THE SYNTHESIS AND CHARACTERISATION OF DIHYDRIDOBIS-(TRIALKYLTIN)(PENTAMETHYLCYCLOPENTADIENYL)-RHODIUM(V) AND -IRIDIUM(V) COMPLEXES AND RELATED REACTIONS *

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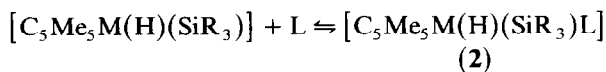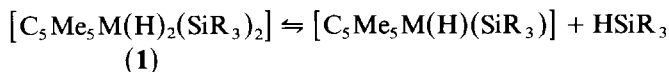(Received November 3rd, 1986)

Summary

The dihydridobis(trialkylstannyl)-rhodium(V) and -iridium(V) complexes [$C_5Me_5M(H)_2(SnR_3)_2$] were made by reaction of R_3SnH and [$(C_5Me_5M)_2Cl_4$] or [$C_5Me_5M(C_2H_4)_2$]. An intermediate in the last reaction was spectroscopically identified as [$C_5Me_5M(H)(SnR_3)(C_2H_4)$] (M = Ir, R = Me), but the rhodium analogues could not be detected. The hydrido-carbonyl complexes, [$C_5Me_5M(H)(SnR_3)(CO)$] were readily obtained by reaction of R_3SnH with [$C_5Me_5M(CO)_2$]; they were more stable than their silyl analogues, but the rhodium complexes slowly decomposed. The complexes [$C_5Me_5M(H)_2(SnR_3)_2$] were very resistant to attack by nucleophiles but the rhodium complexes slowly reacted with PPh_3 to give [$C_5Me_5Rh(PPh_3)(SnR_3)_2$]; this behaviour was in marked contrast to that shown by [$C_5Me_5Rh(H)_2(SiR_3)_2$]. The complex [$C_5Me_5Rh(H)_2(SnMe_3)_2$] was deprotonated by n-butyllithium to give [$C_5Me_5Rh(H)(SnMe_3)_2$]$^-$; this was reversed on addition of methanol.

Introduction

The synthesis, structures and reactivities of the novel rhodium(V) and iridium(V) complexes [$C_5Me_5M(H)_2(SiR_3)_2$] (**1**, R = alkyl, M = Rh or Ir) have been reported [1–5]. The compounds are surprisingly stable under normal conditions, and react only slowly with ligands (L = R_3P, C_2H_4, etc.) to give **2**. This appears generally to

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* Dedicated to Professor Geoffrey Coates with all best wishes for his 70th birthday.

occur by reductive elimination of one trialkylsilane, giving the coordinately un-saturated $[C_5Me_5M(H)(SiR_3)]$, which then combines with L,

$$[C_5Me_5M(H)_2(SiR_3)_2] \rightleftharpoons [C_5Me_5M(H)(SiR_3)] + HSiR_3$$
$$(1)$$

$$[C_5Me_5M(H)(SiR_3)] + L \rightleftharpoons [C_5Me_5M(H)(SiR_3)L]$$
$$(2)$$

The reasons behind this type of reactivity have been considered, as has the lack of direct (bimolecular) reaction with most nucleophiles [1,2]. Electrophiles reacted more readily, but in unexpected ways, for example [1],

$$4[C_5Me_5Rh(H)_2(SiEt_3)_2] + 2H^+ + 4H_2O \rightleftharpoons$$

$$[(C_5Me_5Rh)_4H_4]^{2+} + 4(Et_3Si)_2O + 7H_2$$
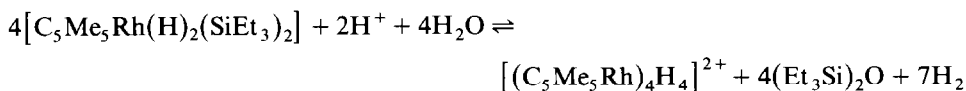
The existence of complexes 1 made it of great interest to investigate related trialkyltin complexes and to compare them to their silyl analogues. This paper describes that work.

Results and discussion

Dihydridobis(trialkyltin)rhodium(V) and -iridium(V) complexes

When the rhodium chloride complex 3a was stirred with tri-n-butyltin hydride in toluene, a smooth reaction took place which yielded the dihydridobis(tri-n-butyltin)rhodium(V) complex 4a in 70% yield

$$[(C_5Me_5M)_2Cl_4] + Bu_3SnH \rightarrow [C_5Me_5M(H)_2(SnBu_3)_2]$$
$$(3) \hspace{4cm} (4)$$
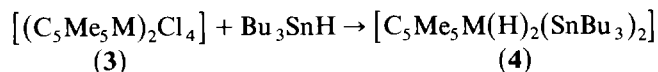
(a, M = Rh; b, M = Ir)

The complex 4a could also be prepared (73%) by irradiation of the bis-ethylene complex 5a

$$[C_5Me_5M(C_2H_4)_2] + R_3SnH \xrightarrow{h\nu} [C_5Me_5M(H)_2(SnR_3)_2]$$
$$(5) \hspace{4cm} (4, R = n\text{-}Bu;$$
$$6, R = Me)$$
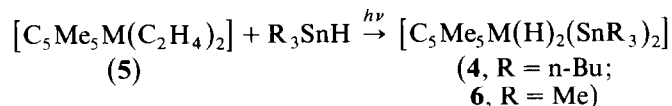
The analogous iridium(V) complex 4b was made by identical routes except that to make it from 3b required the addition of base (triethylamine). Both the rhodium and the iridium tributyltin complexes are oils at room temperature, melting at -18 and $-16°C$, respectively.

The dihydridobis(trimethyltin)-rhodium(V) and -iridium(V) complexes 6 (colour-less crystalline solids at room temperature) were obtained from 5 analogously.

The complexes 4a, 4b, 6a and 6b were characterised by microanalysis and spectroscopically (Tables 1 and 2). The NMR spectra of the rhodium complexes were especially helpful. Thus, for example, the ^{103}Rh NMR (using an INEPT sequence) of the tributyltin complex 4a showed an out-of-phase doublet $(-1: +1)$ at δ -1837, with a separation of of 54.6 Hz, indicating coupling to two hydrides, $J(Rh-H)$ 27.3 Hz. That resonance also showed satellites indicating coupling to $^{117/119}Sn$ [^{117}Sn, $I = 1/2$, 7.7% abundance; ^{119}Sn, $I = 1/2$, 8.7% abundance; $J(Sn-Rh)$ 146 Hz]. The $^{119}Sn\{^1H\}$ spectrum showed a doublet at δ 91.1 and

TABLE 1

NMR SPECTRA OF $[C_5Me_5M(H)_2(SnR_3)_2]$ AND RELATED COMPLEXES

Complex	$\delta(^1H)$ [a]				$\delta(^{13}C)$ [b]		
	H	C_5Me_5	R	Other	C_5Me_5	R	Other
4a	−13.73 [27.5]{25.9}	1.88(7.5)	1.05t(8) 1.17m 1.53m 1.70m	–	11.3 99.2 [3]	13.3 14.2 28.1{61.5} 30.8{17}	–
4b	−17.18 {33}	1.90 {6.3}	1.05t(8) 1.14m 1.54st(8) 1.68m	.	11.0 95.0	11.9 14.1 28.0{58.1} 30.9	
6a	−13.70 [28.8] {37.5}	1.73 {8.7}	0.48 {47.5}	–	11.1 99.4	−2.95 {25.7}	
6b	−17.20 {26.3}	1.78 {7.5}	0.53 {46.3}	–	10.7 95.2	−4.4	
7	–	1.47 J(P–H)2.5	0.39 {37}	Ph, 7.0– 8.2m			
8b	−17.69 {74}	1.67 {4}	0.36 {21}	C_2H_4,1.47 2.19bd 3.46m	9.8 94.1	−8.56	C_2H_4,70.4 71.2
10a	−11.72 [29]{42}	1.82	1.00t(7.5) 1.18m 1.49st(7.5) 1.71m	–	11.1 100.5	12.5 14.0 28.0 30.8	CO,193.1 [75.7]
10b	−15.92 {84}	1.87 {7.5}	1.02t(7.5) 1.19m 1.52st(7.5) 1.73m	–	10.7 96.7	10.5 14.1 28.0 30.9	CO,172.7
11a	−11.85 [29]{40}	1.77 {8}	0.48 {45}	–	10.7 100.2	−5.4	CO,192.6 [74.4]
11b	−16.08 {94}	1.82 {8}	0.53 {46}	–	10.3 96.5	10.2	CO,172.6

[a] ^1H NMR spectra in C_6D_6 at 25°C; [ ] coupling to Rh, { } coupling to Sn, ( ) coupling to H, all in Hz.
[b] ^{13}C NMR spectra in C_6D_6 at +25°C; [ ] coupling to Rh, { } coupling to Sn, all in Hz.

confirmed the bonding of the tins to rhodium. These data were further supported by the ^1H NMR spectrum which showed, apart from the signals due to the pentamethylcyclopentadienyl and the butyl groups, a doublet at δ −13.73 [J(Rh–H) 27.5 Hz, indicating coupling of the hydrides to one rhodium] with satellites (ratios found 2/10/4/10/2; expected, 1.9/10/3.9/10/1.9) showing that the hydrides were also coupled to two tin atoms. The ^{13}C NMR was in agreement with the formulations too. Spectroscopic data for the trimethyltin complex **6a** were very similar indeed.

The data for the iridium complexes **4b** and **6b** were again similar to those for **6a**, even though the metal centre was not NMR active. Thus, for example, **4b** showed a singlet at δ −17.18 in the ^1H spectrum, which had satellites (ratios found, 2/10/2;

TABLE 2

^{103}Rh AND ^{119}Sn NMR AND IR SPECTRA OF $[C_5Me_5M(H)_2(SnR_3)_2]$ AND RELATED COMPLEXES

Complex	IR ^{a}	^{103}Rh		^{119}Sn	
	ν(M–H), ν(CO) (cm^{-1})	δ ^{b}	J(Rh–H)	δ ^{c}	J(Rh–Sn)
		(ppm)	(Hz)	(ppm)	(Hz)
4a	1928	−1837.5	27.3	91.1	146
4b	2087			−50.9	
6a	1938	−1757.1	28.3	59.7	151
6b	2088			−98.5	
7	–			8.9	358
				J(Sn–P), 222Hz ^{d}	
8b	2112			−104.7	
10a	2019, 1976	−1553.2	29.3	100.0	210
10b	2109, 1964			−45.2	
11a	n/o, 1981	−1532	29.6	63.5	221
11b	2107, 1967			−95.9	

^{a} IR spectra measured on Perkin–Elmer 1710 FT spectrometer; complexes **10a**, **10b**, **11a**, and **11b** in C_6H_6 solution, complexes **4a**, **4b**, **6a**, **6b**, **7**, **8b** in cyclohexane solution; ν(M–H) largely obscured by ν(CO) in **11a**. ^{b} ^{103}Rh NMR spectra (via INEPT) measured relative to $\equiv 3.16$ MHz = 0 ppm. ^{c} ^{119}Sn NMR spectra measured with low power decoupling of the alkyltin protons; relative to external SnMe$_4$. ^{d} ^{31}P NMR spectrum, δ 52.5 [J(Rh–P) 167.7; J(Sn–P) 221.8].

expected, 1.9/10/1.9) indicating coupling to two tin atoms, J(Sn–H) 32.5 Hz. This was confirmed by the ^{119}Sn{^{1}H} spectrum which showed a singlet at δ −50.9.

The trialkyltin complexes **4** and **6** were surprisingly unreactive. Thus, no reaction occurred when triphenylphosphine was either irradiated (cyclohexane, 20°C, 4 d) or heated (toluene, 80°C) with **4a** in a 2/1 ratio. Similarly, there was no reaction when **4a** was heated with ethylene (50 atm, 90°C, 25 h) and no H/D exchange was detected when it was irradiated in benzene-d_6 for 4 d. [For comparison, both the rhodium and iridium silyl complexes **1** underwent extensive exchange with C_6D_6 under these conditions.]
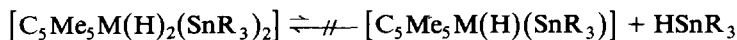
The trimethyltin complex **6a** was equally unreactive towards triphenylphosphine on irradiation in cyclohexane for 10 d. Reaction only occurred under quite drastic conditions, and then to give a completely unexpected product. Only a small residual amount of **6a** was left (by NMR) after it had been heated with triphenylphosphine in benzene (1/1; 100°C, 15 h). The product could not be isolated, but was characterised spectroscopically as **7**. It showed no hydride either in the ^{1}H NMR or in the IR spectra; the ^{31}P NMR showed coupling to Rh [J(Rh–P) 167.7 Hz] with satellites arising from coupling to two tin atoms (ratio 2/10/2/2/10/2). Lastly, the ^{119}Sn NMR spectrum showed a double doublet (δ 8.9) arising from coupling of the equivalent tins to one rhodium [J(Rh–Sn) 358 Hz] and one phosphorus [J(Sn–P) 222 Hz].

$$[C_5Me_5Rh(H)_2(SnMe_3)_2] + PPh_3 \rightleftharpoons [C_5Me_5Rh(PPh_3)(SnMe_3)_2] + H_2$$
$$\text{(6a)} \qquad\qquad\qquad\qquad\qquad \text{(7)}$$
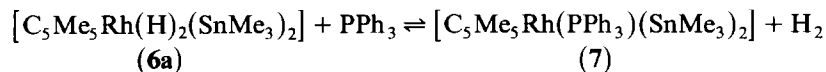
When the tributyltin complex **4a** was treated with triphenylphosphine (1/1) in toluene only about half of the original complex had disappeared after 3 d at 120°C. The high temperature needed for this reaction also caused decomposition, but the

^{31}P{^{1}H} NMR spectrum gave clear indication that the analogue of **7**, [C$_5$Me$_5$RhPPh$_3$(SnBu$_3$)$_2$] was present [doublet at δ 53.0, J(Rh–P) 169 Hz, with tin satellites, J(Sn–P) 302 Hz]. The iridium complex **6b** did not react at all with triphenylphosphine under these conditions.

Although in many other ways (for example in the methods of preparation) these molecules closely resemble the trialkylsilyl complexes **1**, the reductive elimination **1a** → **2a** has no parallel here; the reaction,

$$\left[C_5Me_5M(H)_2(SnR_3)_2\right] \;\overset{}{\underset{}{\rightleftharpoons\!\!\!/\!\!\!-}}\; \left[C_5Me_5M(H)(SnR_3)\right] + HSnR_3$$

does not take place at all. This may be due to a higher stability of the M–Sn than of the M–Si bonds. However, a more likely explanation is that the trialkylstannane (forming an Sn–H bond) that would be produced in such a reaction is much less favoured than is the analogous trialkylsilane (containing an Si–H bond) in the reductive elimination of **1**. This suggestion is supported by the substantially higher bond energy of Si–H (323 kJ/mol in SiH$_4$) compared with Sn–H (251 kJ/mol in SnH$_4$) [6].

The trimethylsilyl complex **1a** undergoes deprotonation with butyllithium to give a monohydrido anion, which with methanol regenerates the original complex [7]

$$\left[C_5Me_5Rh(H)_2(SiMe_3)_2\right] \underset{+H^+}{\overset{-H^+}{\rightleftharpoons}} \left[C_5Me_5Rh(H)(SiMe_3)_2\right]^-$$
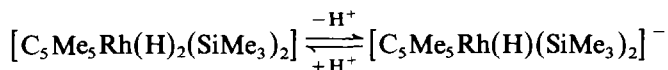
A very similar reaction occurred with the rhodium-trimethyltin complex **6a**, to form [C$_5$Me$_5$Rh(H)(SnMe$_3$)$_2$]$^-$Li$^+$. This was shown by the ^{1}H, the ^{119}Sn, and the ^{103}Rh NMR spectra of solutions containing the anion [^{1}H NMR δ at -17.0 {J(Rh–H) 23, J(Sn–H) 180 Hz}; ^{103}Rh NMR spectrum (via INEPT) δ -1359 {J(Rh–H) 24, J(Rh–Sn) 463 Hz}]. On addition of methanol, the complex **6a** was regenerated.

$$\left[C_5Me_5Rh(H)_2(SnMe_3)_2\right] \underset{MeOH}{\overset{n\text{-}BuLi}{\rightleftharpoons}} \left[C_5Me_5Rh(H)(SnMe_3)_2\right]^-Li^+$$
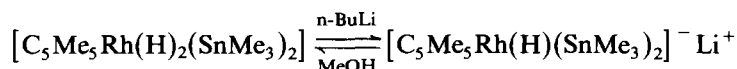
Hydrido(ethylene)(trimethyltin)(pentamethylcyclopentadienyl)iridium (8b)
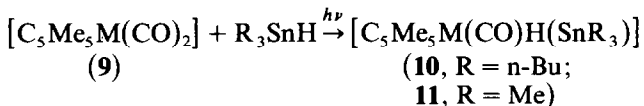
When the irradiation reaction between the bis-ethylene iridium complex **5b** and trimethylstannane (in cyclohexane) to make **6b** was stopped after 75 min, the NMR spectrum showed the presence of three species, **5b** 6%, **6b** 41%, and another complex, **8b** 53%. The components of the mixture could not be separated, but **8b** was identified spectroscopically as [C$_5$Me$_5$Ir(C$_2$H$_4$)(H)(SnMe$_3$)].

The hydride signal in the ^{1}H NMR spectrum of complex **8b** (at δ -17.69) showed satellites with intensity ratio 10/100/10, which indicated the presence of one tin atom in the complex [J(Sn–H) 74.0 Hz]. The ^{1}H spectrum also showed, by integration, the presence of one hydride, one C$_5$Me$_5$, and one Me$_3$Sn, and broad resonance (at δ 1.47, 2.19, and 3.46) which we assign to the inequivalent H's of the coordinated C$_2$H$_4$. The ^{13}C NMR spectrum showed, apart from signals at δ -8.56 (SnMe$_3$), 9.8, and 94.1 (C$_5$Me$_5$), resonances at 70.4 and 71.2, which again we assign to the inequivalent carbons of the coordinated ethylene. Finally, the ^{119}Sn NMR with low power decoupling of the SnMe$_3$ protons showed a doublet at δ -104.7 [J(Sn–H) 74 Hz] confirming that the centre to which the tin was bonded was also bonded to one hydride. Analogous complexes were not observed in the rhodium

reactions, suggesting that they were too reactive to be seen. However, these are exactly analogous to the species **2** ($L = C_2H_4$) which are intermediates in the reactions of **5a** with silanes or of **1a** with ethylene [3,4,8].

Carbonyl(hydrido)(trialkylstannyl)pentamethylcyclopentadienyl-rhodium and -iridium (10, 11)

The reaction to give the hydrido-ethylene complex has an exact parallel in the reactions of **1** in the formation of the rather unstable carbonyl-hydrido-silyl complexes $[C_5Me_5M(H)CO(SiR_3)]$ [7,8]. We have therefore also made the corresponding carbonyl-hydrido-trialkylstannyl complexes **10** and **11**, by irradiation of the metal dicarbonyls **9** with the appropriate trialkylstannane.

$$[C_5Me_5M(CO)_2] + R_3SnH \xrightarrow{h\nu} [C_5Me_5M(CO)H(SnR_3)]$$
$$\mathbf{(9)} \qquad\qquad\qquad \mathbf{(10}, R = n\text{-Bu};$$
$$\mathbf{11}, R = Me)$$

The complexes were isolated and characterised (microanalysis, IR, and NMR spectroscopy). Thus, for example, the iridium complex **11b** showed a hydride in the ^1H NMR spectrum at δ -16.08, with satellites indicating coupling to one tin atom, J(Sn–H) 94 Hz. The presence of the carbonyl is clear from the IR [ν(CO) 1967 cm^{-1}; also ν(Ir–H) 2107 cm^{-1}] and the ^{13}C NMR spectrum (s at δ 172.6). ^{103}Rh NMR spectroscopy (via INEPT) was used additionally to identify the rhodium complex **10a**; this showed an out-of-phase doublet ($-1: +1$) with satellites [δ -1532, J(Rh–H) 29.6, J(Rh–Sn) 220 Hz]. The form of the resonances indicated clearly the attachment of the rhodium to one hydride and one tin.

The reactions to form **10** and **11** were complete after a little over an hour; increased irradiation or increased amounts of the tin hydride gave no sign of the formation of complexes **4** or **6**. The iridium complexes **10b** and **11b** were reasonably stable; however the rhodium analogues **10a** and **11a** were rather unstable when solvent was removed from the product. The formation of hydrogen as well as the blue dimeric carbonyl [$\{C_5Me_5Rh(CO)\}_2$] [ν(CO) 1733 cm^{-1}] was noted in those reactions; complex **11a** could not be obtained pure for that reason.

Support for these points comes from recent observations by Perutz and Haddleton that irradiation of $[C_5H_5Rh(CO)(C_2H_4)]$ in the presence of triethylsilane gave $[C_5H_5Rh(CO)(SiEt_3)H]$ and $[C_5H_5Rh(H)(C_2H_4)SiEt_3]$ by loss of ethylene and carbon monoxide respectively [8]. Previous work had shown that the normal route followed by reaction of Me_3EH (E = Si, Ge, or Sn) with $[C_5H_5Rh(CO)_2]$ gave not the carbonyl hydride found here but $[C_5H_5Rh(CO)(Me_3E)_2]$; however Ph_3SiH and Benzyl$_3$SiH both gave $[C_5H_5Rh(CO)H(SiR_3)]$ [9,10].

Conclusions

The trialkylstannyl-hydrido-rhodium and -iridium complexes are formed very easily and show quite similar properties to the trialkylsilyl-hydrido-rhodium and -iridium species prepared earlier. One major difference is that the tin complexes do not appear to undergo the reductive elimination reactions which we found to be characteristic of the trialkylsilyl complexes; instead they very slowly lose hydrogen. The reason probably lies in the relative strengths of Sn–H and Si–H bonds.

Experimental

All reactions were carried out under nitrogen or argon. Typical preparations are given below; microanalytical and spectroscopic data are collected in Tables 1–3. Spectra were recorded on a Perkin–Elmer 1710 FT infra-red spectrometer, and on Bruker WH400 and AM250 NMR spectrometers; microanalyses are by the University of Sheffield Microanalytical Service. Irradiations were carried out using a Hanovia medium pressure mercury lamp.

Preparation of [$C_5Me_5Rh(H)_2(SnBu_3)_2$] (4a)

A suspension of [($(C_5Me_5Rh)_2Cl_4$] (0.5 g, 0.8 mmol) and tri-n-butyltin hydride (2 g, 6.9 mmol) was stirred in dry toluene (10 cm^3; 14 h at 60°C). Solvent and other volatiles were removed in vacuo, and the residue extracted with pentane and chromatographed on Florisil in pentane. The solvent was removed from the eluate to leave an oil, which was crystallised from diethyl ether/methanol at −78°C to give colourless crystals of [$C_5Me_5Rh(H)_2(SnBu_3)_2$], m.p. −18°C (0.92 g, 70%).

The complex [$C_5Me_5Rh(H)_2(SnBu_3)_2$] (0.41 g, 73%) was also obtained by irradiation of [$C_5Me_5Rh(C_2H_4)_2$] (0.2 g, 0.68 mmol) and n-Bu$_3$SnH (0.8 g, 2.75 mmol) in cyclohexane (3 cm^3, 14 h/20°C).

The iridium complex [$C_5Me_5Ir(H)_2(SnBu_3)_2$] (4b) (m.p. −16°C) was prepared identically in 60 and 64% yields, respectively by the two routes.

Preparation of [$C_5Me_5M(H)_2(SnMe_3)_2$] (6a, M = Rh; 6b, M = Ir)

The rhodium complex 6a, m.p. 66–70°C, was obtained (89%) by irradiating [$C_5Me_5Rh(H)_2(SnBu_3)_2$]; the iridium complex 6b, m.p. 100–104°C, was made similarly in 94% yield.

Preparation of [$C_5Me_5Ir(H)(SnBu_3)CO$] (11b)

A solution of [$C_5Me_5Ir(CO)_2$] (80 mg, 0.2 mmol) and Me$_3$SnH (0.05 cm^3) in cyclohexane (0.7 cm^3) was irradiated (90 min/20°C). The product 11b (97 mg, 90%) was isolated after the removal of volatiles in vacuo.

TABLE 3

YIELDS AND MICROANALYTICAL DATA FOR [$C_5Me_5M(H)_2(SnR_3)_2$] AND RELATED COMPLEXES

Complex	Yield (%)	Microanalyses (Found (calc) (%))	
		C	H
4a	70 [from 3]	49.8 (49.8)	8.7 (8.7)
	73 [from 5]		
4b	60 [from 3]	45.2 (44.9)	7.7 (7.9)
	64 [from 5]		
6a	89 [from 5]	34.4 (33.9)	6.4 (6.2)
6b	94 [from 5]	30.0 (29.3)	5.4 (5.4)
10a	90	47.8 (49.6) [a]	7.6 (7.8)
10b	95	43.1 (42.7)	6.7 (6.7)
11b	90	33.1 (32.3)	5.0 (4.8)

[a] The sample decomposed very quickly in the solid state; the microanalysis was performed 10 min after isolation.

The rhodium complexes **10a** and **11a** were also made by this route but they were quite unstable, and slowly decomposed to form blue $[(C_5Me_5RhCO)_2]$, identified by IR spectroscopy.

Preparation of $[C_5Me_5Ir(C_2H_4)(H)(SnMe_3)]$ (8b)

A solution of $[C_5Me_5Ir(C_2H_4)_2]$ (**5b**), (125 mg, 0.3 mmol) and Me_3SnH ((0.13 cm^3) in cyclohexane (0.7 cm^3) was irradiated (75 min/20 °C). The NMR spectrum of the residue remaining after removal of volatiles showed the presence of **5b** 6%, **8b** 53%, and **6b** 41%; attempts to separate this mixture by column chromatography were unsuccessful.

Reaction of $[C_5Me_5Rh(H)_2(SnMe_3)_2]$ (6a) with triphenylphosphine

A mixture of $[C_5Me_5Rh(H)_2(SnMe_3)_2]$ (100 mg, 0.18 mmol) and triphenylphosphine (50 mg, 0.19 mmol) in benzene (0.5 cm^3) was heated in a sealed NMR tube (15 h/100 °C). The spectrum showed the presence of only a small residual amount of **6a**. After removal of all volatiles an unstable material was isolated, the NMR spectrum of which was consistent with that expected for $[C_5Me_5Rh(PPh_3)(SnMe_3)_2]$ (**7**).

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