Journal of Organometallic Chemistry, 281 (1985) 365–378
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

HYDRIDO-1,5-CYCLOOCTADIENEIRIDIUM(III) COMPLEXES STABILIZED BY TRICHLOROSTANNATE LIGANDS AND THE STRUCTURE OF $[IrH_2(SnCl_3)(PPh_3)_3]$

MATTHIAS KRETSCHMER, PAUL S. PREGOSIN*

Laboratorium für Anorganische Chemie, ETH-Zentrum, Universitätstrasse 6, CH-8092 Zürich (Switzerland)

ALBERTO ALBINATI* and ANTONIO TOGNI

Istituto di Chimica Farmaceutica dell'Università di Milano Viale Abruzzi 42, I-20131 Milano (Italy)

(Received August 31st, 1984)

Summary

The complexes $[IrH(SnCl_3)_2(1,5\text{-COD})L]$, $[IrH_2(SnCl_3)(1,5\text{-COD})L]$ and $[IrH_2(SnCl_3)L_3]$, L = tertiary arylphosphine, have been isolated and characterized by ^1H, ^{31}P and ^{119}Sn NMR spectroscopy. The coordinated 1,5-COD ligand is stable with respect to insertion into an iridium–hydride bond at room temperature, in contrast to the cationic complexes $[IrH_2(1,5\text{-COD})L_2]^+$ which are known to react rapidly at this temperature. The complexes $[IrH_2(SnCl_3)(1,5\text{-COD})L]$ exist as *cis,cis*- and *cis,trans*- (L *trans* to $SnCl_3^-$) isomers in solution. $[IrH_2(SnCl_3)(1,5\text{-COD})(PPh_3)]$ is a poor hydrogenation catalyst for the olefins styrene, cyclohexene and 1,5-COD at room temperature in CH_2Cl_2.

The structure of $[IrH_2(SnCl_3)(PPh_3)_3]$ has been determined by crystallographic methods. The three phosphines are in a pseudo-meridional arrangement and the two hydrides are *cis* to one another. The phosphine ligands are displaced toward the hydrido ligands relative to their position in a typical octahedral complex. Relevant bond lengths (Å) and bond angles (°) are as follows: Ir–Sn, 2.623(1); Ir–P, 2.318(4), 2.340(4), 2.395(3) (with the latter for P *trans* to H); Sn–Ir–P, 97.54(10), 97.35(9), 99.97(9); P–Ir–P, 102.11(12), 105.21(11), 145.95(9) (P *trans* to P). The hydride ligands have been located at a distance of ca. 1.7 Å from the metal.

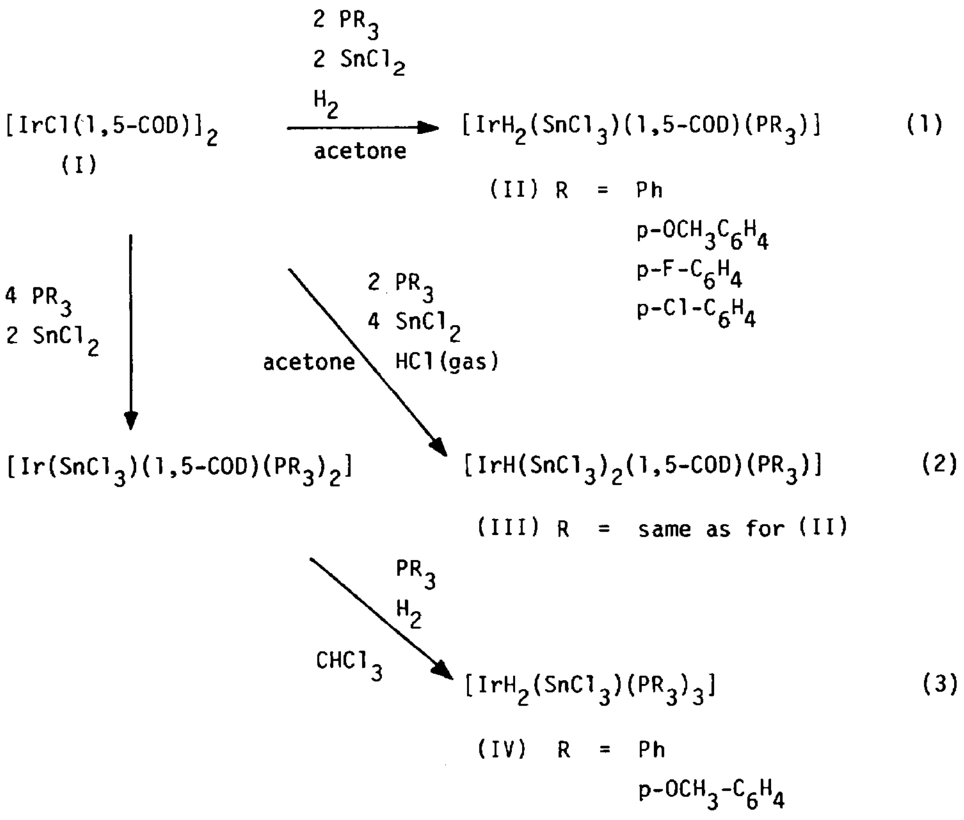
1. Introduction

Trichlorostannate complexes of Group VIII transition metals are recognized to be useful catalysts for homogeneous hydrogenation and hydroformylation [1]. Although there are now many known stable compounds containing the $SnCl_3^-$ ligand [2–8], its exact role in catalysis is still uncertain. The $SnCl_3^-$ may dissociate, thereby affording a labile, active cationic complex [9], or several $SnCl_3^-$ ligands may coordinate, thus imparting an enhanced reactivity to the resulting complex [10]. In view of the general interest in hydride complexes in homogeneous catalysis, we have expanded our studies on $SnCl_3^-$ complexes [11] to include molecules of the type $[Ir(H)_a(SnCl_3)_bL_cL'_d]$, $(a+b)=3$, $(c+d)=3$. The decision to look at iridium complexes was based on the known robust characteristics of iridium hydride complexes [12], combined with the recent reports from Crabtree and co-workers [13] and earlier studies by Osborn and co-workers [14] on the activity of 1,5-cyclooctadiene iridium (1,5-COD) complexes as hydrogenation catalysts. We report here the preparation and characterization of the complexes $[IrH(SnCl_3)_2(1,5\text{-COD})L]$, $[IrH_2(SnCl_3)(1,5\text{-COD})L]$ and $[IrH_2(SnCl_3)L_3]$, L = a tertiary arylphosphine, as well as the structure determination of $[IrH_2(SnCl_3)(PPh_3)_3]$.

2. Results and discussion

a. Synthesis and characterization

The hydridotrichlorostannate complexes can be readily prepared beginning from $[Ir(\mu\text{-Cl})(1,5\text{-COD})]_2$ as shown in Scheme 1. Table 1 contains microanalytical, and Table 2 NMR data for the new complexes.



SCHEME 1

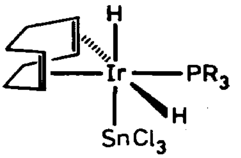
TABLE 1

MICROANALYTICAL DATA

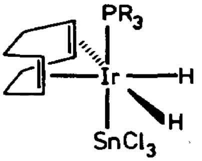
Complex	Found (calcd.) (%)		
	C	H	Cl
$[IrH_2(SnCl_3)(1,5\text{-}COD)(PPh_3)]$	40.83 (41.08)	4.10 (4.16)	12.90 (12.55)
$[IrH_2(SnCl_3)(1,5\text{-}COD)(P(p\text{-}OCH_3\text{-}C_6H_4)_3)]$	39.87 (39.59)	4.14 (4.01)	11.95 (12.09)
$[IrH_2(SnCl_3)(1,5\text{-}COD)(P(p\text{-}F\text{-}C_6H_4)_3]\cdot 0.5\ (CH_3)_2CO$	37.68 (37.84)	3.28 (3.35)	12.20 (12.19)
$[IrH(SnCl_3)_2(1,5\text{-}COD)(PPh_3)]$	30.86 (30.80)	2.74 (2.78)	21.30 (20.98)
$[IrH(SnCl_3)_2(1,5\text{-}COD)(P(p\text{-}Cl\text{-}C_6H_4)_3)]\cdot CH_2Cl_2$	27.39 (26.98)	2.24 (2.26)	32.15 (32.44)
$[IrH_2(SnCl_3)(P(p\text{-}OCH_3\text{-}C_6H_4)_3)_3]$	50.74 (51.25)	4.57 (4.44)	

The solution structures of complexes II *–IV were determined by ^{1}H, ^{31}P and ^{119}Sn NMR methods.

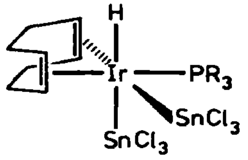
The ^{1}H NMR spectra for IIa show two different hydride absorptions separated by 2.56–2.94 ppm. The low field hydride resonance is *trans* to $SnCl_3^-$ but *cis* to ^{31}P, based on the values $^2J(^{119}Sn, ^1H)$, 961–987 Hz [15], and $^2J(^{31}P, ^1H)$, 14.8–15.4 Hz [12], respectively. The $^{31}P\{^1H\}$ spectra show ^{117}Sn and ^{119}Sn satellites, $^2J(^{119}Sn,^{31}P)$ 230–236 Hz, consistent with a *cis* geometry for these two spins [11a,15] and the ^{119}Sn spectra show doublets arising from coupling to a single ^{31}P spin, thereby confirming the number of coordinated PR_3 groups. The NMR spectra for the complexes IIb can be analysed analogously. It should be noted that for the compounds IIb the hydride ligands are now chemically equivalent and the *trans* orientation of ^{119}Sn and ^{31}P



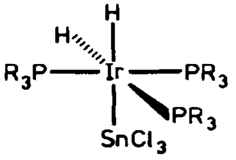
IIa



IIb



III



IV

---

* IIa and IIb were not separated and were characterized spectroscopically as a mixture of isomers.

TABLE 2

NMR DATA [a] FOR THE COMPLEXES

Compound		$\delta(^1H)$ (ppm)	$^2J(^{31}P,^1H)$ (Hz)	$^2J(^{119}Sn,^1H)$ (Hz)	$\delta(^{31}P)$ (ppm)	$^2J(^{119}Sn,^{31}P)$ (Hz)	$\delta(^{119}Sn)$ (ppm)
$[IrH_2(SnCl_3)(1,5\text{-COD})L]^b$							
	IIa/IIb						
$L = PPh_3$	78/22	−11.09, −13.82	15.0	987, 143	10.67	232	−274
		(−14.25)	(14.1)	(23)	(10.90)	(2144)	(−314)
$L = P(p\text{-OCH}_3\text{-C}_6H_4)_3$	84/16	−11.20, −13.76	14.8	985, 142	4.77	231	−278
		(−14.25)	(13.9)	(30)	(4.89)	(2162)	−319)
$L = P(p\text{-F-C}_6H_4)_3$	84/16	−11.16, −13.88	15.4	961, 138	7.80	236	−265
		(−14.35)	(14.4)	(18)	(7.88)	(2275)	(−311)
$L = P(p\text{-Cl-C}_6H_4)_3{}^c$	80/20	−11.02, −13.96	14.9	965, 140	9.43	230	−267
		(−14.47)	(14.5)	(20)	(9.50)	(2204)	(−315)
$[IrH(SnCl_3)_2(1,5\text{-COD})L]$							
$L = PPh_3$		−10.19	11.9	847, 43 [d]	−4.40	215, 156 [d]	−237, −307 [d]
$L = P(p\text{-OCH}_3\text{-C}_6H_4)_3$		−10.27	12.2	832, 50 [d]	−9.32	209, 159 [d]	−240, −309 [d]
$L = P(p\text{-F-C}_6H_4)_3$		−10.35	11.8	880, 45 [d]	−6.78	214, 160 [d]	−229, −298 [d]
$L = P(p\text{-Cl-C}_6H_4)_3$		−10.35	11.1	867, 42 [d]	−4.49	218, 162 [d]	−227, −295 [d]
$[IrH_2(SnCl_3)(PPh_3)_3]$		−14.64, −11.92 [e]	106 [h]	1164, 115 [e]	7.50, 4.97 [f]	195, 136 [g]	−269 [i]
$[IrH_2(SnCl_3)(P(p\text{-OCH}_3\text{-C}_6H_4)_3)_3]$		−14.91, −12.00 [e]	106 [h]	1157, 112 [e]	3.37, −0.30 [f]	183, 136 [g]	−271

[a] Chemical shifts in ppm, coupling constants in Hz, $CDCl_3$ solutions unless otherwise specified. [b] Mixture of *cis,cis*- and *cis,trans*-(*L trans* to $SnCl_3$). The data in parentheses refer to the *cis,trans*-complexes. [c] In CD_2Cl_2. [d] First value refers to $SnCl_3^-$ *trans* to hydride, second value to $SnCl_3^-$ *cis* to hydride. [e] First value refers to hydride *trans* to $SnCl_3^-$, second value to hydride *cis* to $SnCl_3^-$. $^2J(H,H)$ ca. 4 Hz for PPh_3, 3.4 Hz for $P(p\text{-OCH}_3\text{-C}_6H_4)_3$. [f] First value refers to P *trans* to hydride, integral = 1. [g] First value refers to ^{119}Sn coupling to P *trans* to hydride. [h] *trans* coupling of P and H. Remaining $^2J(P,H)_{cis}$ couplings are: PPh_3: hydride *trans* to P, 20.1; hydride *trans* to $SnCl_3^-$, 12.5 to the single phosphorus, 16.5 to the two equivalent phosphorus spins. $P(p\text{-OCH}_3\text{-C}_6H_4)_3$: hydride *trans* to P, 20.2; hydride *trans to* $SnCl_3^-$, 12.5 to the single phosphorus, 15.8 to the two equivalent phosphorus spins. [i] CH_2Cl_2/C_6D_6, 4/1.

spins produces relatively large $^2J(^{119}Sn,^{31}P)$ values [11a]. For the PPh_3 complex, as a mixture of IIa and IIb, the ^{13}C signals of the coordinated 1,5-COD fall in the range δ 78.4–84.5.

The complexes III exist in the isomeric form having $SnCl_3^-$ groups *cis* to each other and to the PR_3 ligand. There is a single ^1H hydride (see Fig. 1) which shows two different two-bond coupling constants to the tin, one of which is relatively large, 832–880 Hz. This places the hydride *trans* to one $SnCl_3^-$ [15] but *cis* to the other. The modest $^2J(^{31}P,^1H)$ doublet couplings of 11.1–12.2 Hz are consistent with the ^{31}P spin *cis* to the hydride. Since the ^1H spectra also show resonances attributable to coordinated 1,5-COD, the six positions of the octahedral complex must be as shown. The various coupling constants from the ^{31}P and ^{119}Sn NMR spectra also support the proposed structure. Unfortunately, the complexes were not sufficiently soluble for determination of $^2J(^{119}Sn,^{117}Sn)$.

The tris phosphine complexes IV are best obtained from I by first preparing the known five-coordinate complexes $[Ir(SnCl_3)(1,5\text{-}COD)(PR_3)_2]$ (R = Ph, *p*-OCH_3CH_4) [16]. Treatment of these with H_2 and PR_3, in chloroform gives the desired products. Their ^1H NMR spectra show two hydride signals, but no resonances for coordinated 1,5-COD. The lower field hydride has a $^2J(^{31}P,^1H)$ coupling of 106 Hz and consequently is *trans* to ^{31}P, whereas the higher field hydride shows a $^2J(^{119}Sn,^1H)$ coupling of ~ 1160 Hz and is therefore *trans* to ^{119}Sn. The observed A_2X $^{31}P\{^1H\}$ spectra for IV confirm the presence of three PR_3 ligands and are consistent with either a meridional or facial arrangement of ^{31}P spins; however, the absence of a $^2J(^{119}Sn,^{31}P)$ coupling > 3 kHz eliminates the possibility of a *trans*

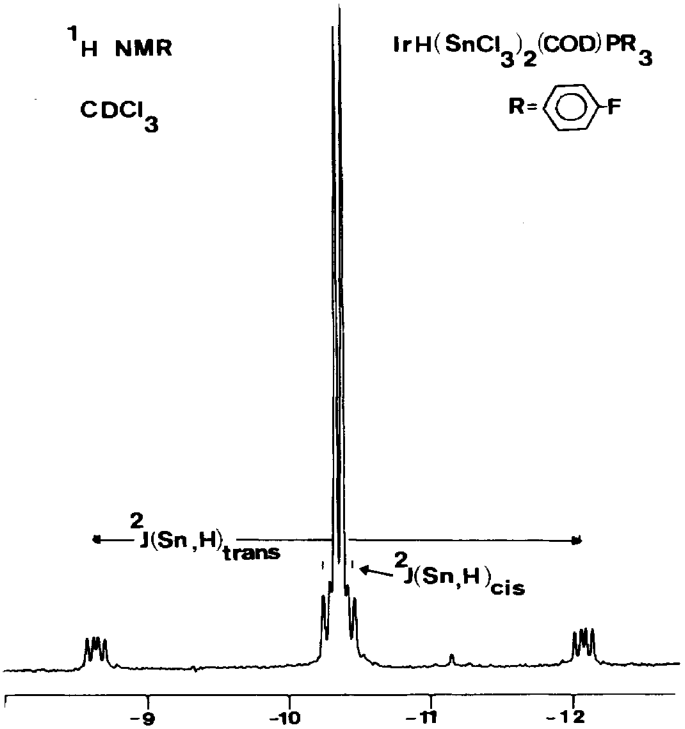


Fig. 1. ^1H NMR signals of the hydride ligand in $[IrH(SnCl_3)_2(1,5\text{-}COD)(P(p\text{-}F\text{-}C_6H_4)_3]$.

R_3P-Ir-$SnCl_3$ fragment, and therefore the facial isomer. The ^{119}Sn proton coupled NMR spectra are compatible with three *cis* $^2J(^{119}Sn,^{31}P)$ values, one *cis* $^2J(^{119}Sn,^1H)$ and one *trans* $^2J(^{119}Sn,^1H)$ coupling, thereby confirming that we have the meridional isomer. The chemistry leading to IV is similar to that found by Schrock and Osborn [14] and Crabtree and co-workers [13,17] who reported that cationic iridium complexes with two PPh_3 ligands of the type $[Ir(1,5\text{-COD})L_2]^+$ ($L = PR_3$), react rapidly with H_2 to form cyclooctane and $[IrH_2(\text{solvent})_2L_2]^+$. This later complex has *cis* hydrides and *trans* L ligands [13,17].

We have previously observed [15] isomer selectivity in iridium(III) trichlorostannate chemistry, so that the presence of only one isomer in both III and IV does not come as a surprise. It is curious, however, that the $SnCl_3^-$ ligand *trans* to hydride in IIa, III and IV, are not especially labilized. All of our NMR spectra were recorded at room temperature, and we have not observed line broadening due to ligand exchange. This is in contrast to our earlier findings for *trans*-$[PtH(SnCl_3)(PR_3)_2]$, for which low temperature measurements were required before sharp ^1H and ^{119}Sn spectra were obtained [18]. Obviously, the relatively robust nature of iridium(III) hydride complexes is not altered by the presence of $SnCl_3^-$ ligands.

It is interesting that with two coordinated tertiary phosphines per metal, the 1,5-COD of $[Ir(SnCl_3)(1,5\text{-COD})(PR_3)_2]$ is readily reduced with H_2 to give IV, whereas in the iridium(III) hydride complexes with only one PR_3 ligand, e.g II or III, the coordinated diolefin is relatively immune to further reaction. Indeed, both the *cis,cis* isomer (IIa) and the *cis,trans* form (IIb) exist without significant * reduction of the 1,5-COD. Presumably, replacement of PR_3 by $SnCl_3^-$, a weaker σ-donor [11], leaves the iridium somewhat electron poorer, with the result that the hydride coordinates strongly, thereby reducing its capability to undergo reactions with the coordinated 1,5-COD.

To make a qualitatively assessment of the catalytic activity of $[IrH_2(SnCl_3)(1,5\text{-COD})(PPh_3)]$ we mixed this complex with styrene (1/1000) in CH_2Cl_2 and treated the solution with gaseous hydrogen for 3 h at 22°C. After work-up ^1H NMR showed ~ 85% unreacted styrene and ~ 15% ethylbenzene. Similar runs with cyclohexene and 1,5-COD show essentially no reduction of olefin. Clearly, this complex is inferior to the cationic derivatives mentioned above with respect to hydrogenation, and we conclude that the presence of coordinated $SnCl_3^-$ ligands is not in itself sufficient to enhance catalytic activity.

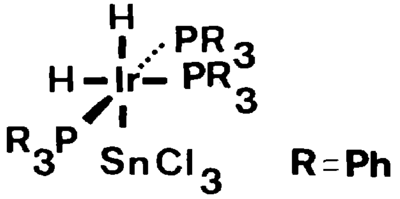
b. The structure of $[IrH_2(SnCl_3)(PPh_3)_3]$

In our earlier [2,10,11c] structural studies on trichlorostannate complexes of platinum(II) we observed considerable variation in Pt–Sn bond distances as a function of the ligand *trans* to $SnCl_3$. Since hydrides often have a strong *trans* influence [20] we determined the structure of $[IrH_2(SnCl_3)(PPh_3)_3]$ in order to see to what extent the iridium–tin bond length is influenced by this ligand. To our knowledge this is the first structure determination of an octahedral iridium trichlorostannate complex, and the first for any transition metal in which the $SnCl_3$ is *trans* to a hydride ligand.

---

* Our yields are always less than 80% so that some olefin reduction may have occurred. We observe only mixtures of IIa and IIb in all of our NMR spectra and, in analogy with Crabtree and co-workers, assume that IIa is formed first [17,19].

Figure 2 shows an ORTEP drawing of the structure of [$IrH_2(SnCl_3)(PPh_3)_3$] and a list of bond distances and bond angles may be found in Table 3. The hydride ligands were refined [21] (see experimental), and found to be separated from the metal by 1.68(9) and 1.70(9) Å; these are reasonable separations in the light of available information [22]. The H–Ir–H angle has a value of 84(3)°. The phosphines and $SnCl_3$ ligands are situated about the iridium so as to form a distorted



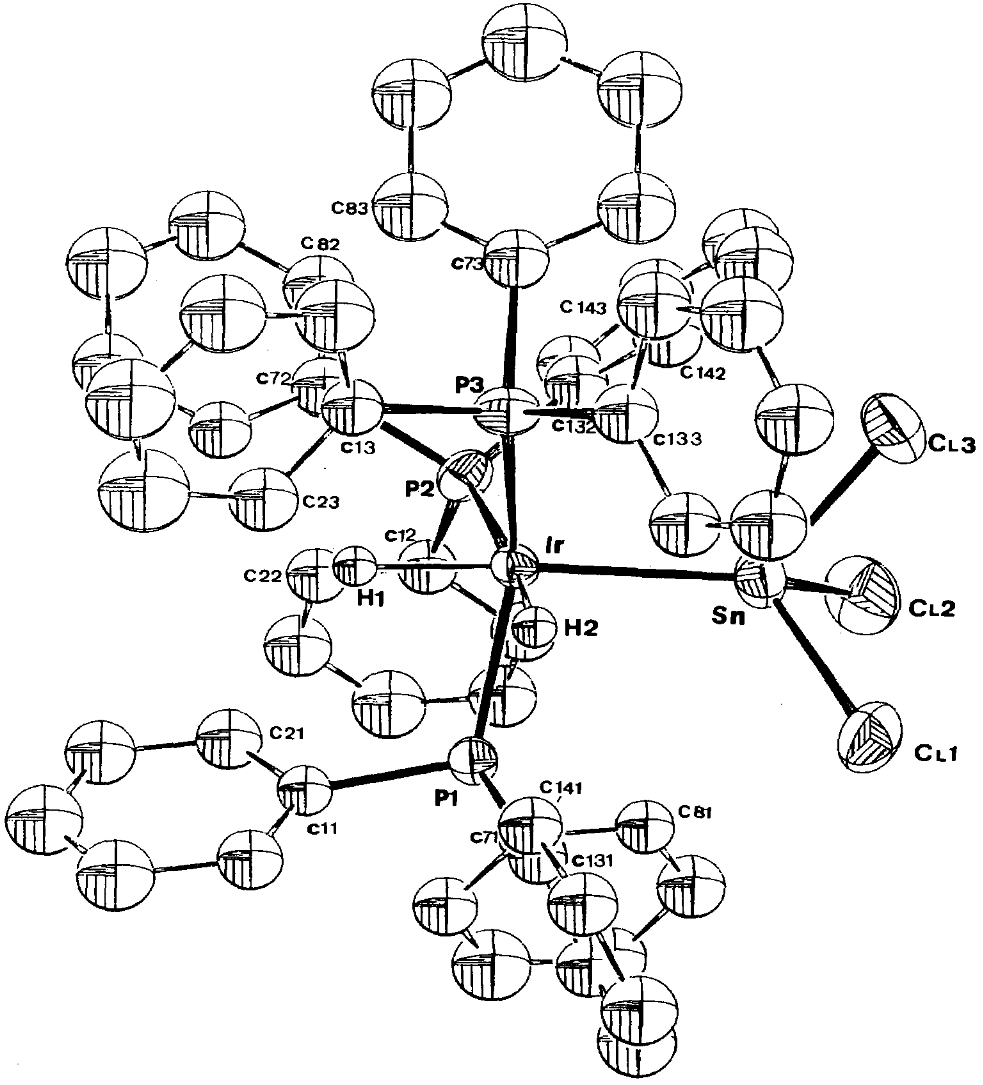


Fig. 2. ORTEP drawing showing the structure of [$IrH_2(SnCl_3)(PPh_3)_3$].

octahedron. The angles Sn–Ir–P fall in the range 97–100°, and two of the three P–Ir–P angles are 102 and 105°. The major deviation from ideal geometry arises from the third P–Ir–P angle, ca. 146°, and involves the two chemically equivalent PPh_3 groups which are pseudo *trans* to one another. Angular distortions in hydride complexes are not unusual, e.g. for $[RhH(PPh_3)_4]$, the phosphines are disposed in a tetrahedral arrangement about the rhodium [23]. Consequently, we consider the three Sn–Ir–P, as well as the P(1)–Ir–P(3) and P(2)–Ir–P(3) bond angles in $[IrH_2(SnCl_3)(PPh_3)_3]$ to be a reflection of the tendency of the sterically more demanding ligands to avoid each other. With regard to the 146° angle, we note that (a) in *mer*-$[IrH_3(PPh_3)_3]$, the bond angle for the two *trans*-PPh_3 groups is 153° [24], (b) for $[PPh_3Au(\mu\text{-}H)IrH_2(PPh_3)_3]^+$ [25] with pseudo-meridional PPh_3 groups, the analogous angle is 149° and (c) for *mer*-$[IrH_2(CO)(PPh_3)_3]^+$ this same angle is 151° [26]. This last CO complex is pertinent in that its geometry is similar to that of $[IrH_2(SnCl_3)(PPh_3)_3]$ since the angles OC–Ir–P are 93.1(1)–100.5(1)° and the remaining P–Ir–P angles are 100.7(1) and 104.4(1)°.

The bond distances in $[IrH_2(SnCl_3)(PPh_3)_3]$ are of interest, especially that for Ir–Sn, 2.623(1) Å. We know of only two other structures involving iridium and

TABLE 3

SELECTED BOND DISTANCES (Å), BOND ANGLES (°), AND TORSION ANGLES FOR $[IrH_2(SnCl_3)(PPh_3)_3]$

Ir–Sn	2.623(1)	Ir–Sn–Cl(1)	120.43(8)
Ir–P(1)	2.318(4)	Ir–Sn–Cl(2)	118.10(9)
Ir–P(2)	2.340(4)	Ir–Sn–Cl(3)	124.50(8)
Ir–P(3)	2.395(3)	Sn–Ir–P(1)	97.54(10)
Ir–H(1)	1.68(9)	Sn–Ir–P(2)	97.35(9)
Ir–H(2)	1.70(9)	Sn–Ir–P(3)	99.97(9)
Sn–Cl(1)	2.397(5)	Sn–Ir–H(1)	168.(2)
Sn–Cl(2)	2.382(5)	Sn–Ir–H(2)	86.(3)
Sn–Cl(3)	2.394(5)	P(1)–Ir–P(2)	145.95(9)
P(1)–C(11)	1.864(15)	P(1)–Ir–P(3)	102.11(12)
P(1)–C(71)	1.837(15)	P(2)–Ir–P(3)	105.21(11)
P(1)–C(131)	1.856(17)	P(1)–Ir–H(2)	75 (4)
P(2)–C(12)	1.845(14)	P(2)–Ir–H(2)	76.(4)
P(2)–C(72)	1.829(14)	P(3)–Ir–H(2)	173.(4)
P(2)–C(132)	1.859(14)	$\langle P–Ir–H_1\rangle_{average}$	83.(6)
P(3)–C(13)	1.860(17)	Cl(1)–Sn–Cl(2)	96.72(16)
P(3)–C(73)	1.837(15)	Cl(1)–Sn–Cl(3)	95.81(16)
P(3)–C(133)	1.838(17)	Cl(2)–Sn–Cl(3)	94.92(18)
$\langle C–C\rangle_{average}$	1.39(4)	Ir–P(1)–C(11)	112.0(4)
		Ir–P(1)–C(71)	115.8(4)
		Ir–P(1)–C(131)	121.3(4)
		Ir–P(2)–C(12)	113.0(4)
		Ir–P(2)–C(72)	111.3(4)
		Ir–P(2)–C(132)	123.0(4)
		Ir–P(3)–C(13)	113.0(4)
		Ir–P(3)–C(73)	117.0(4)
		Ir–P(3)–C(133)	120.3(4)
		P(1)–Ir–Sn–Cl(1)	10.9(2)
		P(1)–Ir–Sn–Cl(2)	−107.0(2)
		P(1)–Ir–Sn–Cl(3)	134.0(2)

trichlorostannate and these are in the five-coordinate iridium(I) complexes $[Ir(SnCl_3)(1,5\text{-}COD)_2]$ and $[Ir(SnCl_3)(norbornadiene)(PMe_2Ph)_2]$ for which the Ir–Sn separations are 2.642(2) [7] and 2.5867(6) Å [27], respectively. Consequently, our Ir–Sn separation is not unusual; however, viewed against other six-coordinate complexes, e.g. $[RuCl(SnCl_3)_5]^{4-}$, Ru–Sn 2.553(2) and 2.579(1) Å [28], $[RuCl(SnCl_3)(CO)(acetone)(PPh_3)_2]$ ($SnCl_3$ *trans* to Cl), Ru–Sn 2.5935(9) Å [29] or $[(CO)_2(SnCl_3)Ru(\mu\text{-}Cl)_3Ru(CO)_3]$, Ru–Sn 2.565(4) Å [30], our observed value of 2.623(1) Å lies at the upper end of the range. Moreover, when compared to M–Sn separations in some square planar platinum complexes, e.g. 2.356(8), 2.482(3) and 2.501(1) Å for *cis*-$[PtCl_2(SnCl_3)_2]^{2-}$ [3b], $[Pt_2(SnCl_3)_2(PEt_3)_2(\mu\text{-}Cl)_2]$ [26] and $[PtCl(SnCl_3)(PEt_3)(PhC(NH_2)\text{=}NOH)]$ [4], respectively, our Ir–Sn distance is certainly rather long.

Turning to the metal–phosphorus separations, the PPh_3 ligand *trans* to hydride shows a rather long Ir–P distance of 2.395(3) Å. For the PPh_3 ligand *trans* to hydride in *mer*-$[IrH_3(PPh_3)_3]$, the Ir–P distance is only 2.347(3) Å [24] and for *fac*-$[IrH_3(PMe_2Ph)_3]$ even shorter at 2.294(3) Å (average value) [31]. Interestingly, the previously mentioned cation *mer*-$[IrH_2(CO)(PPh_3)_3]^+$ has the unique phosphine separated from the metal by 2.426(4) Å [26]. The two pseudo *trans*-P atoms are separated from iridium by 2.318(4) and 2.340(4) Å which is quite normal for a *trans*-P–Ir–P fragment (see Table 4).

Considering both the Ir–Sn and Ir–P bond separations it seems clear that the hydride ligands are exerting a sizeable *trans*-influence such that these distances are

TABLE 4

SOME Ir–P BOND LENGTHS IN IRIDIUM PHOSPHINE COMPLEXES

Compound	Ir–P	Ref.
$[IrH_2(SnCl_3)(PPh_3)_3]$	2.395(3)	This work
	2.318(4)	
	2.340(4)	
$[IrH_2(CO)(PPh_3)_3]SiF$	2.426(4)	26
	2.334(4)	
	2.345(4)	
fac-$[IrH_3(PMe_2Ph)_3]$	2.294(3) (average)	31
mer-$[IrH_3(PPh_3)_3]$	2.347(3)	24
	2.287(3)	
	2.285(3)	
mer-$[IrHCl(CH_2CHO)(PMe_3)_3]$	2.337(1)	32
	2.312(1)	
	2.337(1)	
fac-$[IrCl_3(PMe_2Ph)_3]$	2.289(2) (average)	33
mer-$[IrCl_3(PMe_2Ph)_3]$	2.377(1)	33
	2.363(1)	
	2.278(1)	
$[IrH_2(acetone)_2(PPh_3)_2]BF_4$	2.313(2)	34
	2.321(2)	
fac-$[IrH(PMe_2C_6H_4)(PMe_2Ph)_3]PF_6$	2.380(3) P *trans* to H	35

relatively long. Despite this the molecule shows no inclination to undergo dissociation of either $SnCl_3$ or PPh_3 at room temperature in $CDCl_3$ solution, as indicated by the NMR results. We feel that this stability suggests that the chemistry of this trichlorostannate complex will be determined by the metal, i.e., a neutral, stable iridium(III) hydride complex, of which there are many known examples [12], and not any special characteristic of the $SnCl_3$ ligand. Further studies of this topic are in progress.

3. Experimental

NMR spectra were measured using a Bruker WM-250 instrument as described previously [11d,e]. Solvents were dried and, unless otherwise specified, reactions were carried out under nitrogen. Microanalyses were performed in the microanalytical laboratory of the ETH Zürich. $[IrCl(1,5\text{-}COD)(PPh_3)]$ was prepared from $[Ir(\mu\text{-}Cl)(1,5\text{-}COD)]_2$ plus two equivalents of PPh_3. $[Ir(SnCl_3)(1,5\text{-}COD)(PPh_3)_2]$ was prepared as described previously [16]. Representative syntheses for II–IV are shown below.

$[IrH_2(SnCl_3)(1,5\text{-}COD)(PPh_3)]$. Solid anhydrous tin(II) chloride (0.076 g, 0.4 mmol) was added to a suspension of $[IrCl(COD)(PPh_3)]$ (0.120 g, 0.2 mmol) in 3 ml acetone. The yellow solution was then treated with dihydrogen for one hour. During this period colorless crystalline $[IrH_2(SnCl_3)(COD)(PPh_3)] \cdot x(CH_3)_2CO$ precipitated and was filtered off and dried in vacuum (0.090 g, 53.1%).

$[IrH(SnCl_3)_2(1,5\text{-}COD)(PPh_3)]$. Solid anhydrous tin(II) chloride (0.076 g, 0.4 mmol) was added to a suspension of $[IrCl(COD)(PPh_3)]$ (0.120 g, 0.2 mmol) in 3 ml acetone. The resulting yellow solution was then concentrated under a stream of nitrogen gas and the residue dissolved in 3 ml methylene chloride. A slow stream of dry HCl gas was passed over the solution and after 5 minutes a white crystalline material precipitated. This was filtered off and dried in vacuum (0.159 mg, 78.3%).

$[IrH_2(SnCl_3)(PPh_3)_3]$. Solid triphenylphosphine (0.013 g, 0.05 mmol) was added to a solution of $[Ir(SnCl_3)(COD)(PPh_3)_2]$ (0.053 g, 0.05 mmol) in 3 ml chloroform. The yellow solution was then treated with dihydrogen for 3 h. Addition of 3 ml ethanol to the colourless solution precipitated a colourless crystalline material which was filtered off and dried in vacuum (0.048 g, 79%).

$[IrH_2(SnCl_3)(P(C_6H_4OCH_3)_3)_3]$ was prepared analogously. (Yield 0.043 g, 58%). Suitable stable crystals for X-ray diffraction were obtained by crystallization from $CHCl_3/EtOH$.

Data were collected on Nonius CAD4 diffractometer under the conditions listed in Table 5 with variable scan speed to obtain a constant statistical precision of the collected intensities. Three standard reflections (measured every hour) were used to check the stability of the crystal and of the experimental conditions; no significant variation was detected. The orientation of the crystal was checked every 300 reflections.

Data were corrected for Lorentz and polarization effects; an empirical absorption correction was applied using azimuthal (ψ) scans of 6 reflections at increasing θ values: $\bar{3}\,\bar{4}\,\bar{4}$, $\bar{5}\,\bar{1}\,\bar{5}$, $\bar{5}\,\bar{1}\,\bar{6}$, $\bar{6}\,\bar{1}\,\bar{8}$, $\bar{8}\,\bar{0}\,\bar{8}$, $\overline{10}\,\bar{0}\,\overline{10}$, using the data reduction programs of the CAD4-SDP package [36]; transmission factors were in the range 0.85–0.96. Intensities were considered as observed if $I_{net} \geqslant 3\sigma(I_{tot})$ while an $I_{net} = 0.0$ was given to reflections with negative observed intensities.

The structure was solved by a combined use of Patterson and Fourier methods and refined by block diagonal least squares using anisotropic temperature factors for Ir, Sn, P, and Cl atoms, isotropic for the others. The real part of the anomalous scattering was taken into account using tabulated values [37]; scattering factors were taken from ref. 37. A Cruickshank weighting scheme was used throughout the refinement [38].

The contribution of the aryl hydrogen atoms (fixed in idealized positions at C–H 0.95 Å) was taken into account during the last stage of the refinement. Upon convergence that last Fourier map showed two strong peaks in acceptable positions for the hydride atoms. As the refinement of the hydrogen *trans* to P gave an unsatisfactory geometry, the H ligand positions were recalculated minimizing the potential energy arising from non-bonded interactions [21,39] using the program Hydex [21] (assuming M–H 1.70 Å). Two positions were found, one corresponding to the experimentally determined hydride *trans* to $SnCl_3$. These new positional parameters calculated for the two hydrides, when included in the refinement, (B_{iso} kept constant) refined satisfactorily. Final atomic coordinates are listed in Table 6. A list of the aryl hydrogen coordinates, thermal parameters, and a Table of F_{obs}/F_{calc} may be obtained from the authors.

TABLE 5

CRYSTALLOGRAPHIC AND EXPERIMENTAL DATA FOR $[IrH_2(SnCl_3)(PPh_3)_3]$

Formula	$IrSnCl_3P_3C_{54}H_{47}$
Mol.wt.	1206.14
Crystal dimensions (mm)	0.2×0.2×0.3
Crystal system	Monoclinic
Space group	$P2_1/n$
a (Å)	13.874(3)
b (Å)	23.571(5)
c (Å)	15.261(3)
β (deg)	96.10(2)
Z	4
V (Å^3)	4962.6
ρ (calc. g cm^{-3})	1.61
μ (cm^{-1})	34.5
Radiation	Mo K_α (λ 0.71069 Å)
Measured reflections	$\pm h, +k, +l$
2θ range (deg)	$2.4 \leq 2\theta \leq 22.0$
Scan type	$\omega/2\theta$
max. scan speed (deg/min)	10.5
max. counting time (sec)	60
Scan width (deg)	1.00+0.35 tanθ
Background time (sec)	0.5×scan time
Receiving aperture hor (mm)	1.85+tanθ {vert (mm) 4.0}
Prescan rejection limit	0.5 (2σ)
Prescan acceptance limit	0.03 (33σ)
No. of independent data (obs. data)	6167 (4400)
R [a]	0.048
R_w [b]	0.061

[a] $R = \Sigma(|F_0| - |F_c|)/\Sigma|F_0|$. [b] $R_w = [\Sigma_w(|F_0| - |F_c|)^2/\Sigma_w F_0^2]^{1/2}$.

TABLE 6

FINAL POSITIONAL PARAMETERS FOR $[IrH_2(SnCl_3)(PPh_3)_3]$ (E.s.d.'s are given in parentheses)

	x/*a*	*y*/*b*	*z*/*c*		*x*/*a*	*y*/*b*	*z*/*c*
Ir	0.20034(4)	0.14679(2)	0.23758(3)	C(17)P(1)	0.07969(163)	0.09294(86)	0.57185(150)
Sn	0.20711(7)	0.03565(4)	0.23197(7)	C(18)P(1)	0.06613(149)	0.09575(83)	0.47313(141)
Cl(1)	0.10772(32)	−0.02027(18)	0.31799(30)	C(2)P(2)	0.09033(109)	0.14512(63)	0.00380(104)
Cl(2)	0.16069(39)	−0.00985(19)	0.09459(31)	C(3)P(2)	0.03233(113)	0.12492(70)	−0.07186(109)
Cl(3)	0.35130(35)	−0.01940(21)	0.26548(35)	C(4)P(2)	0.07128(139)	0.09918(77)	−0.14144(131)
P(1)	0.06465(26)	0.15478(17)	0.31325(25)	C(5)P(2)	0.16789(144)	0.09597(78)	−0.13914(135)
P(2)	0.26635(24)	0.16417(14)	0.10528(23)	C(6)P(2)	0.23030(109)	0.11428(68)	−0.06556(105)
P(3)	0.32951(25)	0.16472(16)	0.35120(25)	C(8)P(2)	0.33412(112)	0.27352(66)	0.14091(106)
H(1)	0.19540(980)	0.21910(640)	0.23460(936)	C(9)P(2)	0.33703(127)	0.33186(77)	0.13043(122)
H(2)	0.10350(930)	0.14200(660)	0.15950(916)	C(10)P(2)	0.27904(141)	0.35737(81)	0.06012(132)
C(1)P(1)	0.0338(101)	0.22474(61)	0.29396(98)	C(11)P(2)	0.22162(139)	0.32596(84)	0.00119(132)
C(7)P(1)	−0.03597(109)	0.10655(66)	0.27779(105)	C(12)P(2)	0.21850(111)	0.26590(67)	0.01320(107)
C(13)P(1)	0.07408(111)	0.14965(65)	0.43521(107)	C(14)P(2)	0.40573(107)	0.08007(62)	0.09515(102)
C(1)P(2)	0.18887(97)	0.13833(59)	0.00767(95)	C(15)P(2)	0.48883(122)	0.05510(73)	0.07120(113)
C(7)P(2)	0.27235(94)	0.24024(57)	0.08267(91)	C(16)P(2)	0.55834(129)	0.08940(70)	0.03172(122)
C(13)P(2)	0.38608(97)	0.13602(58)	0.08163(95)	C(17)P(2)	0.53905(150)	0.14703(86)	0.02028(142)
C(1)P(3)	0.31070(112)	0.23026(67)	0.41510(108)	C(18)P(2)	0.45034(112)	0.17120(68)	0.04296(106)
C(7)P(3)	0.44988(104)	0.17878(61)	0.31611(98)	C(2)P(3)	0.27543(107)	0.27832(63)	0.36779(102)
C(13)P(3)	0.36225(111)	0.11139(69)	0.43715(109)	C(3)P(3)	0.26449(127)	0.32927(77)	0.41392(121)
C(2)P(1)	0.02899(115)	0.26345(70)	0.23156(110)	C(4)P(3)	0.29482(147)	0.32996(90)	0.50729(140)
C(3)P(1)	−0.02273(162)	0.31631(95)	0.22042(154)	C(5)P(3)	0.32721(135)	0.28377(83)	0.55049(126)
C(4)P(1)	−0.10376(154)	0.32323(92)	0.26213(143)	C(6)P(3)	0.33827(131)	0.23138(77)	0.50451(123)
C(5)P(1)	−0.13264(150)	0.28385(90)	0.31730(140)	C(8)P(3)	0.49735(105)	0.22945(63)	0.32376(102)
C(6)P(1)	−0.07980(134)	0.23453(82)	0.33496(127)	C(9)P(3)	0.58990(123)	0.23637(74)	0.29482(117)
C(8)P(1)	−0.04572(119)	0.08178(69)	0.19095(112)	C(10)P(3)	0.63494(135)	0.19185(83)	0.26121(128)
C(9)P(1)	−0.12890(128)	0.04999(78)	0.16379(119)	C(11)P(3)	0.58828(123)	0.13896(72)	0.25459(117)
C(10)P(1)	−0.20234(130)	0.04187(79)	0.21861(123)	C(12)P(3)	0.49606(113)	0.13200(67)	0.27916(107)
C(11)P(1)	−0.19081(143)	0.06327(86)	0.30040(137)	C(14)P(3)	0.29438(123)	0.07176(76)	0.45399(116)
C(12)P(1)	−0.10950(130)	0.09674(72)	0.33481(124)	C(15)P(4)	0.31659(145)	0.02978(86)	0.52151(134)
C(14)P(1)	0.09771(130)	0.19597(80)	0.48363(123)	C(16)P(3)	0.40715(153)	0.03026(90)	0.56796(141)
C(15)P(1)	0.11063(139)	0.19456(86)	0.57785(132)	C(17)P(3)	0.47141(139)	0.06862(86)	0.55054(128)
C(16)P(1)	0.10143(160)	0.14378(92)	0.61677(149)	C(18)P(3)	0.45663(117)	0.11084(72)	0.48493(113)

Acknowledgements

We thank the Swiss National Science Foundation for support for M.K. and the Johnson Matthey Research Center, England, for the loan of platinum metals.

References

1 G. Consiglio, P. Pino, L.I. Flowers and C.H. Pittman Jr. J. Chem. Soc. Chem. Comm., (1983) 612; Y. Kawabata, T. Hayashi and I. Ogata, ibid., (1979) 462; J.C. Bailar Jr. in R.B. King (Ed.), Inorganic Compounds with Unusual Properties, American Chemical Society, 1979, p. 1.

2 A. Albinati, P.S. Pregosin and H. Rüegger, Angew. Chem. Int. Ed. Engl. 23 (1984) 78; A. Albinati, R. Naegeli, K.H.A. Ostoja Starzewski, P.S. Pregosin and H. Rüegger, Inorg. Chim. Acta, 76 (1983) L231.

3 M.S. Holt, J.J. MacDougall, F. Mathey and J.H. Nelson, Inorg. Chem. 23 (1984) 449; J.H. Nelson and N.W. Alcock, ibid., 21 (1982) 1196; N.W. Alcock and J.H. Nelson, J. Chem. Soc. Dalton Trans., (1982) 2415.

4 A.B. Goel and S. Goel, Inorg. Chim. Acta, 77 (1983) L5.

5 H. Moriyama, T. Aoki, S. Shinoda and Y. Saito, J. Chem. Soc. Dalton Trans., (1981) 639.

6 L. Farrugia, B.R. James, C.R. Lassigne and E.J. Wells, Can. J. Chem., 60 (1982) 1304.

7 P. Porta, H.M. Powell, R.J. Mawby and L.M. Venanzi, J. Chem. Soc. A, (1967) 455.

8 J.F. Young, R.D. Gillard and G. Wilkinson, J. Chem. Soc., (1964) 5176.

9 G.K. Anderson, H.C. Clark and J.A. Davies, Organometallics, 1 (1982) 64; Inorg. Chem., 22 (1983) 427; 22 (1983) 434; G.K. Anderson, C. Billard, H.C. Clark, J.A. Davies and C.S. Wong, Inorg. Chem., 22 (1983) 439.

10 A. Albinati, P.S. Pregosin and H. Rüegger, Inorg. Chem., 23 (1984) 3223.

11 (a) P.S. Pregosin and S.N. Sze, Helv. Chim. Acta, 61 (1978) 1848; (b) K.H.A. Ostoja Starzewski, P.S. Pregosin and H. Rüegger, ibid., 65 (1982) 785; (c) A. Albinati, R. Naegeli, H. Rüegger and P.S. Pregosin, Angew. Chem., 94 (1982) 310; (d) M. Kretschmer, P.S. Pregosin and H. Rüegger, J. Organomet. Chem., 241 (1983) 87; (e) M. Kretschmer, P.S. Pregosin and M. Garralda, ibid., 244 (1983) 175; (f) M. Kretschmer, P.S. Pregosin, P. Favre and C.W. Schläpfer, ibid., 253 (1983) 17.

12 J.P. Jesson in E.L. Muetterties (Ed.), Transition Metal Hydrides, Marcel Dekker, Inc., New York, 1971, p. 75 and ref. therein.

13 R.H. Crabtree, Accts. Chem. Res., 12 (1979) 331 and ref. therein.

14 R.R. Schrock and J.A. Osborn, J. Am. Chem. Soc., 98 (1976) 2134, 2143, 4450; J.R. Shapely, R.R. Schrock and J.A. Osborn, ibid., 91 (1968) 2816; J.R. Shapely and J.A. Osborn, ibid., 92 (1970) 6976.

15 P.S. Pregosin and M. Kretschmer, Inorg. Chim. Acta, 61 (1982) 247.

16 M. Garralda, V. Garcia, M. Kretschmer, P.S. Pregosin and H. Rüegger, Helv. Chim. Acta, 64 (1981) 1150; R. Uson, L.A. Oro, M.T. Pinillas, A. Arruebo, K.H.A. Ostoja Starzewski and P.S. Pregosin, J. Organomet. Chem., 192 (1980) 227.

17 R.H. Crabtree, H. Felkin, T. Fillebeen-Khan and G.E. Morris, J. Organomet. Chem., 168 (1979) 183; R.H. Crabtree, M.F. Mellea, J.M. Mihelcic and J.M. Quirk, J. Am. Chem. Soc., 104 (1982) 107.

18 K.H.A. Ostoja Starzewski and P.S. Pregosin, Angew. Chem. Int. Ed. Engl., 19 (1980) 316.

19 R.H. Crabtree and R.J. Uriarte, Inorg. Chem., 22 (1983) 4152.

20 T. Appleton, H.C. Clark and L.E. Manzer, Coord. Chem. Rev., 10 (1973) 335.

21 A.G. Orpen, J. Chem. Soc. Dalton Trans., (1980) 2509.

22 (a) N.L. Jones and J.A. Ibers, in L. Pignolet (Ed.), Homogeneous Catalysis with Metal Phosphine Complexes Plenum Press, 1983, p. 111; (b) R. Bau, W.E. Carroll, D.W. Hart, R.G. Teller and T.F. Koetzle, Accts. Chem. Res., 12 (1979) 176.

23 R.W. Baker and P. Pauling, Chem. Comm., (1969) 1495.

24 G.R. Clark, B.W. Skelton and T.N. Waters, Inorg. Chim. Acta, 12 (1975) 235.

25 H. Lehner, D. Matt, P.S. Pregosin, L.M. Venanzi and A. Albinati, J. Am. Chem. Soc., 104 (1982) 6825.

26 P. Bird, J.F. Harrod and K.A. Than, J. Am. Chem. Soc., 96 (1974) 1222.

27 M.R. Churchill and K.G. Lin, J. Am. Chem. Soc., 96 (1974) 76.

28 L.F. Farrugia, B.R. James, C.R. Lossigne and E.J. Wells, Can. J. Chem., 60 (1982) 1304.

29 R.O. Gould, W.J. Sime and T.A. Stephenson, J. Chem. Soc. Dalton, (1978) 76.

30 M. Elder and D. Hall, J. Chem. Soc. A, (1979) 245.

31 Cited in ref. 25b, p. 81.

32 D. Milstein and J.C. Calabrese, J. Am. Chem. Soc., 104 (1982) 3773.
33 G.B. Robertson and P.A. Tucker, Acta Cryst. B, 37 (1981) 814.
34 R.H. Crabtree, G.G.H. Latky; C.P. Pornell, B.E. Segmüller and R.J. Uriorte, Inorg. Chem., 23 (1984) 354.
35 R.H. Crabtree, J.M. Quirk, H. Felkin, T. Fillebeen-Khan and C. Pascard, J. Organomet. Chem., 187 (1980) C32.
36 Enraf–Nonius Structure Determination Package (SDP): Enraf–Nonius, Delft, Holland, 1980.
37 International Tables for X-ray Crystallography, vol. IV, Birmingham, The Kynoch Press.
38 D.W.J. Cruickshank in A. Ahmed (Ed.), Computing Methods in Crystallography, A. Munksgaard, Copenhagen, 1972.
39 G. Ciani, D. Giusto, M. Manassero and A. Albinati, J. Chem. Soc., Dalton Trans., (1976) 1943.