

THE ROLE OF GROUP 14 ELEMENT CARBENE ANALOGUES IN TRANSITION METAL CHEMISTRY

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A. INTRODUCTION AND CLASSIFICATION OF COMPLEXES

This article is concerned with the role of heavy group 14 element carbene analogues MX_2 in transition metal (M') chemistry ($\text{M} = \text{Ge}, \text{Sn}$ or Pb ; $\bar{\text{X}}$ is a bulky monohapto ligand: $\text{X} = \text{CHR}_2, \text{NR}_2, \text{OAr}^{\text{R}'}, \text{or } \text{SAr}^{\text{Bu}'}$; $\text{R} = \text{SiMe}_3$, $\text{Ar}^{\text{R}'} = \text{C}_6\text{H}_2\text{Bu}'_2\text{-2,6-R}'_4$, $\text{R}' = \text{H}, \text{Me}$ or Bu'). Various types of complexes, many of them containing an $\text{M}'\text{--M}$ bond, may result from reactions between the germylene, stannylene or plumbylene MX_2 and the transition metal compound $\text{L}_n\text{M}'\text{--X}'$, as illustrated in Scheme 1. Thus MX_2 may behave in one of seven principal ways, designated Type 1 to Type 7: MX_2 may act as either a terminal (Type 1) or bridging (Type 2) ligand; it may insert into an $\text{M}'\text{--X}'$ bond thus generating the new ligand $\text{MX}_2\text{X}'$ (Type 3); it may behave as an N -centred nucleophile with respect to a compound containing an $\text{M}'\text{--H}$ bond, thus generating a new MX_2 species in which $\text{X} = \text{M}'\text{L}_n$ (Type 4); it may act as an $\bar{\text{X}}$ transfer reagent (Type 5); if $\text{X} = \text{NR}_2$ ($\text{R} = \text{SiMe}_3$), it may oxidatively add to a low oxidation state M' centre by virtue of a C--H bond in $\text{M}(\text{NR}_2)_2$ with concomitant cyclometallation (Type 6); or it may function as a reducing agent (Type 7).

In Tables 1 and 2 we summarize data on transition metal complexes derived from various MX_2 precursors; typical syntheses are illustrated in Schemes 1–9 and eqns. (1)–(4).

There have been three reviews dealing with transition metal complexes based on MX_2 [1–3], of which two have dealt explicitly with the role of

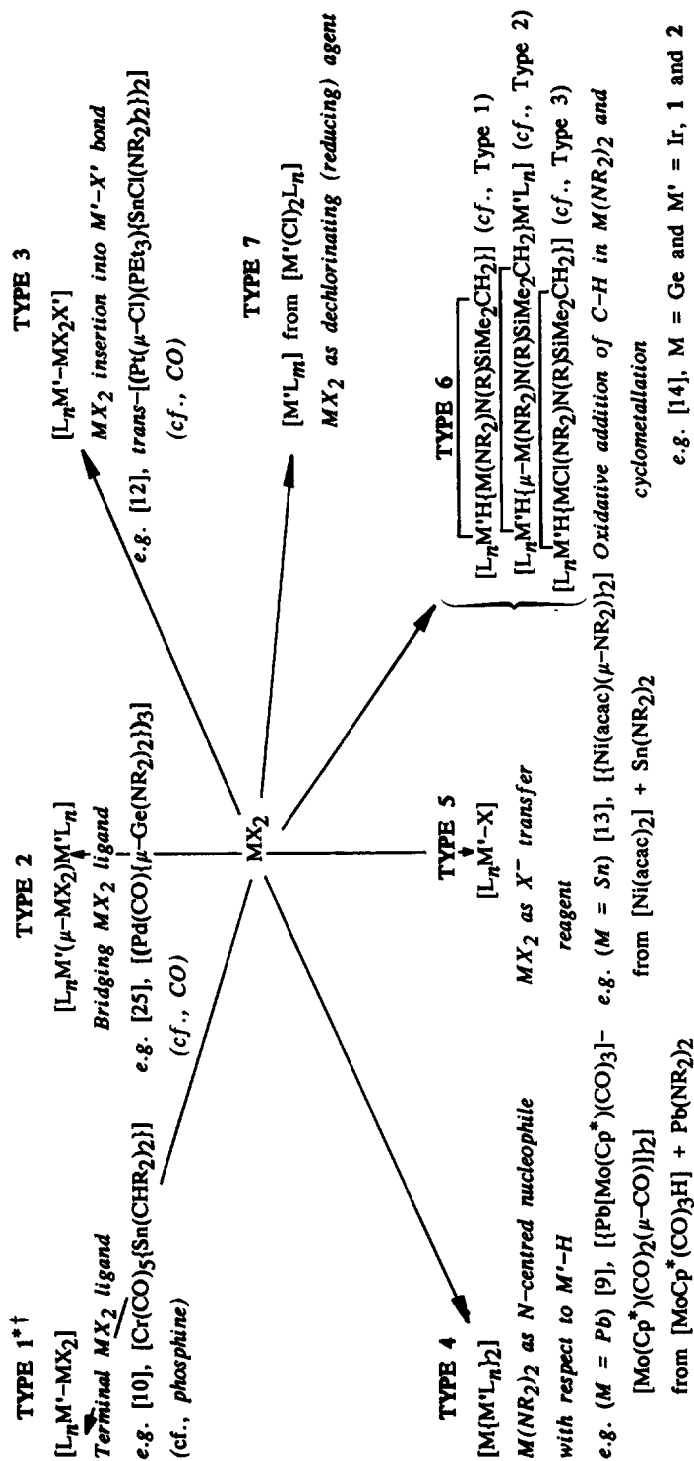
MX_2 as precursors for their complexes with transition metals [1,2]. Excluded from Tables 1 and 2 are complexes containing (i) SnHal_2 , e.g. $[\text{SnCl}_2\{\text{Co}(\text{CO})_4\}_2]$ [16]; (ii) SnHal_3 , e.g. $[\text{PtCl}(\text{PEt}_3)_2(\text{SnCl}_3)]$ and their germanium(II) or lead(II) analogues [17]; and (iii) a base adduct, e.g. $[\text{Cr}(\text{CO})_5\{\text{GeBr}_2(\text{NMe}_3)\}]$ [18]; these are well documented elsewhere [3,19] and fall outside the scope of the present work. Also excluded are complexes (iv) prepared from an $\text{M}(\text{IV})$ precursor ($\text{M} = \text{Ge}, \text{Sn}$ or Pb) by either reduction, e.g. $[\text{Fe}(\text{CO})_4\{\text{SnPh}_2(\text{THF})\}]$ [20], or oxidative addition, e.g. $[\text{PtCl}(\text{PPh}_3)_2\{\text{Sn}(\text{CH}_2\text{Ph})_2\text{Cl}\}]$ [21]; (v) containing a polymeric group 14 metal-centred ligand, e.g. $[\text{W}(\text{CO})_5\{\text{Sn}(\text{OH})_2\}]_n$ [22]; and (vi) containing a porphyrinato- M ligand, e.g. $[\text{Mn}(\text{CO})_5(\mu\text{-Hg})\text{Mn}(\text{CO})_4\{\text{Sn}(\text{tpp})\}]$ (tpp = tetraphenylporphinato) [58]. Some exceptions to the exclusions (i)–(vi) are made for X-ray characterized complexes.

The sole monomeric MX_2 precursors ($\bar{\text{X}}$ being a monohapto ligand) which have been used as sources of transition metal complexes have been those in which $\text{X} = \text{CHR}_2$ (a monomer in solution), NR_2 , $\text{OAr}^{\text{R'}}$ or $\text{SAr}^{\text{Bu'}}$ ($\text{R} = \text{SiMe}_3$; $\text{Ar}^{\text{R'}} = \text{C}_6\text{H}_2\text{Bu}'_2\text{-2,6-R'-4}$, $\text{R}' = \text{H}, \text{Me}$ or Bu'). Apart from the work by Cardin and collaborators (Scheme 8), such chemistry has emerged exclusively from our laboratory. (Added in proof: The paper by Veith, Stahl and Huch [81] reports on rhodium(I) complexes of $\text{SnN}(\text{Bu}')\text{SiMe}_2\text{NBu}'$ in which there is unusual Cl^- bridging of adjacent tin atoms.)

The first heavy group 14 element carbene analogue ("methylene")-derived transition metal complex was $[\text{Cr}(\text{CO})_5\{\text{MX}_2(\text{THF})\}]$ ($\text{MX}_2 = \text{GeMe}_2$, SnMe_2 or SnBu'_2), obtained in 1971 [7]. Such a complex is classified in Tables 1 and 2 as being of Type 1'. Related complexes may have the base stabilization provided by intramolecular neutral donor ligation, with M being in either a four-coordinate environment, as in $[\text{Cr}(\text{CO})_5\{\text{Sn}(\text{SCH}_2\text{CH}_2)_2\text{NBu}'\}]$ [6], or a five-coordinate environment, as in $[\text{Pt}(\text{PPh}_3)_2\{\text{Sn}(\text{acac})_2\}]$ (acacH = $\text{MeCOCH}_2\text{COMe}$) [8]. The first Type 1 complex derived directly from an MX_2 precursor was $[\text{Cr}(\text{CO})_5\{\text{Sn}(\text{CHR}_2)_2\}]$ ($\text{R} = \text{SiMe}_3$) [28], reported in 1974. A rather special case of a complex bearing a terminal MX_2 ligand is one in which there is a short bond between a ligand attached to the transition metal and M ; we refer to this as a Type 1'' complex, and it is exemplified by *cis*- $[\text{Rh}(\text{Cl})(\text{PPh}_3)_2\{\text{Sn}(\text{NR}_2)_2\}]$ in which there is a close $\text{Cl} \cdots \text{Sn}$ interaction; this was described in 1988 [68].

There are several complexes having MX_2 as a bridging ligand; the atom M can then be regarded as having become tetravalent. The Type 2 complexes $[(\text{M}'(\text{CO})\{\mu\text{-M}(\text{NR}_2)_2\})_3]$ ($\text{M}' = \text{Pd}$ or Pt , $\text{M} = \text{Ge}$ or Sn) were reported in 1985 [70]; they were obtained by treating the appropriate Type 1 precursor $[\text{M}'\{\text{M}(\text{NR}_2)_2\}_3]$ with carbon monoxide.

A coordinated MX_2 moiety may not only be stabilized by a neutral but



Scheme 1. The role of the heavy group 14 element carbene analogues MX_2 ($M = Ge, Sn$ or Pb ; $X = \bar{X}$ is a monohapto ligand) in transition metal (M') chemistry. Abbreviations: $R = SiMe_3$, $Cp^* = \eta - C_5Me_5$, $L_n =$ the sum of all other ligands within the coordination sphere of M' . * Type 1' refers to a complex containing a neutral base-stabilized terminal MX_2 ligand, e.g. $[Cr(CO)_5(Sn(Bu')_2(py))]$ [7]. † Type 1' refers to a chloro-transition metal complex containing a terminal MX_2 ligand in which the Cl^- is semi-bridging (short $Cl \cdots M$ distance), e.g. $cis - [Rh(Cl)(PPh_3)_2(Sn(NR_2)_2)]$ [68].

TABLE 1

Transition metal (M') complexes containing $M(NR_2)_2$ (M = Ge, Sn or Pb; R = SiMe₃) or a derivative

Complex ^a	Type	Comments	M' - M (Å)	Ref.
$[Sn(\eta-C_5H_5)_2Me\{Sn(NR_2)_2\}]$	1	IR, ¹ H NMR		1
$[M'(CO)_5\{M(NR_2)_2\}]$ (M' = Cr, Mo or W; M = Ge or Sn)	1	IR, ¹ H NMR		1
<i>trans</i> - $[M'(CO)_4\{M(NR_2)_2\}_2]$ (M' = Mo or W; M = Ge or Sn)	1	IR, ¹ H NMR		1
$[W(CO)_5\{Sn(C_{10}H_6NMMe_{1.8})_2\}]$	1'	IR, ¹ H NMR, X-ray; five-coordinate Sn	2.822(1)	82
$[Mn(CO)_5\{SnBr(NR_2)_2\}]$	3	IR, ¹ H NMR		1
$[Fe(\eta-C_5H_5)(CO)_2\{Sn(NR_2)_2X\}]$ (X = F, I or Me)	3	IR, ¹ H NMR		1, 4
$[Rh(\eta-PhMe)(\eta-C_2H_4)\{SnCl(NR_2)_2\}]$	3	¹ H NMR, X-ray	2.5637(8)	23
$[Rh(\eta-ArH)(\eta-alkene)\{SnCl(NR_2)_2\}_2]$ (alkene = <i>trans</i> -hex-3-ene, ArH = PhMe; alkene = C ₈ H ₁₄ , ^b ArH = C ₆ H ₆ , PhMe ^b or C ₆ H ₃ Me ₃ - 2,4,6)	3	¹ H NMR, X-ray	2.554(1)	24
$[(Rh(\mu-Cl)\{Sn(NR_2)_2\}_2)_2]$	1	¹ H NMR		24
$[Rh(cod)(L^{Me})\{SnMe(NR_2)_2\}]$	3	¹ H, ¹³ C and ¹¹⁹ Sn NMR		68
$[Rh(cod)(L^{Me})\{SnCl(NR_2)_2\}]$	3	IR, ¹ H, ¹³ C and ¹¹⁹ Sn NMR, X-ray	2.685(1)	68
$[Rh(cod)(PEt_3)\{SnCl(NR_2)_2\}]$	3	¹ H, ¹³ C, ³¹ P and ¹¹⁹ Sn NMR, X-ray	2.647(1)	68
$[Rh(cod)(\{Sn(NR_2)_2\}_2(\mu-Cl))]$	3	IR, ¹ H, ¹³ C and ¹¹⁹ Sn NMR; singly bridging Cl ⁻		68
$[Rh(cod)(\mu-Sn(NR_2)_2)\{SnCl(NR_2)_2\}_2]$	2, 3	¹ H, ¹³ C and ¹¹⁹ Sn NMR		68
<i>cis</i> - $[RhCl\{Ge(NR_2)_2\}(PPh_3)_2]$	1'' ^c	¹ H and ³¹ P NMR, X-ray (semi-bridging Cl ⁻ ; Ge...Cl, 2.723(4) Å)	2.39(1)	68
<i>cis</i> - $[Rh\{Sn(NBu')_2SiMe_2\}(\mu-Cl, Sn, Sn)(PPh_3)_2]$	1, 3	¹ H and ³¹ P NMR, X-ray; Cl ⁻ bridges the two tin atoms	2.576(2)	81

$[\text{Rh}\{\text{Sn}(\text{N}(\text{Bu}')_2\text{SiMe}_2)_3(\mu\text{-Cl}, \text{Sn}, \text{Sn})]$	1, 3	^1H and ^{31}P NMR, X-ray; trigonal bipyramidal Rh; $\cdot\text{Cl}^-$ bridges two tin atoms	2.526(1)– 2.568(1)	81
$[\text{Rh}(\text{CO})(\text{dppe})\{\text{SnCl}(\text{NR}_2)_2\}]$	3	IR, ^1H , ^{13}C , ^{31}P , ^{29}Si and ^{119}Sn NMR		68
<i>cis</i> - $[\text{RhCl}(\text{PPh}_3)_2\{\text{Sn}(\text{NR}_2)_2\}]$	1'' ^c	^1H and ^{31}P NMR, X-ray (semi-bridging Cl^- ; $\text{Sn}\cdots\text{Cl}$, 2.743(3) Å)	2.564(1)	23, 68
<i>trans</i> - $[\text{Rh}(\text{CO})(\text{PPh}_3)_2\{\text{SnCl}(\text{NR}_2)_2\}]$	3	IR and ^{119}Sn NMR		68
$[\text{Ir}\{\text{SnCl}(\text{NR}_2)_2\text{N}(\text{R})\text{SiMe}_2\text{CH}_2\}(\text{cod})\text{H}\{\text{Sn}(\text{NR}_2)_2\}]$	3/6	IR, ^1H , ^{13}C and ^{119}Sn NMR	2.325(3)	68
$\{[\text{CH}_2\text{Me}_3\text{SiN}(\text{R})(\text{NR}_2)\text{Ge}\}\text{Ir}(\mu\text{-Cl})_2\}$	1/6	^1H NMR, X-ray	2.468(3) _{av} 2.331(3)	14
$\{\text{Ge}(\text{NR}_2)\text{N}(\text{R})\text{SiMe}_2\text{CH}_2\}[\text{IrH}\{\text{Ge}(\text{NR}_2)_2\}]$	2/6			
$[\text{Ir}\{\text{GeCl}(\text{NR}_2)\text{N}(\text{R})\text{SiMe}_2\text{CH}_2\}(\text{CO})_2\text{H}\cdot\{\text{Ge}(\text{NR}_2)_2\}]$	1	^1H NMR, X-ray	2.460(1) 2.418(1)	14
<i>cis</i> - $[\text{Pd}(\eta\text{-C}_3\text{H}_5)\text{Cl}\{\text{M}(\text{NR}_2)_2\}]$ (M = Sn or Pb)	1	^1H NMR		1
<i>trans</i> - $[\text{Pd}(\text{CNBu}')_2\{\text{SnCl}(\text{NR}_2)_2\}]$	3	^1H NMR, X-ray	2.636(1)	13
$[\text{Pt}\{\text{M}(\text{NR}_2)_2\}(\text{PPh}_3)_2]$ (M = Ge or Sn)	1	^1H , ^{31}P , ^{195}Pt and (for M = Sn; no py adduct) ^{119}Sn NMR		68
<i>cis</i> - $[\text{Pt}(\text{cod})\{\text{SnCl}(\text{NR}_2)_2\}_2]$	3	^1H NMR		1
$[\text{Pt}(\mu\text{-Cl})\{\text{MCl}(\text{NR}_2)_2\}(\text{PEt}_3)_2]$ (M = Ge, Sn ^b or Pb; <i>cis</i> or <i>trans</i> ^b)	3	^{31}P NMR, X-ray	2.534(1)	1, 12
$[\text{M}'\{\text{M}(\text{NR}_2)_2\}_3]$ (M' = Pd, M = Ge or Sn ^b ; M' = Pt, M = Ge or Sn ^b)	1, 7(Pd)	^{195}Pt and ^{119}Sn NMR, X-ray	2.53(1) _{av} 2.487(6) _{av}	5, 12
$[(\text{M}'\text{CO})\{\mu\text{-Sn}(\text{NR}_2)_2\}_3]$ (M' = Pd, M = Ge or Sn ^b ; M' = Pt, M = Ge or Sn ^b)	1	^{195}Pt and ^{119}Sn NMR, X-ray	2.621(5) _{av} 2.620(4) _{av}	25, 70

^a Abbreviations: R = SiMe₃, L^{Me} = $\text{C}(\text{N}(\text{Me})(\text{CH}_2)_2\text{NMe})$ and cod = cycloocta-1,5-diene.

^b Designates those of the series which have been X-ray characterized.

^c Type 1'' refers to a complex having a terminal MX_2 ligand, but in which there is also $\text{M}\cdots\text{ClM}'$ semi-bridging.

TABLE 2

Transition metal (M') complexes containing group 14 metal (M)-centred ligands other than $M(NR_2)_2$ (M = Ge, Sn or Pb; R = SiMe₃)

Complex ^a	Type	Comments	M' - M (Å)	Ref.
$[Cr(CO)_5\{Ge(C_6H_5Me_3-2,4,6)_2(L)\}]$ (L = absent or THF)	1, 1' ^c	IR, ¹ H NMR		26
$[M'(CO)_5\{M(CHR_2)_2\}]$ (M' = Cr, M = Ge or Sn ^b , M' = Mo, M = Sn or Pb)	1	IR, ¹ H NMR, ¹¹⁹ Sn Mössbauer, X-ray	2.562(5)	10, 27, 28
<i>trans</i> - $[M'(CO)_4\{M(CHR_2)_2\}_2]$ (M' = Cr, M = Ge, M' = Cr or Mo, M = Sn)	1	IR, ¹ H NMR, ¹¹⁹ Sn Mössbauer		10, 29
$[Mo(\eta-C_3H_5)(CO)_3\{Sn(CHR_2)_2X\}]$ (X = H or Me)	3	IR, ¹ H NMR, ¹¹⁹ Sn Mössbauer		10, 28
$[W(CO)_2(S_2CNR'_2)_2\{Sn(CHR_2)_2\}]$ (R' = Me or Et)	1	IR, ¹ H and ¹¹⁹ Sn NMR		69
$[Cr(CO)_5\{Sn(Bu')_2(py)\}]$	1' ^c	IR, ¹ H NMR, ¹¹⁹ Sn Mössbauer, X-ray (Sn ^{IV} precursor)	2.653(3)	7
$[M'(CO)_5\{M(\eta-C_3Me_5)Cl\}]$ (M' = Cr, M = Ge or Sn; M' = W, M = Ge ^b or Sn)	1	IR, ¹ H and ¹³ C NMR, X-ray	2.511(1)	31, 32
$[W'(CO)_5\{Ge(\eta-C_3Me_5)R'\}]$ (R' = Me, CHR ₂ ^b or NR ₂)	1	IR, ¹ H, ¹³ C and ²⁹ Si NMR, X-ray	2.632(2)	31
$[M'(CO)_5\{Ge(\eta-C_3H_5)Cl(THF)\}]$ (M' = Cr or W)	1' ^c	IR, ¹ H NMR		32
$[Cr(\eta-C_3H_5)(CO)_5(SnPh_3)]$	3	IR, ¹ H NMR, X-ray	2.85	33
$[M'(CO)_5\{Ge(NPh_2)_2(L)\}]$ (M' = Cr, L = absent; M' = W, L = absent, py or HNPh ₂)	1' ^c	IR, ¹ H NMR		18
$[W(CO)_5\{Ge(NPr_1^i)Cl(py)\}]$	1' ^c	IR, ¹ H NMR		18
$[M'(CO)_5\{Sn(\mu-NMe_2)(NMe_2)\}_2]$ (M' = Cr, Mo or W)	1' ^c	IR (monomeric THF adduct exists in THF solution)		34
$[M'(CO)_5\{Sn(NBu')_2SiMe_3\}]$ (M' = Cr, Mo or W)	1	IR, ¹ H NMR		35
$[Cr(CO)_5\{Ge(SR')_2(L)\}]$ (R' = Me, Et, Ph or CH ₂ Ph, L = absent or N=S(CH) ₆ H ₄ -4)	1, 1' ^c	IR, ¹ H NMR		36, 37
$[M'(CO)_5\{Ge(SC_6H_5Me_3-2,4,6)_2(L)\}]$ (M' = Cr, L = absent ^b , NMe ₃ , py, PPh ₃ or N=S(CH) ₆ H ₄ -4; M' = W, L = absent)	1, 1' ^c	IR, ¹ H NMR, X-ray	2.367(2)	18, 36, 37
$[Cr(CO)_5\{Sn(SCH_2CH_2)_2NBu'\}]$	1' ^c	IR, ¹ H and ¹³ C NMR, X-ray	2.622(1)	7

$[\text{Cr}(\text{CO})_3\{\text{Sn}(\text{SC}_6\text{H}_4\text{Bu}'_3-2,4,6)_2\}]$	1	IR, ^1H NMR	38, 79
$[(\text{M}'(\text{CO})_5\{\text{SnCl}(\mu\text{-SBu}')\})_2] (\text{M}' = \text{Cr or W})$	$1'^c$		39
$[\text{Cr}(\text{CO})_3\{\text{Sn}(\text{SCH}_2\text{CH}_2)_2\text{-PPh}\}]$	$1'^c$	^{13}C , ^{31}P and ^{119}Sn NMR	41
$[\text{W}(\text{CO})_5\{\text{Sn}(\text{SCH}_2\text{CH}_2)_2\text{X(L)}\}] (\text{X} = \text{O, S or NMe, L = absent or py; X = NBU}', \text{L = absent})$	$1'^c$	IR, ^1H , ^{13}C , ^{15}N and ^{119}Sn NMR	40
$[\text{W}(\text{CO})_5\{\text{Sn}(\text{C}_6\text{H}_4\text{Bu}'_3-2,4,6)_2\}]$	1	IR, ^1H NMR	79
$[\text{W}(\text{CO})_5\{\text{Sn}(\text{C}_6\text{H}_4\text{PPh}_2-2)_2\}]$	$1'^c$	^{13}C , ^{31}P and ^{119}Sn NMR, ^{119}Sn Mössbauer	42
$[(\text{M}'(\text{CO})_5\{\text{Sn}(\mu\text{-OCH}_2\text{CH}_2\text{N(R')CH}_2\text{CH}_2\text{O}))_2] (\text{M}' = \text{Cr, Mo or W; R}' = \text{Me or Bu}')$	$1'^c$	IR, ^1H , ^{13}C , ^{15}N and ^{119}Sn NMR	40
$[(\text{M}'(\text{CO})_5\{\text{Sn}(\text{NCS})_2\})] (\text{M}' = \text{Cr or W})$	1	IR	43, 44
$[(\text{M}'(\text{CO})_5\{\text{M}(\text{OCOCH}_3)_2[\text{O}(\text{COCH}_3)_2]\})] (\text{M}' = \text{Cr, Mo or W; M} = \text{Sn or Pb})$	$1'^c$	IR	43–45
$[(\text{M}'(\text{CO})_5\{\text{Sn}(\text{OH})_2(\text{THF})\})] (\text{M}' = \text{Cr or W})$	$1'^c$	IR, ^{119}Sn NMR, stable in THF solution (base-free species is polymeric)	22
$[(\text{M}'(\text{CO})_5\{\text{Sn}[\text{OC}(\text{NMe}_2)_2\text{Fe}(\text{CO})_4]\})] (\text{M}' = \text{Cr, Mo or W})$	$1'^c$	IR, ^1H and ^{13}C NMR	34
$[(\text{Cr}(\text{CO})_5\{\text{Sn}(\mu\text{-OSiMe}_3)(\text{OSiMe}_3))_2]$	$1'^c$	IR	46
$[(\text{W}(\text{CO})_5\{\text{Sn}(\mu\text{-OSiPh}_3)(\text{OSiPh}_3))_2]$	$1'^c$	IR, ^{13}C and ^{119}Sn NMR	46
$[(\text{M}'(\text{CO})_5\{\text{Sn}(\text{OC(R')CHC(R'')O})_2\})] (\text{M}' = \text{Cr, Mo or W, R}' = \text{R}'' = \text{Me or CF}_3, \text{ or R}' = \text{Me and R}'' = \text{Ph, or R}' = \text{Me and R}'' = \text{CF}_3)$	$1'^c$	IR, ^1H and ^{19}F NMR	47, 48
$[\text{W}(\text{CO})_5\{\text{M}[\text{W}(\text{CO})_5]_2(\text{L})\}] (\text{M} = \text{Ge, L = absent}^b, \text{M} = \text{Sn, L = absent}^b \text{ or THF}^b)$	1/4	IR, X-ray (shortest W–M distances); M^{IV} precursor	49, 50
$[\text{Sn}\{\text{M}'(\text{CO})_5\}_2] (\text{M}' = \text{Cr or W})$	4	IR, linear $\text{M}'\text{–Sn–M}'$ array; Sn^{IV} precursor	2.505(2) 2.702(2) 2.713(2)
$[\text{Pb}\{\text{Mo}(\text{R}')(\text{CO})_3\}_2(\text{L})] (\text{R}' = \eta\text{-C}_5\text{H}_5, \eta\text{-C}_3\text{H}_3(\text{SiMe}_3)_{2-1,3} \text{ or } \eta\text{-C}_3\text{Me}_5^b; \text{L} = \text{absent or THF})$	$4'^c, 4$	IR, X-ray; base-free species ^d is dimeric in the solid state	2.935(1) ^d 2.989(1) ^d 2.989(2) 3.019(2)
$[(\text{M}'(\eta\text{-C}_5\text{H}_5)(\text{CO})_3\{\text{Sn}(\text{PR}'_2)_2\text{CX}\})] (\text{M}' = \text{Mo, R}' = \text{Me, X} = \text{SiMe}_3; \text{M}' = \text{W, R}' = \text{Ph, X} = \text{PPh}_2)$	$4'^c$	^{31}P and ^{119}Sn NMR	52

TABLE 2 (continued)

Complex ^a	Type	Comments	M' - M (Å)	Ref.
[Mn(η-C ₃ H ₄ Me)(CO) ₂ (Sn{OC(R')CHC(R'')O) ₂ }] (R' = R'' = Me, CF ₃ or Ph; R' = Me and R'' = Ph or CF ₃)	1' ^c	IR		53
[Mn(η-C ₃ H ₄ R')(CO) ₂ (M(Mn(η-C ₅ H ₄ R')(CO) ₂) ₂)] (M = Ge, R' = H ^b or Me ^b ; M = Sn, R' = Me ^b ; M = Pb, R' = Me ^b)	1/4	IR, X-ray (shortest Mn-M distances); M ^{IV} precursor	2.250(1) 2.260(2) 2.424(8) 2.490(1)	54-57
[M(Mn(η-C ₃ R ₄ R'')(CO) ₂) ₂](M = Ge, R' = H, R'' = Me ^b or R' = R'' = Me ^b ; M = Pb, and R' = R'' = H ^b)	4	IR, X-ray, linear Mn-M-Mn array; M ^{IV} precursor	2.204(1) 2.18(2) 2.463(1)	54, 55, 59, 60
[Fe(η-C ₃ H ₅)(CO)(μ-CO) ₂ Fe(η-C ₃ H ₅){Sn(CHR ₂) ₂ }] [Fe(η-C ₃ H ₅)(CO) ₂ {Sn(CHR ₂) ₂ X}](X = F, Cl, Br, I, OMe, H or Me)	1 3	IR IR, ¹ H and ¹¹⁹ Sn NMR, ¹¹⁹ Sn Mössbauer		10(a), 28 10, 28, 30
[Os ₃ Sn(μ-H) ₂ (CO) ₁₀ (CHR ₂) ₂] [(Fe(CO) ₄) ₂ {μ-Sn(CHR ₂) ₂ }] [(Fe(CO) ₃ {μ-Sn(CHR ₂) ₂ }) ₂] [M ₃ (CO) ₉ (μ-CO){μ-Sn(CHR ₂) ₂ }] (M' = Ru ^b or Os ^b)	1' ^c 2 2 2	Ir, ¹ H NMR, X-ray IR, ¹ H NMR, ¹¹⁹ Sn Mössbauer X-ray, details unpublished X-ray	2.658(1)	61 10, 11, 28 11 11
[Os ₃ (CO) ₈ (μ-dppm){μ-Sn(CHR ₂) ₂ }]	2	IR, X-ray, asymmetric Sn bridges	2.735(2) _{av} 2.732(7) _{av} 2.870(3) _{av} 2.650(3) _{av}	62
[Fe(CO) ₄ {M(OC ₆ H ₂ Bu ₂ -2,6-Me-4) ₂ }] (M = Ge ^b or Sn ^b)	1	IR, ¹ H NMR, X-ray	2.240(2) 2.408(1)	63
[Fe(CO) ₄ {Sn{OC(R')CHC(R'')O) ₂ (py)}](R' = Me, R'' = Ph or CF ₃ ; R' = R'' = CF ₃)	1' ^c	IR, ⁵⁷ Fe Mössbauer		48
[(Fe(CO) ₄) ₂ (μ-Sn{OC(Me)CHC(Ph)O) ₂ }]	2' ^c	IR		64

$[\text{Fe}(\text{CO})_4(\text{Sn}(\eta\text{-C}_5\text{H}_5(\text{CO})_2)_2(\text{L}))]$ (L = absent ^b , THF or py ^b)	1/4	IR, ^1H , ^{13}C and ^{119}Sn NMR, X-ray(isocarbonyl-bridged dimer in the solid state) ^d (shortest Fe-Sn distances); Sn^{IV} precursor	2.527(1) ^d 2.581(1)	69
$[\text{Cr}(\text{CO})_5(\text{Sn}(\eta\text{-C}_5\text{H}_5(\text{CO})_2)_2)]$	1/4	IR, ^1H and ^{13}C NMR, X-ray (isocarbonyl-bridged dimer in the solid state) ^c ; Sn^{IV} precursor	2.624(1) (Cr) 2.570(1) (Fe) 2.550(2) (Fe)	69
$[\text{Ge}(\text{Co}(\text{CO})_4)\text{X}]$ (X = F or $\text{Co}(\text{CO})_4$)	4	IR, trapping with 1,3-dimethyl- buta-1,3-diene		65
<i>cis</i> - $[\text{RhCl}(\text{PPh}_3)_2\{\text{Sn}(\text{CHR}_2)_2\}]$	1	^1H , ^{31}P and ^{119}Sn NMR		10(a), 28, 68
<i>cis</i> - $[\text{RhCl}(\text{PPh}_3)_2\{\text{Sn}(\text{OC}_6\text{H}_4\text{Bu}'_2-2,6)_2\}]$	1	^1H and ^{31}P NMR		68
$[\text{PtCl}(\text{PEt}_3)\{\text{Sn}(\text{CHR}_2)_2\}(\text{SnCl}(\text{CHR}_2)_2)]$ (<i>cis</i> or <i>trans</i>)	1, 3	IR, ^1H and ^{31}P NMR, ^{119}Sn Mössbauer		10, 22, 28
<i>trans</i> - $[\text{Pt}(\mu\text{-Cl})(\text{PEt}_3)\{\text{SnCl}(\text{CHR}_2)_2\}]_2$	3	^{31}P NMR		22
$[\text{Ni}(\text{CO})_3\{\text{Sn}(\mu\text{-OSiMe}_3\text{XOSiMe}_3)_2\}]$	1' ^c	IR		46
$[\text{Ni}(\text{CO})_3\{\text{M}(\mu\text{-OBu}')(\text{OBu}')_2\}]$ (M = Ge ^b or Sn)	1' ^c	IR, ^{13}C and ^{119}Sn NMR, X-ray	2.283(2)	46, 66
$[\text{Pt}(\text{PPh}_3)_2\{\text{Sn}(\text{acac})_2\}]_2$	1' ^c	^{31}P , ^{119}Sn and ^{195}Pt NMR, X-ray	2.558(1) _{av}	8
$[\text{Pt}_2(\text{PPh}_3)_2\{\mu\text{-Sn}(\text{acac})_2\}]_3$	2' ^c	^{31}P , ^{119}Sn and ^{195}Pt NMR, X-ray	2.680(1) _{av}	8
$[\text{PtH}(\text{PEt}_3)\text{XSnR}'_2\{\mu\text{-O}(\text{R}'')\text{SnR}'_2\}_2\text{X}(\text{SnR}'_3)]$ (R' = $\text{C}_6\text{H}_4\text{Me}-4$, R'' = H or Me ^b)	1' ^c , 3	IR, ^1H , ^{31}P and ^{119}Sn NMR, X-ray	2.616(1)	67
$[\text{Pt}(\text{CO})_2\{\text{Sn}(\text{CHR}_2)_2\}]_2$	1	^1H , ^{13}C and ^{195}Pt NMR		15
$[\text{Pt}(\text{PPh}_3)_2\{\text{Sn}(\text{OC}_6\text{H}_4\text{Bu}'_2-2,6)_2\}]$	1	^1H , ^{31}P and ^{195}Pt NMR		68

^a Abbreviations: R = SiMe₃, Ar = C₆H₂Bu'₂-2,6-Me-4, acacH = MeCOCH₂COMe, dppm = (Ph₂P)₂CH₂.

^b Designates those of the series which have been X-ray characterized.

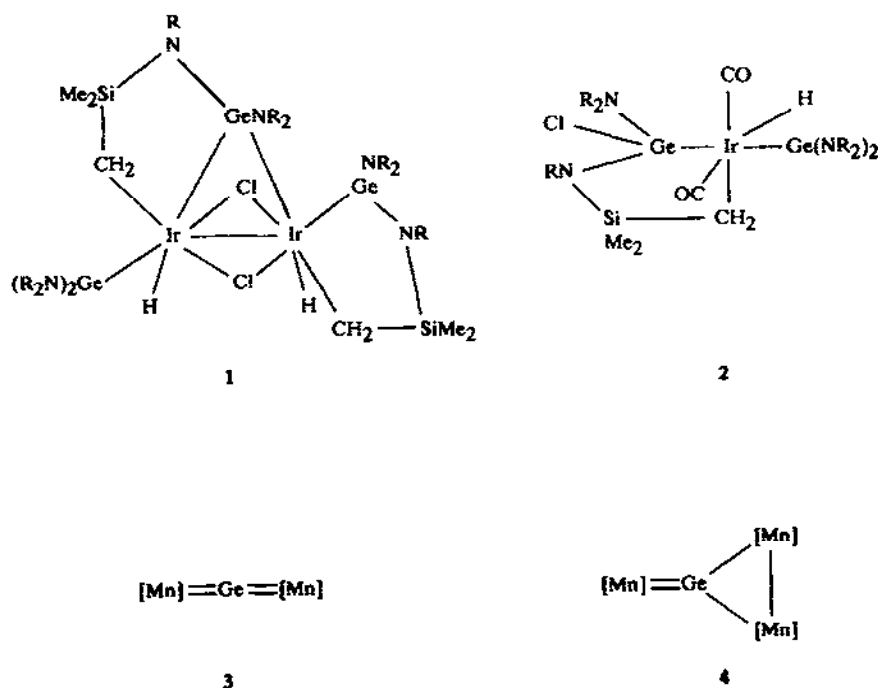
^c Types 1', 2' or 4' refer to the appropriate (see types 1, 2 or 4 respectively) transition metal (M') base-stabilized MX₂ complex.

^d Base-free species.

also by an anionic base $\bar{X}'$; the ligand $\overline{MX}_2X'$ results from insertion of MX_2 into a transition metal (M') $M'-X'$ bond. The first such Type 3 complex derived from an MX_2 precursor was $[Mo(\eta-C_5H_5)(CO)_3-\{Sn(CHR_2)_2X\}]$ ($X = H$ or Me), described in 1974 [28].

Attempts have been made to obtain a dimetallastannylene or dimetallaplumbylene MX_2 in which $X = M'L_n$ (Type 4 behaviour). The only compounds that have been made and well characterized to date in which the metal M has an open-shell configuration are the lead(II) species of Scheme 5; the crystalline complexes have three-coordinated lead, and included $Pb[MoCp^*(CO)_3]_2(THF)$ (there is evidence for the isoleptic Sn compound [75]) and $\{Pb[MoCp^*(CO)_3]_2\}_2$ ($Cp^* = \eta-C_5Me_5$); they were reported in 1987 [9]. Other two- or three-coordinate main group 14 metal- $M'L_n$ complexes are known in which M is in oxidation state +4, such as compounds 3 or 4 ($[Mn] = [Mn(\eta-C_5H_4Me)(CO)_2]$) [54]. It is not inevitable that complexes of type $[M(M'L_n)_3]$ have a cyclic three-membered $M'MM'$ ring structure; indeed acyclic analogues have been made, one of which (see Fig. 1) is of mixed-metal type [69].

As the ligand $\bar{X}$ in MX_2 is in principle capable of acting as a leaving group, it is possible that a compound MX_2 may behave as an $\bar{X}$ transfer reagent (Type 5 behaviour). The reaction between the tin(II) amide and $[Ni(acac)_2]$, illustrated in Scheme 1, was established in 1987 [13].

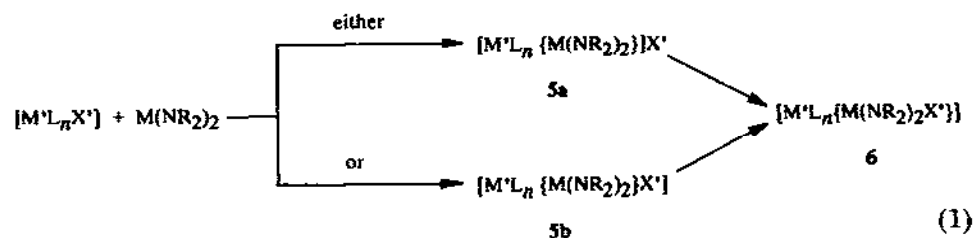


Compound 1 is made from $[\{\text{Ir}(\eta\text{-C}_8\text{H}_{14})_2(\mu\text{-Cl})\}_2]$ and $\text{Ge}(\text{NR}_2)_2$; treating 1 with carbon monoxide generates a further complex, 2; both exemplify Type 6 behaviour, as noted in 1986 [14].

That a methylene may function as a chlorine-atom-abstracting reagent (Type 7 behaviour) in a transition metal context was first observed in 1985 [12]; thus $[\text{Sn}(\text{CHR}_2)_2\text{Cl}]_2$ was one of the products isolated from $[\{\text{PtCl}(\mu\text{-Cl})(\text{PEt}_3)\}_2]$ and $\text{Sn}(\text{CHR}_2)_2$.

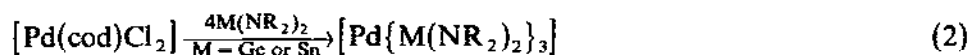
B. SYNTHESIS OF METHYLENE-BASED TRANSITION METAL COMPLEXES

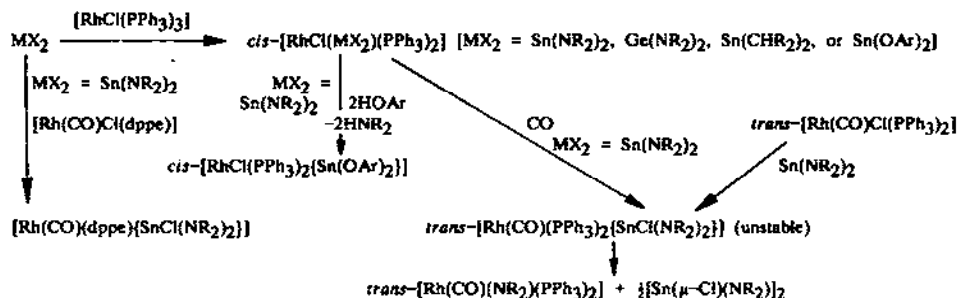
Typical reactions of a methylene MX_2 with a transition metal substrate $[\text{M}'\text{L}_n\text{X}']$ are illustrated in Schemes 2–8. The most intensively studied reactions refer to the amides $\text{M}(\text{NR}_2)_2$ ($\text{R} = \text{SiMe}_3$). In Scheme 2 selected $[\text{M}'\text{L}_n\text{X}']$ substrates are shown with M' ranging from a group 3 to a group 10 transition metal, in low or high oxidation state. It is envisaged that the reaction pathway leading to any product of Scheme 2 invariably involves an initial Type 1 complex 5; however, 5 may undergo rearrangement to yield the Type 3 isomer 6, as a result of a 1,2-shift of an anionic ligand $\bar{\text{X}}$ from the outer or inner coordination sphere of the transition metal M' to M (eqn. (1)):



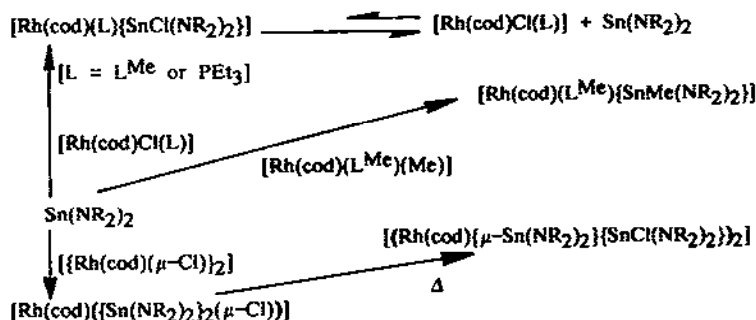
The transformation $\text{M}(\text{NR}_2)_2 \rightarrow \text{6}$ is a carbene-like (or CO-like) insertion of MX_2 into an $\text{M}'\text{-X}'$ bond. The $\text{M}(\text{NR}_2)_2$ reactions leading to 5 or 6 demonstrate the ability of MX_2 to act as a metal-centred nucleophile or substrate for insertion (Type 1 or Type 3 behaviour respectively). The former mode shows that MX_2 has a transition metal reactivity analogous to that of a tertiary phosphine or carbon monoxide.

The fact that MX_2 may function as a bridging ligand (Type 2 behaviour) shows a further analogy with CO. The methylene MX_2 in its Type 2 reaction may also be considered as acting as a reducing agent, in the sense that an $\text{M}(\text{II})$ precursor is converted into an $\text{M}(\text{IV})$ product. A clearer example of MX_2 as a reducing agent, although concomitantly as a ligand, is illustrated in eqn. (2) [70]:

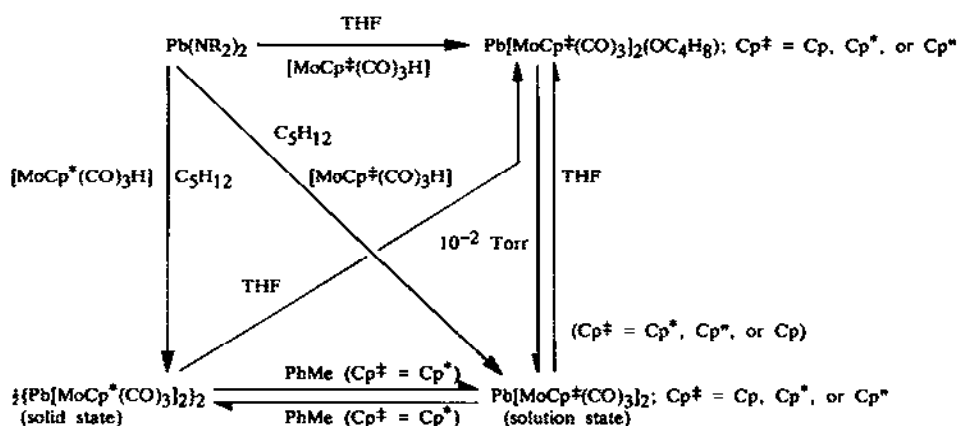




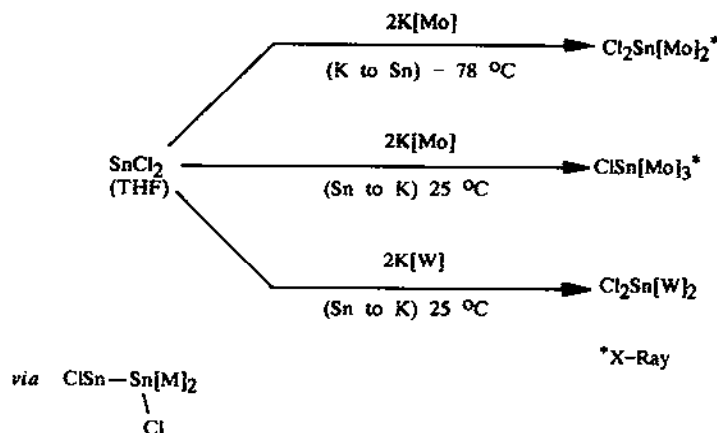
Scheme 3. Some phosphinerhodium(I) complexes derived from MX_2 ($\text{MX}_2 = \text{Sn}(\text{NR}_2)_2$, $\text{Ge}(\text{NR}_2)_2$, $\text{Sn}(\text{CHR}_2)_2$ or $\text{Sn}(\text{OAr})_2$; dppe = $(\text{Ph}_2\text{PCH}_2)_2$, $\text{R} = \text{SiMe}_3$, $\text{Ar} = \text{C}_6\text{H}_3\text{Bu}'_2\text{-2,6}$) [68].



Scheme 4. Some cycloocta-1,5-dienerrhodium(I) complexes derived from $\text{Sn}(\text{NR}_2)_2$ ($\text{R} = \text{SiMe}_3$, $\text{L}^{\text{Me}} = \text{CN}(\text{Me})(\text{CH}_2)_2\text{NMe}$) [68].



Scheme 5. Routes to some Pb(II)-Mo(0) complexes from $[\text{MoCp}^\ddagger(\text{CO})_3\text{H}]$ and $\text{Pb}(\text{NR}_2)_2$ ($\text{R} = \text{SiMe}_3$, $\text{Cp} = \eta\text{-C}_5\text{H}_5$, $\text{Cp}^* = \eta\text{-C}_5\text{Me}_5$, $\text{Cp}'' = \eta\text{-C}_5\text{H}_3\text{R}_{2-1,3}$) [9].



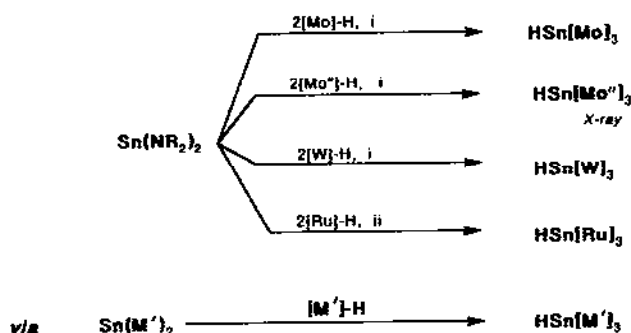
Scheme 6. Interaction of SnCl_2 and $[\text{MCp}(\text{CO})_3]^-$ ($\text{M} = \text{Mo}$ or W , $[\text{Mo}] = [\text{MoCp}(\text{CO})_3]$, $[\text{W}] = [\text{WCp}(\text{CO})_3]$) [75].

analogue from $\text{Sn}(\text{NR}_2)_2$ ($\text{R} = \text{SiMe}_3$) failed, probably because the intermediate dimetallastannylenes were unstable with regard to oxidative addition; the isolated compounds were the hydridotrimetallatin(IV) complexes (Scheme 7) [75]. Alternative efforts at generating the dimetallatin(II) complexes from SnCl_2 likewise led to tin(IV) products (Scheme 6); in this case the reaction pathway might well have also involved a transient dimetallastannylenes which rapidly underwent insertion into one of the $\text{Sn}-\text{Cl}$ bonds of SnCl_2 .

A similar type of isocarbonyl-metal interaction has been found in some polycarbonylchromium(0) and polycarbonyl-iron(0) complexes in which $\text{Sn}[\text{FeCp}(\text{CO})_2]_2$ (abbreviated as SnFp_2) may be considered as the putative dimetallastannylenes intermediate [69]; details are shown in Scheme 9.

C. REACTIONS

Various reactions of a complex containing a coordinated stannylenes or stannate(II) anion are shown in Schemes 3, 5 and 9. These include the conversion of a rhodium(I)-coordinated $\text{Sn}(\text{NR}_2)_2$ complex to the corresponding $\text{Sn}(\text{OAr})_2$ derivative by treatment of the former with the phenol ArOH ($\text{Ar} = \text{C}_6\text{H}_3\text{Bu}'_{2-2,6}$). Such a reaction represents a nucleophilic displacement at tin in a Type 1 complex. Similar nucleophilic substitutions, but in Type 3 complexes, are illustrated in eqn. (4) ($\text{X}' = \text{F}$ (via $[\text{NBu}_4]^+\text{F}^-$), OMe (via NaOMe) or H (via $\text{K}[\text{BHEt}_3]$)) [30]. $[\text{FeCp}(\text{CO})_2\{\text{Sn}(\text{CHR}_2)_2\text{H}\}]$ underwent H/Cl exchange at tin by reaction with aqueous HCl or PhCOCl

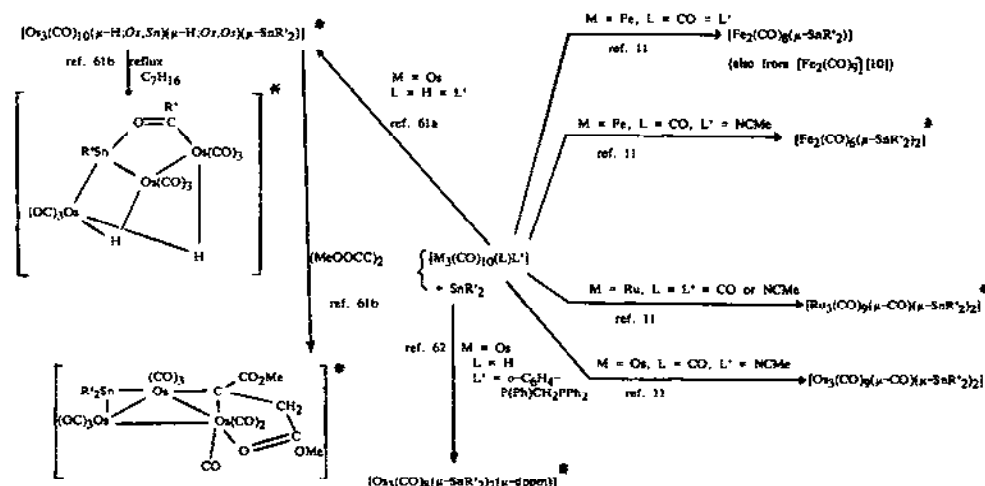


Scheme 7. Interaction of $\text{Sn}(\text{NR}_2)_2$ ($\text{R} = \text{SiMe}_3$) and a transition metal hydride $[\text{M}'\text{Cp}(\text{CO})_3\text{H}]$ ($\text{M}' = \text{Mo}$ or W), $[\text{Mo}(\eta\text{-C}_5\text{H}_3\text{R}_2\text{-1,3})(\text{CO})_3\text{H}]$ or $[\text{RuCp}(\text{CO})_2\text{H}]$ (abbreviated as $[\text{M}']\text{-H}$, $[\text{Mo}']\text{-H}$ and $[\text{Ru}]\text{-H}$ respectively). Reaction conditions: i, C_6H_{14} , 25°C ; ii, C_7H_{16} , reflux [75].

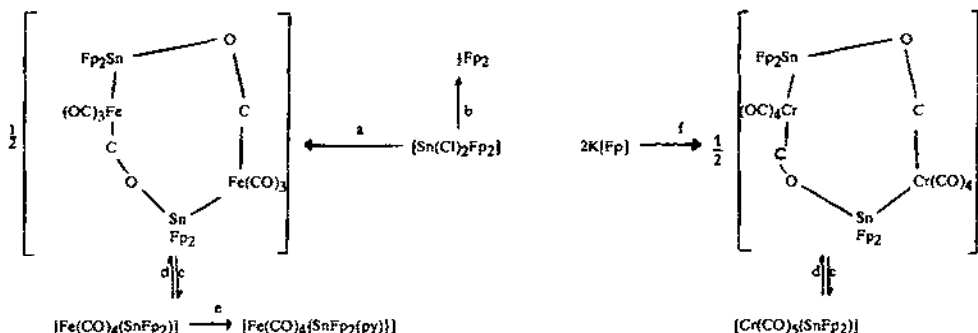
(also yielding PhCHO) [30]:



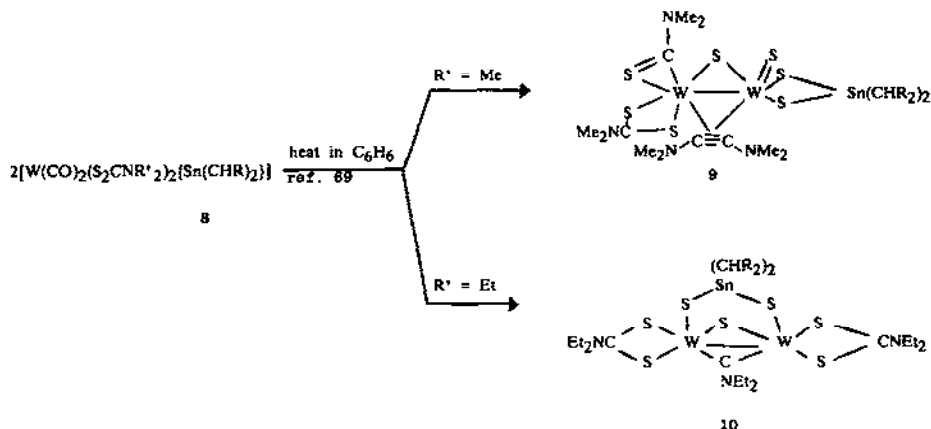
The conversion of a Type 1 complex into a Type 2 complex by reaction of the former with CO has already been cited in the context of the transformation of $[M'\{M(NR_2)_2\}_3]$ into $[(M'\{\mu-M(NR_2)_2\}(CO))_3]$ (7) ($M' = Pd$ or Pt , $M = Ge$ or Sn) [15,25,70]. Likewise the Type 1/6 complex **1** was converted with CO into the Type 3/6 complex **2** [14].



Scheme 8. Reactions of SnR'_2 ($\text{R}' = \text{CHR}_2$, $\text{R} = \text{SiMe}_3$, $\text{dppm} = \text{Ph}_2\text{PCH}_2\text{PPh}_2$ with some carbonyltrimetallal clusters of Fe, Ru or Os [11,61(a),61(b),62]; * X-ray.



Scheme 9. Some polycarbonylchromium(0) and polycarbonyliron(0) SnFp_2 complexes ($\text{Fp} = [\text{Fe}(\eta\text{-C}_5\text{H}_5)(\text{CO})_2]$) [69]. Reagents: a, $\text{Na}_2[\text{Fe}(\text{CO})_4] \cdot 1,5\text{-dioxane}$; b, $\text{Na}_2[\text{Cr}(\text{CO})_5]$; c, PhMe ; d, $\sim \text{PhMe}$; e, py; f, $[\text{Cr}(\text{CO})_5\{\text{SnCl}_2(\text{THF})\}]$.



The complexes **7** underwent reversible one-electron electrochemical reduction in tetrahydrofuran at approximately -1.2 V to yield ESR-characterized reduction products containing, in the case of the tin compounds, a Pd_nSn_2 or Pt_3Sn_3 core [25]. This was established by analysis of their frozen solution ESR spectra, the samples being generated by controlled potential electrolysis of **7** in the cavity of the spectrometer.

The dithiocarbamatotungsten(II) complexes **8**, containing a dialkylstannylene ligand, were partially desulfurized to yield the remarkable X-ray characterized complexes **9** and **10** (eqn. (5)) [69].

D. STRUCTURE AND BONDING

The X-ray structures of some representative complexes are shown in Figs. 1–7. These include two examples showing the methylene ligand functioning in

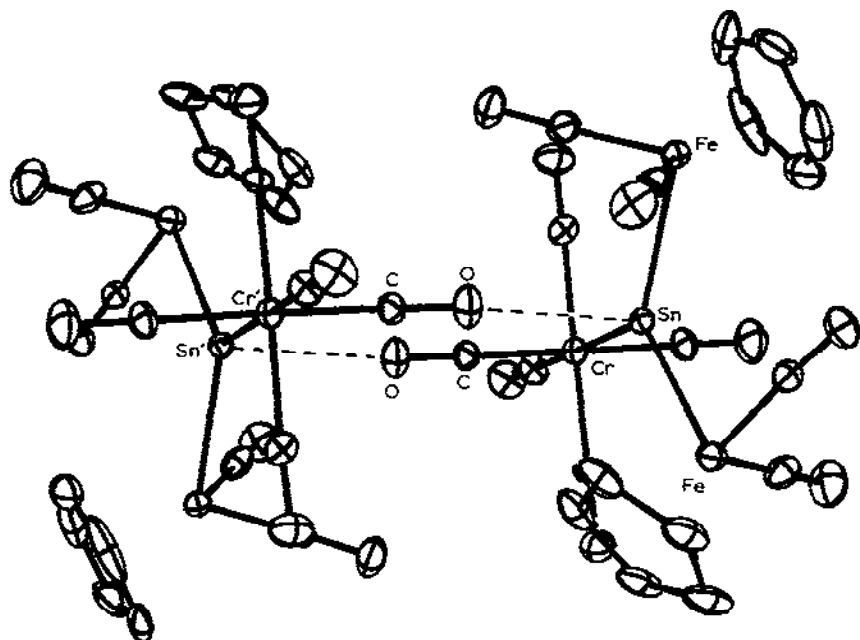


Fig. 1. X-ray structure of $[\{Cr(CO)_4(\mu-CO)\}(SnFp_2)]_2 \cdot 2PhMe$ (O, Cr) (toluene solvent not shown: $Fp = [Fe(\eta-C_5H_5)(CO)_2]$) [69]. Selected structural data: $Cr-Sn$ 2.624(1) Å, $Fe-Sn$ 2.570(1) and 2.550(2) Å, $Sn-O$ 2.976(7) Å, $Cr-CO(\mu)$ 1.862(9) Å, $\mu-C-O$ 1.166(2) Å; $Cr-Sn-Fe$ 121.81(5)° and 121.46(4)°, $Fe-Sn-Fe$ 115.74(4)°, $O-Sn-Cr$ 98.5(1)°, $Sn-O-C$ 169.4(7)°, $Cr-C-O(\mu)$ 176.9(6)°.

a Type 1 fashion (Figs. 1 and 5). Figure 3 illustrates the structures of two Type 1' complexes [76,77]; although these are formally of structure $cis-[RhCl\{M(NR_2)_2\}(PPh_3)_2]$, they nevertheless reveal a rather close $Cl \cdots M$ ($M = Ge$ or Sn) interaction. Figures 4 and 6 exemplify structures of Type 3 complexes, while Fig. 7 refers to one of Type 2. X-ray data on a Type 4 complex are shown in Fig. 2 and similar information is also available for the Type 6 species 1 and 2 [14].

From Table 2 it is evident that X-ray data are available on complexes other than those having a bis(amido)methylene precursor, including $M(CHR_2)_2$ and $M(OAr^{Me})_2$ ($R = SiMe_3$, $Ar^{Me} = C_6H_2Bu'_2-2,6-Me-4$).

In Table 3 selected results are given on some typical $[M'(MX_2)L_n]$ complexes having $X = CHR_2$, NR_2 or OAr^{Me} ; for comparison similar data are provided on the parent monomeric methylene MX_2 . It can be noted that there is no monotonic trend in either the MX_2 angle or the $M-X$ bond length as between MX_2 and $[M'L_n(MX_2)]$.

^{119}Sn NMR chemical shifts of various SnX_2 -derived complexes are listed in Table 4. They are of considerable diagnostic value, although no interpretation of these data is proposed at this time.

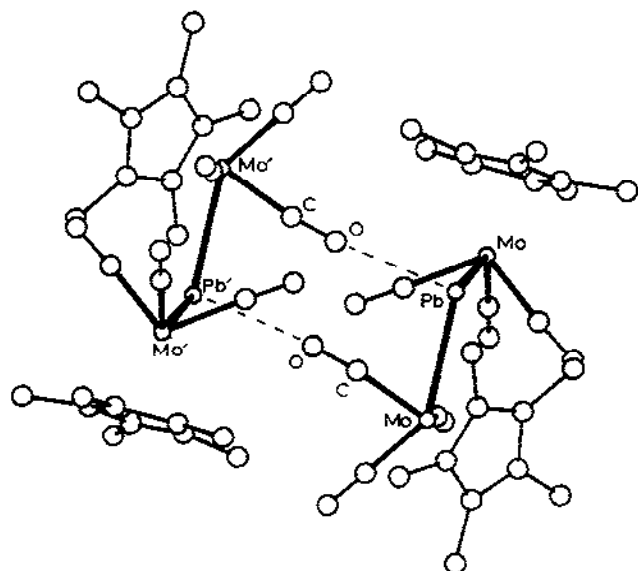


Fig. 2. X-ray structure of $\{Pb[MoCp^*(CO)_3][MoCp^*(CO)_2(\mu-CO)]\}_2$ (O, Pb) ($Cp^* = \eta-C_5Me_5$) [9]. Selected structural data: Mo–Pb 2.935(1) and 2.989(1) Å, Pb–O 2.918(8) Å; Mo–Pb–Mo 120.71(2)°.

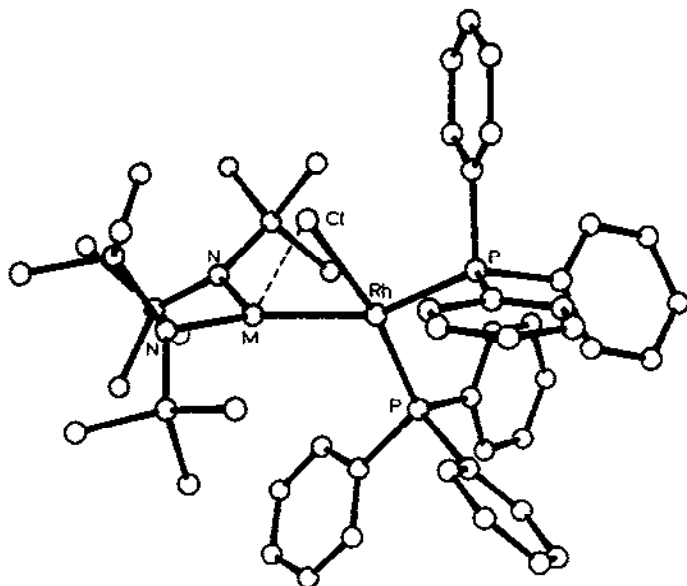


Fig. 3. X-ray structure of $cis-[RhCl(M(NR_2)_2)(PPh_3)_2]$ ($M = Ge$ [76] or Sn [77], $R = SiMe_3$) [68]. Selected structural data for $M = Ge$ ($M = Sn$ in parentheses): Rh–M 2.391(1) (2.564(1)) Å, Rh–Cl 2.388(3) (2.418(3)) Å, Rh–P 2.218(3) and 2.335(3) (2.210(2) and 2.296(3)) Å, M–N 1.881(8) and 1.849(9) (2.085(7) and 2.058(7)) Å, M···Cl 2.723(4) (2.743(3)) Å; M–Rh–Cl 69.46(9)° (66.74(6)°), M–Rh–P 103.47(9)° and 157.42(9)° (103.46(7)° and 156.83(7)°), Cl–Rh–P 170.9(1)° and 88.5(1)° (168.86(9)° and 90.64(9)°), P–Rh–P 99.0(1)° (99.51(9)°), Rh–M···Cl 55.23(7)° (54.07(5)°), N–M···Cl 119.8(3)° and 91.3(3)° (117.9(2)° and 91.9(2)°).

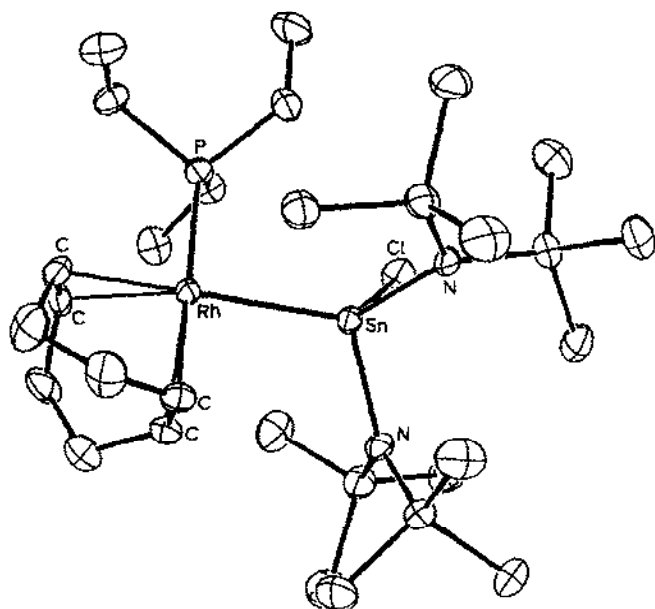


Fig. 4. X-ray structure of $[\text{Rh}(\text{cod})(\text{PEt}_3)\{\text{SnCl}(\text{NR}_2)_2\}]$ ($\text{R} = \text{SiMe}_3$) [68,78]. Selected structural data: Rh-Sn 2.647(1) Å, Rh-P 2.318(1) Å, Rh-C 2.180(5), 2.189(5), 2.229(5) and 2.252(5) Å, Sn-Cl 2.449(1) Å, Sn-N 2.120(4) and 2.099(4) Å; Sn-Rh-P 91.3(1)°, P-Rh-C 89.3(1)°, 96.0(1)°, 167.0(2)° and 157.1(1)°, Rh-Sn-N 113.7(1)° and 123.6(1)°, Rh-Sn-Cl 114.5(1)°, Cl-Sn-N 96.3(1)° and 95.3(1)°, N-Sn-N 108.7(1)°.

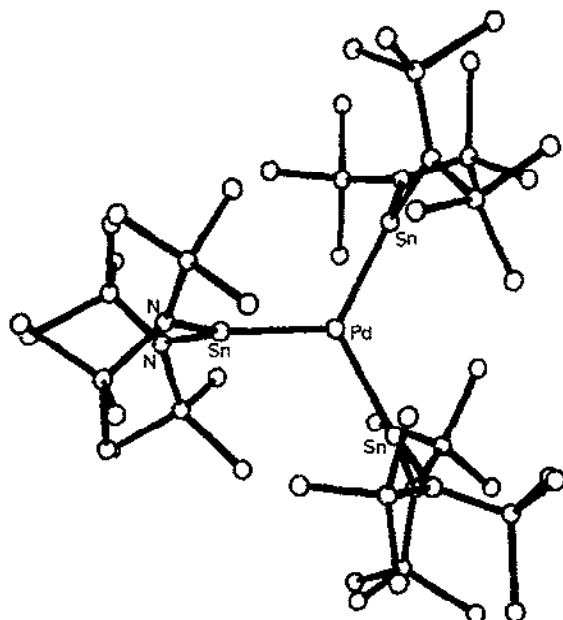


Fig. 5. X-ray structure of $[\text{Pd}\{\text{Sn}(\text{NR}_2)_2\}_3]$ ($\text{R} = \text{SiMe}_3$) [70]. Selected structural data: Pd-Sn 2.533(1), 2.540(1) and 2.517(1) Å; Sn-Pd-Sn 118.82(4)°, 120.78(4)° and 120.40(4)°.

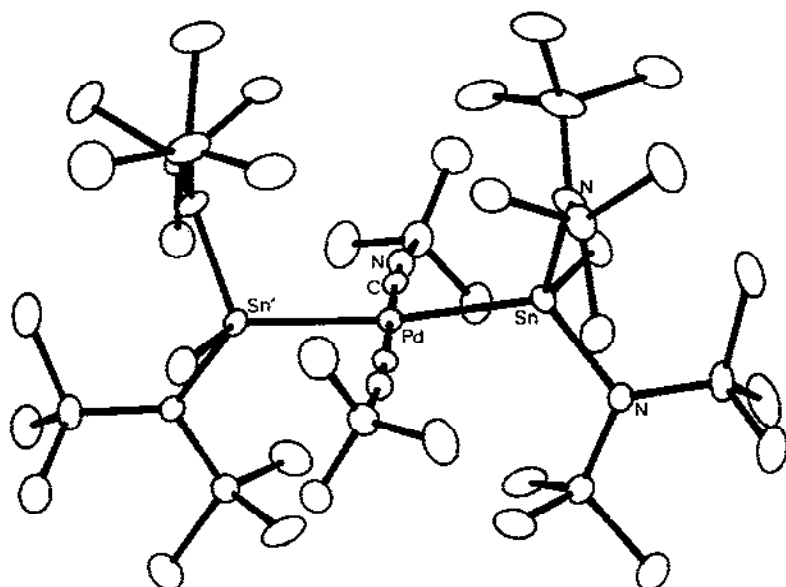


Fig. 6. X-ray structure of *trans*-[Pd(CNBu')₂{SnCl(NR₂)₂}₂] (R = SiMe₃) [13]. Selected structural data: Pd–Sn 2.636(1) Å, Pd–C 1.978(1) Å, Sn–N 2.083(7) and 2.075(8) Å, Sn–Cl 2.406(3) Å; Pd–Sn–Cl 112.57(7)°, Pd–Sn–N 121.9(2)° and 109.9(3)°, Cl–Sn–N 93.9(2)° and 100.1(2)°.

TABLE 3

Comparative structural data for selected group 14 metal(II) compounds MX₂ and some of their transition metal complexes (A) ^a

Compound MX ₂ or (A)	MXM (deg)	⟨M–X⟩ (Å)	Ref.
GeR' ₂	107(2) ^b	2.04(2) ^b	71
SnR' ₂	97(2) ^b	2.22(2) ^b	71
[Cr(CO) ₅ (GeR' ₂)]	102.8(2)	1.98(2)	27
[Cr(CO) ₅ (SnR' ₂)]	98	2.18(1)	10(a)
Ge(NR ₂) ₂	101(1.5) ^b	1.89(1) ^b	72
Sn(NR ₂) ₂	96 ^b , 104.7(2)	2.09(1) ^b , 2.09(1)	73
[Pd{Sn(NR ₂) ₂ } ₃]	107(1)	2.08(2)	70
[Pt{Sn(NR ₂) ₂ } ₃]	104(1)	2.1(2)	12
Ge(OAr) ₂	92.0(4)	1.80(2)	74
Sn(OAr) ₂	88.4(2)	2.01(2)	74
<i>eq</i> -[Fe(CO) ₄ {Ge(OAr) ₂ }]	93.5(2)	1.777(8)	63
<i>eq</i> -[Fe(CO) ₄ {Sn(OAr) ₂ }]	92.2(2)	1.974(15)	63

^a Abbreviations: R' = CHR₂, R = SiMe₃, Ar = C₆H₂Bu'₂-2,6-Me-4.

^b In the vapour (gas-phase electron diffraction); other data are for the crystal (X-ray).

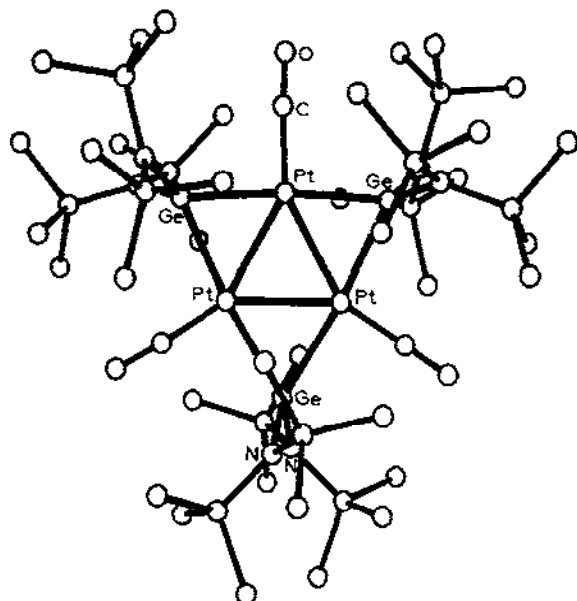


Fig. 7. X-ray structure of $[(Pt\{\mu\text{-Ge}(\text{NR}_2)_2\}(\text{CO})_3)]$ ($\text{R} = \text{SiMe}_3$) [15,80]. Selected structural data: Pt–Pt, 2.735(2), 2.727(2) and 2.723(2) Å, Pt–Ge 2.473(3), 2.482(3), 2.466(3), 2.481(3), 2.473(4) and 2.479(4) Å, Ge–N 1.87(2), 1.86(2), 1.89(2), 1.91(2), 1.88(2) and 1.93(2) Å, Pt–C 1.77(3), 1.78(3) and 1.88(3) Å.

From X-ray, NMR and IR data it is clear that in Type 1 complexes the MX_2 ligand can be regarded as being not only an effective σ donor, but also a powerful π acceptor. This is consistent with the complexes $[\text{Fe}(\text{CO})_4\text{-}\{\text{M}(\text{OAr}^{\text{Me}})_2\}]$ ($\text{M} = \text{Ge}$ or Sn) having the MX_2 ligand in the equatorial position in their trigonal bipyramidal structure [63]. They have the MO_2 plane of $\text{M}(\text{OAr}^{\text{Me}})_2$ tilted from the $\text{Fe}(\text{CO})_{\text{axial}}\text{M}$ plane by only 4.9° for $\text{M} = \text{Ge}$ or 5.2° for $\text{M} = \text{Sn}$. Likewise in octahedral complexes, including $[\text{Cr}(\text{CO})_5\{\text{Sn}(\text{CHR}_2)_2\}]$, the conformation of the MX_2 ligand is such as to maximize the possibility of π bonding to the transition metal (the plane containing the methine carbon atoms, tin and chromium is coplanar with the mutually axial COs and the CO *trans* to tin) [10].

From X-ray data for some rhodium(I) complexes, the relative *trans* influence appears to be $\text{L}^{\text{Me}} \approx \text{PEt}_3 > \bar{\text{SnCl}}(\text{NR}_2)_2 \gg \bar{\text{Cl}}$ ($\text{L}^{\text{Me}} = \text{:CN}(\text{Me})(\text{CH}_2)_2\text{NMe}$) [68].

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TABLE 4
 ^{119}Sn NMR data ^a for transition metal complexes containing tin-centred ligands derived from a stannylene SnX_2

Compound	$\delta(^{119}\text{Sn})$		$\Delta\delta_{\text{L}}$	$^1J(\text{M}', ^{119}\text{Sn})^{\text{k}}$	Sn coordination		Hybridiza- tion at Sn	Ref.
	Complex	Ligand			No.	"Type" ¹		
[Fe(Cp)(CO) ₂ (SnR' ₂ X')]								
X' = F ^g	322	721 ^m	-399	-	4	3	<i>sp</i> ³	30
X' = Cl ^g	311	721 ^m	-410	-	4	3	<i>sp</i> ³	30
X' = Br ^h	292	721 ^m	-429	-	4	3	<i>sp</i> ³	30
X' = I ^d	228	721 ^m	-493	-	4	3	<i>sp</i> ³	30
X' = OMe ^g	267	721 ^m	-454	-	4	3	<i>sp</i> ³	30
X' = H ^g	35	721 ^m	-686	-	4	3	<i>sp</i> ³	30
[Fe(CO) ₄ (Sn{Fe(Cp)(CO) ₂ } ₂)]	724	(535 ⁿ)	-	-	3	1	<i>sp</i> ²	69
[Fe(CO) ₄ (Sn{Fe(Cp)(CO) ₂ } ₂ (THF) _x)] ⁱ	888	(535 ⁿ)	-	-	3 + x	1'	<i>sp</i> ²	69
[Fe(CO) ₄ (Sn{Fe(Cp)(CO) ₂ } ₂ (py))] ^h	762	(535 ⁿ)	-	-	4	1'	<i>sp</i> ²	69
[W(CO) ₂ (S ₂ CNEt ₂) ₂ (SnR' ₂)] ^g	174	721 ^m	-547	- ^o	3	1	<i>sp</i> ²	69
[W(CO) ₂ (S ₂ CNMe ₂) ₂ (SnR' ₂)] ^g	188	721 ^m	-533	- ^o	3	1	<i>sp</i> ²	69
<i>cis</i> -[RhCl(PPh ₃) ₂ (SnR' ₂)] ^j	434	721 ^m	-287	497	3	3/6 ^t	<i>sp</i> ²	68
[Rh(CO)(dppe){SnCl(NR ₂) ₂ }] ^j	36	775	-739	739	4	3	<i>sp</i> ³	68
<i>trans</i> -[Rh(CO)(CO)(PPh ₃) ₂ (SnCl(NR ₂) ₂)] ^j	-60	775	-835	560	4	3	<i>sp</i> ³	68
[Rh(cod)(L ^{Me}){SnMe(NR ₂) ₂ }] ^j	31	775	-744	815	4	3	<i>sp</i> ³	68

$[\text{Rh}(\text{cod})(\text{L}^{\text{Me}})\{\text{SnCl}(\text{NR}_2)_2\}]^j$	-25	775	-800	$_{-P}$	4	3	sp^3	68
$[\text{Rh}(\text{cod})(\text{PET}_3)\{\text{SnCl}(\text{NR}_2)_2\}]^{j,c}$	-12	775	-787	928	4	3	sp^3	68
$[\text{Rh}(\text{cod})\{\text{Sn}(\text{NR}_2)_2\}_2\{\mu\text{-Cl}\}]^{j,d}$	-4	775	-779	860	4	"3"	sp^3	68
$[(\text{Rh}(\text{cod})\{\mu\text{-Sn}(\text{NR}_2)_2\}-\{\text{SnCl}(\text{NR}_2)_2\})_2]^{j,d}$	144	775	-631	840	4	2	sp^3	68
$[\text{Ir}\{\text{SnCl}(\text{NR}_2)_2\}_2]^{j,d}$	118	775	-657	655	4	3	sp^3	68
$[\text{Ir}\{\text{SnCl}(\text{NR}_2)_2\}\text{N}(\text{R})\text{SiMe}_2\text{CH}_2\}-\{\text{cod}\}\text{H}\{\text{Sn}(\text{NR}_2)_2\}]^j$	-193	775	-968	-	4	3(6)'	sp^3	68
$[(\text{IrCl}\{\mu\text{-Sn}(\text{NR}_2)_2\}\{\text{Sn}(\text{NR}_2)_2\})_2]^{j,r}$	356	775	-419	-	3	1'	sp^2	68
	221	775	-554	-	4	2	sp^3	68
	237	775	-538	-	3	1	sp^2	68
$[\text{Pt}(\text{PPh}_3)_2\{\text{Sn}(\text{NR}_2)_2\}]^h$	963	775	188	16650	3	1	sp^2	68
$[\text{Pt}\{\text{Sn}(\text{NR}_2)_2\}_3]^{g,e}$	885	775	110	27874	3	1	sp^2	70
$[\text{Pd}\{\text{Sn}(\text{NR}_2)_2\}_3]^{g,c}$	815	775	40	-	3	1	sp^2	70
$[\text{Pt}(\text{PPh}_3)_2\{\text{Sn}(\text{acac})_2\}]^{b,f}$	-601	-702	101	12891	5	1'	$sp^3d(?)^s$	8

Abbreviations: $\text{R}' = \text{CHR}_2$, $\text{R} = \text{SiMe}_3$, $\text{L}^{\text{Me}} = \text{:CN(Me)(CH}_2)_2\text{NMe}$; $\Delta\delta_{\text{L}} = \delta(\text{complex}) - \delta(\text{ligand})$.

^a Recorded at 134.3 MHz except ^b 93.3 MHz, and at ambient temperature except ^c 273 K, ^d 193 K and ^e 343 K and ^f not reported; the following solvents were used: ^g benzene- d_6 , ^h toluene- d_8 , ⁱ THF- d_8 (presumably coordinated), ^j 10% toluene- d_8 /toluene; δ in ppm relative to SnMe_4 , positive shifts to higher frequency. ^k Coupling constants J in Hertz. ^l Types 1-6 are identified in Scheme 1. ^m Value reported for dimer in solution [18]. ⁿ Value for $[\{\text{Fe}(\text{Cp})(\text{CO})_2\}_2\text{SnCl}_2]$ [15]; $[\{\text{Fe}(\text{Cp})(\text{CO})_2\}_2\text{Sn}]$ is not known. ^o Not observed. ^p Not resolved. ^q Relative assignment based on coupling patterns. ^r Structure tentatively assigned on the basis of limited data on crude sample. ^s Not reported. ^t The Type 6 ligand $\text{SnCl}(\text{NR}_2)\text{N}(\text{R})\text{SiMe}_2\text{CH}_2^-$ is inserted into the Ir-Cl bond, so the Sn environment is essentially Type 3

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