

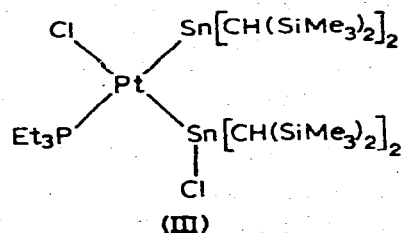
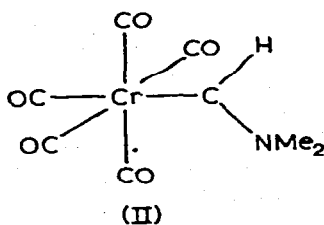
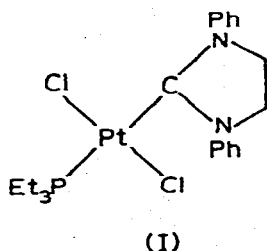
THE COORDINATION CHEMISTRY OF BIVALENT GROUP IV DONORS; NUCLEOPHILIC-CARBENE AND DIALKYLSTANNYLENE COMPLEXES

M.F. LAPPERT

School of Molecular Sciences, University of Sussex, Brighton BN1 9QJ (Great Britain)

I. Introduction

The principal aim of this article is to review the chemistry of bivalent Group IV donors MXY ($\text{M} = \text{C}, \text{Si}, \text{Ge}, \text{Sn}$ or Pb) as ligands in transition metal chemistry. The simplest products of such reactions are the derived carbene-metal complexes $\text{LM}'\text{-MXY}$, such as I or II, or heavier Group IV analogues such as III. The main emphasis here will be on the carbene complexes.



I shall restrict the scope to exclude the chemistry of such compounds when these are not obtained from the carbene or carbenoid precursors (e.g., the original method for obtaining such complexes, applied to the Cr, Mo and W Group by E.O. Fischer and his co-workers, employed procedures whereby a coordinated CO ligand was converted to a coordinated carbene; this will not be discussed); however, the literature of carbenometal derivatives up to 1972 has been comprehensively summarised elsewhere [1,2]. Also omitted is the situation wherein the carbenometal complex, usually derived from an electrophilic carbene, is a transient intermediate, as is often the case in various transition metal-catalysed organic reactions; this field has also been surveyed [3].

Because of the special nature of this volume of reviews, it may be of interest in this introduction briefly to place our researches on bivalent Group IV donors in the context of our earlier and current work in organometallic chemistry.

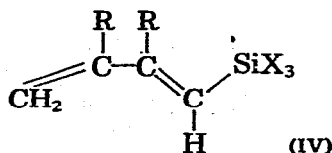
My doctorate was completed under the supervision of W. Gerrard, and

concerned the reactions of alcohols or ethers, including optically-active compounds, with boron trichloride. (This formed a part of Gerrard's commitment to the problem of interaction of an alcohol and a non-metal halide in connection with the reaction sequences of alkyl halide formation.) The work was extended to include reactions of boron trichloride with organic compounds generally [4] and, much later, to inorganic compounds [5]. The first review of organoboron chemistry was published in 1956 [6], and further contributions made to other areas of boron chemistry: B—O [7], B—N [8], B—C [9], B—S [10], B—halide [11], B—pseudohalide [12], and cyclic boron compounds [13]. Work on boron halides was enlarged to include Lewis acid—base adducts, including structural and calorimetric investigations [14].

Physicochemical approaches to bonding problems, in collaboration with J.B. Pedley, were initiated in the early 1960's and continue to the present time. Methods used involve calorimetry, nuclear magnetic resonance, He(I) photoelectron spectroscopy (PES), mass spectrometry, and analysis of data by molecular orbital (MO) procedures. Compounds examined include simple derivatives of B, Si, P, and the heavier Group III-V elements, as well as of transition metals. The objectives are to obtain, for series of compounds, reliable standard heat of formation, bond energy, bond dissociation energy, and orbital energy data, and thereby contribute to an understanding of bonding. These experiments are, for the most part, related to the synthetic programme. For example, researches on metal alkyls (vide infra) have encompassed PES and ΔH_f^0 measurements [15].

The use of organotin for the synthesis of organoboron species led to involvement in Group IV chemistry in 1960. Organotin—nitrogen compounds were examined in detail [16]. Metal amides, including $\text{Me}_3\text{SnNMe}_2$, were shown to be versatile reagents in synthesis: involving their reactions with unsaturated moieties (insertion reactions generally were reviewed in 1967 [17]), including monomers (in collaboration with A.D. Jenkins) [18]; protic species, such as cyclopentadienes and acetylenes; and metal and non-metal halides. Amides examined were derived from B, Al, Si^{IV} , Ge^{IV} , Ge^{III} , Ge^{II} , Sn^{IV} , Sn^{III} , Sn^{II} , Pb^{II} , P^{III} , As^{III} , Tl^{IV} , Tl^{III} , Zr^{IV} , Hf^{IV} , V^{III} , and V^{IV} [16,19]. The study was extended to derivatives of aldimines and ketimines such as $\text{Me}_3\text{SnN}=\text{C}(\text{CF}_3)_2$ and *cis*-[Pt(PPh₃)₂Cl{N=C(CF₃)₂}] [20].

Reactions of amides with diazomethane afforded the first volatile organometallic diazoalkanes, $\text{Me}_3\text{SiCHN}_2$ and $(\text{Me}_3\text{Sn})_2\text{CN}_2$ [21], and this in turn led to their use in the synthesis of organic heterocycles, metal alkylazo complexes such as $[\text{Mo}(\pi\text{-C}_5\text{H}_5)(\text{CO})_2(\text{N}=\text{NCH}_2\text{SiMe}_3)]$, and, in part, in our interest in carbenometal complexes. Reactions of amides with metal hydrides yielded compounds having metal—metal bonds, such as $[\text{Ta}(\pi\text{-C}_5\text{H}_5)_2\text{H}_2(\text{SnMe}_3)]$ [22]. This discovery stimulated our work on silyl—transition metal compounds [23] and subsequently transition metal-catalysed (especially using Ziegler systems) hydrosilylation [24]; for example, $\text{RC}\equiv\text{CH}$ was converted regio- and stereo-specifically into IV. We found, in collaboration with C. Eaborn, that strained Si heterocycles undergo ring opening with various transition metal complexes [25].



We have contributed to synthetic organosilicon chemistry (e.g., perfluorophenylsilanes [26]) and the use of organosilicon compounds in organic synthesis (e.g., Wittig-type reactions of 2-lithio-2-trimethylsilyl-1,3-dithian and related reactions for providing C₁ homologation [27]).

Studies on the chemistry of homoleptic metal alkyls, MR_n [28], using bulky ligands without β-hydrogen such as Me₃SiCH₂⁻, (R')⁻, and (Me₃Si)₂CH⁻, (R)⁻, commenced in 1968 and stemmed from our interest in the amido ligand including (Me₃Si)₂N⁻ [16], compounds having M—Si bonds [23], and the chemistry of other *monohapto* organometallics (carbene complexes [1,3], and alkenyls and alkynyls [29]). Among the thermally stable alkyls to be synthesised and characterised were the first paramagnetic Main Group neutral alkyls MR₃ (M = Si, Ge or Sn), Group IIIA, IVA, and VIA alkyls, e.g., YR₃, ZrR'₄ and CrR₃, and the square planar (CuR')₄ which has alkyl-bridges between Cu atoms [28].

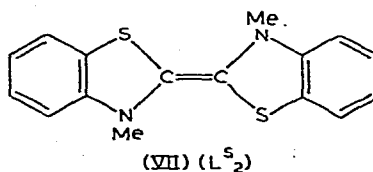
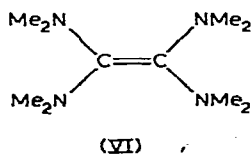
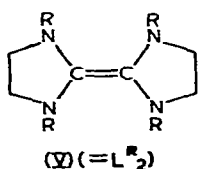
The behaviour of a metal-alkyl bond is also a theme of a project begun in 1972, in collaboration with A.W. Johnson, on coenzyme-B₁₂-dependent enzyme reactions [30]. The organometallic chemistry of free radicals and the use of ESR spectroscopy, in collaboration with A. Hudson, features in this work, in the study of metal-centred radicals MR₃ [31], in S_H2 reactions at transition metal centres [32], and in efforts to elucidate the mechanism of reactions such as oxidative-addition of MeI to Pt⁰ [33] or M—R photolysis [34]. Previously we had considered researches on model-B₁₂-systems; hydrogen transfer involving an alkylcobalt(III) reagent was then in principle viable via a carbene- or alkenyl-cobalt moiety, and this in part prompted our involvement in those areas.

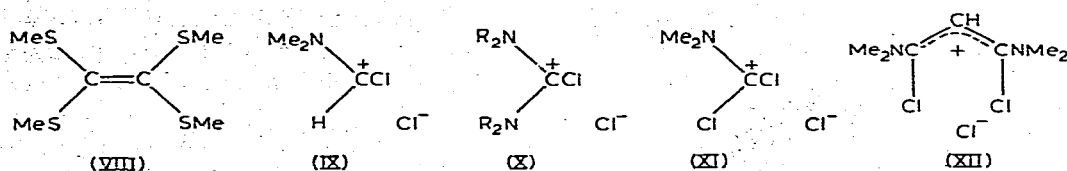
II. Nucleophilic-carbenometal complexes and related chemistry

A. Electron-rich olefins and other electron-rich carbenoids: general considerations

A major field of transition metal organometallic chemistry has concerned the interaction between a metal complex and an organic molecule. Almost invariably, the metal complex has been the nucleophile with the metal atom as the electron-rich centre. Typically, such a reaction has been an oxidative-addition to a low valent coordinatively unsaturated metal complex, using various organic substrates. Examples of the latter are olefins such as C₂F₄ or C₂-(CN)₄, acetylenes including EtOOC≡CCOOEt, or alkyl or acyl halides; unactivated olefins such as C₂H₄, C₄H₆, or C₈H₈ are not regarded as formally causing the oxidation of the metal, but the borderline between a complex and a metallocycle is often blurred.

Our own studies, however, are distinct in that we have been interested in the *transition metal chemistry of electron-rich olefins or carbonium ions*, e.g., V-XII.





The PE spectra of V ($R = \text{Me}$) and VI show that for each olefin there are five bands below 10.5 eV, with the energetically most accessible orbital at the remarkably low first vertical ionisation potential (IP) of ca. 6.0 eV (cf., C_2H_4 or C_2F_4 , 10.5 eV; Na, 5.1 eV) [35]. A simple Hückel π -MO scheme shows this orbital (π_5 in Fig. 1) to be antibonding between four of its six centres and hence of low IP. Not surprisingly, therefore, these olefins readily give rise to cations such as $[\text{L}_2^{\text{R}}]^{\ddagger}$ or $[\text{L}_2^{\text{R}}]^{2+}$ (XIII) [36]. The weak olefinic C=C bond, estimated at ca. 80 kcal mol⁻¹ [36], is consistent with the MO description, and is exemplified by the reaction of V with strong acids to give salts having the cation XIV. Nevertheless, an electron-rich olefin such as V does not dissociate in solution to produce a nucleophilic carbene (cf., [37]), unless a suitable catalyst, e.g., a Rh^{I} complex, is present [38]. Thus, heating two closely-related electron-rich olefins in boiling xylene for 2 h caused no metathesis (e.g., eqn. 1), but in the presence of 1.8 mol % of $[\text{RhCl}(\text{PPh}_3)_3]$ the redistribution was statistical [38]. The catalytic cycle probably involves a sequence like that shown in Fig. 2. Evidence rests on the following observations [38]: (a) compounds XIVa and XIVb are obtained from $[\text{RhCl}(\text{PPh}_3)_3]$ by heating with the appropriate olefin V in boiling xylene and hence step (i) is confirmed; (b) both XIVa and XIVb are effective metathesis catalysts; and (c) the complexes XIVa and XIVb are interconvertible by treatment with excess of the other olefin. Hence the only missing step in the proposed cycle is a Rh^{III} metallocycle such

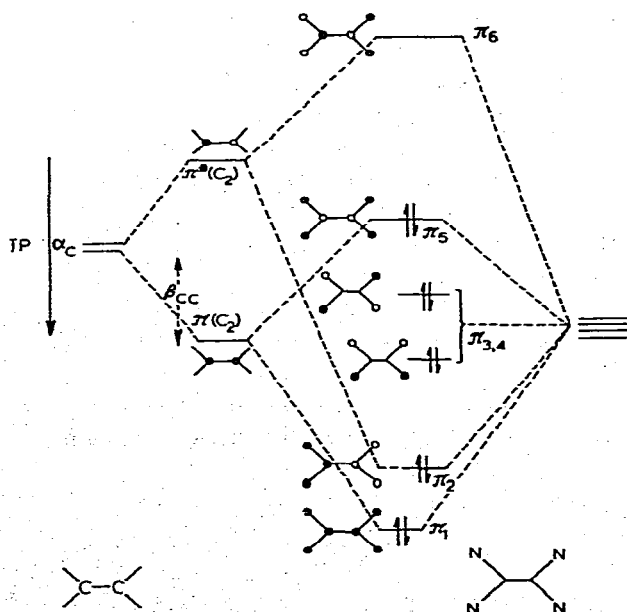
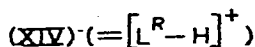
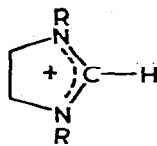
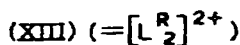
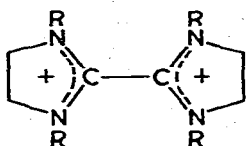
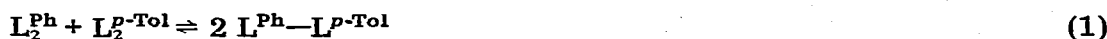


Fig. 1. Schematic π -MO scheme for electron-rich olefins V or VI.



as XV. However related (stable) RhC_4 rings are known, and both Rh^{I} and an electron-rich olefin are known to be good nucleophiles; hence a transition state of type XVI is plausible. (It remains a speculation to suppose that the well-known olefin metathesis reaction, involving simple hydrocarbons, also proceeds via carbenemetal intermediates.)



B. The reactions of transition metal complexes with electron-rich olefins

Our initial objective was to seek synthetic procedures for carbenemetal complexes from organic precursors, or carbenoids. It soon became clear that such complexes were likely to be stable only if the carbene ligand is electron-rich, i.e., a nucleophilic carbene. Nevertheless, we did attempt to prepare electrophilic carbenemetal complexes, but instead obtained the reaction products shown in eqns. 2 and 3 [39,77].

The initial experiments (eqn. 4) which led to our first carbenemetal complex, I [39], were designed to generate the nucleophilic carbene L^{Ph} and trap this by means of reagent XVII, known to undergo bridge-cleavage by bases such as amines or phosphines [40].

We now consider it unlikely that a free nucleophilic carbene is an inter-

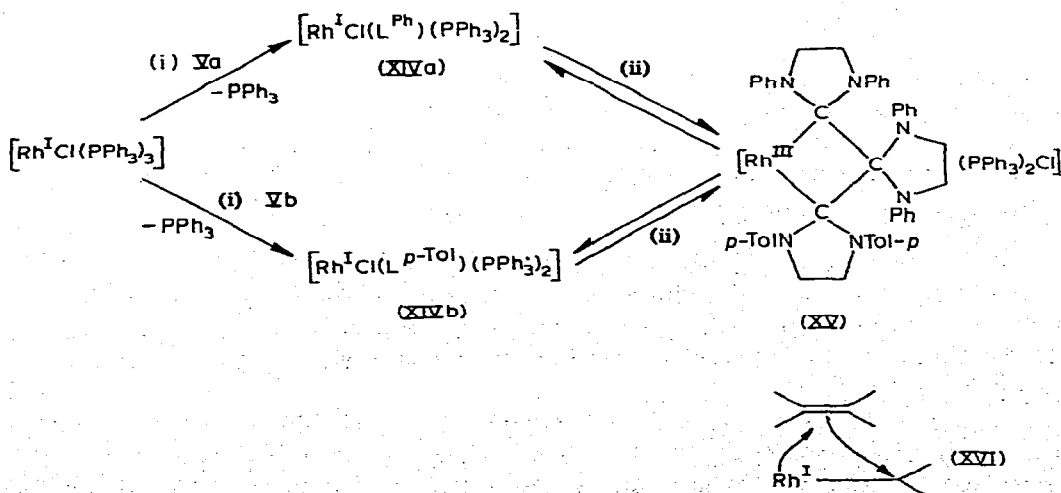
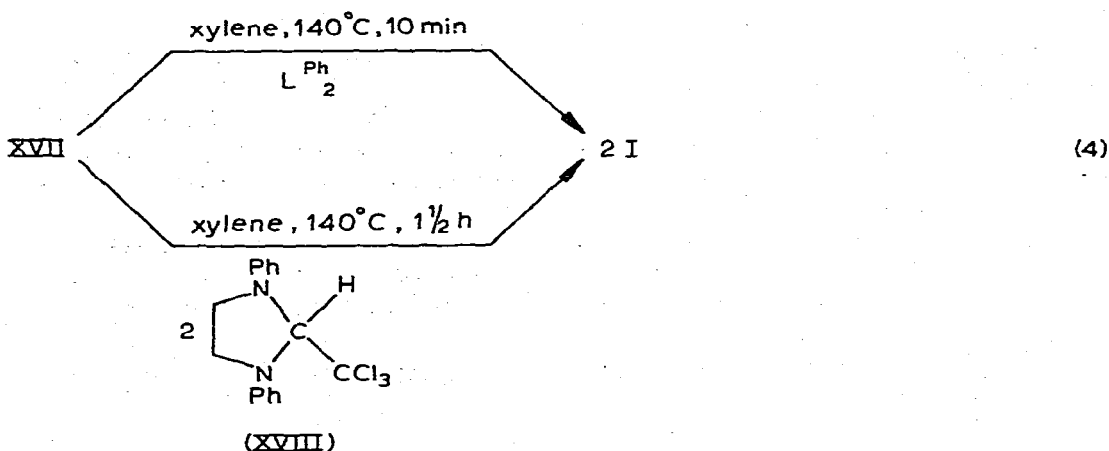
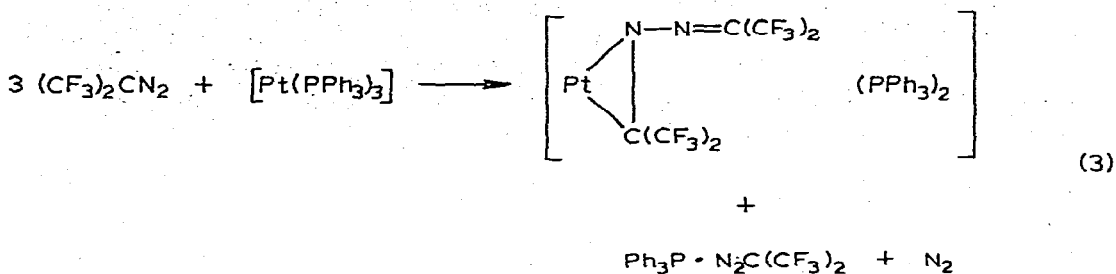
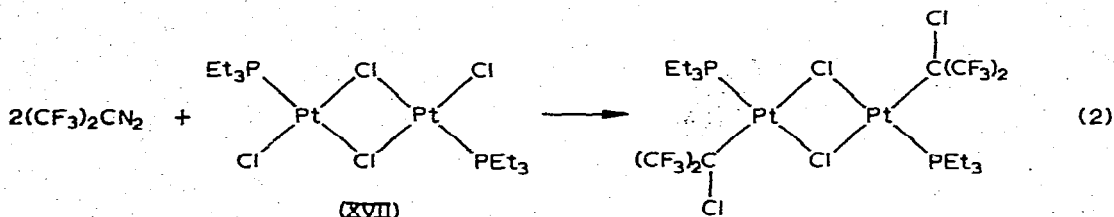


Fig. 2. Proposed catalytic cycle for electron-rich olefin dismutation, using Rh^{I} catalysts.



mediate in reactions such as those shown in eqn. 4, because for a Group VI metal carbonyl as the transition metal reagent, other products can be isolated under milder conditions [41] (see below). The electron-rich olefin can be generated in situ from XVIII or an aminoacetal (eqn. 5) [41]. Reaction 5 may

$$\text{HC}(\text{NMe}_2)(\text{OMe})_2 + \text{RNH}(\text{CH}_2)_2\text{NHR} \rightarrow \text{V} + 2\text{MeOH} + \text{Me}_2\text{NH} \quad (5)$$

be modified by using a 1,3-propylenediamine derivative to make the six-membered cyclic homologue of V, which has proved to be much less reactive than V in its transition metal chemistry [41]. The *N*-arylolefins (V) are considerably less reactive than the alkyls and somewhat less reactive than the thiazole derivative L_2^{S} (VII) [39].

Reaction 4 suggested to us that electron-rich olefins like V or VII might have an extensive carbene-ligand chemistry, in some ways analogous to that of tertiary phosphines. Stable complexes having 1, 2, 3, or 4 carbene ligands have been made from olefins for Cr^0 , Mo^0 , Mo^{II} , W^0 , W^{II} , Fe^0 , Fe^{I} , Ru^0 , Ru^{II} , Rh^{I} , Rh^{III} , Ir^{I} ,

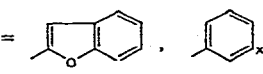

TABLE 1
CARBENOMETAL COMPLEXES FROM ELECTRON-RICH OLEFINS

Complex	Ref.	Complex	Ref.
$[M(CO)_5L^R]$ M = Cr and R = Me or Et; M = Mo and R = Me, Et, n-Bu, or PhCH ₂ ; M = W and R = Me, Et, or PhCH ₂	41	<i>trans</i> -[RhX(L ^R)(PPh ₃) ₂] X = Cl and R = Me, Ph, or <i>p</i> -MeOC ₆ H ₄ ; X = Br and R = Me or <i>p</i> -Tol; X = I and R = Me; X = Br or N=C(CF ₃) ₂ and R = Me or <i>p</i> -Tol	35,43, 46,48
$[M(CO)_5L^R]$ M = Cr, Mo, or W and L ^R = $\overline{CN(Me)-}$ (CH ₂) ₃ NMe	41	<i>trans</i> -[Rh(CO)CIL ^R (PPh ₃)] L = Me, Et, Ph, <i>p</i> -Tol, or <i>p</i> -MeOC ₆ H ₄	45,48
<i>cis</i> -[M(CO) ₄ (L ^R) ₂] M = Cr and R = Me or Et; M = Mo and R = Me, Et, n-Bu, or PhCH ₂ ; M = W and R = Me, Et, or PhCH ₂	41	<i>trans</i> -[Rh(CO)CILEt(PET ₃)] also L' analogue	47 41
<i>trans</i> -[M(CO) ₄ (L ^R) ₂] M = Cr or W, and R = Me; M = Mo and R = Me, Et, or PhCH ₂	41	<i>trans</i> -[Rh(CO)Cl(L ^R) ₂] R = Me or Et also (L') ₂ analogue	44,45,48 41
<i>cis</i> -[M(CO) ₄ L ^{Me} {C(OR')R''}] M = Cr or Mo and R' = Me = R''; M = W and R' = Et with R'' = Me or Ph	41	<i>cis</i> - or <i>trans</i> -[Rh(CO)L ^{Me} (PPh ₃) ₂] ⁺ X ⁻ <i>cis</i> - or <i>trans</i> -[RhCO(L ^{Et}) ₂ (PPh ₃)] ⁺ Cl ⁻ also L' analogue	46 48 41
<i>cis</i> -[M(CO) ₄ (L ^{Me})Q] M = Cr and Q = AsPh ₃ ; M = Mo and Q = LEt, LCH ₂ Ph, PPh ₃ , or py	41	<i>trans</i> -[Rh(L ^{Me}) ₂ (P) ₂] ⁺ Cl ⁻ P = PPh ₃ or PPhMe ₂	46,48
<i>fac</i> -[W(CO) ₃ (L ^{Me}) ₃] <i>fac</i> -[W(CO) ₃ (L ^{Me}) ₂ py] [Cr(CO) ₂ L ^{Me} (C ₆ H ₆ - η)]	41 41 41	[RhCO(L ^R) ₃] ⁺ Cl ⁻ , R = Me or Et	46
<i>cis</i> -[W(CO) ₄ L ^{Me} {C(O)Ph}] ⁻ Li ⁺ or [L ^{Me} H] ⁺	41	<i>cis</i> -[RhCl(COD)L ^R] R = H, Me, Et, Ph, <i>p</i> -Tol, or <i>p</i> -MeOC ₆ H ₄ also L' analogue	46 (H, 41) 41
[M(CO) ₂ (L ^R) ₂ X ₂] M = Mo and X = Cl, Br, or I, with R = Me or Et; M = W and X = I, with R = Me or Et	41	<i>cis</i> -[Rh(CH ₂ SiMe ₃)(COD)L ^p -Tol or Ph] [RhH(Cl)(L ^{Et}) ₂ SiCl ₃] ₂ <i>cis</i> -[Rh(COD)(L ^{Me}) ₂] ⁺ Cl ⁻	46 47 46
[M(CO) ₃ (L ^R) ₂ X ₂] M = Mo and X = I, with R = Me; M = W and X = Br or I, with R = Me or Et (for I)	41	[IrCOL ^{Me} {N=C(CF ₃) ₂ }]PPh ₃ [IrCO(L ^{Me}) ₃] ⁺ BF ₄ ⁻ [IrCOL ^{Me} (PPh ₃) ₂] ⁺ BF ₄ ⁻	44 44 44
[M(NO) ₂ (L ^R) ₂ X ₂] M = Mo and X = Br, with R = Me; M = W and X = I, with R = Et	41	<i>trans</i> -[NiCl(L ^{Me}) ₂ (PPhEt ₂)] ⁺ BF ₄ ⁻ [NiCl(L ^{Me}) ₃] ⁺ BF ₄ ⁻ <i>cis</i> -[PdCl ₂ L ^{Me} (P)] P = PET ₃ or P-n-Bu ₃	44 44 39,42
[W(CO) ₄ L ^{Me} X ₂] X = Br or I	41	<i>cis</i> - or <i>trans</i> -[PdCl ₂ L ^{Ph} (P)] P = PET ₃ or P-n-Bu ₃ also L'(PET ₃) analogue	39,42 41 44
[W(CO) ₃ L ^R Br ₃] ⁻ [L ^R -H] ⁺ R = Me or Et	41	<i>trans</i> -[PdCIL ^{Me} (PET ₃) ₂] ⁺ BF ₄ ⁻	44
[Fe(CO) ₄ L ^R] R = Me or Et	41	<i>cis</i> -[PdBr ₂ L ^{Ph} (P)] P = PET ₃ or P-n-Bu ₃	42
[Fe(CO) ₃ (L ^{Me}) ₂] <i>cis</i> - or <i>trans</i> -[Fe ₂ (CO) ₃ L ^R (C ₅ H ₅ - η)] R = Me or Et	41 41	<i>trans</i> -[PtCl ₂ L ^R (Q)] R = Me and Q = PET ₃ , P-n-Pr ₃ , P-n-Bu ₃ , or AsEt ₃ ; R = Ph and Q = PET ₃ , P-n-Bu ₃ , PPhMe ₂ or AsPh ₃ ; R = S and Q = PET ₃ or P-n-Bu ₃ also L'(PET ₃) analogue	39 41 41
[Ru ₃ (CO) ₁₁ L ^{Et}] [Ru(L ^R) ₄ Cl ₂] R = Me or Et	41 41		41

(Table continued)

TABLE I (continued)

CARBENEMETAL COMPLEXES FROM ELECTRON-RICH OLEFINS

Complex	Ref.	Complex	Ref.
<i>trans</i> -[PtBr ₂ L ^R (PEt ₃)] R = Me, Ph, or S	39,42	<i>trans</i> -[PtMe ₂ (L ^{Me})Q] Q = PEt ₃ or AsEt ₃	42
<i>cis</i> -[PtCl ₂ L ^R (Q)] R = Me and Q = P- <i>n</i> -Pr ₃ , P- <i>n</i> -Bu ₃ , PPhMe ₂ , or AsEt ₃ ; R = Ph and Q = PEt ₃ , P- <i>n</i> -Bu ₃ , PPhMe ₂ , or AsEt ₃ ; R = S and Q = PEt ₃ , P- <i>n</i> -Bu ₃ , or PPhMe ₂	39,42	<i>cis</i> -[PtMe ₂ (L ^{Me})Q] Q = PEt ₃ , PPh ₃ , PPhMe ₂ , or AsEt ₃	42,44
<i>cis</i> -[PtBr ₂ L ^R (PEt ₃)] R = Me, Ph, or S	39,42	<i>trans</i> -[PtCl(L ^{Me} (P) ₂] ⁺ BF ₄ ⁻ P = PEt ₃ or PPhMe ₂	42
<i>cis</i> - or <i>trans</i> -[PtR ₂ (LEt) ₂] R = 	41	<i>trans</i> -[PtHL ^{Me} (PEt ₃) ₂] ⁺ Cl ⁻ or BF ₄ ⁻ [PtX(L ^{Me}) ₃] ⁺ BF ₄ ⁻ X = H or Cl	42 44
or  : x = OMe or F; y = OMe or Me		<i>cis</i> -[PtCl(L ^{Me}) ₂ (PPh ₃)] ⁺ Cl ⁻ , I ⁻ , or BF ₄ ⁻ [Pt(σ-C ₃ H ₅)Cl(L ^{Me} (PPh ₃))] <i>cis</i> -[Pt(σ-C ₃ H ₅)(L ^{Me}) ₂ (PPh ₃)] ⁺ Cl ⁻ or BF ₄ ⁻ [Au(L ^{Me}) ₂] ⁺ Cl ⁻ or BF ₄ ⁻	44 44 44 44

Ni^{II}, Pd^{II}, Pt^{II} and Au^I (Table 1) [39,41-47]. The phosphine analogy is fortified by noting that these complexes have been prepared by (a) di- μ -chloro- or di- μ -bromo-dimetal bridge-splitting (Rh, Pd, Pt) [39,42,44,46,47]; (b) displacement of a neutral ligand (CO, PR₃, olefin, or L^R) [41,43-47], or (c) displacement of an anionic ligand (e.g., Cl⁻) [44,46]. Some examples are illustrated in Fig. 3. As we are here not concerned particularly with the chemistry of carbenemetal complexes, this is covered only briefly; complexes are made (a) directly from electron-rich olefins, or (b) from other carbene complexes. Illustrations of such reactions are in Figs. 3 and 4. Substitution reactions of

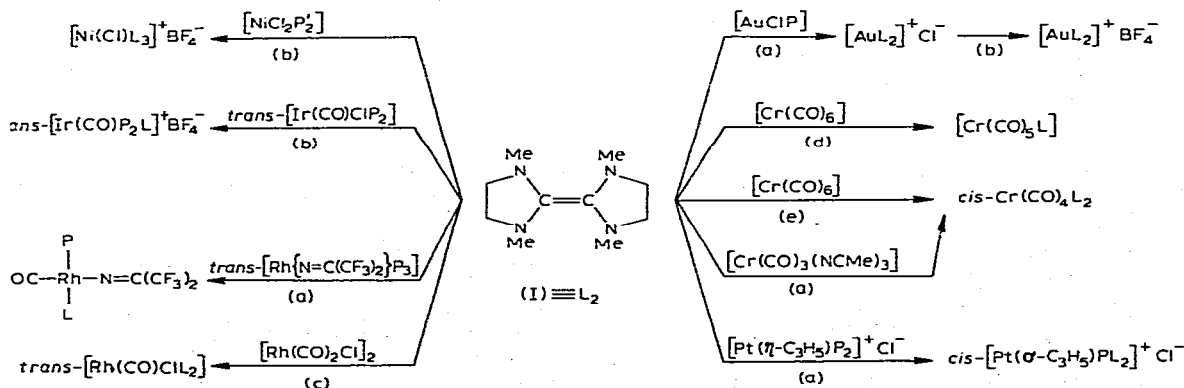


Fig. 3. Some transition metal complex reactions of the electron-rich olefin I (\equiv L₂) (P = PPh₃; P' = PPhEt₂). Reaction conditions: (a) PhMe, reflux, 5-20 min; (b) Me₂CO, NaBF₄, reflux, 3 h; (c) DMF, 110°C, 15-20 min; (d) MeC₆H₁₁, 100°C; (e) dekaline, 160°C, ¼ h.

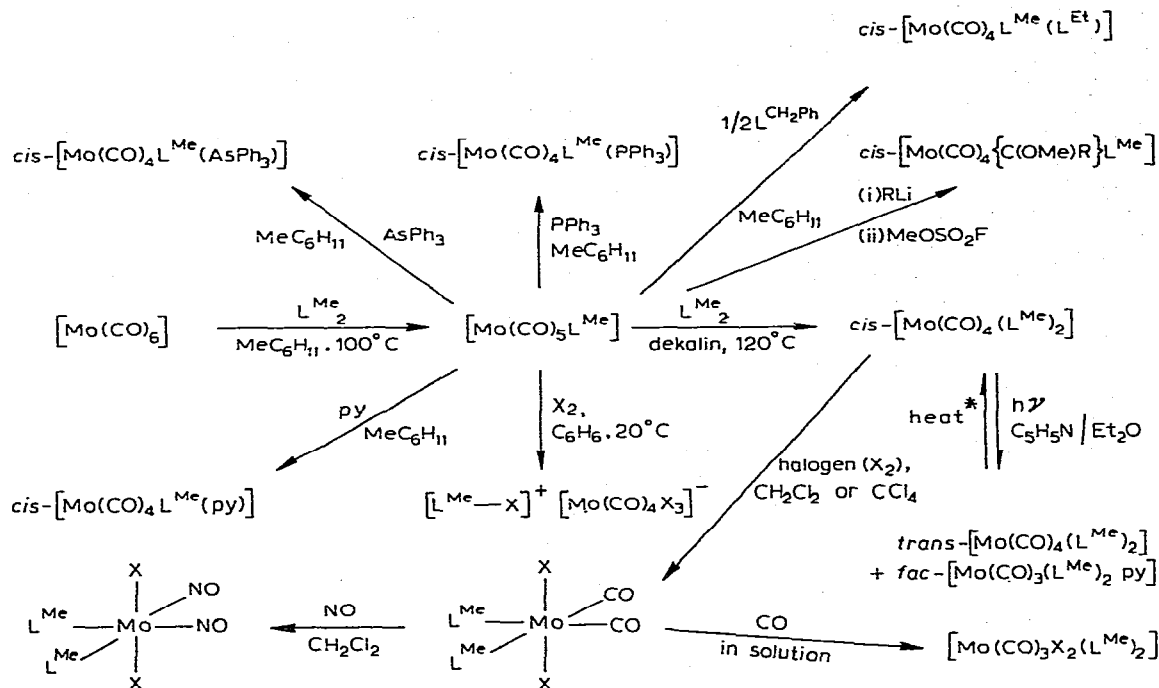


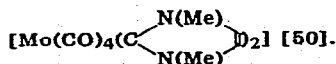
Fig. 4. Some reactions of a Group IV carbonyl(carbene)metal complex [41].

square-planar Rh^{I} complexes of type $[\text{RhCO}(\text{L}^{\text{R}})_n\text{P}_{2-n}\text{X}]$ ($n = 1$ or 2 and $\text{P} =$ a tertiary phosphine) with tertiary phosphines to give cationic carbene complexes $[\text{Rh}(\text{CO})(\text{L}^{\text{R}})_n\text{P}_{3-n}]^+\text{X}^-$ were shown to proceed by a two-step (i then ii) process: substitution with retention of configuration, and subsequent isomerisation, both sensitive to steric effects; an illustration is in eqn. 6.

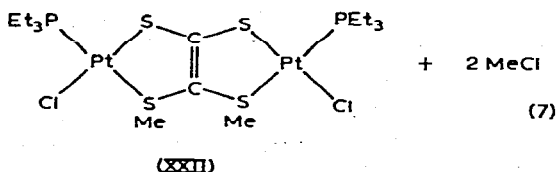
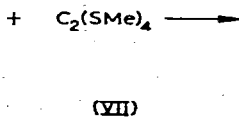
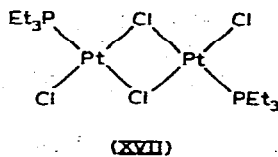
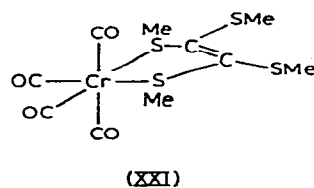
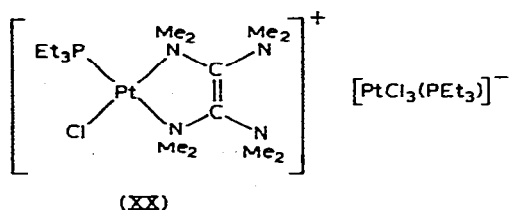
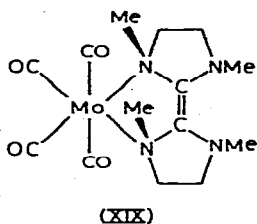
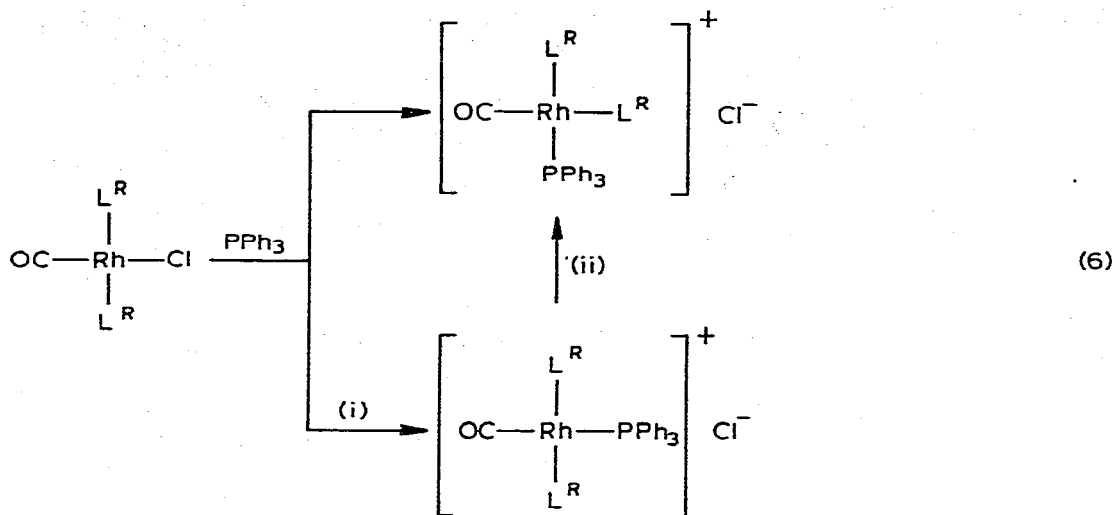
Detailed examination of the nature of the reactions of electron-rich olefins V-VIII with various transition metal complexes reveals a more complex pattern than that so far described. Firstly we may distinguish (i) chelate olefins, such as V and VII, and (ii) the open-chain compounds VI and VIII. For both class i and ii, we find reactions in which the C=C bond of the olefin is not cleaved and these may be of type a or b.

(a). Reactions in which the olefin becomes bound to the metal, forming a metallocycle in which 2 N's or 2 S's act as ligating atoms. At present, structural evidence for XIX [41], XX [51] and XXI [51], rests on analysis and ^1H and ^{13}C NMR spectra, but X-ray diffraction studies are in hand**. For the olefin VII, we have observed another reaction in which S—Me cleavage is observed (eqn. 7)

* Thermal isomerisations of this type and for *trans*- or *cis*- Pd^{II} or -Pt^{II} complexes can be followed by differential scanning calorimetry, to obtain quantitative data; reliable results are not yet to hand [49]; such thermal and photochemical isomerisations have also been demonstrated for



** Completed in XIX [52].



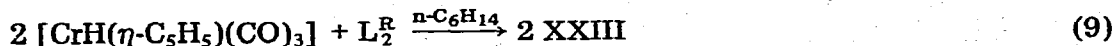
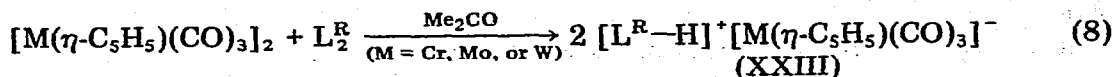
[52]. The structure of XXII was confirmed by a single crystal X-ray analysis. The bridging olefin fragment is intermediate between that found in XXI and a bridging bis(dithiolate). However, we have been unable to convert XXII into such a complex, which would require further loss of 2MeCl.

(b). Reactions in which the olefin is oxidised to the cation XII. The counterion has thus far been $[\text{V}(\text{CO})_6]^-$ [53], $[\text{M}(\eta\text{-C}_5\text{H}_5)(\text{CO})_3]^-$ ($\text{M} = \text{Cr}, \text{Mo}, \text{or W}$) [41,53], $[\text{Mn}(\text{CO})_5]^-$ [41], $[\text{Co}(\text{CO})_4]^-$ [41,53], and $[\text{CuCl}_2]^-$ [41], from respectively $\text{V}(\text{CO})_6$, $[\text{M}(\eta\text{-C}_5\text{H}_5)(\text{CO})_3]_2$, $\text{Mn}_2(\text{CO})_{10}$, $\text{Co}_2(\text{CO})_8$, and $(\text{CuCl})_n$.

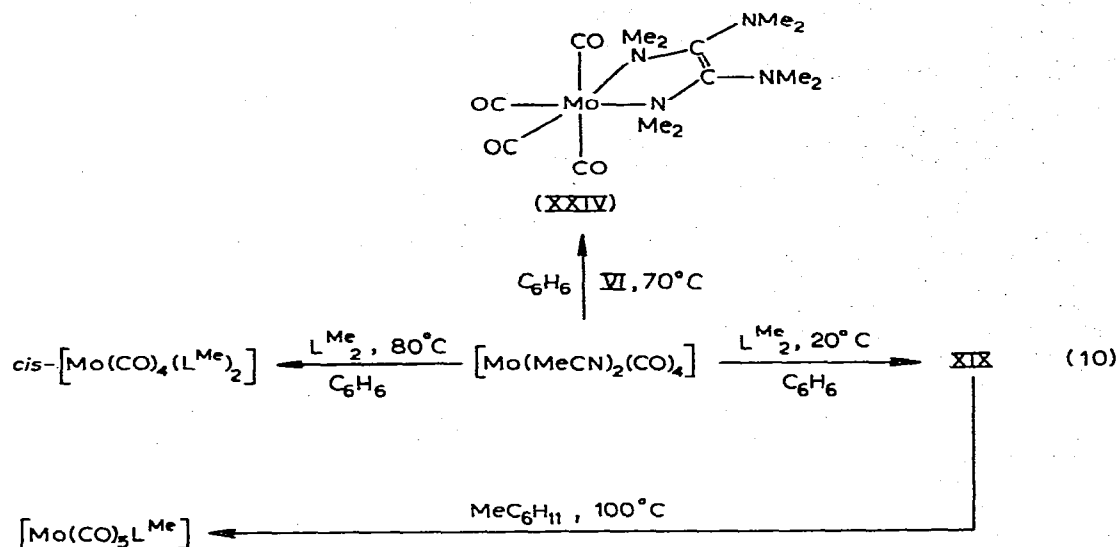
For class *i* only, we find, additionally, reactions in which the C:C olefinic bond is cleaved, and these may be of type *c* or *d*.

(c). Reactions in which nucleophilic-carbenemetal complexes are formed (vide supra).

(d). Reactions in which proton abstraction takes place from solvent (e.g., eqn. 8) or a metal hydride (e.g., eqn. 9) to give the cation XIV [41], or halogen abstraction takes place to form a cation related to XIV, $[\text{L}^{\text{R}}\text{-X}]^+$ (see Fig. 4) [41].



For the chelate olefins, e.g., V (class *i*) *N,N'*-metallocycles such as XXIV are formed under milder conditions than those required for C=C cleavage, as illustrated by eqn. 10 [41].



Reactions in which the olefin is a reducing agent clearly require the transition metal neutral substrate to have accessible stable neighbouring oxidation states: e.g., $[\text{Mo}^{\text{I}}] \rightarrow [\text{Mo}^0]^-$; $[\text{Mn}^0] \rightarrow [\text{Mn}^{-1}]$; or $[\text{Co}^0] \rightarrow [\text{Co}^{-1}]$. The $[\text{CuCl}_2]^-$ salt was formed, we believe, from Cl^-/CuCl , after initial $\text{L}_2^{\text{R}}/\text{CuCl}$ reaction (to give $[\text{L}_2^{\text{R}}]^{2+}(\text{Cl}^-)_2 + \text{Cu}$) [41]. Efforts to make a carbenetene(IV) complex, by treating L^{Me}_2 , L^{Et}_2 , or L^{Ph}_2 with Me_3SnCl , or related compounds, led to a complicated redox reaction, in which the radical cation $[\text{L}^{\text{Ph}}_2]^{\cdot+}$ and the ions $[\text{L}^{\text{R}}\text{-H}]^+$ and $[\text{Me}_3\text{SnCl}_2]^-$ were identified [54].

Complexes other than carbenometal compounds, which are directly accessible from electron-rich olefins are shown in Table 2.

C. Reactions of imidoyl chlorides with low valent transition metal complexes

The imidoyl chlorides are the nitrogen analogues of carboxylic acid chlorides. The transition metal chemistry of the latter is well-documented, whereas the nitrogen compounds had not been explored prior to our work, begun in 1971. Using a Rh^{I} substrate we observed that a carbenerhodium(III) complex could be isolated by one of two distinct processes, depending on whether the hydrogen chloride was rigorously excluded [55,56] or was present [55,57]. This is illustrated for the case of $[\text{Rh}(\text{CO})_2\text{Cl}]_2$ and $\text{PhC}(\text{Cl})=\text{NMe}$ in eqn. 11, and the derived carbene complexes are listed in Table 3. The structure of the iodo-analogue of XXV, $[\text{Rh}(\text{CO})\text{C}(\text{Ph})\text{NMeC}(\text{Ph})=\text{NMeI}_3]$, was confirmed by a single crystal X-ray analysis [56]. Possible reaction sequences

TABLE 2

OTHER TRANSITION METAL COMPLEXES FROM ELECTRON-RICH OLEFINS

Complex	Ref.	Complex	Ref.
<i>(a). Olefin complexes via 2 N's or 2 S's</i>		<i>(c). Electron-rich carbonium-ion salts</i>	
<i>cis</i> -[M(CO) ₄ (N,N'-LR ₂)] M = Mo and R = Me; M = W and R = Me or Et	41	[LMe-H] ⁺ [M(η-C ₅ H ₅)(CO) ₃] ⁻ M = Cr, Mo, or W or [W(CO) ₃ LMeBr ₃] ⁻	41
<i>cis</i> -[M(CO) ₄ {N,N'-C ₂ (NMe) ₂ (CH ₂) ₃ }] M = Mo or W	41	[LEt-H] ⁺ [Mo(η-C ₅ H ₅)(CO) ₃] ⁻ or [W(CO) ₃ LEtBr ₃] ⁻	41
<i>cis</i> -[Mo(CO) ₄ {N,N'-C ₂ (NMe) ₂ }]	41	[(CH ₂) ₃ N(Me) C-H N(Me)] ⁺ [M(η-C ₅ H ₅)- (CO) ₃] ⁻ M = Mo or W	41
<i>cis</i> -[Cr(CO) ₄ {S,S'-C ₂ (SMe) ₂ }]	51		
[PtCl(PEt ₃)SC=C(SMe)SMePtS- (PEt ₃)Cl] (XXII)	52	[LMe-X] ⁺ [Mo(CO) ₄ X ₃] ⁻ X = Br or I	41
<i>(b). [Olefin] 2⁺ complexes</i>		[LMe-X] ⁺ [W(CO) ₄ I ₃] ⁻	41
[C ₂ (NMe) ₂] ₂ ²⁺ [V(CO) ₆] ₂ ⁻ or [Mo(η-C ₅ H ₅)(CO) ₃] ₂ ⁻ or [Mn(CO) ₅] ₂ ⁻ or [Co(CO) ₄] ₂ ⁻ or [PtCl ₃ (PEt ₃)] ₂ ⁻ [LMe ₂] ₂ ²⁺ [M(η-C ₅ H ₅)(CO) ₃] ₂ ⁻ M = Cr, Mo, or W, or [Mn(CO) ₅] ₂ ⁻ or [Co(CO) ₄] ₂ ⁻ or [CuCl ₂] ₂ ⁻	41,53 41		
[(CH ₂) ₃ N(Me) C N(Me)] ²⁺ or [LEt ₂] ₂ ²⁺ [Mo- (η-C ₅ H ₅)(CO) ₃] ₂ ⁻			

are shown in Fig. 6. The overall reactions c are three-fragment oxidative reactions, but both the pathways a with a' (reactions of a coordinated imidoyl

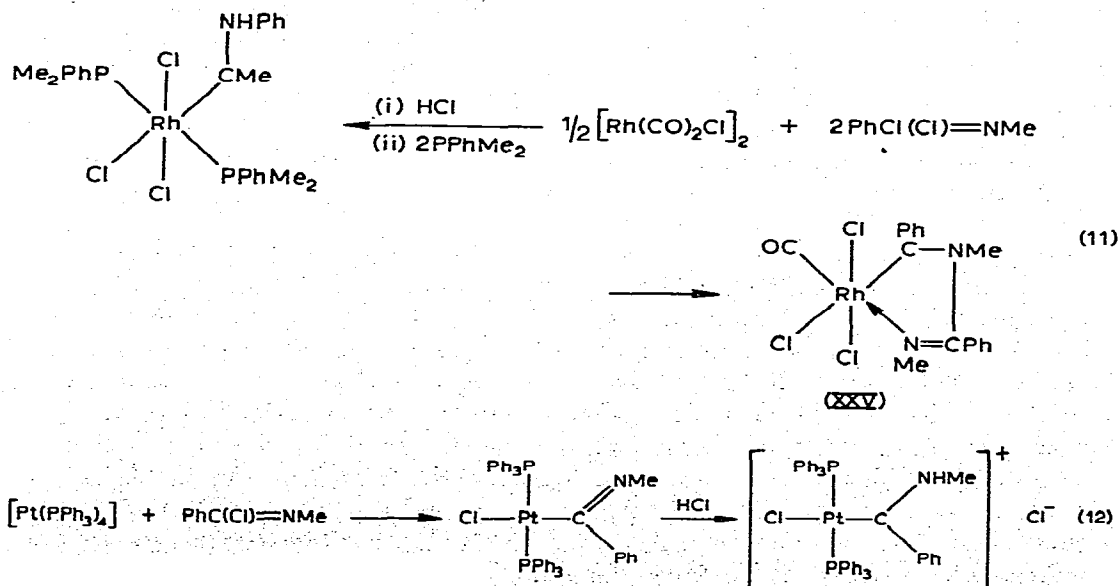


TABLE 3
CARBENE METAL COMPLEXES BY THREE-FRAGMENT OXIDATIVE ADDITION

Complex	Ref.	Complex	Ref.
(a) From an imidoyl chloride and HCl [Rh(CO)Cl ₃ {C(Ph)NHR}P] P = PPh ₃ and R = Me, Et, i-Pr, or o-Tol; P = PPh ₂ Me and R = Me	55,57	[RhCl ₃ (CHNR ₂)(P) ₂] R = Me, Et, or i-Pr and P = PPh ₃ or PEt ₃	59
[Rh(CO)Cl ₃ {C(Ph)NHR}] _n R = Me or i-Pr	55,57	[RhX ₃ (CHNMe ₂)(PPhMe ₂) ₂] X = Cl or Br	59
[Rh(CO)Cl ₃ {C(Me)NHTol-o}] _n	55,57	[Rh(CO)I ₃ (CHNMe ₂)] ₂	59
[RhCl ₃ {C(Me)NHTol-o}(PPhMe ₂) ₂]	55,57	[RhI ₃ (CHNMe ₂)(PEt ₃) ₂]	59
[PtCl{C(Ph)NHMe}(PPh ₃) ₂] ⁺ Cl ⁻	43	[PtCl ₄ (CHNMe ₂)(PEt ₃)]	58
(b) From an imidoyl chloride		[Ir(CO)Cl ₂ (CHNMe ₂)(PPh ₃) ₂] ⁺ Cl ⁻	54,63
[Rh(CO)X ₃ {C(Ph)N(Me)C(Ph)NMe}] X = Cl, Br, or I	55,56	[Ir(CO)Cl ₃ (CHNMe ₂)(PPh ₂ Me)]	54
[RhCl ₃ {C(Ph)N(Me)C(Ph)NMe}(PPhMe ₂) ₂]	55,56	[PtCl ₃ (CHNMe ₂)(PPhMe ₂)] ⁺ Cl ⁻	54
[Rh(CO)Cl ₃ {C(Ph)N(Et)C(Ph)NEt}]	55,56	(d) From (PhHN) ₂ CCl ₂ [Rh(CO)Cl ₃ {C(NHPh) ₂ }(PPh ₃)]	54,58
(c) From R ₂ NCHCl ₂		[Rh(CO)Cl ₃ {C(NHPh) ₂ }] ₂	54
[M(CO) ₅ (CHNMe ₂)] ^a (M = Cr or Mo)	58,59	[RhCl ₃ {C(NHPh) ₂ }(PPhR ₂) ₂] R = Me or Ph	54
cis-[Mn(CO) ₄ CH(CHNMe ₂)] ^a	78	(e) From Me ₂ NCCL ₃ [Cr(CO) ₅ (CCINMe ₂)] ^a	54
[Fe(CO) ₄ (CHNMe ₂)] ^a	58,59	[Rh(CO)Cl ₃ (CCINMe ₂) ₂]	54
[Rh(CO)Cl ₃ (CHNR ₂)] ₂ R = Me, Et, i-Pr, or n-Bu	59	[RhCl ₃ (CCINMe ₂)(PR ₃) ₂] R = Et or Ph	54
[Rh(CO)Cl ₃ (CHNR ₂)(PPh ₃)] R = Me, Et, or i-Pr	59		

^a By salt elimination.

ligand) or b with b' [reactions of a methyleneammonium salt, see Sect. II. D] have support. Thus the formation of coupled products, derived from two imidoyl chloride molecules per Rh atom, can only reasonably proceed by the former process. Moreover in the Pt⁰ → Pt^{II} system (eqn. 12) this procedure has been exemplified [43].

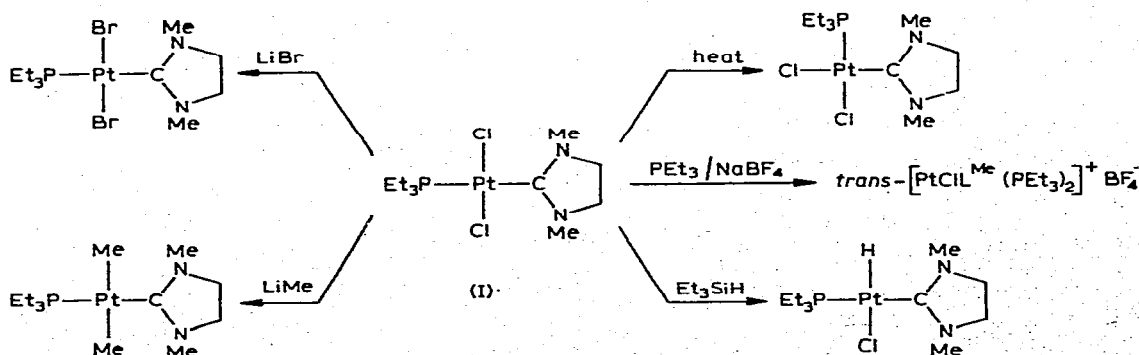


Fig. 5 Some reactions of a carbeneplatinum(II) complex [42].

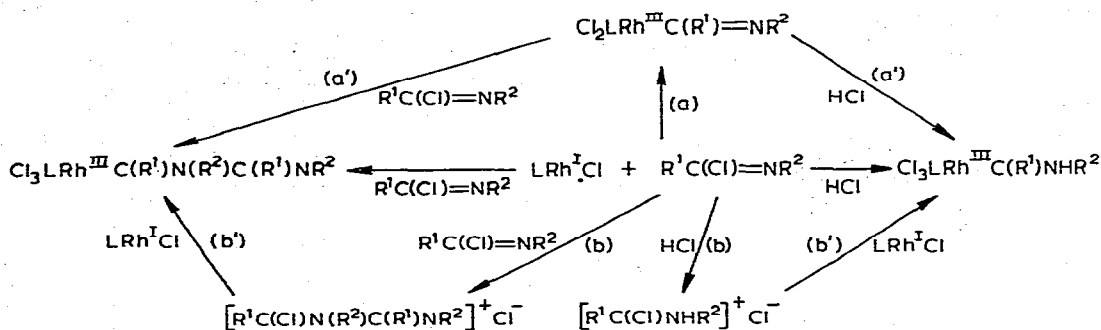


Fig. 6. Reaction sequences in imidoyl chloride/Rh^I systems leading to carbene complexes.

D. Oxidative addition reactions of low valent transition metal complexes with electron-rich geminal dihalides

The reaction of a dialkyl(chloromethylene)ammonium chloride R_2NCHCl_2 , R_2NCCl_3 , or $(R_2N)_2CCl_2$ [which has ionic character, (IX-XI)] and a Rh^I substrate leads similarly to the carbene product of a three-fragment oxidative addition [54,58,59]. Compounds of type XXVI (which has been confirmed by X-ray analysis [59]) were named secondary carbenemetal complexes to differentiate them from those which had both H's of CH_2 substituted, the tertiary complexes. The C-chlorocarbenemetal complexes, e.g., the C-chloro analogue of XXVI, $[RhCl_3\{CCl(NMe_2)\}(PEt_3)_2]$, [54], are also of interest, in part because they may be intermediates in Fischer's carbynemetal synthesis from alkoxy-carbenemetal precursors and BX_3 . In Fig. 7 are shown some reactions leading to carbenerhodium(III) complexes (these and others are listed in Table 3) from such electron-rich gem-dichlorides. Alternative reaction sequences are in Fig. 8. Secondary carbenemetal(0) complexes (Cr^0 , Mo^0 , Mn^I , Fe^0) [58,59,-

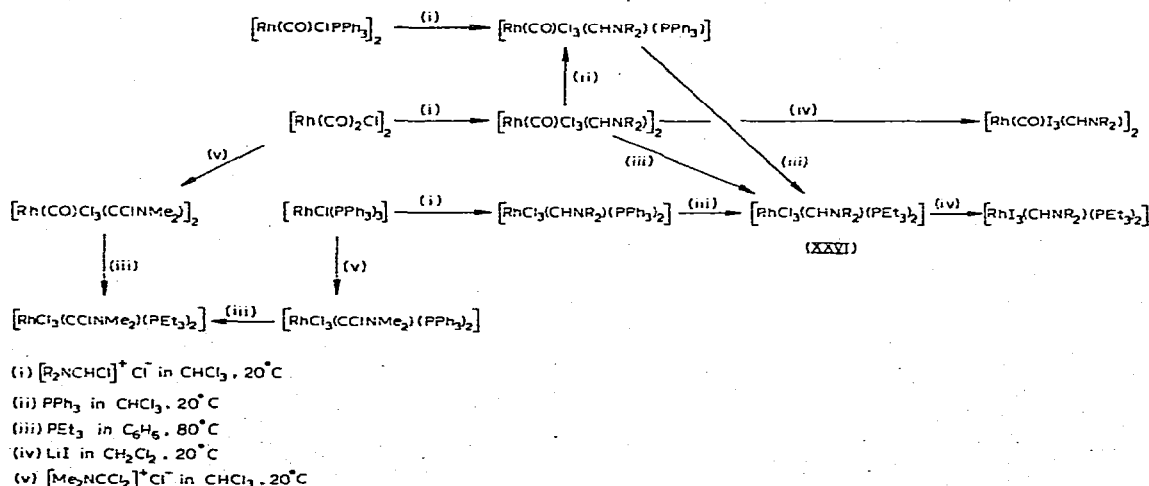
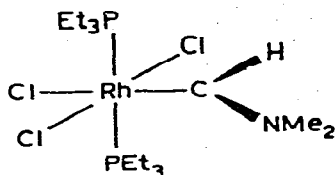


Fig. 7. Some reactions leading to Rh^{III} secondary carbene- or C-chlorocarbene-metal complexes.



(XXVI)

78] and $[\text{Cr}(\text{CO})_5(\text{CCINMe}_2)]$ [54] have also been made by salt elimination using $[\text{Mo}(\text{CO})_5]^{2-}$, $[\text{Mn}(\text{CO})_5]^-$ or $[\text{Fe}(\text{CO})_4]^{2-}$ as sodium salts.

There are analogies for some of these reactions. Thus, Öfele has used

$\text{Ph}\overline{\text{C}=\text{C}(\text{Ph})\text{CCl}_2}$ and $\text{Na}_2^+[\text{Cr}(\text{CO})_5]^{2-}$ to prepare $[\text{Cr}(\text{CO})_5(\text{C} \begin{smallmatrix} \text{Ph} \\ \diagup \\ \text{Ph} \end{smallmatrix})]$ [61] and has converted palladium metal to $[\text{PdCl}_2(\text{C} \begin{smallmatrix} \text{Ph} \\ \diagup \\ \text{Ph} \end{smallmatrix})]_2$ [60]; whereas chloromethylenammonium salts having the non-coordinating anion BF_4^- have yielded cationic thiazolocarbenometal complexes of Ir^{III} , Pd^{II} , or Pt^{II} from d^8 or d^{10} precursors [62].

Methylenammonium chlorides do not necessarily yield carbenometal products, as exemplified by eqns. 13 and 14 [54]. A parallel is with two-fragment oxidation of an alkyl halide RX to $[\text{Pt}(\text{PPh}_3)_3]$ which gives $[\text{PtX}(\text{R})(\text{PPh}_3)_2]^+$ unless steric effects supervene when $[\text{PtX}_2(\text{PPh}_3)_2]$ or $[\text{PtH}(\text{X})(\text{PPh}_3)_2]$ are obtained [33]. Some reactions of the secondary complexes are in eqns. 15-17 [54].

1,3-Dichloromalonilycyaminium chloride (XII) was expected to yield chelating dicarbene species. However, reaction with $[\text{Rh}(\text{CO})_2\text{Cl}]_2$ afforded complex XXVII, in which the ligand is considered to act as a bridge [54].

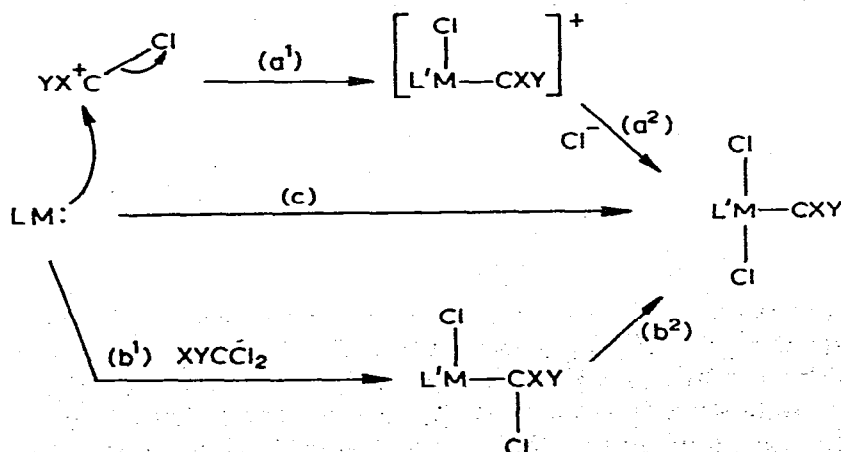
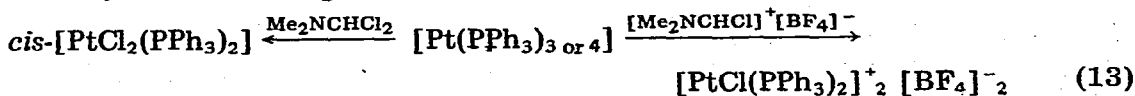
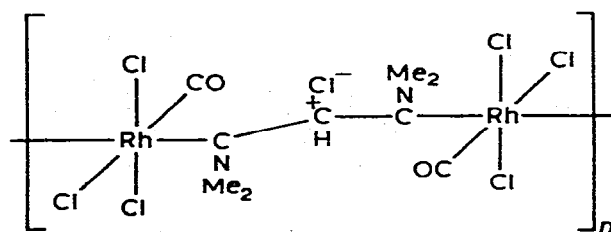
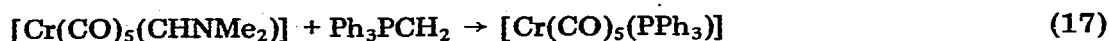
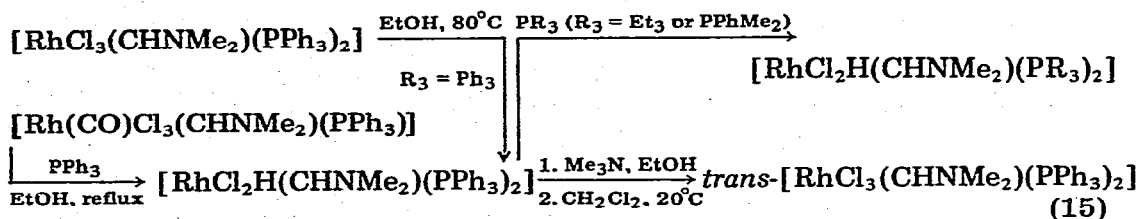
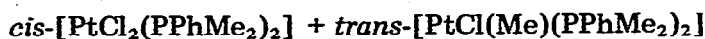
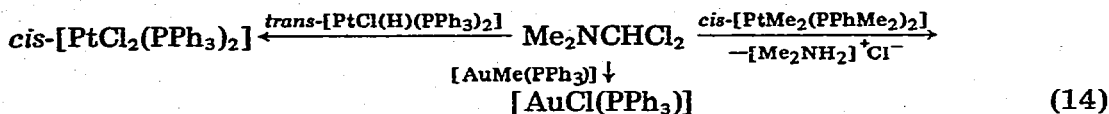


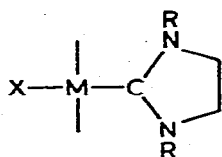
Fig. 8. Reaction sequences leading to three-fragment oxidative addition.



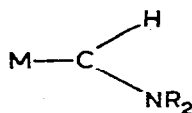
(XXVII)

E. Structural studies on carbenemetal complexes

In the more general context of carbenemetal chemistry, the earlier literature on this topic is dealt with elsewhere [1,2]. In so far as the complexes that we have prepared are concerned, the problem may be discussed with reference to XXV, XXVIII and XXIX.



(XXVIII)



(XXIX)

Crystal structures have been completed on the triiodo analogue of XXV [56], four compounds of type XXVIII and one of type XXIX: I and its *trans*-isomer [42,64], $[\text{RhL}^{\text{Me}}\{\text{N}=\text{C}(\text{CF}_3)_2\}(\text{PPh}_3)_2]$ [43], *cis*- $[\text{Mo}(\text{CO})_4(\text{L}^{\text{Me}})_2]$ [65], and XXVI [59]. These data show that the $\text{M}-\text{C}_{\text{carb}}$ bond is not particularly short, e.g., in the Pt^{II} complexes comparable to that in a platinum(II) alkyl [66]. This suggests that the $\text{M}-\text{C}_{\text{carb}}$ bond has little π -bond character. The nucleophilic car-

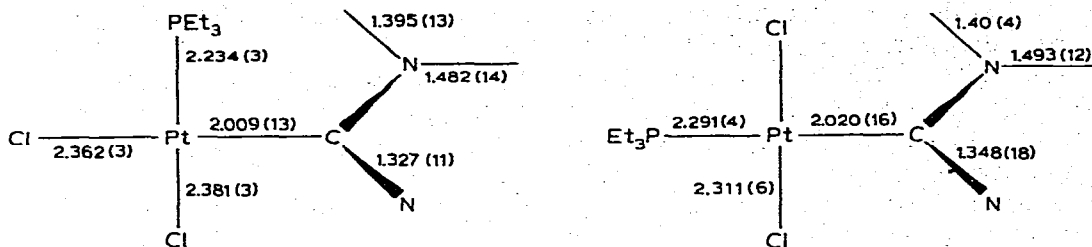


Fig. 9. Bond length data for isomeric complexes $[\text{PtCl}_2\text{L}^{\text{Ph}}(\text{PEt}_3)]$.

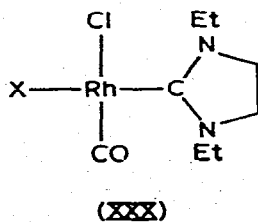
bene ligand, although a poor π -acceptor, must be a good σ -donor because it is difficult to displace from the metal coordination sphere. Comparison of Pt-Cl and Pt-P lengths in I and its *cis*-isomers (see Fig. 9 [42,64]) shows that the *trans*-influence is in the sequence carbene $\approx \text{PR}_3 > \text{Cl}^-$. The $\text{Rh}^{\text{III}}-\text{C}_{\text{carb}}$ bond length is very similar (1.96-1.97 Å) for secondary and tertiary carbene ligands. The $\text{C}_{\text{carb}}-\text{N}$ bond lengths are shorter than in carboxylic acid amides and shortest for the secondary carbene ligand; this shows there is considerable π -bond character in this bond. The coordination plane of the carbene ligand is approximately orthogonal to the coordination plane around the metal.

IR spectroscopic data are useful in a number of ways but $\nu(\text{C}\cdots\cdots\text{N})$ has diagnostic value: 1480-1520 cm^{-1} in tertiary carbenemetal complexes $\text{M}-\text{L}^{\text{R}}$, ca. 1600 cm^{-1} in secondary carbenemetal complexes, ca. 1660 cm^{-1} in $[\text{L}^{\text{R}}]^{2+}$ and ca. 1650 cm^{-1} in $[\text{L}^{\text{R}}-\text{H}]^+$ [41]. $\nu(\text{C}_{\text{carb}}-\text{H})$ is at ca. 3050 cm^{-1} [59]. Far IR assignments of $\nu(\text{PtCl}_2)$ in Pt^{II} complexes, such as those shown in Fig. 9, confirm that nucleophilic carbenes are similar to tertiary phosphines in their *trans*-influence [67].

NMR spectroscopic data serve to identify secondary carbene complexes, especially $\text{C}_{\text{carb}}-\text{H}$ at τ ca. -1 [59]. Variable temperature ^1H spectra in these show that the activation energy to rotation about the C-N bond is greater than in tertiary carbene complexes, and is outside the NMR range (i.e., $> 25 \text{ kcal mol}^{-1}$) [59]. Restricted rotation on the NMR time scale about the $\text{Rh}^{\text{I}}-\text{C}_{\text{carb}}$ bond in complexes $[\text{RhL}^{\text{Et}}(\text{Y})\text{Y}'(\text{Z})]$ has been demonstrated [45]; the ^1H Et signal belongs to the ABX_3 spin system at lower temperature which changes to A_2X_3 on heating. ($\text{M}-\text{C}$ hindered rotation had been observed in *cis*-

$[\text{Cr}(\text{CO})_4(\text{C}(\text{N}(\text{Me})\text{R})_2)]$ [68]. This observation promises to provide a new

approach to the study of the relative *trans*-influence of groups X in complexes such as XXX (in which X is a neutral ligand).



^{13}C NMR of neutral *cis*- and *trans*-monocarbene-palladium(II) and -platinum(II) complexes $[\text{MX}_2(\text{L}^{\text{R}})(\text{ER}'_3)]$ ($\text{X} = \text{Cl}, \text{Br}, \text{or I}$; $\text{E} = \text{P}$ or As) show that the chemical shift of C_{carb} (similar to that found in carbonium ions) is sensitive to the *trans*-ligand and that unusual long range ^{31}P — ^{13}C couplings are found to the ring methylene carbons [69]. The ^{13}C chemical shifts of the carbonyls are particularly useful in assigning stereochemistry in $[\text{M}(\text{CO})_4(\text{L}^{\text{R}})_2]$ [41]; for each of XIX and XXI the methyl signals are found as doublets, and the *cis*-arrangements of the N, N' -Me's in XIX is confirmed by the mutually *trans*-CO's shown as a doublet.

III. Stannylene- and plumbylene-transition metal complexes

By use of the bulky ligand $(\text{Me}_3\text{Si})_2\text{CH}^-$ (R^-) coloured Group IV dialkyls which are monomeric in benzene or cyclohexane have been obtained: SnR_2 [70], PbR_2 [70], and GeR_2 [71]. The coordination transition metal chemistry of the first of these has been explored. The dialkylstannylene is electron-rich, having a first IP of 7.42 eV, corresponding to 1 *5p* lone pair level (7.32 eV in PbR_2) [70]. Consequently it is a good nucleophile, superior to a tertiary phosphine. However, SnR_2 has a more complicated coordination chemistry than the latter, because of the greater tendency of Sn than P to achieve a higher valency state while still being able to bond to metal [72]. Reactions are thus classified into two types: (i) insertion reactions and (ii) simple dialkylstannylene Lewis base reactions. This is illustrated in Fig. 10 and exemplified in Table 4. The crystal structure of one such stannylene complex is complete (Fig. 11) [72], and shows three-coordinate trigonal tin, C(1), C(2), Cr and Sn being coplanar, with $r(\text{Sn}-\text{Cr})$ shorter than in $[t\text{-Bu}_2(\text{py})\text{Sn}-\text{Cr}(\text{CO})_5]$ [2.654(3) Å] [73], and $\text{C}_2\text{SnCRC}(51)\text{C}(53)\text{C}(54)\text{O}(51)\text{O}(53)\text{O}(54)$ essentially coplanar; this is suggestive of $\text{Cr}-\text{Sn}$ ($d \rightarrow p$) π -bonding [72]. The bis(stannylene) complexes have only been obtained in *trans*-form, no doubt due to the bulk of the ligands. ^{119}Sn Mössbauer spectra of the complexes of Table 4 show two classes: type (i) in which Sn is four-coordinate, isomer shifts are low ($1.49 \pm 0.25 \text{ mm s}^{-1}$ relative to BaSnO_3), and with low quadrupole splittings ($< 2.37 \text{ mm s}^{-1}$); and type (ii) in which Sn is three-coordinate, isomer shifts are high ($2.15 \pm 0.1 \text{ mm}$

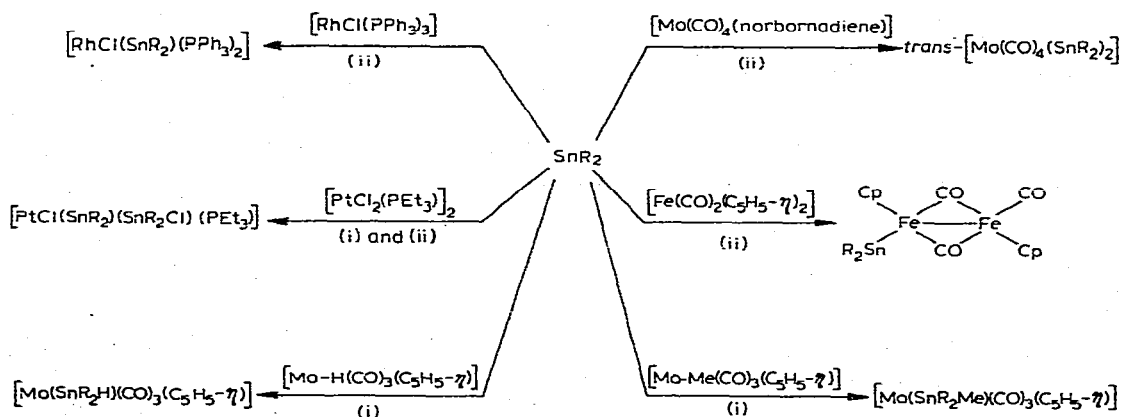


Fig. 10. Reactions of SnR_2 with some transition metal complexes.

TABLE 4
STANNYLENE TRANSITION METAL AND RELATED COMPLEXES

Complex ^a	Ref.	Complex ^a	Ref.
(a) Stannylene complexes [M(CO) ₅ (SnR ₂)] M = Cr or Mo	70,74,75	(b) Stannylene insertion products [Mo(CO) ₃ (C ₅ H ₅ -η)(SnR ₂ X)] X = H or Me	74,75
<i>trans</i> -[Cr(CO) ₄ (SnR ₂) ₂] M = Cr or Mo	70,74,75	[Fe(CO) ₄] ₂ SnR ₂	74,75
[Fe ₂ (CO) ₂ (C ₅ H ₅ -η) ₂ (SnR ₂)	74,75	[Fe(CO) ₂ (C ₅ H ₅ -η)] ₂ SnR ₂	75
[RhCl(SnR ₂)(PPh ₃) ₂]	74,75	[Fe(CO) ₂ (C ₅ H ₅ -η)(SnR ₂ X)] X = H, Cl, or Me	74,75
[PtCl(SnR ₂)(SnR ₂ Cl)(PEt ₃)]	74,75	[PtCl(SnR ₂)(SnR ₂ Cl)(PEt ₃)]	74,75
		(c) A plumbylene complex ^b [Mo(CO) ₅ (PbR ₂)]	75

^a R = (Me₃Si)₂CH. ^b [Cr(CO)₅(GeR₂)] has also been obtained [76].

s⁻¹), and unusually high quadrupole splittings (4.25 ± 0.2 mm s⁻¹) [74]. A feature of the dialkylstannylene complexes here described is their good hydrocarbon solubility, doubtless due to the presence of the many methyl groups.

IV. Conclusions and acknowledgements

I believe that the coordination chemistry of neutral Group IV donors other than CO and RNC is a rapidly developing field of much promise. Both electron-rich olefins and bulky dialkyl-stannylenes or -plumbylenes show aspects of their coordination chemistry which parallels that of tertiary phosphines with, however, considerable differences; accordingly much remains to

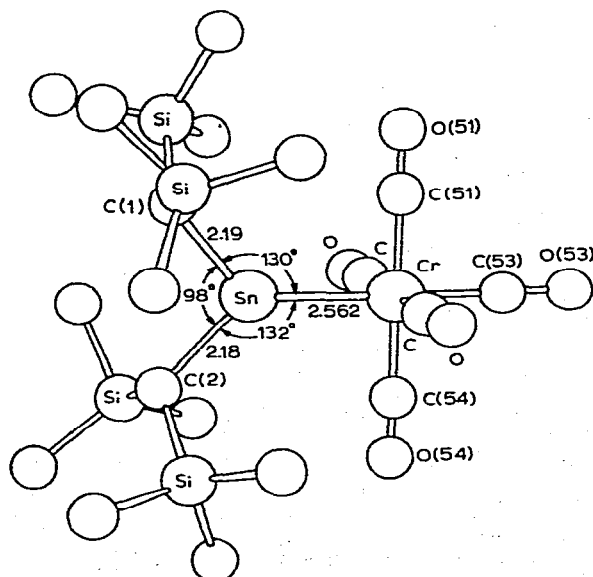


Fig. 11. The crystal and molecular structure of [Cr(CO)₅SnR₂] [72].

be accomplished, although many of the principal lines of development may already have emerged.

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