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# Binuclear Organometallic Compounds. Part II.<sup>1</sup> Reactions of Triorganotin Hydrides with Iridium(1) and Rhodium(1) Complexes

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Hydrostannation of the iridium(1) complexes, trans-IrXCOL<sub>2</sub> (where X = CI, Br, or 1:  $L = PPh_3$ , PPh<sub>2</sub>Me, or PPhEt<sub>o</sub>) by the tri-organotin hydrides,  $R_{a}SnH$  (where R = Me, Et, or Ph), yields the iridium(III) species,  $R_{a}SnIr$ -HXCOL<sub>2</sub>, the stereochemical configurations of which are discussed on the basis of i.r. and n.m.r. data. The rhodium(I) complex, RhClCO(PPhEt<sub>2</sub>)<sub>2</sub> does not react with tri-organotin hydrides, and, although RhCl(PPh<sub>3</sub>)<sub>3</sub> does react, hydrostannation does not occur.

THERE is current interest in compounds containing transition metal-Group IV metal bonds.<sup>2</sup> This paper is concerned with the formation, properties, and structures of complexes containing iridium-tin bonds; the attempted preparation of rhodium-tin complexes is also described. All known iridium (and rhodium)-tin complexes fall into one of two classes, depending on whether they contain trichloro-tin, or alkyl-(aryl)-tin groups.<sup>2</sup> Collman et al.<sup>3</sup> have recently prepared several pentaco-ordinate iridium(I) and rhodium(I) complexes

 Soc. (A), 1970, 2594.
 <sup>2</sup> Cf. N. S. Vyazankin, G. A. Razuvaev, and O. A. Kruglaya, Organometallic Chem. Rev. (A), 1968, 3, 323; F. G. A. Stone, in 'New Pathways in Inorganic Chemistry,' ed. E. A. V. Ebsworth, Combridge University A. G. Maddock, and A. G. Sharpe, Cambridge University Press, 1968, p. 283; M. C. Baird, Progr. Inorg. Chem., 1968, 9, 1; J. F. Young, Adv. Inorg. Chem. Radiochem., 1968, 11, 91.

of the latter type, but this is the first full report 4 on the formation of hexaco-ordinate iridium(III) complexes, containing trialkyl- and triaryl-tin groups bonded to iridium.

Iridium-Tin Complexes.—The formation of octahedral  $d^{6}$  iridium(III) complexes by oxidative-addition reactions of the square planar  $d^8$  iridium(I) complex trans-IrXCOL<sub>2</sub> (where X = halogen; L = tertiary phosphine) is well known,<sup>5</sup> and iridium-silicon complexes <sup>6</sup> have been obtained in this way [equation (1); where  $R^1 = R^2$ = Cl or OEt; n = 0; and  $R^1$  = Et or Ph;  $R^2$  = Cl;

<sup>3</sup> J. P. Collman, F. D. Vastine, and W. R. Roper, J. Amer. Chem. Soc., 1966, 88, 5035; 1968, 90, 2282. <sup>4</sup> M. F. Lappert and N. F. Travers, Chem. Comm., 1968, 1569.

<sup>5</sup> J. P. Coliman and W. R. Roper, Adv. Organometallic Chem., 1968, 7, 54.

<sup>6</sup> A. J. Chalk and J. F. Harrod, J. Amer. Chem. Soc., 1965, 87, 16.

<sup>&</sup>lt;sup>1</sup> D. J. Cardin, S. A. Keppie, and M. F. Lappert, J. Chem.

$$\frac{\mathrm{R}^{1}_{n}\mathrm{R}^{2}_{3-n}\mathrm{SiH} + \mathrm{IrClCO}(\mathrm{PPh}_{3})_{2}}{(\mathrm{R}^{1}_{n}\mathrm{R}^{2}_{3-n}\mathrm{Si})\mathrm{IrHClCO}(\mathrm{PPh}_{3})_{2}} \quad (1)$$

The iridium-silicon compounds were unstable in solution, dissociating to a mixture of the starting materials; this precluded measurements of molecular weights or n.m.r. spectra. Trialkyl- (and triaryl-) silanes do not react with trans-IrClCO(PPh<sub>3</sub>)<sub>2</sub>.<sup>6</sup> However, it seemed conceivable that, in view of their greater reactivity, trialkyl- (and triaryl-) stannanes might add to trans-IrXCOL<sub>2</sub>; moreover, it was anticipated<sup>2</sup> that the compounds having iridium-tin bonds, would be more stable than their silicon analogues. This was indeed found to be the case.

Prior to our preliminary communication,<sup>4</sup> hydrometallation of co-ordinatively unsaturated low-oxidation state complexes was only known for the Si-H addition. In the meantime, Glockling and Wilbey have shown that germanes  $R_3GeH$  (R = Me or Et) react with trans-IrClCO(PPh<sub>3</sub>)<sub>2</sub> in a different way [equation (2)].<sup>7</sup> They proposed that the Ge-Ir product arose from successive oxidative addition, R3GeCl elimination, and further R<sub>3</sub>GeH oxidative addition. An alternative explanation is that the initial product of hydrogermylation is reduced by excess of R<sub>3</sub>GeH; or more probably, as recently demonstrated for the R<sub>3</sub>SiH-IrClCO(PPh<sub>3</sub>)<sub>2</sub> system,<sup>8</sup> that the successive steps are IrClCO(PPh<sub>3</sub>)<sub>2</sub>  $\stackrel{\mathtt{R}_3GeH}{\longrightarrow} \mathrm{IrHCO}(\mathrm{PPh}_3)_2 \stackrel{\mathtt{R}_3GeH}{\longrightarrow} \mathrm{R}_3\mathrm{GeIrH}_2\mathrm{CO}(\mathrm{PPh}_3)_2.$ 

$$\frac{2R_{3}GeH + IrClCO(PPh_{3})_{2} \longrightarrow}{R_{3}GeCl + R_{3}GeIrH_{2}CO(PPh_{3})_{2}}$$
(2)

Trialkyl- and triaryl-tin hydrides (and deuterides) reacted with trans-IrXCOL<sub>2</sub>, in organic media, at room temperature, according to equation (3). When R = Ph,

$$R_3SnH + IrXCOL_2 \longrightarrow R_3SnIrHXCOL_2$$
 (3)

X = Cl, and  $L = PPh_2Me$  or  $PPhEt_2$ , the solvent was benzene or diethyl ether; when R = Me, X = Cl, and  $L = PPh_3$ , the solvent was benzene or an excess of trimethyltin hydride(deuteride); in all other reactions, benzene was the only solvent used.

The properties of the complexes depended markedly on the nature of R and L. Instability in air and solubility in organic solvents increased down the series:  $R/L = Ph/PPh_3 < Ph/PPh_2Me < Me/PPh_3 < Et/$  $PPh_3 < Me/PPh_2Me$ . In contrast to the silane adducts,<sup>6</sup> the soluble stannane adducts did not dissociate in organic solvents, as shown by molecular weight data, i.r. and n.m.r. spectra, and by the fact that they could be recrystallised from solvent mixtures.

I.r. and n.m.r. data for the iridium-tin complexes are

<sup>8</sup> A. J. Chalk, *Chem. Comm.*, 1969, 1207.
 <sup>9</sup> L. Vaska, *J. Amer. Chem. Soc.*, 1966, 88, 4100.
 <sup>10</sup> D. M. Adams, 'Metal-Ligand and Related Vibrations,' Arnold, London, 1967, p. 202; H. Kriegsmann and H. Geissler, *Z. anorg. Chem.*, 1963, 323, 170.

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shown in Table 1. The i.r. spectra of all the iridiumtin complexes, with the exception of Ph<sub>3</sub>SnIrHClCO- $(PPhEt_2)_2$ , exhibited single bands for  $\nu(IrH)$  and  $\nu(CO)$ absorption, indicating that the complexes were single isomers. Proof that the band between 2050 and 2150 cm.<sup>-1</sup> in the spectrum of each hydrido-complex was correctly assigned to the Ir-H stretching frequency was obtained from the spectrum of the corresponding deuterido-complex (Table 1). The ratio v(IrH): v(IrD)was found to be normal [*i.e.*, v(IrH): v(IrD) = 1.39— 1.40], except for those complexes where hydrogen (and consequently deuterium) was assumed to be trans to carbonyl.9

The Ir-Cl stretching mode is readily assigned in the i.r. spectra (400-200 cm.<sup>-1</sup>) of the Me<sub>3</sub>Sn complexes, but for the complexes Ph<sub>3</sub>SnIrHClCOL<sub>2</sub>, two bands were present at ca. 300 and 250 cm.<sup>-1</sup>; the disappearance of the former, and the retention of the latter band, in the spectra of the corresponding bromo- and iodo-complexes leads to the assignment of  $\nu(IrCl)$  at 300 cm.<sup>-1</sup>, and  $\nu_{sym.}(SnPh_3)$  at 250 cm.<sup>-1</sup>.<sup>10</sup> Two weak bands were observed, at 280 and 255 cm.<sup>-1</sup>, in the spectrum of Et<sub>3</sub>SnIrHClCO(PPh<sub>3</sub>)<sub>2</sub>; the former is assigned to the Ir-Cl stretching vibration and the latter, tentatively, to the SnC<sub>2</sub> bending mode.<sup>11</sup> The position of the Ir-Cl stretching mode in the deuterido-complexes was virtually identical to that in the corresponding hydridocomplexes, thus showing that no isomerisation of the complexes had occurred on deuteriation.

The n.m.r. data (Table 1) established the general stoicheiometry of the iridium-tin complexes and, in three cases, the presence of hydrogen bonded to iridium was verified, the  $\tau$  values falling in the correct region for six co-ordinate iridium hydrides.<sup>12</sup>

Rhodium-Tin Complexes.-Wilkinson and his coworkers 13 investigated the hydrosilation of trans-RhClCO(PEt<sub>3</sub>)<sub>2</sub>, but found the rhodium-silicon adducts stable only in presence of an excess of silane; however, stable adducts were formed by interaction of silanes, bearing electronegative substituents, and RhCl(PPh<sub>3</sub>)<sub>3</sub> in dichloromethane or in absence of solvent, with an excess of the silane.<sup>13,14</sup> It seemed, therefore, that hydrostannation of such rhodium(I) complexes might also take place; however, no reaction was observed between triphenyltin hydride—the most effective hydrostannating agent for iridium(I) complexes-and trans-RhClCO(PPhEt<sub>2</sub>)<sub>2</sub>. Trialkyl- and triaryl-stannanes did react with RhCl(PPh<sub>3</sub>)<sub>3</sub>, in the presence or absence of solvent, but, of the products isolated, none was a rhodium hydride (no Rh-H stretching frequency band in the i.r. spectrum); moreover, the analytical data obtained did not correspond to any plausible product.

Cf. A. P. Ginsberg, Transition Metal Chem., 1966, 1, 111.

<sup>13</sup> F. de Charentenay, J. A. Osborn, and G. Wilkinson, J. Chem. Soc. (A), 1968, 787

14 R. N. Haszeldine, R. V. Parish, and D. J. Parry, J. Organometallic Chem., 1967, 9, P13.

<sup>7</sup> F. Glockling and M. D. Wilbey, Chem. Comm., 1969, 286.

<sup>&</sup>lt;sup>11</sup> H. Kriegsmann and K. Ulbricht, Z. anorg. Chem., 1964, **328**, 90; P. Taimsalu and J. L. Wood, Trans. Faraday Soc., 1963, 59, 1754.

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Stereochemistry.—In assigning the configurations of the six-co-ordinate iridium-tin complexes,  $R_3SnIr$ -HXCOL<sub>2</sub>, the simplifying assumption is made that the phosphine ligands are *trans*-, as they are in all the simple adducts of IrXCOL<sub>2</sub>.<sup>15</sup> This was proved for Ph<sub>3</sub>SnIrHClCO(PPh<sub>2</sub>Me)<sub>2</sub> by the observation (in the n.m.r. spectrum) of virtual coupling <sup>16</sup> between the PPh<sub>2</sub>Me ligands (see Table 1). On this basis, the possible configurations for the iridium-tin complexes are shown in formulae (I)—(III).



The Triphenyltin-Iridium Complexes—The observation (see Table 1) that the iridium-hydrogen (and

configuration (I).<sup>17c</sup> With configuration (II), v(IrH)absorption would be expected to be low, owing to the high trans-influence of the carbonyl group; 17d however,  $\nu$ (IrH) absorption values for the triphenyltin complexes are noticeably higher than those for the corresponding yellow trimethyltin complexes. This is evidence both against the assignment of configuration (II) to the triphenyltin complex and for its assignment to the trimethyltin complexes (see below). Moreover, no significant H/CO vibrational interaction <sup>9</sup> was observed, as shown by comparison of the spectra of the hydridoand deuterido-triphenyltin complexes, thus eliminating Consequently, the complexes configuration (II). Ph<sub>3</sub>SnIrHXCOL<sub>2</sub> are assigned the configuration (I). This does not necessarily imply that the mode of addition of triphenyltin hydride to trans-IrXCOL<sub>2</sub>, in benzene, is trans, because rapid isomerisation of a cis-adduct may have supervened.

Trimethyltin-Iridium Complexes.—With  $(Me_3Sn)$ -IrHClCO(PPh<sub>3</sub>)<sub>2</sub>, two different isomers were isolated;

		IABLE 1		
I.r. and n.m.r.	spectral	data for	R <sub>3</sub> SnIr(H	$orD)XCOL_2$

		$1.r. (cm.^{-1})$			N				
R, H or D, X and L in		v(IrH) or							
R <sub>3</sub> SnIr(H or D)XCOL <sub>2</sub>	Configuration	v(IrD)	$\nu(CO)$	v(IrCl)	Ph •	PMe b	R <sub>3</sub> Sn <sup>b</sup>	IrH ?	
Me, H, Cl, PPh <sub>3</sub>	(II)	2080 d	1963 ª	290	2.61 m (33)		10.01s(9)	18.8	
Me, D, Cl, PPh <sub>3</sub>	(II)	1508 <sup>d</sup>	1993 a	290	· ,				
Me, H, Br, PPh <sub>3</sub>	(II)	2080 ª	1963 <sup>a</sup>		2.6m(34)		10·03s (9)		
Me, H, Cl, PPh <sub>3</sub>	(I)	2093 ª	1998 ª	299	. ,				
Me, D, Cl, PPh <sub>3</sub>	(I)	1503 ª	1998 ª	297					
Me, H, Cl, PPh <sub>2</sub> Me	(I)	2065	1980	297					
Et, H, Cl, PPh <sub>3</sub>	(II)	2067	1955	280	2.73m(2)		3·93m (1)	20.4	
Ph, H, Cl, PPh <sub>3</sub> <sup>e</sup>	$(\mathbf{I})$	2138	1998	<b>300</b>	.,				
Ph, D, Cl, PPh <sub>3</sub> <sup>e</sup>	(I)	1530	1998	300					
Ph, H, Br, PPh <sub>3</sub> •	(I)	2138	1998						
Ph, D, Br, PPh <sub>3</sub> •	(I)	1530	1998						
Ph, H, I, PPh <sub>3</sub> •	(I)	2140	1997						
Ph, H, Cl, <b>PPh<sub>2</sub>Me</b> <sup>e</sup>	(I)	2073 ª	2005 ª	305	2·68m (32)	8·2t (6)′		15.3	
Ph, D, Cl, PPh <sub>2</sub> Me <sup>e</sup>	(I)	1483 ď	2005 ª	307					
Ph, H, Cl, PPhEt <sub>2</sub> <sup>e</sup>	g	2092	2002	300					
-	2	2047	1990						

<sup>a</sup> Chemical shift ( $\tau$ ); coupling pattern indicated by: s (singlet), m (multiplet), t (triplet); relative integral intensities in parentheses. <sup>b</sup> Recorded in CDCl<sub>3</sub>. <sup>c</sup> Recorded in PhH. <sup>d</sup> KBr disc; all other spectra measured as Nujol mulls (solution spectra in CHCl<sub>3</sub> are very similar). <sup>e</sup>  $\nu_{sym}$  (SnPh<sub>3</sub>), 247—248 cm.<sup>-1</sup>. <sup>f</sup>  $J_{P-H}$  (apparent), 9 c./sec. <sup>g</sup> Presumably a mixture of isomers.

iridium-deuterium) stretching frequencies for the adducts  $Ph_3SnIrHXCOL_2$  (X = Cl, Br, or I; L =  $Ph_3P$ ) are independent of the nature of the halogen (X) in the starting complex suggests (on the basis that the *trans*influence of X is likely to be more profound than its *cis*-influence) that hydrogen (or deuterium) cannot be *trans* to X, as in configuration (III).<sup>17a</sup> Moreover, if the triphenyltin complexes had configuration (III), v(IrCl) absorption would be expected in the region 250—270 cm.<sup>-1</sup>, in accordance with the high *trans*influence of the hydride ligand; <sup>17b</sup> in fact, v(IrCl)absorption is at *ca*. 300 cm.<sup>-1</sup>, and this is consistent with

they were obtained not as a mixture, but in separate experiments. No attempt was made to interconvert isomers. The *yellow isomer*, to which configuration (II) is assigned, was obtained by allowing equimolar proportions of trimethyltin hydride and *trans*-IrClCO(PPh<sub>3</sub>)<sub>2</sub> to react, in benzene at room temperature. From the i.r. data (Table 1), it is evident that v(IrH) absorption in the complex Me<sub>3</sub>SnIrHXCO(PPh<sub>3</sub>)<sub>2</sub> is unaffected by a change in X from Cl to Br, and thus, on the basis of *trans*-influence theory, configuration (III) seems unlikely; <sup>17a</sup> also, v(IrCl) absorption was located at *ca*. 290 cm.<sup>-1</sup>, a value too high to be compatible with a

<sup>16</sup> J. M. Jenkins and B. L. Shaw, Proc. Chem. Soc., 1963, 279.
<sup>17</sup> (a) L. Vaska, J. Amer. Chem. Soc., 1966, 88, 5325; (b)
J. M. Jenkins and B. L. Shaw, J. Chem. Soc., 1965, 6789; (c)
M. A. Bennett, R. J. H. Clark, and D. L. Milner, Inorg. Chem., 1967, 6, 1647; (d) J. Chatt, N. P. Johnson, and B. L. Shaw, J. Chem. Soc., 1964, 1625.

<sup>&</sup>lt;sup>15</sup> (a) J. A. Ibers and S. J. La Placa, Science, 1964, 145, 920;
J. Amer. Chem. Soc., 1965, 87, 2581; Inorg. Chem., 1966, 5, 405; (b) J. A. McGinnety, R. J. Doedens, and J. A. Ibers, *ibid.*, 1967, 6, 2243; (c) D. J. Hodgson and J. A. Ibers, *ibid.*, 1968, 7, 2345; (d) J. P. Collman and C. T. Sears, *ibid.*, 1968, 7, 27; (e) L. Vaska and R. E. Rhodes, J. Amer. Chem. Soc., 1965, 87, 4970.

configuration where chlorine is *trans* to hydrogen.<sup>17b,c</sup> Evidence for the appreciable H/CO vibrational interaction,<sup>9</sup> anticipated for a complex with configuration (II), was obtained by comparison of the spectra of the hydrido- and deuterido-trimethyltin complexes; moreover, the low <sup>12</sup>  $\tau$ (IrH) values, observed for the Me<sub>3</sub>SnIrHXCO(PPh<sub>3</sub>)<sub>2</sub> complexes, suggest that H is *trans* to CO, as is thought to be the case in other six-coordinate iridium complexes having similar  $\tau$  values.<sup>17a,18</sup>

The magnitude of the *trans*-influence of the trimethyltin group, in six-co-ordinate iridium-tin complexes, is unknown. However, from previous work, the *trans*influence of a trimethyltin group in square-planar platinum(II) complexes is known to be approximately However, as for the  $Ph_3SnH$  adducts, these are not necessarily mechanistic differences.

The complex  $Me_3SnIrHClCO(PPh_2Me)_2$  is only tentatively assigned configuration (I), in the absence of spectral data for the corresponding deuterido-complex; the value of v(IrCl), approximately the same as that for  $Me_3SnIrHClCO(PPh_3)_2$  [configuration (I)] supports this assignment.

The Triethyltin-Iridium complex.—The value of v(IrCl) for the triethyltin complex is more compatible with configuration (II), than with (I) or (III), for the reasons discussed above; the magnitude of the *trans*-influence of the triethyltin group is unknown. In the n.m.r. spectrum,  $\tau(IrH)$  is approximately the same as that for

TABLE 2 Analytical data for  $R_3SnIr(H \text{ or } D)XCOL_2$ 

R. Hor D. X and L in	Found				Required					
$R_3SnIr(H \text{ or } D)XCOL_2$	C (%)	H (%)	X (%)	P (%)	M °	C (%)	H (%)	X (%)	P (%)	$\overline{M}$
Me, H, Cl, PPh <sub>3</sub> <sup>a</sup>	50.85	4.3	$4 \cdot 0$	6.65	967	50.85	4.25	3.75	6.55	945
Me, D, Cl, PPh <sub>3</sub> <sup>a</sup>	$51 \cdot 15$	4.65				50.8	4.35			
Me, H, Br, PPh <sub>3</sub>	50.0	$4 \cdot 3$			1025	48.55	4.05			989
Me, H, Cl, PPh <sub>3</sub> <sup>b</sup>	50.6	$4 \cdot 2$	3.7			50.88	4.25	3.75		
Me, D, Cl, PPh <sub>3</sub> <sup>b</sup>	50.25	$4 \cdot 3$				50.8	4.35			
Me, H, Cl, PPh <sub>2</sub> Me	43.7	4.45	4.5		811	43.9	4.4	$4 \cdot 3$		821
Et, H, Cl, PPh <sub>3</sub>	52.3	4.7	3.75	5.8	978	52.3	4.7	3.6	6.25	987
Ph, H, Cl, PPh <sub>3</sub>	58.4	4.1	$3 \cdot 0$	$5 \cdot 3$	d	58.4	<b>4</b> ·1	3.12	5.45	
Ph, D, Cl, PPh <sub>3</sub>	58.2	$4 \cdot 2$				58.35	$4 \cdot 2$			
Ph, H, Br, PPh <sub>3</sub>	56.15	$3 \cdot 9$	6.75	5.15	d	56.2	3.95	6.8	5.25	
Ph, D, Br, PPh <sub>3</sub>	$55 \cdot 9$	4.15				56.15	4.05			
Ph, H, I, PPh <sub>3</sub>	54.35	3.85	9.35		d	54.05	$3 \cdot 8$	10.4		
Ph, H, Cl, PPh <sub>2</sub> Me	53.55	$4 \cdot 2$	3.55		1004	53.65	$4 \cdot 2$	3.5		1007
Ph, D, Cl, PPh <sub>2</sub> Me	53.7	4.4				53.6	<b>4</b> ·3			
Ph, H, Cl, PPhEt <sub>2</sub>	49.85	5.0				49.9	4.95			

• Yellow isomer (configuration II). • White isomer [configuration (I)]. • In benzene. • Solubility too low to permit measurement.

the same as that of a methyl group.<sup>19</sup> Such information is compatible with the observation that v(IrCl) absorption in Me<sub>3</sub>SnIrHClCO(PPh<sub>3</sub>)<sub>2</sub> is virtually identical to v(IrCl)absorption in MeIrIClCO(PPh<sub>3</sub>)<sub>2</sub>, where methyl is *trans* to chlorine.<sup>17c</sup>

The white isomer, to which configuration (I) is assigned, was obtained by reaction of excess of trimethyltin hydride with trans-IrClCO(PPh<sub>3</sub>)<sub>2</sub> in absence of solvent. The value of  $\nu$ (IrCl) absorption for the complex is compatible with configuration (I), but not with (III), as discussed above.<sup>17b,c</sup> No evidence was found for H/CO vibrational interaction. Furthermore,  $\nu$ (IrH) absorption is too high for a configuration where H is trans to CO (see above); consequently, (II) may be eliminated.

Isomerisation of the white trimethyltin complex [configuration (I)] to the yellow trimethyltin complex [configuration (II)] was observed (i.r. and n.m.r. spectra) when the former was dissolved in chloroform.

In benzene, the adduct of trimethyltin hydride to trans-IrClCO(PPh<sub>3</sub>)<sub>2</sub> apparently results from *cis*-addition, whereas, in absence of solvent but in presence of excess of stannane, the mode of addition is apparently *trans*.

other six-co-ordinate iridium complexes where H is trans to  $CO.^{17d,18}$  The complex  $Et_3SnIrHClCO(PPh_3)_2$  is thus tentatively assigned configuration (II).

#### EXPERIMENTAL

All manipulations were carried out either *in vacuo*, or in an atmosphere of pure, dry nitrogen. Diethyl digol [bis-(2-ethoxyethyl) ether] was dried over molecular sieves (4A), and then distilled from lithium aluminium hydride under reduced pressure; all other solvents were purified by conventional methods and degassed several times, *in vacuo*, before use.

I.r. spectra were recorded as Nujol mulls, KBr discs, or in chloroform solution, on Perkin-Elmer models 237 and 337 spectrophotometers; high-resolution spectra were measured on a Perkin-Elmer 125 spectrometer; far-i.r. spectra (400—200 cm.<sup>-1</sup>) were recorded on a Grubb-Parsons DM4 spectrometer. N.m.r. spectra were measured on a Varian Associates model A60 spectrometer and on a Perkin-Elmer R10 spectrometer.

Molecular weights were determined in benzene, with a Mechrolab Osmometer, model 301 A. Analytical data for the complexes  $R_3SnIr(H \text{ or } D)XCOL_2$  are given in Table 2.

<sup>&</sup>lt;sup>18</sup> (a) R. C. Taylor, J. F. Young, and G. Wilkinson, *Inorg. Chem.*, 1966, **5**, 20; (b) H. Singer and G. Wilkinson, *J. Chem. Soc.* (A), 1968, 2516.

<sup>&</sup>lt;sup>19</sup> D. M. Adams, J. Chatt, J. Gerratt, and A. D. Westland, J. Chem. Soc., 1964, 734; (b) D. J. Cardin and M. F. Lappert, Chem. Comm., 1966, 506.

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The complexes IrClCO(PPh<sub>3</sub>)<sub>2</sub>,<sup>20 a, c</sup> IrBrCO(PPh<sub>3</sub>)<sub>2</sub>,<sup>20 b</sup> IrICO(PPh<sub>3</sub>)<sub>2</sub>,<sup>15b</sup> IrClCO(PPh<sub>2</sub>Me)<sub>2</sub>,<sup>20c</sup> IrClCO(PPhEt<sub>2</sub>)<sub>2</sub>,<sup>20a</sup> RhClCO(PPhEt<sub>2</sub>)<sub>2</sub>,<sup>21a</sup> and RhCl(PPh<sub>3</sub>)<sub>3</sub> <sup>21b</sup> were prepared by literature procedures.

Triphenyltin hydride,<sup>22a</sup> trimethyltin hydride,<sup>23a</sup> and trimethyltin deuteride 23b were obtained by standard methods. Reduction of triethyltin chloride with an excess of lithium aluminium hydride, in anhydrous diethyl digol at 80-90° for 1 hr. yielded triethyltin hydride,<sup>24</sup> which was distilled from the reaction mixture (b.p. 37- $40^{\circ}/10$  mm.). Triphenyltin deuteride was obtained as follows. A mixture of triphenyltin bromide and excess of lithium aluminium deuteride, in tetrahydrofuran, was stirred (1 hr.) at room temperature, and was then deuteriolysed, (D<sub>2</sub>O) at 0°, and filtered; the filtrate was dried (molecular sieves) and the solvent was removed in vacuo; distillation of the residue, with a pre-heated oil-bath (200°), vielded triphenyltin deuteride (b.p. 148°/0.001 mm.; v(SnD) <sup>22b</sup> 1321 cm.<sup>-1</sup>).

For reactions with trimethyltin hydride, trimethyltin deuteride, or triethyltin hydride, the hydride was freshly distilled in vacuo, and temporarily stored at  $-196^{\circ}$ , before a reaction was carried out on the same day with the appropriate iridium(I) or rhodium(I) complex. In all the hydrostannation experiments, the reaction flask was covered in aluminium foil to prevent photochemical decomposition of the stannane reactant.

Hydrostannation of trans-IrXCOL<sub>2</sub>.-(1) Me<sub>3</sub>SnIrHClCO-PPh<sub>3</sub>)<sub>2</sub> [yellow isomer-configuration (II)]. Trimethyltin hydride (0.21 g., 1.27 mmoles) was distilled in vacuo, into a suspension of trans-IrClCO(PPh<sub>3</sub>)<sub>2</sub> (0.76 g., 0.97 mmoles) in benzene (25 ml.), which was cooled to  $-196^{\circ}$ . When the mixture was warmed to room temperature, a clear yellow solution was formed which was stirred overnight under nitrogen. After evaporation of solvent to a lower volume (ca. 8 ml.), some trans-IrClCO(PPh<sub>3</sub>)<sub>2</sub> (0.17 g., 0.22 mmoles) was filtered off, and the filtrate was evaporated to dryness in vacuo. The yellow solid residue was stirred with hexane (8 ml.), filtered, washed with hexane, and dried in vacuo (yield: 0.46 g., 0.49 mmoles, 50%); recrystallisation (CH<sub>2</sub>Cl<sub>2</sub>-MeOH) yielded yellow crystals.

Me<sub>3</sub>SnIrDClCO(PPh<sub>3</sub>)<sub>2</sub> [yellow isomer-configuration (II)]. This was prepared by a reaction analogous to (1), with trimethyltin deuteride.

(2) Me<sub>3</sub>SnIrHBrCO(PPh<sub>3</sub>)<sub>2</sub>. As in (1) above, trimethyltin hydride (0.2 g., 1.21 mmoles) and trans-IrBrCO(PPh<sub>3</sub>)<sub>2</sub> (0.7 g., 0.85 mmoles) in benzene (20 ml.) yielded some unchanged iridium starting material (0.1 g., 0.12 mmoles), and the required complex (0.37 g., 0.37 mmoles, 43%).

(3) Me<sub>3</sub>SnIrHClCO(PPh<sub>3</sub>)<sub>2</sub> [white isomer-configuration (I)]. A large excess of trimethyltin hydride (4.7 g., 28.5 mmoles) was distilled in vacuo onto solid trans-IrClCO- $(PPh_3)_2$  (0.58 g., 0.74 mmoles) contained in a small flask, cooled to  $-196^{\circ}$ . The flask was warmed to room temperature, filled with nitrogen, and the reaction mixture was stirred. Within a few minutes, conversion of the yellow, crystalline  $IrClCO(PPh_3)_2$  to a white powder had begun. The mixture was stirred for 1.5 hr. after which the bulk of

the trimethyltin hydride was allowed to distil off, in vacuo. The solid was pumped (2 hr.) to remove the last traces of the tin hydride; the white solid residue (0.71 g., 0.75 mmoles) was stirred with light petroleum (b.p.  $30-40^{\circ}$ ) (6 ml.) and then filtered off, and washed with further light petroleum. The white, microcrystalline product (0.53 g., 0.56 mmoles, 76%) was dried in vacuo.

Me<sub>3</sub>SnIrDClCO(PPh<sub>3</sub>)<sub>2</sub> [white isomer-configuration (I)]. This was prepared by a reaction analogous to (3), with trimethyltin deuteride.

(4)  $Me_3SnIrHClCO(PPh_2Me)_2$ . Trimethyltin hydride (0.25 g., 1.5 mmoles) was distilled in vacuo into a solution of trans-IrClCO(PPh2Me)2 (0.66 g., 1.0 mmoles) in benzene (25 ml.), which was cooled to  $-196^{\circ}$ . When the mixture warmed to room temperature, a clear, almost colourless solution was obtained, which was stirred (2 hr.) under nitrogen, and then evaporated, in vacuo. The pale yellow solid residue was digested with light petroleum (b.p. 30-40°) (10 ml.), and was then filtered off, and washed with more light petroleum to yield a white solid (0.64 g., 0.78 mmoles, 78%).

(5) Et<sub>3</sub>SnIrHClCO(PPh<sub>3</sub>)<sub>2</sub>. Triethyltin hydride (0.56 g., 2.7 mmoles) was distilled in vacuo into a suspension of trans-IrClCO(PPh<sub>3</sub>)<sub>2</sub> (1.45 g., 1.86 mmoles) in benzene (30 ml.), which was cooled to  $-196^{\circ}$ . The mixture was warmed to room temperature, and then allowed to reflux gently (20 min.) under nitrogen; the resultant clear, deep vellow solution was stirred overnight. After removal of some unchanged IrClCO(PPh<sub>3</sub>)<sub>2</sub> (0.41 g., 0.52 mmoles) by filtration, the solution was evaporated, in vacuo, to yield an orange syrup. After being pumped under high vacuum overnight, the hard syrup was digested with light petroleum (b.p. 30-40°) (15 ml.) to give a yellow-orange solid, which was filtered off, washed with light petroleum, and dried, in vacuo (1.03 g., 1.04 mmoles, 56%). Recrystallisation (PhH-MeOH) afforded yellow crystals.

(6)  $Ph_3SnIrHClCO(PPh_3)_2$ . Triphenyltin hydride (0.46 g., 1.31 mmoles) in benzene (4 ml.) was added to a solution of trans-IrClCO(PPh<sub>3</sub>)<sub>2</sub> (0.91 g., 1.17 mmoles) in the same solvent (160 ml.). The mixture immediately became very pale yellow, and was stirred (2 days), during which time a white precipitate was slowly formed. The product was filtered off and washed with benzene to give white microcrystals which were dried in vacuo (1.02 g., 0.9 mmoles, 77%).

Ph<sub>3</sub>SnIrDClCO(PPh<sub>3</sub>)<sub>2</sub>. This was prepared by a reaction analogous to (6) with triphenyltin deuteride.

(7)  $Ph_3SnIrHBrCO(PPh_3)_2$ . In a reaction analogous to (6), triphenyltin hydride (0.08 g., 0.24 mmoles) and trans-IrBrCO(PPh<sub>3</sub>)<sub>2</sub> (0.14 g., 0.17 mmoles) were stirred overnight in benzene (25 ml.), to yield the required bromocomplex, as a pale, buff-coloured precipitate (0.13 g., 0.11 mmoles, 65%).

 $Ph_3SnIrDBrCO(PPh_3)_2$ . This was prepared by a reaction analogous to (7), with triphenyltin deuteride.

(8) Ph<sub>3</sub>SnIrHICO(PPh<sub>3</sub>)<sub>2</sub>. In a reaction analogous to (6), triphenyltin hydride (0.2 g., 0.56 mmoles) and trans-IrICO(PPh<sub>3</sub>)<sub>2</sub> (0.38 g., 0.43 mmoles) were stirred overnight,

<sup>&</sup>lt;sup>20</sup> (a) J. Chatt, N. P. Johnson, and B. L. Shaw, J. Chem. Soc. (A), 1967, 604; (b) P. B. Chock and J. Halpern, J. Amer. Chem. Soc., 1966, **88**, 3511; (c) J. P. Collman and J. W. Kang, *ibid.*, 1967, **89**, 844.

 <sup>&</sup>lt;sup>21</sup> (a) J. Chatt and B. L. Shaw, J. Chem. Soc. (A), 1966, 1437;
 (b) J. A. Osborn, F. H. Jardine, J. F. Young, and G. Wilkinson, ibid., 1966, 1711.

<sup>&</sup>lt;sup>22</sup> H. G. Kuivila and O. F. Beumel, J. Amer. Chem. Soc., 1961, 83, 1246; (b) W. P. Neumann and R. Sommer, Angew. Chem.,

 <sup>85, 1240, (</sup>b) W. P. Neumann and R. Sommer, Angew. Chem., 1963, 75, 788; K. Kuhlein, W. P. Neumann, and H. Mohring, Angew. Chem. Internat. Edn., 1968, 7, 455.
 <sup>23</sup> (a) R. H. Fish, H. G. Kuivila, and I. J. Tyminski, J. Amer. Chem. Soc., 1967, 89, 5861; (b) C. R. Dillard and L. May, J. Mol. Spectroscopy, 1964, 14, 250.
 <sup>24</sup> W. P. Neumann, Angew. Chem. Internat. Edn., 1963, 2, 165.

in benzene (25 ml.), to yield the required iodo-complex as a pale-yellow precipitate (0.23 g., 0.19 mmoles, 44%).

(9) Ph<sub>3</sub>SnIrHClCO(PPh<sub>2</sub>Me)<sub>2</sub>. Triphenyltin hydride (0·38 g., 1·08 mmoles), in benzene (3 ml.), was added to a solution of *trans*-IrClCO(PPh<sub>2</sub>Me)<sub>2</sub> (0·57 g., 0·87 mmoles) in the same solvent (15 ml.). The resultant pale yellow solution was stirred overnight. Evaporation of solvent, *in vacuo*, left a white, microcrystalline solid, which was stirred with light petroleum (b.p. 30—40°) (12 ml.) and was then filtered off, washed with light petroleum, and dried *in vacuo* (0·79 g., 0·78 mmoles, 90%). Recrystallisation (PhH/ MeOH) yielded white crystals.

Similarly, triphenyltin hydride reacted with *trans*-IrClCO(PPh<sub>2</sub>Me)<sub>2</sub> in diethyl ether, to yield the white, crystalline, ether-soluble complex  $Ph_3SnIrHClCO(PPh_2-Me)_2$ .

 $Ph_3SnIrDClCO(PPh_2Me)_2$ . This was prepared by a reaction analogous to (9), with triphenyltin deuteride.

(10) Ph<sub>3</sub>SnIrHClCO(PPhEt<sub>2</sub>)<sub>2</sub>. Triphenyltin hydride (0·36 g., 1·03 mmoles) in diethyl ether (3 ml.) was added to a solution of *trans*-IrClCO(PPhEt<sub>2</sub>)<sub>2</sub> (0·56 g., 0·95 mmoles) in the same solvent (50 ml.). The solution immediately became colourless, and was stirred overnight; the mixture was reduced to a low volume (5 ml.) by evaporation of the solvent. Addition of light petroleum (b.p. 30-40°) (5 ml.) to this precipitated white crystals, which were filtered off, washed with light petroleum, and dried *in vacuo* (0·52 g., 0·55 mmoles, 58%).

Attempted Hydrostannation of trans-RhClCO(PPhEt<sub>2</sub>)<sub>2</sub>.... No reaction occurred between equimolar proportions of triphenyltin hydride and *trans*-RhClCO(PPhEt<sub>2</sub>)<sub>2</sub> in benzene at room temperature, as indicated by the almost quantitative recovery of the latter reactant (authentic i.r. spectrum). Attempted Hydrostannation of RhCl(PPh<sub>3</sub>)<sub>3</sub>.—(1) With triphenyltin hydride. (a) Addition of triphenyltin hydride (1 mole) to RhCl(PPh<sub>3</sub>)<sub>3</sub> (1 mole) in benzene caused the solution to deepen in colour. After being stirred overnight at room temperature, the solution was evaporated to low volume, in vacuo; addition of ethanol to it precipitated a brick-red solid [no  $\nu$ (RhH) (Found: C, 60.45; H, 4.85. Calc. for Ph<sub>3</sub>SnRhHCl(PPh<sub>3</sub>)<sub>2</sub>: C, 63.95; H, 4.55. Calc. for (Ph<sub>3</sub>Sn)<sub>2</sub>RhCl(PPh<sub>3</sub>)<sub>2</sub>: C, 63.45; H, 4.45].

(b) Similarly, addition of triphenyltin hydride (5 moles) to RhCl(PPh<sub>3</sub>)<sub>3</sub> (1 mole) in benzene, and work-up as in (a), produced a yellow-brown solid [no v(RhH) (Found: C, 48.0; H, 3.85)].

(2) With triethyltin hydride. (a) Triethyltin hydride (8 moles) reacted with RhCl(PPh<sub>3</sub>)<sub>3</sub> (1 mole) in benzene to give a clear orange-brown solution, from which a light brown solid [no  $\nu$ (RhH)] was isolated by evaporation of solvent and addition of methanol.

Similarly, reaction of an excess of triethyltin hydride with  $RhCl(PPh_3)_3$  in tetrahydrofuran, gave a brown solution; work up, as in (a), yielded a brown solid [no v(RhH)].

(3) With trimethyltin hydride. Reaction of a large excess of trimethyltin hydride—which also served as solvent—with RhCl(PPh<sub>3</sub>)<sub>3</sub>, at room temperature *in vacuo*, yielded a dark brown solid [no v(RhH) (Found: C, 43.2; H, 3.85. Calc. for Me<sub>3</sub>SnRhHCl(PPh<sub>3</sub>)<sub>2</sub>: C, 56.6; H, 4.85. Calc. for (Me<sub>3</sub>Sn)<sub>2</sub>RhCl(PPh<sub>3</sub>)<sub>2</sub>: C, 50.9; H, 4.9].

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