrow CH_4 + TiMe(\eta^5\text{-}C_5Me_5)(C_5Me_4CH_2)$$

(42)

$$[Cr(CH_2Ph)_3(THF)_3] \xrightarrow{\text{heat}} Cr(\eta^6\text{-}PhCH_2\text{---}\underset{Me}{\bigcirc})(\eta^6\text{-}PhMe)^+$$

(43)

$$Zr(CH_2Ph)_4 \xrightarrow{h\nu} Zr(H)(CH_2Ph)_2(CH_2C_6H_4CH_2Ph)$$ (44)

 + PhH (45)

$$TiR(NEt_2)_3 \longrightarrow [Ti\{N\overset{|}{C}HMe(Et)\}(NEt_2)_2]_n + RH$$

(46)

(R = Me, Et)
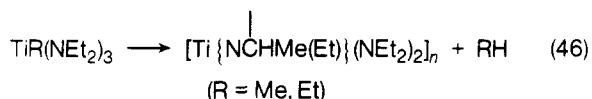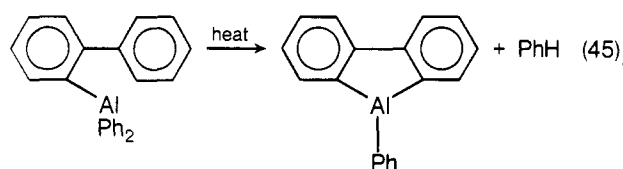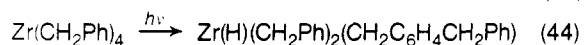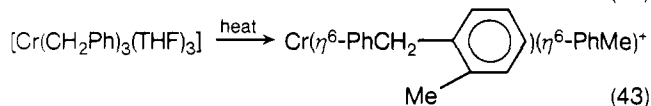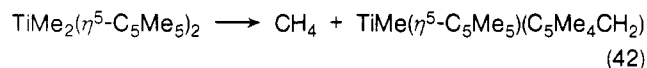
ing cyclopentadienyl and σ-hydrocarbyl groups (R) are (i) intramolecular transfer of R to the C_5 ring with formation of a coordinated pentadiene, a reaction which has analogies with reductive eliminations; and (ii) elimination of RH, the hydrogen deriving from the cyclopentadienyl group. Examples of (i) are shown in eq 47[260] and eq 48.[261]

$$V(\eta^5\text{-}C_5H_5)_2Ph \xrightarrow{CO} \text{} \xrightarrow{-H_2}$$

$$V(\eta^5\text{-}PhC_5H_4)(\eta^5\text{-}C_5H_5)CO \quad (47)$$

$$Mo(\eta^5\text{-}C_5H_5)_2Cl(Et) \xrightarrow{PR_3} \text{} \quad (48)$$
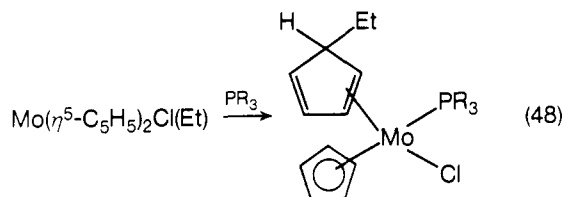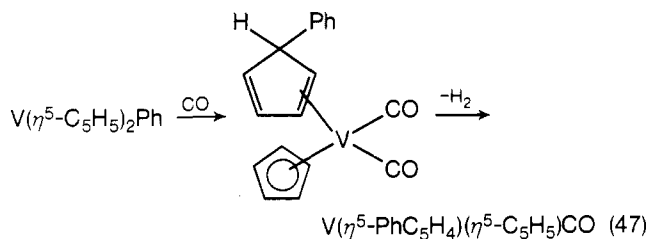
Decompositions of $M(\eta^5\text{-}C_5H_5)CH_2Ph(CO)_n$ (M = Mo, n = 3; M = Fe, n = 2) to give inter alia $M(\eta^5\text{-}C_5H_5)(CO)_nM(\eta^5\text{-}C_5H_4CH_2Ph)(CO)_n$ possibly also involve this pathway (cf. eq 47).[262] Process ii is illustrated by the decompositions of $Ti(\eta^5\text{-}C_5H_5)_2R_2$ (R = e.g., Ph or C_6H_4Me),[183] $Ti(\eta^5\text{-}C_5H_5)_2R$ (R = e.g., Ph or $C_6H_4Me\text{-}p$),[236] and $U(\eta^5\text{-}C_5H_5)_3R$ (R = e.g., Me, Bu, cis-CMe=CHMe, or CH_2CMe_3),[263] studied in some detail using D labeling. Primary decomposition pathways were identified as follows: for $Ti(\eta^5\text{-}C_5H_5)_2R_2$ there are contributions from intramolecular H abstraction from both a cyclopentadienyl group and an aryl group (cf. section III.B), Scheme IV.

SCHEME IV

$$[Ti(\eta^5\text{-}C_5H_5)_2C_6D_4] + C_6D_6$$

contribution $\overset{2}{\nearrow}_3$

$$Ti(\eta^5\text{-}C_5H_5)_2(C_6D_5)_2 \qquad \begin{matrix} [C_{10}H_8Ti] + C_6D_4H_2 \\ [C_{10}H_8Ti] + C_6D_5H \end{matrix}$$

contribution $\overset{1}{\searrow}_3$

$$[C_{10}H_9TiC_6D_5] + C_6D_5H$$

For $Ti(\eta^5\text{-}C_5H_5)_2R$, RH arises primarily via intermolecular H abstraction from a cyclopentadienyl, possibly proceeding as shown in eq 49, while, for $U(\eta^5\text{-}C_5H_5)_3R$, RH arises intramolecularly, possibly as shown in eq 50. A radical reaction within the coordination sphere without inversion of configuration of R· (there is retention of configuration at the α-carbon of R

in the product RH) would, as mentioned previously, also be a possibility, but it would be difficult to distinguish this from eq 50.

$$\text{}$$

$$[(\eta^5\text{-}C_5H_5)_2TiC_5H_4Ti(\eta^5\text{-}C_5H_5)R] + RH \quad (49)$$

$$\text{} \longrightarrow [U(\eta^5\text{-}C_5H_5)_2(C_5H_4)] + RH \quad (50)$$

IV. General Relationships Affecting Stability

Although broad rationalizations relating stability to the nature of the metal, the alkyl, or supporting ligands or solvents are rarely generally valid, the following points are identified. Table VI provides comprehensive coverage for well-characterized transition metal complexes, and representative data for thermolysis of homoleptic main group compounds are in Table VII.

A. Effect of Changes in the Ligand R⁻

An invariant order of stability cannot be drawn up because the various factors are a function of reaction mechanism which, as has been noted, can vary widely. The hydrocarbyl groups show differing trends within the various pathways. However, the following sequences of decreasing stability appear to be the most generally applicable: (i) 1-norbornyl > $PhCH_2$ > $Me_3SiCH_2 \sim Me_3CCH_2$ > Ph > Me ≫ Et > sec- or tert-alkyls;[6,16,75,90,103] (ii) R_F > R_H;[6] (iii) C_6F_5 > C_6H_5;[6] and (iv) chelating > nonchelating hydrocarbyls.[18,74,178,179,271] The abrupt change in stability on passing from Me to higher alkyl (other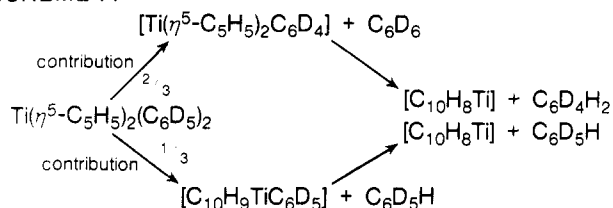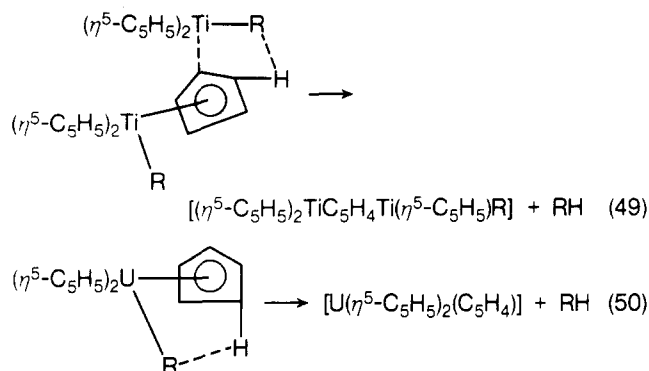 than a neopentyl type) is the main feature and generally reflects a change in decomposition pathway. That even subtle changes in R can influence the pathway is shown by the complexes $M(CH_2SiMe_3)_4$ and $M(CH_2SnMe_3)_4$ (M = Ti, Zr, or Hf). The former give $SiMe_4$,[16b] whereas the latter give $(Me_3SnCH_2)_2$ as the organic product.[252]

Distinctions are only useful when referring to complexes of the same coordination number; for example, it is not valid to discuss the relative stabilities of complexes having Me_3SiCH_2 (R) or $(Me_3Si)_2CH$ (R') ligands by reference to CrR_4 and CrR'_3. The role of the ligand in determining coordination number has already been observed (cf. Tables I–IV).

B. Effect of Changes of Metal and Its Oxidation State

Comparisons can only usefully be made within an isostructural series. Suitable examples in the transition series are MR_4 (R = Me_3SiCH_2,[1,8] Me_3CCH_2,[79,90,111] or $PhCH_2$;[103,106] and M = Ti, Zr, Hf, V, or Cr), $M(1\text{-norbornyl})_4$ (M = Ti, Zr, Hf, V, Cr, Mn, Fe, or Co),[75] and MR_3 [R = $(Me_3Si)_2CH$; M = Sc, Y, Ti, V, Cr,[76] or Yb[76b]]. Stability increases on descending a triad (group 4B)[90] in contrast to the situation in the main group (e.g., 4A) where M–C bond strengths significantly decrease. Trends across the transition series are as yet unclear. Electronic configuration, in the context of kinetically labile or inert complexes, may play a role. Some stable (substitution-inert) octahedral d^3 or d^6 (low spin) alkyls of Cr^{III}, Co^{III}, and Rh^{III} with aquo or ammine ligands are known; and we draw attention to the remarkably stable Cr^{III} complexes

TABLE VI. Thermal Decomposition of Homoleptic Transition Metal Alkyls[a]

Compound	Decomposition conditions	Products and comments	Ref
$TiMe_4$	Ether or hydrocarbon, 10–20°	CH_4 + black solid (contains C, H, Ti), hydrogen in CH_4 not derived from solvent	226, 249
$TiPh_2$	200–250°	Ph_2 + Ti	101
$TiPh_4$	Benzene, −10°	Ph_2 + Ph_2Ti	101
$Ti(CH_2CMe_3)_4$	Benzene, 60° $t_{1/2}$ ~ 14.5 h	Me_4C + black solid, hydrogen in Me_4C not derived from solvent	90
$Ti(CH_2SiMe_3)_4$	Benzene, 80° $t_{1/2}$ ~ 125 h	$SiMe_4$ + black solid, hydrogen in $SiMe_4$ not derived from solvent	16, 90
$Ti(CH_2SnMe_3)_4$	Benzene, 80° $t_{1/2}$ ~ 30 min	$(SnMe_3CH_2)_2$ + black solid + $SnMe_4$	252
$Ti(CH_2Ph)_4$	Toluene, hydrocarbon	PhMe + solid containing Ti^{III}. No D incorporation from deuterated solvents	103
$ZrPh_4$	Et_2O, 0°	$[ZrPh_2·Et_2O]_2$, Ph_2, PhH	207
$Zr(CH_2CMe_3)_4$	Benzene, 80° $t_{1/2}$ ~ 80 h	Me_4C + black solid, hydrogen in Me_4C not derived from solvent	90
$Zr(CH_2SiMe_3)_4$	Benzene, 80° $t_{1/2}$ ~ 150 h	$SiMe_4$ + black solid, hydrogen in $SiMe_4$ not derived from solvent	16, 90
$Zr(CH_2SnMe_3)_4$	Benzene, 80° $t_{1/2}$ ~ 30 min	$(SnMe_3CH_2)_2$ + black solid + $SnMe_4$	252
$Zr(CH_2Ph)_4$	~130°	C_6H_6 + PhMe + $(PhCH_2)_2$ + Ph_2CH_2 + black solid (but see ref 103 and 228)	227
$Hf(CH_2CMe_3)_4$	Benzene, 90° $t_{1/2}$ ~ 900 h	Me_4C + black solid, hydrogen in Me_4C not derived from solvent	90
$Hf(CH_2SiMe_3)_4$	Benzene, 90° $t_{1/2}$ ~ 350 h	$SiMe_4$ + black solid, hydrogen in $SiMe_4$ not derived from solvent	16, 90
$Hf(CH_2SnMe_3)_4$	Benzene, 80° $t_{1/2}$ ~ 30 min	$(SnMe_3CH_2)_2$ + black solid + $SnMe_4$	252
VPh_4	Et_2O, −50°	$VPh_2·nEt_2O$ + Ph_2	208
$V(CH_2Ph)_4$	Et_2O, 90°	PhMe (3.3–3.7 mol) + black solid	274
$TaMe_5$	~25°, neat	CH_4 + Ta + black solid	38
$CrBu^t_4$	Heptane, 70°	Principally Me_3CH + $Me_2C{=}CH_2$ + Cr (with 5% C) [$Cr(CH_2CMe_3)_4$ stable under these conditions]	110
WMe_6	Neat, 25°	CH_4 + C_2H_6 (trace) + black solid (contains C, H, W)	39
MnR_2 (R = e.g., Me, Et, Pr^i, Bu^t, $PhCH_2$)		RH + R(−H); proportions and extent of decomposition depend on R	231
$(CuMe)_n$	Neat, 0°	C_2H_6	264
$(CuR)_n$ (R = e.g., Me, Et, Pr^i, Ph, $PhCH_2$)	THF, ~25°	R–R + RH + R(−H); proportions and extent of decomposition depend on R	233
$(CuAr)_n$ (Ar = o, m, p-MeC_6H_4, or o-$MeOC_6H_4$)	~100	Ar_2	120
$(CuC_6F_5)_4$	210–220°	$(C_6F_5)_2$ + Cu	121
$(CuC_6H_4CF_3-m)_8$	Benzene, heat	$(m-C_6H_4CF_3)_2$ + $Cu_8(C_6H_4CF_3-m)_6$	122
$(CuCH_2SiMe_3)_4$	Toluene, 80°	Cu + $SiMe_4$ + $(SiMe_3)_2CH_2$ + $(SiMe_3CH_2)_2$ + $PhCH_2CH_2SiMe_3$ + $(PhCH_2)_2$	45
$(AgC_6F_5)_n$	150°	$(C_6F_5)_2$	265
$[Au(C_6F_5)_3]_n$	Heat	$(C_6F_5)_2$ + Au	266
$(AuC_5H_4N-o)_n$	120–150°	α,α-bpy + Au	135
$Th(CH_2Ph)_4$	85°	$(PhCH_2)_2$ + PhMe + C_6H_6 + C_2H_6 + black solid	99

[a] Studies on the decomposition of other species, generally less well characterized and prepared in situ, are to be found in ref 110, 166, 230, 246, 267, 268, and 269.

CrR_3 [R = $Me_2P(CH_2)_2$ or o-$CH_2PPh_2C_6H_4$,[73] or $(Me_3Si)_2CH$].[76] However, it appears that, for the early transition metals at least, the electronic configuration of the metal is relatively unimportant.

C. Effect of Charge

The formation of complex anions generally leads to an increase in stability, as has already been noted. However, the degree to which this reflects the effect of charge rather than the blocking of vacant coordination positions (e.g., in Li-$TiMe_5$)[137] or the formation of metal–metal bonds or clusters (e.g., in $Li_4Cr_2Me_8$[140] or $LiCuMe_2$[149]) is uncertain. Cationic species have been little studied and appear to be of relatively low stability (cf. ref 217).

D. Effect of Additional Neutral Ligands

If a vacant coordination position is a necessary requirement for a particular decomposition pathway (e.g. α-, β-, or

TABLE VII. Thermal Decomposition of Representative Homoleptic Main Group Element σ-Hydrocarbyls

Compound	Decomposition conditions	Products and comments	Ref
Group 1			
$(LiEt)_n$	98–130°	>98% $CH_2{=}CH_2$	164
$(LiBu^s)_n$	78–104°	1-Butene (29–34%), cis-2-butene (51–54%), trans-2-butene (15–17%)	164
Group 2			
$(BeMe_2)_n$	200°	$CH_4 + (BeCH_2)_n \rightarrow (Be_2C)_n$	2
$(BeEt_2)_n$	190°	C_2H_6, C_2H_4, C_4H_8 (in ratio 2:1:1.5)	2
$BeBu^t{}_2$	Room temp	$BeBu^i{}_2 \xrightarrow{80°} Me_2C{=}CH_2 + BeH_2$	2, 50
$(MgMe_2)_n$	250°	$CH_4, (MgCH_2)_n$	2
$(MgEt_2)_n$	175–200°	$CH_2{=}CH_2, MgH_2$	2
$(MgPh_2)_n$	280°	Ph_2, Mg	2
MR_2 (M = Zn, Cd, or Hg)		M + mixture of products from R·	7
Group 3			
BMe_3	450°, 1–2 h sealed tube	$(MeB)_6(CH)_4$	220
$BBu^s{}_3$	"reflux"	$BBu^n{}_3$	270
$BBu^n{}_3$	200–300°	Bu^{n}B⬠, Bu^{s}B⬠, C_4H_8, H_2	37
$AlEt_3$	162–192°	$C_2H_4 + AlEt_2H \rightarrow C_2H_6$ (+ other hydrocarbons) + $AlH_3 \rightarrow Al + H_2$	91
$Al(CH_2CMe_3)_3$	~200°	$Me_2C{=}CH_2, AlMe_3$	91
$(AlPh_3)_2$	>200°	C_6H_6 + residue which with D_2O gives $C_6H_5D, C_6H_4D_2$, and $C_6H_3D_3$	91
Group 4			
$SiMe_4$	~700°	Mixture of products mainly containing Si–C–Si linkages	255, 256
$PbMe_4$	400–700°	$Me_3Pb\cdot + Me'$ (rate-controlling step)	7
$PbEt_4$	233–267°	Pb, $n{-}C_4H_{10}, C_2H_4, C_2H_6, H_2$	7
Group 5			
$AsMe_5$	100–122°	$(AsMe_3 + C_2H_6) + (Me_3AsCH_2 + CH_4) \rightarrow AsMe_3 + C_2H_4 + (CH_2)_n$	96a
$SbMe_3$	475–603°	Sb + products from Me·	7
$SbPh_5$		$SbPh_3 + Ph_2$	2

bimolecular elimination), coordinating ligands, which may be the solvent, lead to an enhancement of stability. For example, Lewis base complexes of $TiMe_4$ are more stable than $TiMe_4$, of which $TiMe_4(PMe_3)_2$ is less stable than $TiMe_4$-$(Me_2PCH_2CH_2PMe_2)$;[272] and $TaMe_5(Me_2PCH_2CH_2PMe_2)$ is stable to 110° whereas free $TaMe_5$ decomposes at or below 25°C.[38]

V. Appendix (Added December 1975)

This section, added in proof, provides information on additional literature[273-305] (see also ref 76b, 86, 253, 306-315, 322, and 323 incorporated in the text, and to ref 25, 59, 62, 71, 76a, 112, 137, 171, 172, 187, 203, 210, 214, and 220) (to December 1975) that has come to our attention since the submission of the manuscript. Data on new complexes have been added to Tables II and III while publications relating to stability and decomposition pathways (in ref 274, 276-278, 283, 287, 289-305, and 324-329) are briefly mentioned below.

A cautionary note to the handling of some simple metal alkyls comes from reports on WMe_6,[276] $ReMe_6$,[293] and $TaMe_5$[293] which, like $(CuMe)_x$, can decompose explosively when isolated in a reasonably pure state. Olefin metathesis catalysts are now better understood: recent reports show the active species to be metal carbene complexes $LMCX_2$, produced via α-elimination from metal alkyl precursors,[304] as had been proved for electron-rich olefin dismutation, with

metallocycles $\overline{LMCX_2CY_2}CY_2$ as postulated intermediates.[305] Reductive elimination from $PtAr_2L_2$ (Ar = Ph or p-MeC_6H_4; L_2 = e.g., $(PPh_3)_2$ or $Ph_2PCH_2CH_2PPh_2$) is enhanced by addition of excess ligand L (steric acceleration to elimination from a postulated five-coordinate intermediate), in marked contrast to earlier reports (section III.E) on related systems in which ligand dissociation is rate determining.[294] The thermal decomposition product of $Th(\eta^5-C_5H_5)_3Bu$ (cf. the related U complexes, section III.I) has been characterized as the novel C_5H_4 bridged $[Th(\eta^1,\eta^5-C_5H_4)(\eta^5-C_5H_5)_2]_2$.[296]

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