

BASICITY OF TRANSITION METAL CARBONYL COMPLEXES

XI *. REACTIONS OF $C_5H_5Mn(CO)_2L$ WITH STANNIC CHLORIDE AND STRUCTURE OF REACTION PRODUCTS

A.G. GINZBURG *, N.G. BOKYI, A.I. YANOVSKY, Yu.T. STRUCHKOV, V.N. SETKINA and D.N. KURSANOV

Institute of Organo-Element Compounds, USSR Academy of Sciences, Moscow (U.S.S.R.)
(Received March 9th, 1977)

Summary

Adducts of 1 : 2 composition were obtained by reacting $C_5H_5Mn(CO)_2L$ complexes ($L =$ tertiary phosphines, $AsPh_3$ and $SbPh_3$) with stannic chloride. The crystal and molecular structure of $C_5H_5Mn(CO)_2PPh_3 \cdot 2SnCl_4$ was established by X-ray structural analysis. It has an ionic structure that corresponds to formula $[C_5H_5Mn(CO)_2(PPh_3)(SnCl_3)]^+SnCl_5^-$. The coordination environment of the manganese atom is a distorted square pyramid with a C_5H_5 ligand at the apex. Using IR spectroscopy it was established that in certain cases a mixture of two isomers is formed in solution. In $C_5H_5Mn(CO)_2L$ complexes the central manganese atom is the site of attack by aprotic acids and is the most basic site of the molecule.

Introduction

The concept of basicity for transition metal complexes has been considerably developed recently [2,3]. This problem is closely related to the study of the reactivity of these complexes with respect to electrophilic reagents. It has been shown that the direction of the primary attack by an electrophil and the site to which it is finally attached greatly depends on the nature of the electrophil and the substrate structure, in particular on the central metal atom and its ligand environment [4,5]. Under the action of acids (CF_3COOH , HCl), $RC_6H_5Cr(CO)_2L$ [6] and $C_5H_5Mn(CO)_2L$ (where L is a phosphine) [7] are protonated, the proton being attached to the central metal atom; obviously the latter is the most basic site in the molecule. The formation of $Cr-H$ and $Mn-H$ bonds in these reactions has been reliably established by IR and NMR studies [6-8].

* For part X, see ref. 1.

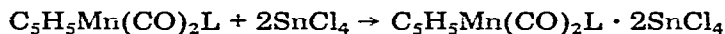
(π -ligand) $M(\text{CO})_x\text{L}_y$ complexes may also interact with other electrophilic reagents, for instance with aprotic EHal_4 acids, forming adducts such as $\text{C}_5\text{H}_5\text{Co}(\text{CO})_2 \cdot \text{HgCl}_2$ the structure of which has already been determined [9]. The chemical bond in these adducts is of the donor—acceptor type, the donor being the electron-rich organometallic complex and the acceptor the aprotic acid with vacant orbitals. However, the nature of bonding between the donor and acceptor may vary considerably for different adducts. They may be neutral or salt-like and are formed by oxidative addition or oxidative elimination. It should be noted that in these adducts the formal oxidation state of the metal always increases and dative interaction always weakens, since it has been established that the $\nu(\text{CO})$ frequencies in metalcarbonyl moieties increase by 50–90 cm^{-1} in relation of the initial complexes.

The reactions of organometallic π -complexes with EHal_4 ($\text{E} = \text{Ti, Ge, Sn}$; $\text{Hal} = \text{Cl, Br}$) were previously studied mainly in solution [4,5,10]; solid crystalline adducts were obtained in reactions of SnCl_4 with ferrocene [11] and ruthenocene [12], however their structure has not been determined precisely.

The aim of the present work was to determine the structure of products formed in reactions of $\text{C}_5\text{H}_5\text{Mn}(\text{CO})_2\text{L}$ with stannic chloride.

Results and discussion

Interaction of $\text{C}_5\text{H}_5\text{Mn}(\text{CO})_2\text{L}$ (I a–e, $\text{L} = \text{PPh}_3, \text{AsPh}_3, \text{SbPh}_3, \text{P}(\textit{iso}\text{-C}_3\text{H}_7)_3, \text{P}(\text{C}_6\text{H}_{11})_3$) with an excess of SnCl_4 in thoroughly dried $\text{CH}_2\text{Cl}_2, \text{CHCl}_3$ or in benzene brings about an abrupt change of colour from yellow to red or brown; crystalline $\text{C}_5\text{H}_5\text{Mn}(\text{CO})_2\text{L} \cdot 2\text{SnCl}_4$ adducts (IIa–e) are isolated from the solution (see also preliminary communication [13]). IIa, IIb and IIc are practically insoluble in the solvents used and rapidly precipitate; IId and IIe are more soluble. In solid state IIa–e readily hydrolyze, in air they decompose after several minutes forming I with quantitative yields and products of SnCl_4 hydrolysis. Nucleophilic solvents (ether, alcohol, acetone, amines, acetonitrile, etc) rapidly decompose II with formation of I.



(I)

(II)

Ia, IIa, $\text{L} = \text{PPh}_3$; Ib, IIb, $\text{L} = \text{AsPh}_3$; Ic, IIc, $\text{L} = \text{SbPh}_3$; Id, IId, $\text{L} = \text{P}(\textit{i}\text{-C}_3\text{H}_7)_3$; Ie, IIe, $\text{L} = \text{P}(\text{C}_6\text{H}_{11})_3$

Adducts II are insoluble in nonpolar solvents (hydrocarbons, $\text{CCl}_4, \text{CS}_2$), while in polar solvents (acetone, nitromethane or nitrobenzene) they dissociate forming I. Consequently NMR study and conductivity measurements cannot be used for determining their structure.

In IR spectra of solutions and in solid state (Nujol mulls) both $\nu(\text{CO})$ frequencies are shifted to the region of higher wave numbers. This indicates weakening of dative interaction in $\text{Mn}-\text{CO}$ bonds and increase of the positive charge on the Mn atom. The direction and value of the $\nu(\text{CO})$ shift during formation of II coincides with previously studied situations when the Mn atom acquires a partial positive charge as a result of: protonation at the metal [7]; substitution of CO for NO^+ [14]; or formation of a carbenium center in the side chain of a substituent in the Cp-ring [15]. On the basis of this similarity it can only be suggested

that during formation of II, an acceptor SnCl_x group is attached to the Mn atom and no conclusion can be made about coordination of the second Sn atom.

To determine the structure of the adducts we carried out an X-ray study of IIa ($L = \text{PPh}_3$). IIa has a salt-like structure. The crystal consists of $[\pi\text{-C}_5\text{H}_5\text{Mn}(\text{CO})_2\text{PPh}_3(\text{SnCl}_3)]^+$ cations and SnCl_5^- anions (Fig. 1 shows the cation structure). Manganese has a tetragonal pyramid coordination (assuming that the cyclopentadienyl ring occupies only one coordination place). PPh_3 and SnCl_3 groups are in *trans*-positions and the P-Mn-Sn(2) and C(1)-Mn-C(2) angles are $131.1(1)$ and $115.1(4)^\circ$ respectively. The angle values are in good agreement with seven-coordinated, $\pi\text{-C}_5\text{H}_5\text{M}(\text{CO})_3\text{R}$ complexes of Mo and W where angles $\text{R-M-CO}(\text{trans}) = 125\text{--}133^\circ$ and $\text{OC-M-CO}(\text{trans}) = 107\text{--}116^\circ$ [16] and also agree with the structure of $\pi\text{-C}_5\text{H}_5\text{Re}(\text{CO})_2(\text{CH}_3)\text{Br}$ where angles $\text{Br-Re-C(3)}(\text{trans}) = 139.1(1)^\circ$ and $\text{C(2)-Re-C(1)}(\text{trans}) = 102.0(1)^\circ$ [17]. Although syntheses of $\text{C}_5\text{H}_5\text{Mn}(\text{CO})_2(\text{SnCl}_3)(\text{SiCl}_3)$ complexes was described by Graham in 1971 [18], the structure of IIa is the first X-ray study of a mononuclear 7-coordinated π -complex of Mn. Recently the structure of the product of the SnCl_4 reaction with $(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2)\text{Mo}(\text{CO})_4$ was reported [30] and was found to be ionic; and ionic structure was also assumed for the $(\text{C}_5\text{H}_5)_2\text{Ru} \cdot 1.5\text{SnCl}_4$ adduct [12].

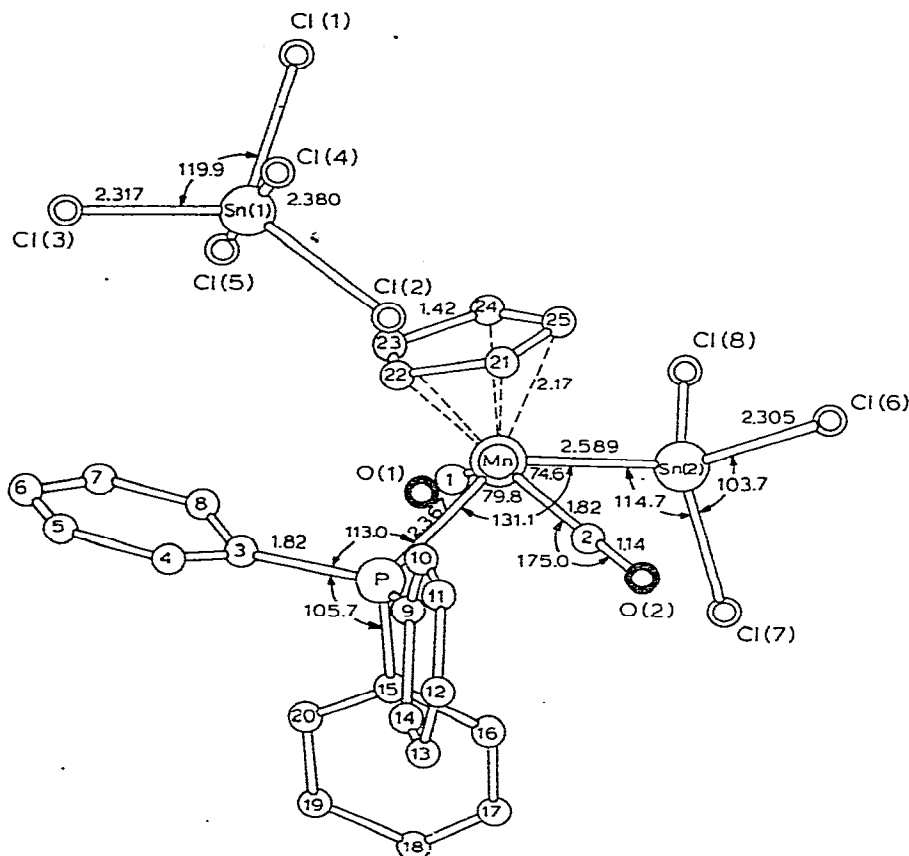


Fig. 1. A view of complex IIa showing the atom numbering.

The projection of the Mn coordination environment on the plane of the cyclopentadienyl ring is shown in Fig. 2. The Sn(2)—Mn—C(1) and Sn(2)—Mn—C(2) angles are equal (74.9(3) and 74.4(3)°) and are considerably smaller than the P—Mn—C(1) and P—Mn—C(2) angles (80.0(4) and 79.5(4)° respectively). This is apparently due to repulsion of the carbonyl groups by phenyl rings (distances C(1)...C(15) = 2.95, C(2)...C(9) = 3.00, and C(1)...C(16) = 3.19 Å are shortened, whereas C...Cl is not less than the sum of the corresponding Van der Vaals radii; the minimal distance of C(2)...Cl(6) is 3.58 Å).

Much interest is presented by the length of the Sn—Mn bond. Several authors have pointed out the strong dependence of the Sn—Mn length (and, in general, of bonds between nontransition and transition metals) upon the ligand environment of both atoms [19,20] that is caused by a change of the multiplicity of the bond due to *d*—*d* interaction of the filled orbitals of the transition metal with vacant orbitals of the nontransition metal. The presence of acceptor ligands at the Sn atom and of donor PPh₃ ligand in the coordination environment of Mn should increase multiplicity and shorten the Sn—Mn bond.

These considerations agree with data obtained for several complexes of iron. Thus, in π -C₅H₅Fe(CO)₂-SnPh₃ the Fe—Sn bond is 2.536 Å [21], while in π -C₅H₅Fe(CO)₂-SnCl₃ it is only 2.467 Å [22]. The Mn—Sn bond of 2.598(2) Å in IIa is shorter than the corresponding distances established previously for Ph₃SnMn(CO)₄PPh₃ (2.63(1) Å, [19]), Me₃SnMn(CO)₅ (2.674(4) Å [20]), Ph₂Sn[Mn(CO)₅]₂ (2.70(1) Å [23]) and for H₂Sn[Mn(CO)₅]₂ (2.67 Å [24]). The Mn—P bond (2.367(4) Å), on the other hand, is considerably longer as compared with 2.236 Å in Ia [25] and with 2.234, 2.239 Å in π -C₅H₅Mn(CO)(PPh₃)₂ [26]. The longer Mn—P bond is probably connected with reduction of its multiplicity due to weakening of dative interaction.

The Mn—CO bonds (1.82 and 1.83(1) Å) are also longer than in the binuclear 7-coordinated [π -C₅H₅Mn(CO)₂]₂- μ -C=CHPh complex (1.74–1.77 Å [27]) and in Ia (1.74, 1.77 Å [25]). Lengthening of the Mn—CO bonds conforms with the increase of ν (CO) frequencies when passing from Ia to IIa.

The Sn(2) atom has a distorted tetrahedral configuration: the Mn—Sn—Cl angle of 114.7(1)° is bigger and the Cl—Sn—Cl angle of 103.6(1)° is smaller than the ideal value of 109.5°. The SnCl₅⁻ anion is a trigonal bipyramid with axially

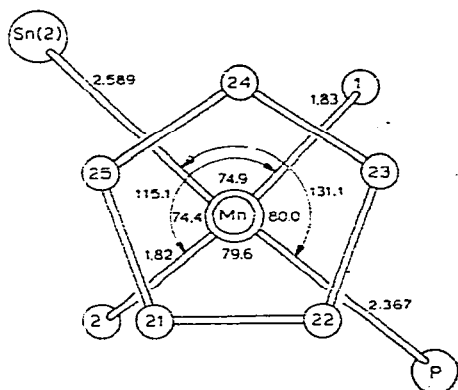
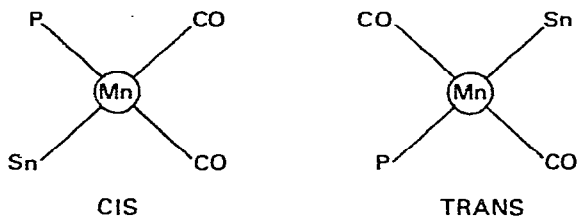


Fig. 2. The projection of Mn coordination environment on the plane of the cyclopentadienyl ring.

arranged Cl(4) and Cl(5) atoms; the axial Sn—Cl bonds (average 2.380(4) Å) are, as usual, slightly longer than the equatorial Sn—Cl bonds (average 2.317(2) Å). The interionic contacts in the structure are normal. The shortest distances are Cl...Cl = 3.57, Cl...C = 3.41 and Cl...O = 3.27 Å.

Thus an important conclusion can be made from the structure of IIa, namely, that the cation is evidently formed by direct attack of the aprotic acid molecule at the central Mn atom which, as for protonation, is the site with highest basicity. The intermediate formed is stabilized by transfer of Cl⁻ to the external sphere where it is bonded to the second SnCl₄ molecule producing a SnCl₅⁻ counterion.

Formation of the Mn—SnCl₃ bond may lead to two isomers with *cis*- and *trans*-arrangements of CO ligands in the base of the square pyramid:



From the above-mentioned it follows that in crystal form the cation IIa has a *trans*-structure, whereas, according to IR data, both isomers may exist in solution.

Formation of II leads to an increase in $\nu(\text{CO})$ frequencies; depending on the amount of SnCl₄ and on the basicity of the complex either the $\nu(\text{CO})$ frequencies of both I and II are present in the spectrum or (with a large excess of SnCl₄) only the frequencies of II (Table 1). It should be noted that adducts with SnCl₄ are formed only when the basicity of the central Mn atom is sufficiently increased by donor ligands. Unsubstituted $\pi\text{-C}_5\text{H}_5\text{Mn}(\text{CO})_3$ does not react with SnCl₄ (the basicity of the metal is insufficient) and in the case of I with L = P(OPh)₃, although an adduct is formed, the equilibrium is strongly shifted towards the initial compounds (according to IR data) and we were unable to isolate crystalline II.

In several instances four new absorption bands belonging to II were observed in the IR spectra instead of two (see Fig. 3).

Formation of II also brings about a sharp change in the relative intensities of $\nu(\text{CO})$. The shape of the spectrum in the region of $\nu(\text{CO})$ frequencies depends on several factors: the nature of the donor atom in L (P, As or Sb), the radical at the phosphorus atom, the ratio of the reagent concentrations, and the solvent. Usually the shape of the spectrum changes in time. For a solution of IIa at moderate SnCl₄ concentrations four bands are observed (Fig. 3a), whereas with a large excess of SnCl₄ only two bands are present (at 1995 and 2035 cm⁻¹). The position and relative intensities of these two bands practically coincide with those in the spectrum of solid IIa (in Nujol mulls), the structure of which was determined independently. On this basis we assigned the bands at 1995vs and 2035m cm⁻¹ to the *trans*-isomer of IIa and the other two bands at 1970(sh) and 2050 cm⁻¹ to the *cis*-isomer that is present in small quantities in the solution at moderate concentrations of SnCl₄. At high SnCl₄ concentrations IIa exists

TABLE I
THE CO STRETCHING MODE FREQUENCIES FOR I AND II

Ligand L	$\nu(\text{CO})$ frequencies in CH_2Cl_2 solution (cm^{-1})				$\nu(\text{CO})$ frequencies in the solid state (Nujol mulls)		Isomer of II in the solid state, based on IR data	
	starting I in CH_2Cl_2	1.5-2 mol Sn: 1 mol Mn	6-10 mol Sn: 1 mol Sn	$\nu(\text{CO})$ frequencies in CH_2Cl_2 solution (cm^{-1})	$\nu(\text{CO})$ frequencies in the solid state (Nujol mulls)	Isomer of II in the solid state, based on IR data		
	$\nu(\text{as})$ $\nu(\text{s})$	<i>Cis</i>	<i>Trans</i>	<i>Cis</i>	<i>Trans</i>			
PPh ₃	1870	1037	1970(sh)	2050	1995	2035	2050m	<i>trans</i>
AsPh ₃	1868	1036	1970(sh)	2050	1995	2035	2036m	<i>trans</i>
SnPh ₃	1870	1037			1984	2025	2035th	<i>trans</i>
P(iso-C ₃ H ₇) ₃	1856	1025	1962	2043	1986	2025	2040s	<i>cis</i>
P(C ₆ H ₁₁) ₃	1853	1024	1960	2042	1985	2025(sh)	2040s	<i>cis</i>

(sh) = shoulder; vs = very strong; s = strong; m = medium.

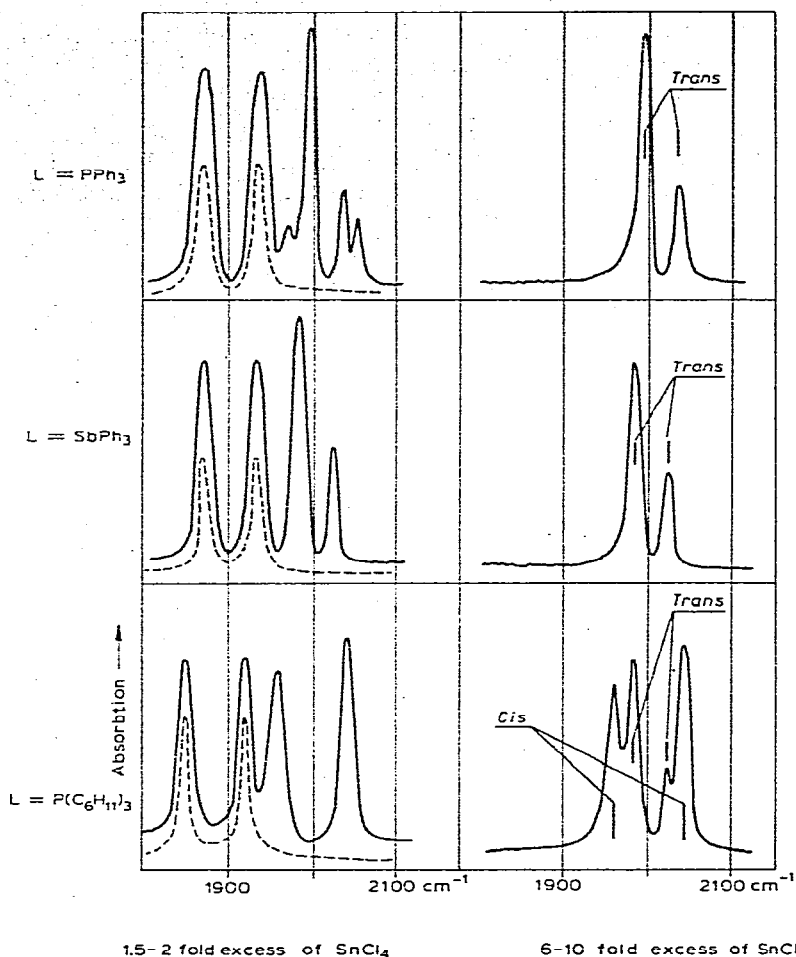


Fig. 3. CO stretching frequencies for CH_2Cl_2 solutions: left, 1.5–2 fold excess of SnCl_4 ; right, 6–10 fold excess of SnCl_4 . Upper, $\text{L} = \text{PPh}_3$; middle, $\text{L} = \text{SbPh}_3$; lower, $\text{L} = \text{P}(\text{C}_6\text{H}_{11})_3$. $\nu(\text{CO})$ frequencies for the starting I shown by the dotted line.

only in the *trans* form, whereas adducts with $\text{L} =$ trialkylphosphines (IIa and IIe) form a mixture of isomers.

Analysis of the variation of intensity ratio of both bands in the IR spectra confirms the possibility of formation of both *cis*- and *trans*-isomers. It is known that the ratio of integral intensities for the $\text{M}(\text{CO})_2$ fragment depends on the angle between the carbonyl groups (α): $A_{\text{asym}}/A_{\text{sym}} = \text{tg}^2\alpha/2$ (expression 1 [28,29]). When the angle hardly differs from 90° , the ratio of the optical densities of $\nu(\text{CO})$ bands in pseudo-octahedral $\text{C}_5\text{H}_5\text{Mn}(\text{CO})_2\text{L}$ is close to unity: $D_{\text{asym}}/D_{\text{sym}} \approx 1.0\text{--}1.2$. Strictly speaking, the ratio of optical densities is not equal to the ratio of integral intensities, however, in our case such substitution is possible since the half-widths of the asymmetrical and symmetrical $\nu(\text{CO})$ bands in CH_2Cl_2 or CHCl_3 solutions differ only slightly. When the angle considerably exceeds 90° , i.e. for the *trans*-isomer, the ratio of optical densities should be noticeably higher than unity and the asymmetrical band should be more inten-

sive than the band of symmetrical vibration exhibited at higher wave number. Due to the approximate nature of expression 1, the angle values calculated from the intensity ratios are not sufficiently accurate and provide only semi-quantitative estimation. For the 1995 and 2035 cm^{-1} frequencies in the IIa spectrum, $D_{1995}/D_{2035} = 3.5$ which corresponds to an angle of 120–122°. This value satisfactorily agrees with the value of 115° obtained from X-ray data for the crystal. Close values of α are obtained from $D_{\text{asym}}/D_{\text{sym}}$ ratios for *trans*-isomers of other II adducts (3.5 for $L = \text{AsPh}_3$, 3.0 for $L = \text{SbPh}_3$). Due to considerable overlap of bands we were unable to measure the corresponding ratio for *cis*-isomers. It can only be said that the intensity ratio is less than unity for *cis*-isomers (symmetrical vibration band is more intensive), e.i. angle α is less than 90°.

Conclusions

Interaction of $\text{C}_5\text{H}_5\text{Mn}(\text{CO})_2\text{L}$ with stannic chloride proceeds by direct attack at the central Mn atom by the aprotic acid. IR spectral data are in good agreement with a $[\pi\text{-C}_5\text{H}_5\text{Mn}(\text{CO})_2\text{PPh}_3(\text{SnCl}_3)]^+\text{SnCl}_5^-$ structure of the adduct determined by X-ray analysis. The close similarity of properties and IR spectra in the region of $\nu(\text{CO})$ frequencies makes it possible to consider that the other adducts have a similar salt-like structure with Mn–SnCl₃ bonds. The Mn–Sn bond readily ruptures during hydrolysis or under the action of nucleophilic solvents. Attack at the central metal atom shows that it is the reaction site with highest basicity.

Experimental

Synthesis of $[\pi\text{-C}_5\text{H}_5\text{Mn}(\text{CO})_2\text{PPh}_3(\text{SnCl}_3)]^+\text{SnCl}_5^-$

The reaction was carried out under an atmosphere of thoroughly dried argon in a cylindrical funnel with a porous plate (height 70–100 mm, diameter 20 mm). 1.1 g (4 mmol) of SnCl_4 in 5 ml of dry CH_2Cl_2 was added to 0.44 g (1 mmol) of $\pi\text{-C}_5\text{H}_5\text{Mn}(\text{CO})_2\text{PPh}_3$ in 5 ml of CH_2Cl_2 . The solution instantly turned cherry colored and after 10–15 min a cherry-brown crystalline precipitate was formed. After complete precipitation the solvent was filtered under argon pressure, the deposit repeatedly washed with CH_2Cl_2 and then with benzene and hexane (all operations were carried out under argon atmosphere or under a layer of argon-saturated solvent). The remaining solvent was evacuated under vacuum. The crystals are stable in a sealed ampoule or in an inert solvent. Yield 0.85 g (~90%). (Found: C, 31.37; H, 2.35; Mn, 5.70. $\text{C}_{25}\text{H}_{20}\text{MnO}_2\text{PSn}_2\text{Cl}_2$ calcd.: C, 31.30; H, 2.10; Mn, 5.73%). Yellow IIb ($L = \text{AsPh}_3$) and pale yellow IIc ($L = \text{SbPh}_3$) were prepared in the same manner. To isolate II d and II e where L are trialkylphosphines, after adding the solution of SnCl_4 in CH_2Cl_2 to I in the same solvent, the red solution of II was evacuated under vacuum and the remaining dark red oil was covered with hexane. Red crystals of II are formed after cooling the oil to -78°C and trituration under hexane. Elemental analyses (C, H and Mn) of II b–e also give satisfactory results.

X-ray structural analysis

Crystals of $[\pi\text{-C}_5\text{H}_5\text{Mn}(\text{CO})_2\text{PPh}_3\text{SnCl}_3]\text{SnCl}_5$ are monoclinic: $a = 13.018(6)$;

$b = 19.396(8)$, $c = 13.293(6)$ Å, $\beta = 104.84(4)^\circ$, $V = 3244(3)$ Å³, $d_{\text{cal}} = 1.975$ g/cm³, $Z = 4$, spaced group $P2_1/c$. Cell constants were determined with an automatic 4-circle Syntex $P2_1$ diffractometer and refined by the least-squares method. The three-dimensional set of intensities was obtained with the same diffractometer (λ Mo- $K\alpha$, graphite monochromator, $2\theta \leq 40^\circ$, $\theta/2\theta$ scan technique, 2245 independent reflections with $F^2 \geq 3\sigma$). Computer programs [31] were used.

The structure was determined by the heavy-atom method and refined by the least-squares method first in the isotropic ($R = 11.6\%$) and then in the anisotropic ($R = 4.5\%$) approximations. Atomic coordinates and temperature factors are given in Table 2, bond distances and angles in Tables 3 and 4.

IR spectra of solutions (0.1 mm NaCl cells) and of Nujol mulls were recorded

TABLE 2

ATOMIC ($\times 10^4$) AND THERMAL ($\times 10^4$) PARAMETERS

Anisotropic thermal parameters are of the form $T = \exp[-(B_{11}h^2 + B_{22}k^2 + B_{33}l^2 + B_{12}hk + B_{13}hl + B_{23}kl)]$

Atom	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Sn(1)	4079(1)	2152(0)	201(1)	66	25	19	-7	39	3
Sn(2)	7887(1)	3788(0)	4462(1)	74	24	13	-1	36	4
Mn	7392(1)	4431(1)	2702(1)	43	17	134	-2	23	-5
Cl(1)	2516(3)	1854(2)	626(3)	84	39	38	-10	1	-12
Cl(2)	5581(3)	2229(2)	1580(3)	85	61	61	36	11	10
Cl(3)	4006(3)	2610(4)	3470(3)	93	86	86	-20	52	-50
Cl(4)	3735(3)	3341(2)	456(4)	111	24	24	-1	-18	-12
Cl(5)	4451(4)	980(2)	67(4)	180	27	110	-10	261	-33
Cl(6)	7770(3)	4441(2)	5890(2)	140	48	18	20	56	-26
Cl(7)	9584(3)	3345(2)	4934(3)	82	39	112	22	16	11
Cl(8)	6882(3)	2818(2)	4516(3)	112	33	103	-35	73	27
P	8418(2)	4710(1)	1523(2)	46	15	33	3	22	-4
O(1)	7978(6)	3023(3)	2186(6)	92	17	28	3	59	-6
O(2)	9027(7)	5299(4)	4084(6)	90	26	36	-29	20	-25
C(1)	7782(8)	3567(6)	2397(8)	42	28	35	3	36	18
C(2)	8444(9)	4940(5)	3542(8)	83	14	31	-7	56	-19
C(3)	7685(8)	4617(5)	173(8)	52	26	42	-12	45	-14
C(4)	7648(8)	5175(5)	-525(8)	81	21	5	7	46	15
C(5)	7073(9)	5083(6)	-1558(9)	61	34	6	-7	13	14
C(6)	6550(9)	4470(6)	-1914(8)	76	34	30	17	22	18
C(7)	6591(11)	3929(7)	1209(10)	103	42	36	-18	17	13
C(8)	7151(9)	4007(6)	-178(8)	82	31	29	-19	37	8
C(9)	8976(8)	5579(5)	1685(7)	61	16	40	3	19	10
C(10)	8326(8)	6142(5)	1745(8)	52	18	74	-5	20	14
C(11)	8784(10)	6791(5)	1938(10)	75	15	103	-8	51	-13
C(12)	9841(9)	6903(6)	1991(9)	66	22	18	-7	39	-7
C(13)	10461(9)	6368(6)	1877(9)	72	29	17	-10	41	-2
C(14)	10043(9)	5683(5)	1716(8)	70	23	25	-31	40	16
C(15)	9562(8)	5150(5)	1676(8)	64	14	25	-16	56	0
C(16)	10304(8)	4137(6)	2666(8)	41	25	24	9	11	7
C(17)	11241(10)	3749(6)	2748(10)	91	26	23	15	64	43
C(18)	11430(10)	3395(7)	1922(11)	63	35	27	12	77	47
C(19)	10691(10)	3410(6)	985(10)	85	28	30	9	101	-13
C(20)	9750(9)	3792(6)	853(9)	76	28	23	-9	67	9
C(21)	6309(9)	5284(6)	2717(11)	51	37	25	-2	37	-7
C(22)	6176(8)	5055(6)	1669(9)	28	24	20	16	10	11
C(23)	5855(8)	4345(6)	1603(10)	28	37	20	-15	1	1
C(24)	5743(9)	4143(7)	2585(10)	41	41	27	-2	35	34
C(25)	6051(9)	4711(7)	3279(9)	57	46	25	15	59	-5

TABLE 3
 BOND LENGTHS d (Å)

Atoms	d	Atoms	d	Atoms	d	Atoms	d
Sn(1)—Cl(1)	2.319(4)	Mn—C(21)	2.18(1)	C(5)—C(6)	1.39(2)	C(17)—C(18)	1.37(2)
Sn(1)—Cl(2)	2.317(3)	Mn—C(22)	2.18(1)	C(6)—C(7)	1.40(2)	C(18)—C(19)	1.37(2)
Sn(1)—Cl(3)	2.316(4)	Mn—C(23)	2.16(1)	C(7)—C(8)	1.39(2)	C(19)—C(20)	1.40(2)
Sn(1)—Cl(4)	2.390(4)	Mn—C(24)	2.18(1)	C(8)—C(3)	1.39(1)	C(20)—C(15)	1.37(2)
Sn(1)—Cl(5)	2.371(4)	Mn—C(25)	2.15(1)	C(9)—C(10)	1.40(1)	C(21)—C(22)	1.43(2)
Sn(2)—Cl(6)	2.313(4)	P—C(3)	1.81(1)	C(10)—C(11)	1.39(1)	C(22)—C(23)	1.43(2)
Sn(2)—Cl(7)	2.301(4)	P—C(9)	1.83(1)	C(11)—C(12)	1.38(2)	C(23)—C(24)	1.40(2)
Sn(2)—Cl(8)	2.301(4)	P—C(15)	1.81(1)	C(12)—C(13)	1.35(2)	C(24)—C(25)	1.43(2)
Mn—Sn(2)	2.589(2)	C(1)—O(1)	1.14(1)	C(13)—C(14)	1.43(2)	C(25)—C(21)	1.42(2)
Mn—P	2.367(4)	C(2)—O(2)	1.14(1)	C(14)—C(9)	1.39(2)		
Mn—C(1)	1.83(1)	C(3)—C(4)	1.41(1)	C(15)—C(16)	1.42(1)		
Mn—C(2)	1.82(1)	C(4)—C(5)	1.40(1)	C(16)—C(17)	1.41(2)		

 TABLE 4
 BOND ANGLES ω (°)

Atoms	ω	Atoms	ω	Atoms	ω
Cl(1)—Sn(1)—Cl(2)	115.9(1)	P—Mn—C(2)	79.6(4)	C(10)—C(9)—C(14)	119.9(9)
Cl(1)—Sn(1)—Cl(3)	118.3(1)	C(1)—Mn—C(2)	115.1(5)	C(9)—C(10)—C(11)	119(1)
Cl(1)—Sn(1)—Cl(4)	89.8(1)	Mn—P—C(3)	112.9(4)	C(10)—C(11)—C(12)	122(1)
Cl(1)—Sn(1)—Cl(5)	91.3(2)	Mn—P—C(9)	114.0(4)	C(11)—C(12)—C(13)	119(1)
Cl(2)—Sn(1)—Cl(3)	125.6(1)	Mn—P—C(15)	112.0(4)	C(12)—C(13)—C(14)	121(1)
Cl(2)—Sn(1)—Cl(4)	88.6(1)	C(3)—P—C(9)	107.5(5)	C(13)—C(14)—C(9)	118(1)
Cl(2)—Sn(1)—Cl(5)	90.9(2)	C(3)—P—C(15)	105.1(5)	P—C(15)—C(16)	117.3(8)
Cl(3)—Sn(1)—Cl(4)	89.2(2)	C(9)—P—C(15)	104.5(4)	P—C(15)—C(20)	121.6(7)
Cl(3)—Sn(1)—Cl(5)	90.0(2)	Mn—C(1)—O(1)	176.9(9)	C(16)—C(15)—C(20)	121(1)
Cl(4)—Sn(1)—Cl(5)	178.7(2)	Mn—C(2)—O(2)	173.0(9)	C(15)—C(16)—C(17)	117(1)
Mn—Sn(2)—Cl(6)	115.0(1)	P—C(3)—C(4)	119.6(7)	C(16)—C(17)—C(18)	122(1)
Mn—Sn(2)—Cl(7)	115.0(1)	P—C(3)—C(8)	120.5(8)	C(17)—C(18)—C(19)	119(1)
Mn—Sn(2)—Cl(8)	114.1(1)	C(4)—C(3)—C(8)	119.8(9)	C(18)—C(19)—C(20)	120(1)
Cl(6)—Sn(2)—Cl(7)	104.0(1)	C(3)—C(4)—C(5)	118(1)	C(19)—C(20)—C(15)	120(1)
Cl(6)—Sn(2)—Cl(8)	105.5(2)	C(4)—C(5)—C(6)	122(1)	C(21)—C(22)—C(23)	108(1)
Cl(7)—Sn(2)—Cl(8)	101.5(1)	C(5)—C(6)—C(7)	119(1)	C(22)—C(23)—C(24)	108(1)
Sn(2)—Mn—P	131.1(1)	C(6)—C(7)—C(8)	120(1)	C(23)—C(24)—C(25)	108(1)
Sn(2)—Mn—C(1)	74.9(3)	C(7)—C(8)—C(3)	121(1)	C(24)—C(25)—C(21)	109(1)
Sn(2)—Mn—C(2)	74.4(3)	P—C(9)—C(10)	120.0(8)	C(25)—C(21)—C(22)	106(1)
P—Mn—C(1)	80.0(4)	P—C(9)—C(14)	120.0(8)		

on a Zeiss UR-20 spectrometer with a LiF prism. Nujol mulls were prepared in a dry box under argon.

References

- 1 B.V. Lokshin, E.B. Nazarova and A.G. Ginzburg, *J. Organometal. Chem.*, 129 (1977) 379.
- 2 J.C. Kotz and D.G. Pedrotty, *Organometal. Chem. Rev.*, A4 (1969) 479.
- 3 D.F. Schriver, *Account Chem. Res.*, 3 (1970) 231.
- 4 B.V. Lokshin, E.B. Rusatch, Z.P. Valueva, A.G. Ginzburg and N.E. Kolobova, *J. Organometal. Chem.*, 102 (1975) 535.
- 5 B.V. Lokshin, E.B. Rusatch, N.E. Kolobova, Yu.V. Makarov, N.A. Ustynuk, V.I. Zdanovich, A.Zh. Zakaeva and V.N. Sétkina, *J. Organometal. Chem.*, 108 (1975) 353.

- 6 D.N. Kursanov, V.N. Setkina, P.V. Petrovsky, V.I. Zdanovitch, N.K. Baranetskaya and I.D. Rubin, *J. Organometal. Chem.*, **37** (1972) 339.
- 7 B.V. Lokshin, A.G. Ginzburg, V.N. Setkina, D.N. Kursanov and I.B. Nemirovskaya, *J. Organometal. Chem.*, **37** (1972) 347.
- 8 A.G. Ginzburg, P.O. Okulevich, V.N. Setkina, G.A. Panosyan and D.N. Kursanov, *J. Organometal. Chem.*, **81** (1974) 201.
- 9 I.W. Nowell and D.R. Russel, *J. Chem. Soc., Dalton*, (1972) 2393, 2396.
- 10 A.G. Ginzburg, B.V. Lokshin, V.N. Setkina and D.N. Kursanov, *J. Organometal. Chem.*, **55** (1973) 357.
- 11 J. Klikorka, J. Pavlik and J. Holecek, *Proceedings of XIII congress of ICC, Zakopane, Sept. 1970, I*, 150.
- 12 K.R. Mann, W.H. Morrison and D.N. Hendrickson, *Inorg. Chem.*, **13** (1974) 1180.
- 13 A.G. Ginzburg, V.N. Setkina and D.N. Kursanov, *Izv. Acad. Nauk SSSR, Ser. Khim.*, N2 (1973) 481.
- 14 T.A. James and J.A. McCleverty, *J. Chem. Soc. A*, (1970) 850.
- 15 A.G. Ginzburg, V.N. Setkina and D.N. Kursanov, *J. Organometal. Chem.*, **77** (1974) C27.
- 16 B.P. Birukov, Yu.T. Struchkov and *Itogi Nauku, Kristallokhimiya*, Moscow, VINITI, 1971, 170.
- 17 G.G. Aleksandrov, Yu.T. Struchkov and Yu.V. Makarov, *J. Strukturnoy Khimii*, **14**, N1 (1973) 98.
- 18 W. Jetz and W.A.G. Graham, *Inorg. Chem.*, **10** (1971) 1547.
- 19 R.F. Bryan, *J. Chem. Soc., A* (1967) 172.
- 20 R.F. Bryan, *J. Chem. Soc., A* (1968) 696.
- 21 G.A. Melson, P.F. Stokely and R.F. Bryan, *J. Chem. Soc., A*, (1970) 2247.
- 22 P.T. Greene and R.F. Bryan, *J. Chem. Soc., A*, (1970) 1696.
- 23 B.T. Kilbourn, J.M. Powell, *Chem. Ind.*, (1964) 1578.
- 24 K.D. Bos, E.S. Bulten, J.G. Noltes and A.L. Spek, *J. Organometal. Chem.*, **92** (1975) 33.
- 25 C. Barbeau, K.R. Dichmann and L. Ricard, *Canad. J. Chem.*, **51** (1974) 3027.
- 26 C. Barbeau and R.J. Dabey, *Canad. J. Chem.*, **52** (1975) 1140.
- 27 A.N. Nesmeyanov, G.A. Aleksandrov, A.B. Antonova, K.N. Anisimov, N.E. Kolobova and Yu.T. Struchkov, *J. Organometal. Chem.*, **110** (1976) C36.
- 28 W. Beck, A. Melnikhoff and R. Stahl, *Ber.*, **99** (1966) 3721.
- 29 S.F.A. Kettle and J. Paul, *Adv. Organometal. Chem.*, **10** (1972) 199.
- 30 F.W.B. Einstein, and J.S. Field, *J. Chem. Soc., Dalton Trans.*, N 16-17 (1975) 1628.
- 31 V.I. Andrianov, Z.Sh. Safina and B.L. Tarnopol'sky, *Structure analysis programmes "Röntgen-75"*. Institute of Chemical Physics, Moscow, 1975.