

BASICITY OF TRANSITION METAL CARBONYL COMPLEXES

XIII *. REACTIONS OF THE π -CYCLOPENTADIENYL COMPLEXES OF MOLYBDENUM AND TUNGSTEN WITH APROTIC ACIDS

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Summary

The aprotic acids HgCl_2 and SnX_4 ($X = \text{Cl}, \text{Br}$) react with the π -complexes $\text{C}_5\text{H}_5\text{M}(\text{CO})(\text{NO})(\text{L})$ (II, $\text{M} = \text{Mo}, \text{W}$; $\text{L} = \text{PPh}_3$) by attack at the metal center. With HgCl_2 complexes II yield stable neutral 1 : 1 adducts $\text{CpM}(\text{CO})(\text{NO})(\text{L}) \cdot \text{HgCl}_2$ (III). In the case of SnCl_4 , complexes II initially produce the ionic 1 : 2 adducts $[\text{CpM}(\text{CO})(\text{NO})(\text{L})(\text{SnCl}_3)]^+\text{SnCl}_5^-$ (IV) which, as a result of oxidative elimination of CO, turn into the neutral complexes $\text{CpM}(\text{NO})(\text{L})(\text{SnCl}_3)(\text{Cl})$ (V). In reactions of II with SnBr_4 the corresponding $\text{CpM}(\text{NO})(\text{L})(\text{SnBr}_3)(\text{Br})$ complexes are formed directly. The formation of III–V is accompanied by a considerable increase of the frequencies $\nu(\text{CO})$ and $\nu(\text{NO})$. The structures of the complexes IV ($\text{M} = \text{Mo}$) and V ($\text{M} = \text{Mo}$) have been established by an X-ray structure analysis.

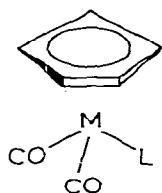
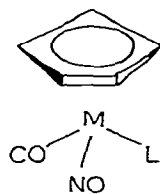
Introduction

In the molecules of π -complexes of the general formula $(\eta^n\text{-C}_n\text{H}_n)\text{M}(\text{CO})(\text{L})(\text{L}')$, where the cyclic ligand $\text{C}_n\text{H}_n = \eta^5\text{-cyclopentadienyl}, \eta^6\text{-benzene}$, L and $\text{L}' = \text{CO}, \text{NO}$ or phosphines, attack of electrophilic reagents is possible at one or more reaction sites, viz. the cyclic η -ligand, the central metal atom M , the oxygen of CO and NO, or the heteroatom of the ligands CS, CN, etc. The direction of attack and the structure of the reaction products depend on the nature of the reagent and the structure of the π -complex, particularly on the ligand environment of the metal atom. Earlier, the authors investigated the

* For part XII and preliminary communication see ref. 1.

reactions of the π -complexes of Group VII metals $C_5H_5M(CO)_2(PPh_3)$ (I) with mercuric chloride [2] and tin halides [3,4]. These aprotic acids attack the metal whose basicity is much higher than that of the corresponding $C_5H_5M(CO)_3$ as a result of substitution of CO by the donor ligand PPh_3 . Such an attack involves coordination of the aprotic acid with the M atoms ($M = Mn, Re$) and yield either neutral (with $HgCl_2$) or ionic (with $SnCl_4$ or $SnBr_4$) complexes with M—Hg and M—Sn bonds.

In this paper the reactions of aprotic acids with the Group VI metal complexes $C_5H_5M(CO)(NO)(PPh_3)$ (II), which are isoelectronic and isostructural with I, are reported.

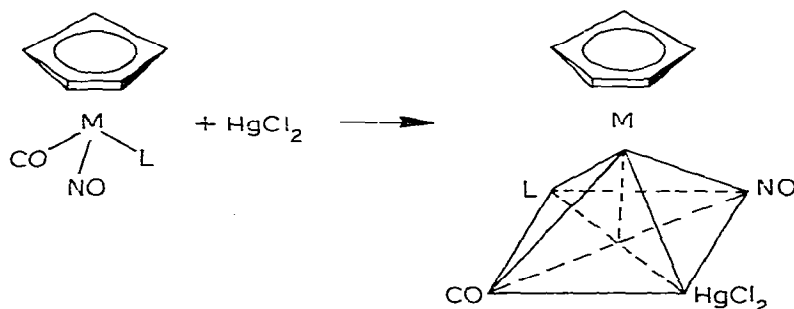
(I , $M = Mn, Re$)(II a , $M = Mo$; II b , $M = W$)

Unlike the derivatives of manganese and rhenium cyclopentadienyltricarbonyl, the chemistry of complexes II has not so far received much attention [5]. Earlier, the frequencies $\nu(CO)$ and $\nu(NO)$ were noticed to increase in reactions between these complexes and $SnCl_4$, however, reaction products were not isolated and their structures not determined [6].

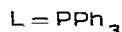
Results and discussion

Reactions with $HgCl_2$

On addition of an equimolar quantity of $HgCl_2$ to red solutions of complexes $C_5H_5M(CO)(NO)(PPh_3)$ in CH_2Cl_2 the mercuric chloride rapidly dissolves although in the absence of II it is practically insoluble in CH_2Cl_2 . This reaction is accompanied by a fast change of the solution color from red to yellow and several minutes later the solid adducts $C_5H_5M(CO)(NO)(PPh_3) \cdot HgCl_2$ are precipitated.



(II a, b)



(III c, b)

In the IR spectra of III (Nujol mulls) the frequencies $\nu(CO)$ and $\nu(NO)$ are

TABLE 1

 $\nu(\text{CO})$ AND $\nu(\text{NO})$ FREQUENCIES (IN CH_2Cl_2 , cm^{-1}) IN THE IR SPECTRA OF COMPOUNDS II–VI

Compound	M = Mo		M = W	
	$\nu(\text{CO})$	$\nu(\text{NO})$	$\nu(\text{CO})$	$\nu(\text{NO})$
II $\text{C}_5\text{H}_5\text{M}(\text{CO})(\text{NO})(\text{PPh}_3)$	1915	1610	1900	1595
III $\text{C}_5\text{H}_5\text{M}(\text{CO})(\text{NO})(\text{PPh}_3)(\text{HgCl}_2)^a$	1985	1680	1960	1660
IV $[\text{C}_5\text{H}_5\text{M}(\text{CO})(\text{NO})(\text{PPh}_3)(\text{SnCl}_3)]^+\text{SnCl}_5^-$	2070	1750	2050	1730
V $\text{C}_5\text{H}_5\text{M}(\text{NO})(\text{PPh}_3)(\text{SnCl}_3)(\text{Cl})$	—	1680	—	1655
VI $\text{C}_5\text{H}_5\text{M}(\text{NO})(\text{PPh}_3)(\text{SnBr}_3)(\text{Br})$	—	1670	—	1645

^a Nujol mulls.

shifted by 60–70 cm^{-1} towards larger wave numbers as compared with initial II (Table 1). The compounds are stable in air, practically insoluble in organic solvents and are nonelectrolytes in acetone. The increased frequencies $\nu(\text{CO})$ and $\nu(\text{NO})$ suggest increased positive charges on the metal and coordination of mercury with the M atoms, similar to mercury chloride adducts with $\text{C}_5\text{H}_5\text{M}(\text{CO})_2\text{PPh}_3$ [3], $\text{C}_5\text{H}_5\text{Co}(\text{CO})_2$ [7] and $\text{C}_6\text{H}_6\text{Cr}(\text{CO})_3$ [8].

Among η^5 -cyclopentadienyl derivatives of Mo and W a large number of 7-coordinate complexes of the type $\text{C}_5\text{H}_5\text{M}(\text{CO})_2(\text{L})(\text{X})$ [5] (where L is a two-electron, and X is a one-electron ligand) is known with a square pyramidal geometry, C_5H_5 being the apical ligand. Compounds III apparently have the same structure, the *trans*-positions of the CO and NO ligands in the pyramid base being most probably due to steric factors.

Reactions with tin halides

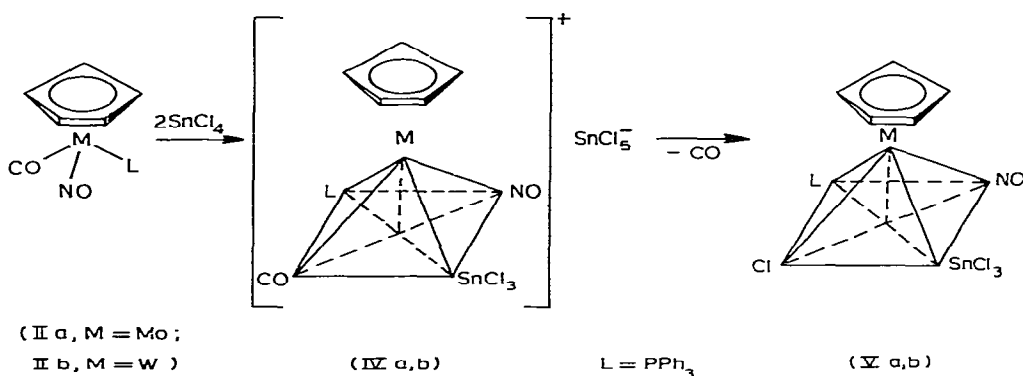
As an excess of SnCl_4 is added to solutions of complexes IIa,b in CH_2Cl_2 the solution instantaneously changes its color from red to yellow and the $\nu(\text{CO})$ and $\nu(\text{NO})$ frequencies of the initial compounds disappear. The reaction products are complexes IVa,b and in their IR spectra the $\nu(\text{CO})$ and $\nu(\text{NO})$ bands are shifted by 130–150 cm^{-1} towards higher wave numbers (Table 1). Such a strong increase in the frequencies is indicative of an ionic structure for IV, the $\text{M}(\text{CO})(\text{NO})$ fragment being a part of the cation. The properties of complexes IV depend on the nature of the M atom and on the reaction conditions.

The solutions containing IVa (M = Mo) are unstable and rapidly lose CO. In the case of a small excess of SnCl_4 (the ratio Mo : Sn \sim 1 : 2.5) a mixture of crystals of brown IVa and orange Va is precipitated from the solution of IVa on storage at 0°C. By an X-ray analysis (see below) IVa was shown to have an ionic structure $[\text{C}_5\text{H}_5\text{Mo}(\text{CO})(\text{NO})(\text{PPh}_3)(\text{SnCl}_3)]^+\text{SnCl}_5(\text{H}_2\text{O})^-$.

Complex IVa is formed as a result of attack of SnCl_4 at the molybdenum atom, the SnCl_3 group becomes attached to Mo and the Cl^- anion is displaced to the outer sphere and forms the SnCl_5^- counterion with the second SnCl_4 molecule. By addition of H_2O * this counterion can be transformed into the octahedral $\text{SnCl}_5(\text{H}_2\text{O})^-$ anion. It should be noted that the highly basic neutral

* Source of water may be traces of H_2O in the solvent, in the SnCl_4 and/or atmospheric moisture.

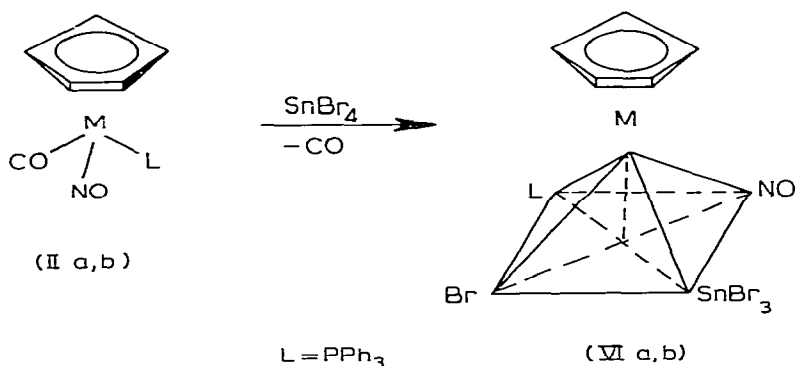
carbonyl complexes of the Group VI metals $M(\text{CO})_4(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2)$ ($M = \text{Mo}, \text{W}$) [9] and the cyclopentadienyl complex $\text{C}_5\text{H}_5\text{Co}(\text{PMe}_3)_2$ [10] also yield ionic products with $\text{SnCl}_5(\text{H}_2\text{O})^-$ anions in reactions with SnCl_4 .



In the case of larger excess of SnCl_4 ($\text{Mo} : \text{Sn} \geq 1 : 3$) in more concentrated solutions and when petroleum ether is added, IVa rapidly (within about 30 minutes) converts, as a result of oxidative elimination of CO , into the neutral covalent complex Va whose structure was also established by an X-ray analysis. The oxidative elimination occurs by an attack of SnCl_5^- or $\text{SnCl}_5(\text{H}_2\text{O})^-$ on the cation IVa with elimination of CO and SnCl_4 . The transformation $\text{IVa} \rightarrow \text{Va}$ is accompanied by pronounced changes in the IR spectra: the characteristic bands of IVa at 2070 and 1750 cm^{-1} disappear while a new band $\nu(\text{NO})$ appears at 1680 cm^{-1} .

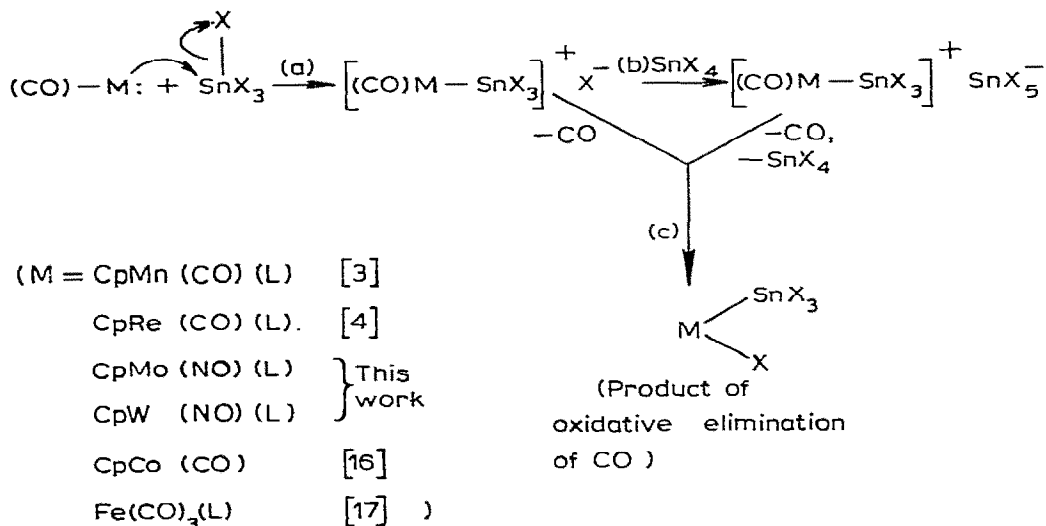
The reaction of SnCl_4 with complex IIb ($M = \text{W}$) yields a yellow solution which, on addition of petroleum ether, gives the stable yellow-brown complex IVb with the structure $[\text{C}_5\text{H}_5\text{W}(\text{CO})(\text{NO})(\text{PPh}_3)\text{SnCl}_3]^+\text{SnCl}_5^-$. In the solid state IVb is stable; on refluxing in CH_2Cl_2 it slowly releases CO and gradually converts to the respective Vb ($\nu(\text{NO}) 1655 \text{ cm}^{-1}$) but this conversion is much slower than in the case of IVa.

Reactions of II with SnBr_4 in CH_2Cl_2 occur via the rapid oxidative elimination of CO and yield neutral complexes $\text{C}_5\text{H}_5\text{M}(\text{NO})(\text{PPh}_3)(\text{SnBr}_3)(\text{Br})$ (VIa, b). In the IR spectra of VI, as in those of V, there are no $\nu(\text{CO})$ bands and only the broad $\nu(\text{NO})$ bands at 1670 cm^{-1} ($M = \text{Mo}$) or 1645 cm^{-1} ($M = \text{W}$) are present. It should be noted that III, IV, V and VI are in fact representatives of rather uncommon chiral complexes wherein the metal atom is simultaneously bonded to five different ligands.



Thus attack of the aprotic acids HgCl_2 and SnX_4 ($\text{X} = \text{Cl}$ and Br) on the cyclopentadienyl complexes of Mo and W takes place at the central metal atom, which in these π -complexes is the most basic site of the molecule just as in the previously investigated η^5 -cyclopentadienyl complexes of Mn and Re.

The formation of complexes IV as well as the previously obtained $[\text{C}_5\text{H}_5\text{Mn}(\text{CO})_2(\text{L})\text{SnCl}_3]^+\text{SnCl}_5^-$ [3] and the corresponding rhenium complexes [4] can be regarded as a nucleophilic substitution of the halogen atom (Cl or Br) at the tin atom in SnX_4 by neutral nucleophiles containing a transition metal. By analogy with O-, S-, N-, P- and other nucleophiles conventional in organic chemistry, the metal complexes exhibiting nucleophilic properties can be referred to as "M-nucleophiles". These reactions can be represented by the following general scheme:



A specific feature of reactions of SnX_4 with the π -complexes of Mn, Re, Mo, W is that the second stage (b) involves addition of the second SnX_4 molecule to the anion X^- with formation of SnX_5^- ; in the case of Mo and W complexes the third stage (c) is the oxidative elimination of CO. In reactions of II with SnBr_4 stages (a) and (b) are too fast to allow identification of the intermediates by IR spectra.

Determination of crystal and molecular structures

The structures of IVa and Va were established by an X-ray study (see Fig. 1). Atomic coordinates and temperature factors are listed in Tables 2 and 3. The bond lengths and bond angles are given in Tables 4 and 5. Geometrical parameters and stereochemistry* of the complex cation $[\text{C}_5\text{H}_5\text{Mo}(\text{CO})(\text{NO})(\text{PPh}_3)(\text{SnCl}_3)]^+$ in IVa are very close to those found in the neutral Va. This fact is quite understandable, since in general IVa and Va are structural analogues and

* Values of certain torsional angles characterizing the mutual orientation of ligands in IVa and Va are given in Table 6.

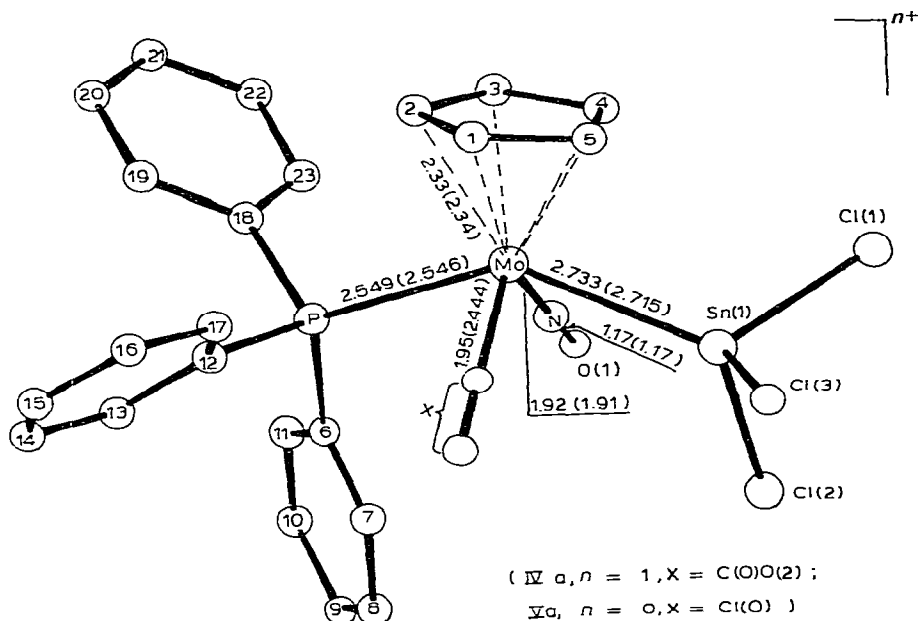


Fig. 1. The structures of the cation IVa and the molecule Va with main bond lengths (for Va in brackets): and atom numbering.

differ only by the charge and one ligand X (X = CO in IVa and X = Cl in Va). The Mo atom coordination in IVa and Va (see Fig. 1) can be regarded as octahedral with a centered face (the Cp ligand occupies three coordination sites) and a Mo coordination number of 7, or as a distorted tetragonal-pyramidal with the Cp ligand (considered now as occupying one coordination site) at the apex and the remaining four ligands at the pyramid base.

In both structures the most bulky ligands PPh_3 and SnCl_3 are in *trans*-positions relative to each other, the Sn—Mo—P angles being $139.24(6)$ and $142.57(3)^\circ$, and the X—Mo—NO angles $107.3(4)$ and $112.3(1)^\circ$ in IVa and Va, respectively. In the structure of the complex $[\text{C}_5\text{H}_5\text{Mn}(\text{CO})_2(\text{PPh}_3)(\text{SnCl}_3)]^+\text{SnCl}_5^-$ [3] the *trans*-angles Sn—Mo—P and OC—Mn—CO are $131.1(1)$ and $115.1(4)^\circ$, respectively. Obviously the differences between the Sn—Mn—P and Sn—Mo—P angles in IVa and Va are due to the different radii of Mn (1.38 \AA) and Mo (1.58 \AA) [11]. As usual, because of the additional d_π — d_π interaction, the Sn—Mo and Mo—P bonds are shorter than the corresponding sums of atomic radii, $r_{\text{Sn}} + r_{\text{Mo}} = 3.00 \text{ \AA}$ [12] and $r_{\text{Mo}} + r_{\text{P}} = 2.72 \text{ \AA}$ [13]. The Mo—Sn and Mo—P bond lengths in IVa ($2.733(1)$ and $2.549(1) \text{ \AA}$) are somewhat greater than in Va ($2.715(1)$ and $2.546(1) \text{ \AA}$), which is due to the greater competition between the ligands for the electron density on the metal in the cation IVa than in the neutral Va. A similar relationship has been observed in the structures of $[(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2)\text{Mo}(\text{CO})_4(\text{SnCl}_3)]^+$ [9] and $(\text{MeSCH}_2\text{CH}_2\text{SMe})\text{Mo}(\text{CO})_3(\text{SnCl}_3)(\text{Cl})$ [9], wherein the Sn—Mo bond lengths are 2.729 and 2.688 \AA , respectively. The Mo—C(Cp) bond lengths of 2.31 – 2.36 \AA (average 2.33 \AA) in IVa and 2.29 – 2.38 \AA (average 2.34 \AA) in Va are usual for η^5 -cyclopentadienyl derivatives of molybdenum (e.g. in the structure of $\text{CpMo}(\text{CO})_2(\text{PPh}_3)$ -

TABLE 2

ATOMIC COORDINATES ($\times 10^5$ FOR Mo AND Sn, $\times 10^4$ FOR OTHER ATOMS) IN STRUCTURES OF IVa AND Va

Atom ^a	IVa			Va		
	x	y	z	x	y	z
Sn(1)	86 277(5)	34 615(7)	6 722(4)	71 482(4)	-11 264(2)	71 890(3)
Sn(2)	60 244(4)	5 691(6)	77 712(3)	—	—	—
Mo	76 826(5)	13 777(7)	7 850(4)	65 329(4)	-22 619(2)	64 759(3)
Cl(0)	—	—	—	4 840(2)	-1 994(1)	7 896(2)
Cl(1)	8 059(3)	4 660(4)	-232(2)	8 950(2)	-637(1)	6 287(2)
Cl(2)	10 081(2)	3 144(5)	653(2)	7 719(3)	7 719(3)	-1 023(1)
Cl(3)	8 865(5)	4 842(4)	1 516(3)	5 559(2)	-347(1)	6 998(2)
Cl(4)	7 139(2)	-246(3)	8 681(1)	—	—	—
Cl(5)	4 834(2)	1 040(3)	6 813(1)	—	—	—
Cl(6)	7 063(2)	486(3)	7 159(1)	—	—	—
Cl(7)	4 923(2)	378(4)	8 328(1)	—	—	—
Cl(8)	6 338(2)	2 677(3)	8 085(2)	—	—	—
P	7 979(2)	-822(2)	1 223(1)	6 069(1)	-3 330(1)	7 203(1)
O(1)	8 879(5)	413(7)	-20(3)	9 333(7)	-2 515(3)	7 371(5)
O(2)	8 878(6)	1 928(7)	2 167(4)	—	—	—
O(3)	5 718(5)	-1 398(6)	7 462(4)	—	—	—
N	8 450(6)	795(8)	299(4)	8 222(5)	-2 408(2)	7 168(5)
C(o)	8 449(7)	1 697(7)	1 654(4)	—	—	—
C(1)	6 313(7)	1 987(10)	965(5)	5 676(6)	-2 675(3)	4 753(5)
C(2)	6 179(6)	864(9)	654(5)	7 072(6)	-2 064(3)	4 654(5)
C(3)	6 283(6)	997(11)	39(5)	7 364(6)	-1 991(3)	4 709(5)
C(4)	6 516(7)	2 223(13)	-21(6)	6 152(7)	-1 668(3)	4 831(5)
C(5)	6 552(7)	2 852(10)	569(6)	5 132(6)	-2 090(3)	4 861(5)
C(6)	9 107(6)	-1 338(8)	1 241(4)	6 700(5)	-3 491(2)	8 641(4)
C(7)	9 840(7)	-697(10)	1 615(5)	7 392(6)	-4 029(3)	8 873(5)
C(8)	10 698(8)	-1 089(13)	1 647(6)	7 757(6)	-4 170(3)	9 987(5)
C(9)	10 851(8)	-2 102(12)	1 324(6)	7 396(6)	-3 794(3)	10 890(5)
C(10)	10 120(9)	-2 759(12)	968(6)	6 696(6)	-3 264(3)	10 672(5)
C(11)	9 260(7)	-2 381(10)	922(5)	6 366(5)	-3 113(3)	9 559(5)
C(12)	7 937(6)	-1 064(7)	2 035(4)	4 352(5)	-3 593(2)	7 298(4)
C(13)	8 344(8)	-2 140(9)	2 343(4)	4 093(5)	-4 147(3)	7 818(5)
C(14)	8 259(8)	-2 417(9)	2 944(5)	2 811(6)	-4 373(3)	7 865(5)
C(15)	7 812(7)	-1 635(10)	3 240(4)	1 786(5)	-4 036(3)	7 389(5)
C(16)	7 432(7)	-564(10)	2 938(5)	2 022(5)	-3 488(3)	6 885(5)
C(17)	7 500(6)	-285(8)	2 343(5)	3 330(5)	-3 258(3)	6 832(4)
C(18)	7 162(6)	-1 900(7)	740(4)	6 872(5)	-3 862(2)	6 219(4)
C(19)	6 621(6)	-2 605(10)	993(4)	6 139(5)	-4 194(3)	5 441(5)
C(20)	5 975(6)	-3 388(10)	608(5)	6 775(7)	-4 519(3)	4 564(6)
C(21)	5 885(8)	-3 464(10)	-28(6)	8 131(7)	-4 427(3)	4 500(6)
C(22)	6 416(8)	-2 762(10)	-306(5)	8 880(5)	-4 198(3)	5 281(5)
C(23)	7 061(7)	-1 985(10)	86(4)	8 266(5)	-3 866(3)	6 135(5)

^a The atoms Sn(2), Cl(4)...Cl(8) and O(3) (of the water molecule) form the anion in IVa and the atoms C(O) and O(2) belong to the CO ligand of its cation. In the molecule of Va the atom Cl(O) acts as a ligand instead of the CO group in IVa (See the figure).

$C(CN)_2C(CN)_2CH_3$ the average Mo—C(Cp) distance is 2.33 Å [14]). The bond lengths Mo—CO of 1.95(1) Å and C—O of 1.15(1) Å in IVa and Mo—Cl of 2.444(2) Å in Va are unexceptional. The nitrosyl ligands * are linearly coordi-

* The closeness of the Mo—NO and Mo—CO as well as the N—O and C—O bond lengths in IVa allows a possibility of disorder with the NO and CO ligands substituting each other.

TABLE 3
ANISOTROPIC TEMPERATURE FACTORS IN THE FORM $T = \exp\left[-\frac{1}{40}(B_{11}h^2a^*2 + \dots + 2B_{12}hka^*b^* + \dots)\right]$ IN STRUCTURES OF IVa AND Va

Atom	IVa											
	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}	B_{11}	B_{12}	B_{13}	B_{22}	B_{33}	B_{23}
Sn(1)	67(1)	41(1)	57(1)	-14(1)	26(1)	2(1)	31(1)	3(1)	0(1)	25(1)	33(1)	2(1)
Sn(2)	34(1)	35(1)	32(1)	-2(1)	6(1)	2(1)	-	-	-	-	-	-
Mo	41(1)	32(1)	35(1)	-2(1)	9(1)	3(1)	24(1)	2(1)	4(1)	23(1)	19(1)	4(1)
Cl(0)	-	-	-	-	-	-	52(1)	0(1)	9(1)	40(1)	51(1)	-2(1)
Cl(1)	101(2)	72(2)	119(3)	-3(2)	24(2)	53(2)	46(1)	13(1)	31(1)	47(1)	109(2)	3(1)
Cl(2)	55(2)	138(3)	100(3)	-18(3)	17(2)	13(2)	83(1)	-1(1)	15(1)	82(1)	45(1)	-22(1)
Cl(3)	275(6)	73(2)	133(4)	-83(4)	142(4)	-47(2)	39(1)	-5(1)	-	32(1)	71(1)	1(1)
Cl(4)	54(1)	60(1)	33(1)	10(1)	4(1)	10(1)	-	-	-	-	-	-
Cl(5)	50(1)	79(2)	48(2)	4(1)	-5(1)	20(1)	-	-	-	-	-	-
Cl(6)	54(1)	101(2)	46(1)	0(1)	19(1)	20(1)	-	-	-	-	-	-
Cl(7)	48(1)	121(3)	56(2)	-6(2)	4(1)	1(2)	-	-	-	-	-	-
Cl(8)	72(2)	38(1)	129(3)	1(1)	-10(2)	-9(2)	-	-	-	-	-	-
P	39(1)	30(1)	27(1)	-6(1)	5(1)	-1(1)	20(1)	-1(1)	0(1)	22(1)	23(1)	1(1)
O(1)	72(4)	60(4)	48(4)	2(3)	33(3)	-2(3)	93(4)	19(3)	-12(3)	50(3)	52(3)	-5(2)
O(2)	103(6)	52(4)	48(4)	-13(4)	2(4)	-9(3)	-	-	-	-	-	-
O(3)	79(4)	41(3)	56(4)	-11(3)	9(3)	-6(3)	-	-	-	-	-	-
N	68(5)	42(4)	37(4)	-6(4)	10(4)	2(3)	22(2)	-3(2)	25(2)	17(2)	50(3)	-4(2)

C(0)	65(5)	29(3)	28(4)	-1(3)	9(4)	-4(3)	-	-	-	-	-	-
C(1)	55(6)	48(5)	56(6)	14(4)	23(5)	3(5)	44(3)	39(3)	22(2)	3(2)	-1(2)	3(2)
C(2)	36(4)	48(5)	49(5)	-1(4)	14(4)	6(4)	46(3)	46(3)	20(2)	-14(2)	14(2)	-1(2)
C(3)	34(4)	66(6)	44(5)	-3(4)	4(4)	0(5)	47(3)	53(3)	22(2)	8(2)	16(2)	-11(2)
C(4)	49(6)	85(8)	55(6)	16(6)	13(5)	29(6)	68(4)	31(3)	22(2)	-10(2)	1(2)	-7(2)
C(5)	52(6)	44(5)	85(8)	11(4)	19(6)	2(5)	32(2)	53(3)	28(2)	-9(2)	0(2)	-5(2)
C(6)	47(5)	28(4)	33(4)	-2(4)	9(4)	5(3)	23(2)	26(2)	26(2)	3(2)	-1(2)	-2(2)
C(7)	43(5)	58(6)	59(6)	-2(5)	0(5)	-8(5)	41(3)	28(2)	34(3)	-4(2)	-5(2)	-3(2)
C(8)	43(6)	63(7)	79(8)	-3(5)	8(6)	8(6)	43(3)	35(3)	38(3)	1(2)	-5(2)	-10(2)
C(9)	53(6)	64(7)	75(7)	4(6)	31(6)	27(6)	44(3)	44(3)	32(3)	12(2)	-9(2)	-8(2)
C(10)	72(7)	66(7)	78(8)	13(6)	43(6)	-6(6)	36(3)	51(3)	27(2)	1(2)	0(2)	4(2)
C(11)	59(6)	52(5)	58(6)	-8(5)	30(5)	-9(5)	28(2)	36(3)	31(2)	-1(2)	1(2)	1(2)
C(12)	40(4)	27(4)	25(4)	-7(3)	5(3)	0(3)	24(2)	26(2)	26(2)	3(2)	3(2)	2(2)
C(13)	65(6)	42(5)	34(4)	-3(4)	18(4)	0(4)	27(2)	33(3)	36(2)	4(2)	5(2)	-1(2)
C(14)	80(6)	37(5)	36(5)	0(5)	14(4)	8(4)	41(3)	31(3)	39(3)	11(2)	9(2)	2(2)
C(15)	62(6)	51(5)	30(4)	-3(5)	16(4)	4(4)	25(2)	48(3)	37(3)	13(2)	6(2)	8(2)
C(16)	60(6)	60(6)	41(5)	5(5)	24(4)	2(5)	20(2)	49(3)	39(3)	2(2)	-3(2)	6(2)
C(17)	46(6)	38(4)	43(5)	6(4)	14(4)	0(4)	25(2)	35(3)	28(2)	4(2)	2(2)	0(2)
C(18)	40(4)	23(3)	31(4)	-6(3)	4(3)	0(3)	25(2)	24(2)	29(2)	-3(2)	3(2)	1(2)
C(19)	45(5)	52(5)	36(4)	-8(4)	8(4)	-5(4)	29(2)	40(3)	32(2)	5(2)	4(2)	8(2)
C(20)	49(5)	63(6)	46(5)	-25(5)	6(4)	0(5)	52(3)	40(3)	43(3)	2(2)	5(2)	20(2)
C(21)	54(6)	51(6)	61(7)	-16(5)	-4(5)	-18(5)	53(3)	46(3)	41(3)	-4(3)	18(3)	16(3)
C(22)	71(6)	50(5)	35(5)	-22(5)	-2(4)	-6(4)	27(2)	40(3)	47(3)	-8(2)	11(2)	-1(2)
C(23)	65(6)	51(5)	31(5)	-11(5)	5(4)	3(4)	28(2)	35(3)	37(3)	-6(2)	1(2)	5(2)

TABLE 4
 BOND LENGTHS (Å)

Bond	IVa	Va	Bond	IVa	Va
Mo—Sn(1)	2.733(1)	2.715(1)	P—C(6)	1.81(1)	1.82(1)
Mo—Cl(O)	—	2.444(2)	P—C(12)	1.81(1)	1.83(1)
Mo—P	2.549(2)	2.546(1)	P—C(18)	1.81(1)	1.83(1)
Mo—N	1.82(1)	1.91(1)	N—O(1)	1.17(1)	1.17(1)
Mo—Co	1.95(1)	—	C(O)—O(2)	1.15(1)	—
Mo—C(1)	2.36(1)	2.36(1)	Av.C—C(Cp)	1.40(2)	1.41(2)
Mo—C(2)	2.33(1)	2.31(1)	Av.C—C(Ph)	1.38(2)	1.39(2)
Mo—C(3)	2.33(1)	2.29(1)	Sn(2)—Cl(4) ^a	2.381(3)	—
Mo—C(4)	2.31(1)	2.35(1)	Sn(2)—Cl(5)	2.399(3)	—
Mo—C(5)	2.31(1)	2.38(1)	Sn(2)—Cl(6)	2.376(3)	—
Sn(1)—Cl(1)	2.305(4)	2.363(2)	Sn(2)—Cl(7)	2.377(3)	—
Sn(1)—Cl(2)	2.290(4)	2.329(2)	Sn(2)—Cl(8)	2.383(3)	—
Sn(1)—Cl(3)	2.310(5)	2.364(2)	Sn(2)—O(3)	2.235(7)	—

^a Sn(2), Sn atom in the anion of IVa.

nated with Mo (the bond lengths Mo—N 1.92(1) Å in IVa and 1.91(1) Å in Va, N—O 1.17(1) and 1.17(1) Å; angles Mo—N—O 176(8) and 167.1(1)°) and act as three-electron donors in both complexes. Accordingly, the Mo atoms in IVa and Va obey the EAN rule.

The SnCl₅(H₂O)[−] anion in IVa has the usual octahedral structure. The bond lengths (Sn—O 2.235(7) Å and Sn—Cl 2.377–2.399 Å) are close to those found (Sn—O 2.24 Å, Sn—Cl 2.37–2.38 Å) in the same anion in the structure of [(Ph₂PCH₂CH₂PPh₂)Mo(CO)₄(SnCl₃)]⁺ SnCl₅(H₂O)[−] [9].

In the crystal of IVa the water molecule of the anion forms a hydrogen bond O(3)—H...Cl(8) (1 − x, 1/2 + y, 3/2 − z) by one of its H atoms with the chlorine atom of the neighbouring anion. This bond is 3.21 Å long, the Sn—O(3)...Cl(8) angle being 120°.

This study therefore shows that π-complexes of Mo and W with the donor ligands PPh₃ exhibit properties of strong organometallic bases and readily react with the aprotic acids HgCl₂ and SnX₄ (X = Cl, Br). Aprotic acids attack the metal atom which is thus the most basic site of the molecular. Products of reactions with aprotic acids have been isolated and their structure established by X-ray and IR spectral study.

Experimental

The starting compounds IIa and IIb were obtained as previously described [15].

Preparation of IIIa and IIIb. To the solution of 0.1200 g of IIa or 0.1425 g of IIb (0.25 mmol) in 6–8 ml of CH₂Cl₂ an exact amount of finely powdered HgCl₂ (0.0680 g, 0.25 mmol) is added under magnetic stirring. Mercuric chloride rapidly dissolves producing a clear yellow solution (the starting IIa and IIb are red in color) and after 5–10 minutes finely crystalline powders of the air-stable yellow complexes IIIa and IIIb precipitate. The precipitate is filtered off, washed with CH₂Cl₂ and the solvent is removed in vacuo. The yield is close to theory.

TABLE 5
BOND ANGLES (DEGREES) IN STRUCTURES IVa AND Va

Angle	IVa	Va	Angle	IVa	Va	Angle	IVa	Va
Sn(1)-Mo-P	139.24(6)	142.57(3)	N-Mo-Cp	126.4	122.8	C(6)-P-C(12)	104.2(4)	102.4(2)
Sn(1)-Mo-Cl	-	74.22(4)	O-C-Mo-Cp	125.9	-	C(6)-P-C(18)	108.5(4)	107.0(2)
Sn(1)-Mo-N	77.5(3)	79.8(2)	Mo-Sn(1)-Cl(1)	117.3(1)	117.4(1)	C(12)-P-C(18)	104.8(4)	104.6(2)
Sn(1)-Mo-CO	75.7(3)	-	Mo-Sn(1)-Cl(2)	115.7(1)	116.4(1)	Av. C-C-C(Cp)	109(1)	109(1)
Sn(1)-Mo-Cp ^a	107(4)	106(1)	Mo-Sn(1)-Cl(3)	115.0(2)	119.1(1)	Av. C-C-C(Ph)	120(1)	120(1)
P-Mo-Cl	-	82.70(5)	Mo-P-C(6)	111.0(3)	114.8(2)	O(3)-Sn(2)-Cl(8)	179.1(2)	-
P-Mo-N	80.2(3)	82.4(2)	Mo-P-C(12)	116.5(3)	119.2(2)	O(3)-Sn(2)Cl(cis)	84.1-87.2	-
P-Mo-CO	79.0(3)	-	Mo-P-C(18)	111.2(3)	107.9(2)	Cl(4)-Sn(2)-Cl(5)	170.5(1)	-
P-Mo-Cp	113.3	111.2	Mo-N-O(1)	176.5(8)	167(1)	Cl(6)-Sn(2)-Cl(7)	172.2(1)	-
Cl(O)-Mo-N	-	112.3(1)	Mo-C-O(2)	177.1(8)	-	Cl-Sn(2)-Cl(cis)	88.9-95.8(1)	-
Cl(O)-Mo-Cp	-	124.2	Cl-Sn(1)-Cl(2)	101.4(2)	101.3(1)	-	-	-
N-Mo-CO	107.3(4)	-	Cl(1)-Sn(1)-Cl(3)	104.5(2)	98.3(1)	-	-	-
-	-	-	Cl(2)-Sn(1)-Cl(3)	100.6(2)	101.1(1)	-	-	-

^a Cp is a centroid of the C₅H₅ ligand.

TABLE 6

MAIN TORSIONAL ANGLES τ (DEGREES) CHARACTERIZING THE MUTUAL LIGAND ORIENTATION IN IV_a AND V_a

Ligand	IV _a	V _a	Angle	IV _a	V _a
	X = CO	X = Cl		X = CO	X = Cl
Sn(1)MoPC(6)	-24.8	-20.6	PMoSn(1)Cl(1)	145.3	130.0
Sn(1)MoPC(12)	94.2	101.4	PMoSn(1)Cl(2)	25.5	9.8
Sn(1)MoPC(18)	-145.7	-139.8	PMoSn(1)Cl(3)	-91.3	-111.7
NMoPC(6)	32.8	41.4	XMoSn(1)Cl(1)	-161.4	-175.9
NMoPC(12)	151.8	163.3	XMoSn(1)Cl(2)	78.9	63.3
NMoPC(18)	-88.1	-77.8	XMoSn(1)Cl(3)	-37.9	-57.6
XMoPC(6)	-77.2	-72.4	NMoSn(1)Cl(1)	86.9	67.3
XMoPC(12)	41.9	49.5	NMoSn(1)Cl(2)	-32.9	-52.9
XMoPC(18)	161.9	168.4	NMoSn(1)Cl(3)	-149.7	-174.4

Preparation of IV_a, V_a. To 0.12 g (0.25 mmol) of II_a in 5 ml of CH₂Cl₂ a 2–3-fold excess of SnCl₄ in 2–3 ml of CH₂Cl₂ is added. The solution color changes instantaneously from red to yellow and in the IR spectrum the $\nu(\text{CO})$ and $\nu(\text{NO})$ bands of II_a disappear and the bands of IV_a appear. On storage of the solutions at 0–2°C, CO is gradually evolved concurrently with a decrease of the intensity of the bands of IV_a and an appearance of the $\nu(\text{NO})$ band of V_a at 1675–1680 cm⁻¹. On addition of 2 to 4 volumes of petroleum ether at 0°C a mixture of IV_a and V_a crystals is formed on the walls of the reaction vessel and can be separated mechanically. Without addition of petroleum ether crystallization is slower and mainly crystals of V_a are formed. IV_a is moderately and V_a is very stable in air.

Preparation of IV_b. To 0.1430 g (0.25 mmol) of II_b in 5 ml of CH₂Cl₂ an excess of SnCl₄ is added, changing the color of the solution from red to yellow and giving rise to the IV_b bands in the IR spectrum. After addition of petroleum ether a yellow-brown oil precipitates which rapidly crystallizes on trituration. The crystals are filtered off, washed with CH₂Cl₂ and the solvent removed in vacuo. The yield is about 90%; IV_b is stable in air.

Preparation of VI_a and VI_b. To 0.25 mmol of II_a or II_b in 5 ml CH₂Cl₂ 0.5 g (1.0 mmol) of SnBr₄ in CH₂Cl₂ is added. CO is rapidly liberated and complexes VI_a or VI_b, which are practically insoluble in CH₂Cl₂, precipitate from the solution with a yield close to theory. The analytical data and properties of the complexes III–VI are given in Table 7.

Determination of the crystal structure of IV_a and V_a

Crystals of IV_a and V_a are monoclinic, the cell parameters being respectively: $a = 15.492(5)$ and $10.086(1)$; $b = 10.787(4)$ and $22.069(3)$; $c = 21.809(9)$ and $11.610(2)$ Å; $\beta = 107.16(3)$ and $89.91(1)^\circ$; $D_{(\text{measured})} = 1.80$ and 1.78 ; $D_{(\text{calcd.})} = 1.86$ and 1.78 g cm⁻³, $Z = 4$, space group $P2_1/c$,

Experimental data were obtained with a Syntex P2₁ automatic diffractometer, λMo , graphite monochromator, $\theta/2\theta$ scan, $2^\circ \leq 2\theta \leq 46^\circ$ for IV_a and $2^\circ \leq 2\theta \leq 50^\circ$ for V_a; 3570 and 3710 independent reflections with $F^2 > 2\sigma$ for IV_a and V_a respectively. Both structures were solved using the heavy atom method and refined by full-matrix least squares with anisotropic thermal

TABLE 7
ANALYTICAL DATA AND PROPERTIES OF III-VI

Compound	Color	M.p. (°C)	Formula	Analysis found (Calcd.) (%)				
				C	H	Hg/Sn	Cl/Br	Other
IIIa	yellow	160(d)	$C_{24}H_{10}NO_2PMoHgCl_2$	38.25 (38.27)	3.14 (2.66)	26.54 (26.65)	—	3.96(P) 4.12
IIIb	yellow	185(d)	$C_{24}H_{20}NO_2PWHgCl_2$	33.98 (24.10)	2.53 (2.38)	23.70 (23.80)	8.84 (8.45)	—
IVa	brown	—	$C_{24}H_{22}NO_3PMoSn_2Cl_8$	28.10 (28.25)	2.36 (2.16)	23.06 (23.26)	28.97 (29.20)	—
IVb	yellow	145-148	$C_{24}H_{20}NO_2PWSn_2Cl_8$	26.50 (26.42)	2.19 (1.83)	21.71 (21.78)	26.27 (26.05)	16.90(W) (16.88)
Va	orange	205-208	$C_{23}H_{20}NOPMoSnCl_4$	38.17 (38.71)	2.84 (2.80)	17.04 (16.95)	20.79 (19.92)	—
VIa	orange	177-180	$C_{23}H_{20}NOPMoSnBr_4$	30.95 (30.95)	2.36 (2.24)	13.86 (13.30)	—	1.51(N) (1.57)
VIb	cherry red	188-190	$C_{23}H_{20}NOPWSnBr_4$	27.72 (28.18)	2.04 (2.04)	11.92 (12.11)	33.54 (32.67)	—

parameters to $R = 0.0516$ ($R_G = 0.0615$) for IVa and $R = 0.0542$ ($R_G = 0.0615$) for Va. Determination of cell parameters indicated that VIa is isostructural with Va.

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