Rhodium Complexes of Group 4B Ligands

By **Robin Hill** and **Selby A. R. Knox,*** Department of Inorganic Chemistry, The University, Bristol BS8 1TS

The reactions of the hydrides MMe_3H (M = Si, Ge, or Sn) with $[Rh(\eta-C_5H_5)(CO)_2]$ have been investigated under both photochemical and thermal conditions. The complex $[Rh(\eta-C_5H_5)(CO)(GeMe_3)_2]$ is formed in highest yield (*ca.* 50%) photochemically and $[Rh(\eta-C_5H_5)(CO)(SnMe_3)_2]$ (*ca.* 80%) thermally (80 °C). Under u.v. irradiation, $SnMe_3H$ and $[Rh(\eta-C_5H_5)(CO)_2]$ afford $[Rh(CO)_3(SnMe_3)_3]$ principally (*ca.* 30%), whose reactions with PPh_3, $P(OMe)_3$, and cyclopentadiene have been studied. The complex $[Rh(\eta-C_5H_5)(CO)(SiMe_3)_2]$ is formed in only trace amounts by either method. Reduction of $[Rh(\eta-C_5H_5)(CO)_2]$ or $[Rh(\eta-C_5H_5)(CO)I_2]$ with sodium amalgam gives an air-sensitive solution with properties characteristic of $[Rh(\eta-C_5H_5)(CO)H]^-$. Addition of MMe_3X (M = Ge, Sn, or Pb; X = halide) gives $[Rh(\eta-C_5H_5)(CO)(MMe_3)_2]$ (M = Ge or Sn) in fair (20—50%) yield, and $[Rh(\eta-C_5H_5)(CO)(PbMe_3)_2]$ in trace amounts. Iodine smoothly cleaves $[Rh(\eta-C_5H_5)(CO)(GeMe_3)_2]$ to afford $[Rh(\eta-C_5H_5)(CO)(GeMe_3)I]$, whose chemistry is described. The complex $[Rh_2(\eta-C_5H_5)_2(CO)_3]$ is formed in 32% yield on irradiation of $[Rh(\eta-C_5H_5)(CO)_2]$, and its reactions with MMe_3H (M = Si, Ge or Sn) and $P(OMe)_3$ have been investigated.

AN extensive chemistry of Group 4B derivatives of iron, ruthenium, and osmium carbonyls now exists,[1] built principally on two synthetic routes to such complexes: (*a*) direct reaction of the metal carbonyls with organogroup 4B hydrides; and (*b*) reduction of the carbonyls to anions and then subsequent reaction with organogroup 4B halides. However, despite the often-quoted similarities in the chemistry of $[Fe(CO)_5]$ and of the complexes $[M(\eta-C_5H_5)(CO)_2]$ (M = Co, Rh, or Ir), relatively little attention has been paid to organogroup 4B derivatives of these latter species. Route (*a*) has been explored to some extent with $[M(\eta-C_5H_5)(CO)_2]$ (M = Co or Rh) in that reaction of $[Rh(\eta-C_5H_5)(CO)_2]$ with triphenyl- or tribenzyl-silane has been observed [2] to yield hydrides $[Rh(\eta-C_5H_5)(CO)H(SiR_3)]$, while trichlorosilane gave $[Rh(\eta-C_5H_5)(CO)(SiCl_3)_2]$. In contrast, trichlorosilane afforded $[Co(\eta-C_5H_5)(CO)H(SiCl_3)]$ with $[Co(\eta-C_5H_5)(CO)_2]$.[3] Other routes to Group 4B derivatives of $[M(\eta-C_5H_5)(CO)_2]$ (M = Co [4] or Rh [2]) have involved treatment with germanium and tin tetrahalides, yielding complexes $[M(\eta-C_5H_5)(CO)(M'X_3)X]$ and $[M(\eta-C_5H_5)(CO)(M'X_3)_2]$ (M′ = Ge or Sn; X = Cl, Br, or I), or with hexamethylditin,[5] a source of $[M(\eta-C_5H_5)(CO)(SnMe_3)_2]$ and $[\{M(\eta-C_5H_5)(CO)(\mu-SnMe_2)\}_2]$; the latter complex (M = Co) has been the subject of an *X*-ray diffraction study.[6] No reports have appeared, however, of attempts to enter Group 4B–cobalt or –rhodium chemistry *via* route (*b*), *i.e. via* anions comparable to the species $[M(CO)_4]^{2-}$ and $[M(CO)_4H]^-$ (M = Fe, Ru, or Os) which have been instrumental in the development of the organometallic chemistry of the iron triad metals. In this paper we describe the synthesis and chemistry of some Group 4B derivatives of $[Rh(\eta-C_5H_5)(CO)_2]$ approached by both routes (*a*) and (*b*). A preliminary account of some aspects of this work has appeared.[7]

RESULTS AND DISCUSSION

Reactions of $[Rh(\eta-C_5H_5)(CO)_2]$.—The reactions of the hydrides MMe_3H (M = Si, Ge, or Sn) with $[Rh(\eta-C_5H_5)(CO)_2]$ differ markedly. Each produces a complex, $[Rh(\eta-C_5H_5)(CO)(MMe_3)_2]$, and some produce trace amounts of a tentatively identified unisolated hydride $[Rh(\eta-C_5H_5)(CO)H(MMe_3)]$, but yields of the former are very sensitive to the conditions employed. Trimethylsilane barely reacted with $[Rh(\eta-C_5H_5)(CO)_2]$ either photochemically or thermally (80 °C) over several days, and identification of the very air-sensitive products $[Rh(\eta-C_5H_5)(CO)(SiMe_3)_2]$ and $[Rh(\eta-C_5H_5)(CO)H(SiMe_3)]$ was by i.r. spectra alone. Ultraviolet irradiation of a hexane solution of $GeMe_3H$ and $[Rh(\eta-C_5H_5)(CO)_2]$, on the other hand, gave $[Rh(\eta-C_5H_5)(CO)(GeMe_3)_2]$ in *ca.* 50% yield in the same time. Only *ca.* 10% yield was achieved, however, on heating (80 °C) the reactants in the same solvent for that time (5 d). The greatest yield on heating was obtained for $[Rh(\eta-C_5H_5)(CO)(SnMe_3)_2]$; after 3 d at 80 °C an 80% yield was obtained from $SnMe_3H$ and $[Rh(\eta-C_5H_5)(CO)_2]$. The reaction pursued a quite different course under u.v. irradiation, $[Rh(\eta-C_5H_5)(CO)(SnMe_3)_2]$ being formed in dramatically reduced yield (*ca.* 15%), with the unusual complex $[Rh(CO)_3(SnMe_3)_3]$ as major product (*ca.* 30%).

The photochemical reactions of $[Rh(\eta-C_5H_5)(CO)_2]$ with MMe_3H can be envisaged as proceeding to the observed products *via* a transient species $[Rh(\eta-C_5H_5)(CO)]$ formed by unimolecular ejection of carbon monoxide. Oxidative addition of MMe_3H will then yield the hydrides $[Rh(\eta-C_5H_5)(CO)H(MMe_3)]$, which in the presence of excess of MMe_3H react to release hydrogen and form the major product $[Rh(\eta-C_5H_5)(CO)(MMe_3)_2]$. The mode of formation of $[Rh(CO)_3(SnMe_3)_3]$ and the mechanism of the thermal reactions are less clear.

The low-melting, hydrocarbon-soluble, air-stable complexes $[Rh(\eta-C_5H_5)(CO)(MMe_3)_2]$ are clearly identified as of formulation (I) by their characteristic spectroscopic properties (Table). The characterisation of $[Rh(CO)_3(SnMe_3)_3]$ was difficult; although formed in good yield and reasonably air stable, it does not handle well. Crystallisation of the complex was hindered by its

---

[1] J. D. Cotton, S. A. R. Knox, I. Paul, and F. G. A. Stone, *J. Chem. Soc.* (*A*), 1967, 264; S. A. R. Knox and F. G. A. Stone, *ibid.*, 1971, 2874, and refs. therein.

[2] A. J. Oliver and W. A. G. Graham, *Inorg. Chem.*, 1971, **10**, 1.

[3] W. Jetz and W. A. G. Graham, *Inorg. Chem.*, 1971, **10**, 4.

[4] R. Kummer and W. A. G. Graham, *Inorg. Chem.*, 1968, **7**, 523.

[5] E. W. Abel and S. Moorhouse, *Inorg. Nuclear Chem. Letters*, 1971, **7**, 905.

[6] J. Weaver and P. Woodward, *J.C.S. Dalton*, 1973, 1060.

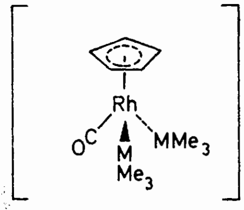
[7] R. Hill and S. A. R. Knox, *J. Organometallic Chem.*, 1975, **84**, C31.

New rhodium complexes

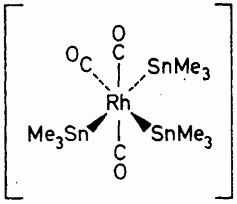
Complex	Colour	M.p. (θ_c/°C) [a]	$\tilde{\nu}$(CO) [b]/cm^{-1}	^{1}H N.m.r. spectra (τ) [c]
$[Rh(\eta\text{-}C_5H_5)(CO)(SiMe_3)_2]$ (I)	pale yellow		2 000s	
$[Rh(\eta\text{-}C_5H_5)(CO)(GeMe_3)_2]$ (I)	pale yellow	(45—50)	1 995s	4.70(5), 9.49(18)
$[Rh(\eta\text{-}C_5H_5)(CO)(SnMe_3)_2]$ (I)	pale yellow	(85)	1 984s	4.31(5), 9.63(18)
$[Rh(\eta\text{-}C_5H_5)(CO)(PbMe_3)_2]$ (I)	pale yellow		1 979s	
$[Rh(\eta\text{-}C_5H_5)(CO)(GeMe_3)(SnMe_3)]$	pale yellow	(50)	1 989s	4.71(5), 9.57(9), 9.67(9)
$[Rh(\eta\text{-}C_5H_5)(CO)(GeMe_3)(SnPh_3)]$	colourless	118—119	1 972s	
$[Rh(\eta\text{-}C_5H_5)(CO)(GeMe_3)I]$	red-purple	79—80	2 031s	4.35(5), 9.09(9)
$[Rh(\eta\text{-}C_5H_5)(CO)I(SnPh_3)]$	red	155—156	2 031s	2.48(15), 4.42(5)
$[Rh_2(\eta\text{-}C_5H_5)_2(CO)_3]$ (IV)	dark red	124—125	1 984s, 1 939m	4.51
$[Rh_2(\eta\text{-}C_5H_5)_2(CO)_2\{P(OMe)_3\}]$(V)	dark red	108—109	1 974s, 1 821m, 1 805s	4.50(10), 6.28(s)(9)[J 12.6 Hz]
$[Rh(\eta\text{-}C_5H_5)(CO)_2\{P(OMe)_3\}]$	yellow	(50)	1 987s, 1 967s	4.28(5), 6.41(d)(9)[J 12.6 Hz]
$[Rh(CO)_3(SnMe_3)_3]$ (II)	yellow		2 066m, 2 034m, 2 004s	9.40

[a] Boiling points at a pressure of 10^{-2} Torr are given in parentheses. [b] For Hexane solutions. [c] For $CDCl_3$ solutions; relative intensities are given in parentheses.

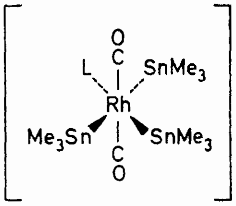
apparently high solubility; cooling of concentrated hexane solutions to −78 °C gave only dark oily solids. The complex decomposes on heating above room temperature, but a small amount was obtained pure as a pale yellow sublimate on one occasion. The mass spectrum (Experimental section) of this substance characterised it clearly as $[Rh(CO)_3(SnMe_3)_3]$, with a sharp cut-off corresponding to the molecular ion, which has a distinctive Sn_3 isotope pattern. Subsequent loss of carbonyl and methyl groups dominated the fragmentation pattern. The i.r. spectrum, which remained unchanged throughout all the stages of purification, exhibited three carbonyl-stretching bands (Table) in a pattern consistent with a *mer*-octahedral configuration, (II), rather than the *fac* isomer. Although the ^{1}H n.m.r. spectrum showed only one signal (at τ 9.40) for the methyltin protons, which are in two different environments in (II), it is reasonable that the resonance should not be very stereochemically sensitive. This signal remains sharp to −90 °C, thus effectively eliminating (in conjunction with the i.r. spectrum) any possibility of $[Rh(CO)_3(SnMe_3)_3]$ being stereochemically non-rigid, like the related $[Os(CO)_4(SnMe_3)_2]$.[8]



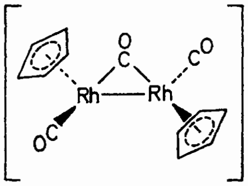
(I)



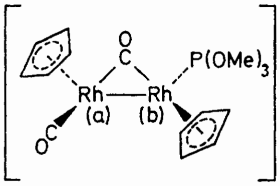
(II)



(III) L = PPh_3 or $P(OMe)_3$



(IV)



(V)

Some precedence for the formation of $[Rh(CO)_3(SnMe_3)_3]$ from $[Rh(\eta\text{-}C_5H_5)(CO)_2]$ and $SnMe_3H$ does exist. Cleavage of the $\eta\text{-}C_5H_5$ ligand from rhodium has been observed[9] in the reaction of $[Rh(\eta\text{-}C_2H_4)_2(\eta\text{-}C_5H_5)]$ with trimethyl phosphite, which affords $[Rh_2\{P(OMe)_3\}_8]$. More relevant, however, are the reactions[3] of $[Co(\eta\text{-}C_5H_5)(CO)_2]$ and $[\{Fe(\eta\text{-}C_5H_5)(CO)_2\}_2]$ with trichlorosilane, which lead to $[Co(CO)_4(SiCl_3)]$ and $[Fe(\eta\text{-}C_5H_5)(CO)H(SiCl_3)_2]$ respectively.

Treatment of $[Rh(CO)_3(SnMe_3)_3]$ with triphenylphosphine or $P(OMe)_3$ in refluxing hexane in each case led to rapid (*ca.* 1h) formation of a species with a single strong carbonyl-stretching frequency (at 1 975 and 1 972 cm^{-1} respectively). Isolation of either in a pure state was not achieved, but, following chromatography of the $P(OMe)_3$ complex, a colourless oil was obtained with a mass spectrum characteristic of $[Rh(CO)_2\{P(OMe)_3\}(SnMe_3)_3]$. It thus seems reasonable to assign the *trans*-dicarbonyl structure, (III), to these products, for which one strong carbonyl band would be expected. Reaction of $[Rh(CO)_3(SnMe_3)_3]$ with cyclopentadiene afforded a 36% yield of (I; M = Sn).

Although effective routes to (I; M = Ge, or Sn) had been established in the work described above, these were relatively tedious compared with any possible synthesis *via* an anion derived from $[Rh(\eta\text{-}C_5H_5)(CO)_2]$. Subsequent treatment of such an anion with an organogroup 4B halide would involve a rapid ionic reaction. We have established that treatment of either $[Rh(\eta\text{-}C_5H_5)(CO)_2]$

---

[8] R. K. Pomeroy and W. A. G. Graham, *J. Amer. Chem. Soc.*, 1972, **94**, 274.

[9] R. Mathieu and J. F. Nixon, *J.C.S. Chem. Comm.*, 1974, 147.

or (preferably) [$Rh(\eta-C_5H_5)(CO)I_2$] [10] briefly in tetrahydrofuran with a sodium amalgam gives an air-sensitive yellow-black solution with properties characteristic of its containing [$Rh(\eta-C_5H_5)(CO)H]^-$. Thus, the i.r. spectrum of the solution showed a single carbonyl absorption at 1 892 cm^{-1}, typical of a uninegative anion rather than of $[Rh(\eta-C_5H_5)(CO)]^{2-}$. The existence of the related $[Fe(CO)_4H]^-$ in aqueous solution is well established,[11] and it is likely that trace amounts of water in the solvent generate $[Rh(\eta-C_5H_5)(CO)H]^-$ here. Attempts to isolate this anion by precipitation with $[Ph_4As]^+$ or $[(Ph_3P)_2N]^+$ were unsuccessful.

Reaction of the anion solution with $GeBrMe_3$ or $SnMe_3Cl$ gave the complexes (I; M = Ge or Sn). These were obtained in better yield (40—50%) when using an anion solution derived from [$Rh(\eta-C_5H_5)(CO)I_2$] than from [$Rh(\eta-C_5H_5)(CO)_2$]; in the latter event yields of 5—20% were common. These products are not inconsistent with $[Rh(\eta-C_5H_5)(CO)H]^-$ being the nucleophile and, significantly, a very air-sensitive pale yellow liquid isolated as a minor product of the reaction with $SnMe_3Cl$ had i.r. and mass spectra indicative of the hydride [$Rh(\eta-C_5H_5)(CO)H(SnMe_3)$]. The reaction of $PbMe_3Cl$ with the anion did not proceed as cleanly as those above. Chromatography and sublimation of the reaction mixture gave a mixture of (I; M = Pb), [$Rh(\eta-C_5H_5)(CO)H(PbMe_3)$], and [$RhMe(\eta-C_5H_5)(CO)(PbMe_3)$], tentatively identified by i.r. and mass spectra (Experimental section). The transfer of a methyl group from lead to rhodium implicit in the formulation of the latter complex has a precedent. Work in this laboratory on the photochemical reaction of [$Mn(CO)_5(PbMe_3)$] with $P(OMe)_3$ identified [$MnMe(CO)_3\{P(OMe)_3\}_2$] as a product.[12] With $SnMe_2Cl_2$ the anion yielded (I; M = Sn) and the known [5] [$\{Rh(\eta-C_5H_5)(CO)(\mu-SnMe_2)\}_2$] in low yield.

It is thus apparent that complexes (I; M = Ge or Sn) can conveniently be prepared from either the interaction of the hydrides MMe_3H with [$Rh(\eta-C_5H_5)(CO)_2$] or of halides MMe_3X with the anion $[Rh(\eta-C_5H_5)(CO)H]^-$, which is best derived from [$Rh(\eta-C_5H_5)(CO)I_2$]. Yields are higher using the first route, but the second is more rapid.

The chemistry of complexes [$Ru(CO)_4(MMe_3)_2$] (M = Si, Ge, or Sn) has been extensively studied,[1,13] and it was of interest to investigate the related species (I) on a comparative basis; (I; M = Ge) was chosen as a subject for this investigation. This complex did not react under even quite vigorous conditions (octane at reflux) with the polyolefins cyclopentadiene, cycloheptatriene, and cyclooctatetraene, each of which exhibits [13] high reactivity with [$Ru(CO)_4(MMe_3)_2$]. In parallel with this stability, (I; M = Ge) was recovered quantitatively after heating *in vacuo* at 120 °C for 2 weeks. This again contrasts with complexes [$Ru(CO)_4(MMe_3)_2$] which give di- and tri-ruthenium MMe_2-bridged complexes on thermolysis, and also with (I; M = Sn) which has been shown [5] to afford [$\{Rh(\eta-C_5H_5)(CO)(\mu-SnMe_2)\}_2$]. Complex (I; M = Ge) does have two reactions in common with [$Ru(CO)_4(GeMe_3)_2$], however, in that treatment with excess of $SnMe_3H$ under u.v. irradiation effects ligand exchange with formation of (I; M = Sn) and [$Rh(\eta-C_5H_5)(CO)(GeMe_3)(SnMe_3)$] (see below), and that a single M–$GeMe_3$ bond is cleaved by iodine. The latter reaction proceeded smoothly at room temperature to give red-purple [$Rh(\eta-C_5H_5)(CO)(GeMe_3)I$] (Table) in high yield. This complex decomposes slowly even in the dark *in vacuo* to release iodine and in the reactions described below, which illustrate its varied chemistry, it was used within a day of being prepared.

The tentative i.r. identification of the hydrides [$Rh(\eta-C_5H_5)(CO)H(MMe_3)$] (M = Si, Ge, Sn, or Pb) has been mentioned. The synthesis of [$Rh(\eta-C_5H_5)(CO)(GeMe_3)I$] presented an opportunity to support this identification, in that treatment of the iodide with sodium tetrahydroborate should yield [$Rh(\eta-C_5H_5)(CO)(GeMe_3)H$]. A deep red diethyl ether solution of the iodide did in fact give a very air-sensitive colourless solution on shaking with $Na[BH_4]$, which showed a single strong carbonyl-stretching frequency at 2 013 cm^{-1}. This is identical to that previously attributed to [$Rh(\eta-C_5H_5)(CO)(GeMe_3)H$]. More important, from a synthetic point of view, was the observation that brief stirring of a tetrahydrofuran solution of the iodide over sodium amalgam generated an air-sensitive solution with the reactivity anticipated of the $[Rh(\eta-C_5H_5)(CO)(GeMe_3)]^-$ anion. Efforts to isolate this species as a salt were unsuccessful. However, on reaction of the 'anion' solution with $SnMe_3Cl$, pale yellow liquid [$Rh(\eta-C_5H_5)(CO)(GeMe_3)(SnMe_3)$] was formed in 41% yield. The complexes (I; M = Ge) and (I; M = Sn) were also obtained as minor products, indicating that the anion may disproportionate to a small extent in solution to give (I; M = Ge) and $[Rh(\eta-C_5H_5)(CO)]^{2-}$ {subsequently converted into $[Rh(\eta-C_5H_5)(CO)H]^-$}. With $SnPh_3Cl$ the anion gave [$Rh(\eta-C_5H_5)(CO)(GeMe_3)(SnPh_3)$] in low yield. It is interesting to note that iodine preferentially cleaves the Rh–Sn bond of [$Rh(\eta-C_5H_5)(CO)(GeMe_3)(SnMe_3)$], as one might expect, forming [$Rh(\eta-C_5H_5)(CO)(GeMe_3)I$] exclusively.

In an effort to prepare a $\sigma-C_5H_5$ derivative, [$Rh(\eta-C_5H_5)(CO)(GeMe_3)I$] was treated with thallium cyclopentadienide, but no reaction was observed. With $Sn(\sigma-C_5H_5)Ph_3$, in a similar attempt, a surprising reaction occurred to give [$Rh(\eta-C_5H_5)(CO)I(SnPh_3)$] in high yield. The anticipated [14] elimination of $SnPh_3I$ is evidently unfavourable relative to the exchange of Group 4B ligands, with the presumed formation of $GeMe_3(\sigma-C_5H_5)$. The exchange is reminiscent of that observed for (I; M = Ge) on reaction with $SnMe_3H$. It is noteworthy that the carbonyl-stretching frequencies of [$Rh(\eta-C_5H_5)(CO)I(SnPh_3)$] and [$Rh(\eta-C_5H_5)(CO)$-

---

[10] R. B. King, *Inorg. Chem.*, 1966, **5**, 82.

[11] J. R. Case and M. C. Whiting, *J. Chem. Soc.*, 1960, 4632.

[12] L. Soden and S. A. R. Knox, unpublished work.

[13] S. A. R. Knox and F. G. A. Stone, *Accounts Chem. Res.*, 1974, **7**, 321.

[14] E. W. Abel and S. Moorhouse, *Angew. Chem. Internat. Edn.*, 1971, **10**, 339.

$(GeMe_3)I]$ are of identical energy, indicating the same electronic effect on rhodium of both $GeMe_3$ and $SnPh_3$.

Reactions of $[Rh_2(\eta\text{-}C_5H_5)_2(CO)_3]$.—The deep red crystalline $[Rh_2(\eta\text{-}C_5H_5)_2(CO)_3]$ was initially thought[15] to be a tetracarbonyl, but was subsequently characterised by *X*-ray crystallography as a tricarbonyl of structure (IV). Apart from a recent study[16] of bridge–terminal carbonyl site exchange by variable-temperature ^{13}C n.m.r. spectroscopy, the chemistry of (IV) is unexplored; not a single reaction has been described. In part this no doubt reflects the lack of a convenient published synthesis. The complex can, however, be obtained in *ca.* 30% yield on u.v. irradiation of a hexane solution of $[Rh(\eta\text{-}C_5H_5)(CO)_2]$ for 168 h, and is thereby readily available for chemical study. The complex is very reactive. The red colour of a hexane solution of the complex with $GeMe_3H$ was quickly discharged on warming to 80 °C. With $SnMe_3H$ reaction was even more rapid, being complete within 10 min at room temperature. In each case i.r. spectra identify the products as $[Rh(\eta\text{-}C_5H_5)(CO)_2]$, $[Rh(\eta\text{-}C_5H_5)(CO)H(MMe_3)]$, and $[Rh(\eta\text{-}C_5H_5)(CO)(MMe_3)_2]$ (M = Ge or Sn). Reaction with $SiMe_3H$ was slower, but after 2 h at 80 °C $[Rh(\eta\text{-}C_5H_5)(CO)_2]$ and $[Rh(\eta\text{-}C_5H_5)(CO)H(SiMe_3)]$ were observed as products.

The reaction of (IV) with slightly more than an equimolar quantity of $P(OMe)_3$ appeared initially to have a resemblance to those with MMe_3H in that the isolated products were $[Rh(\eta\text{-}C_5H_5)(CO)_2]$ and $[Rh(\eta\text{-}C_5H_5)(CO)\{P(OMe)_3\}]$. Taken with the products from the MMe_3H reactions, a bimolecular displacement of $[Rh(\eta\text{-}C_5H_5)(CO)_2]$ from (IV) by L [L = MMe_3H or $P(OMe)_3$] was indicated, with co-formation of $[Rh(\eta\text{-}C_5H_5)(CO)L]$. However, treatment of (IV) with a deficiency of $P(OMe)_3$, under otherwise identical conditions, led to formation of the monosubstituted complex $[Rh_2(\eta\text{-}C_5H_5)_2(CO)_2\{P(OMe)_3\}]$, (V). The above mechanistic conclusion thus evidently represents an oversimplification of the mode of reaction of (IV) with MMe_3H or $P(OMe)_3$. Attack of a further molecule of $P(OMe)_3$ on the obviously intermediate (V) will occur at the least-crowded and more-electrophilic rhodium [*i.e.* (a) in (V)], generating two molecules of $[Rh(\eta\text{-}C_5H_5)(CO)\{P(OMe)_3\}]$. The source of $[Rh(\eta\text{-}C_5H_5)(CO)_2]$ remains obscure.

The i.r. spectra of both (V) and $[Rh(\eta\text{-}C_5H_5)(CO)\{P(OMe)_3\}]$, which is alternatively available *via* u.v. irradiation of $[Rh(\eta\text{-}C_5H_5)(CO)_2]$ with $P(OMe)_3$, exhibited more carbonyl-stretching bands than expected (see Table). We attribute this to a conformational isomerism within the $P(OMe)_3$ ligand, similar to that proposed[17] for related phosphite complexes.

EXPERIMENTAL

I.r. spectra were recorded with a Perkin-Elmer 257 grating spectrophotometer, using cells of 1.0 mm path length with calcium fluoride windows. Solution spectra were measured on an expanded scale, using the 1 601 cm^{-1} absorption of polystyrene as calibration. ^1H N.m.r. spectra were recorded using Varian Associates T60 and HA100 spectrometers; mass spectra were obtained using an A.E.I. MS902 instrument operating at 70 eV ionising potential.* Reactions took place under a nitrogen atmosphere or *in vacuo*, where stated, employing hydrocarbon solvents dried by distillation from calcium hydride. U.v. irradiation was provided by a 250 W mercury lamp. Silica gel (100—200 mesh) or alumina columns of 50 cm length were used in chromatography. The complexes $[\{Rh(CO)_2Cl\}_2]$,[18] $[Rh(\eta\text{-}C_5H_5)(CO)_2]$,[19] and $[Rh(\eta\text{-}C_5H_5)(CO)I_2]$[10] were prepared by literature methods.

Reactions of $[Rh(\eta\text{-}C_5H_5)(CO)_2]$.—(a) *With* $SiMe_3H$. (i) *Photochemically.* Irradiation for 5 d of an evacuated sealed Pyrex tube containing a hexane (25 cm^3) solution of $[Rh(\eta\text{-}C_5H_5)(CO)_2]$ (0.5 g, 2.23 mmol) and $SiMe_3H$ (0.74 g, 10.0 mmol) resulted in a dark yellow-orange coloration. Concentration and chromatography on silica gel gave a yellow band on elution with hexane, which was removed as two fractions. The first, on removal of solvent and sublimation of the residue to a −78 °C probe, gave a pale yellow liquid which decomposed rapidly at room temperature. The i.r. spectrum had ν(CO) bands at 2 050, 2 016, 2 000, and 1 987 cm^{-1}, attributed to a mixture of $[Rh(\eta\text{-}C_5H_5)(CO)_2]$, $[Rh(\eta\text{-}C_5H_5)(CO)H(SiMe_3)]$, and $[Rh(\eta\text{-}C_5H_5)(CO)(MMe_3)_2]$, (I; M = Si). The second fraction yielded only $[Rh(\eta\text{-}C_5H_5)(CO)_2]$.

(ii) *Thermally.* A similar sealed tube containing identical quantities of $SiMe_3H$ and $[Rh(\eta\text{-}C_5H_5)(CO)_2]$ in hexane (20 cm^3) was heated at 80 °C for 43 h giving an orange-black solution. An i.r. spectrum of the solution revealed that little reaction had occurred, but had new ν(CO) bands at 2 016 and 2 000 cm^{-1} assigned to $[Rh(\eta\text{-}C_5H_5)(CO)H(SiMe_3)]$ and (I; M = Si).

(b) *With* $GeMe_3H$. (i) *Photochemically.* Irradiation of $[Rh(\eta\text{-}C_5H_5)(CO)_2]$ (0.5 g, 2.23 mmol) and $GeMe_3H$ (1.2 g, 10.1 mmol) in hexane (20 cm^3) in a sealed evacuated Pyrex tube for 5 d gave a dark yellow-green solution. Removal of solvent and chromatography of the residual dark red liquid on alumina, eluting with hexane, gave a yellow band identified by i.r. spectroscopy as unchanged $[Rh(\eta\text{-}C_5H_5)(CO)_2]$. The solution collected before the yellow band yielded a pale yellow liquid on evaporation, which was sublimed [80—100 °C(10^{-2}Torr)] to a water-cooled probe as pale yellow waxy (I; M = Ge) (0.53 g, 54%) (Found: C, 33.5; H, 5.6%; *M* 432. $C_{12}H_{23}Ge_2ORh$ requires C, 33.3; H, 5.3%; *M* 432).

(ii) *Thermally.* A similar tube containing $[Rh(\eta\text{-}C_5H_5)(CO)_2]$ (1.0 g, 4.46 mmol) and $GeMe_3H$ (1.0 g, 8.41 mmol) in hexane (25 cm^3) was heated at 80 °C for 5 d to give an orange-black solution which yielded (I; M = Ge) (0.08 g, 8%) on treatment as in (i) above.

(c) *With* $SnMe_3H$. (i) *Photochemically.* Irradiation of $SnMe_3H$ (2.3 g, 14.2 mmol) and $[Rh(\eta\text{-}C_5H_5)(CO)_2]$ (1.0 g, 4.46 mmol) in hexane (20 cm^3) in a sealed evacuated Pyrex tube for 5 d gave a dark red solution. Removal of solvent and chromotography of the residual dark red liquid on silica gel with hexane as eluant gave a dark discoloured column with no discernible bands. The first 150 cm^3 of

---

* 1 eV ≈ 1.6 × 10^{-19} J, 1 Torr = (101 325/760) Pa.

[15] E. O. Fischer and K. Bittler, *Z. Naturforsch.*, 1961, **B16**, 835.

[16] J. Evans, B. F. G. Johnson, J. Lewis, and J. R. Norton, *J.C.S. Chem. Comm.*, 1973, 79.

[17] D. A. Brown, H. J. Lyons, and A. R. Manning, *Inorg. Chim. Acta*, 1970, **4**, 428.

[18] J. A. McCleverty and G. Wilkinson, *Inorg. Synth.*, 1966, **8**, 212.

[19] J. Knight and M. J. Mays, *J. Chem. Soc.* (*A*), 1970, 654.

solvent eluted yielded a dark red liquid which solidified when maintained under high vacuum overnight. Attempted sublimation [30—80 °C(10^{-2}Torr)] of the solid (0.95 g, 31%) caused substantial decomposition but gave a small amount of pale yellow solid $\mathrm{[Rh(CO)_3(SnMe_3)_3]}$(II) (Found: C, 21.5; H, 4.1. $\mathrm{C_{12}H_{27}O_3RhSn_3}$ requires C, 21.2; H, 4.0%) as a sublimate on a water-cooled probe. The mass spectrum had principal ions corresponding to the series $[M - n\mathrm{CO}]^+$ (n = 0 or 1), $[M - \mathrm{Me} - n\mathrm{CO}]^+$ (n = 0—3), $[\mathrm{RhSn_3Me}_{2n}]^+$ (n = 0, 2, or 4), $[\mathrm{RhSn_2Me}_n]^+$ (n = 0 and 2—5), and $[\mathrm{SnMe}_n]^+$ (n = 0—3). The next 60 cm^3 of solvent eluted from the column afforded (I; M = Sn) (0.3 g, 14%), identified by i.r. spectroscopy.

(ii) *Thermally*. A similar sealed tube containing $[\mathrm{Rh(\eta\text{-}C_5H_5)(CO)_2}]$ (1.0 g, 4.46 mmol) and $\mathrm{SnMe_3H}$ (2.1 g, 12.7 mmol) in hexane (20 cm^3) was heated at 80 °C for 3 d. Concentration and chromatography on silica gel gave a single yellow band on hexane elution. Removal of solvent gave a yellow liquid which was distilled [85 °C(10^{-2}Torr)] to a water-cooled probe as pale yellow *liquid* (I; M = Sn) (1.9 g, 81%) (Found: C, 28.2; H, 4.6%; *M* 524. $\mathrm{C_{12}H_{23}ORhSn_2}$ requires C, 27.5; H, 4.4%; *M* 524).

Preparation of $[\mathrm{Rh(\eta\text{-}C_5H_5)(CO)H}]^-$.—(a) *From* $[\mathrm{Rh(\eta\text{-}C_5H_5)(CO)_2}]$. After addition of a tetrahydrofuran (70 cm^3) solution of $[\mathrm{Rh(\eta\text{-}C_5H_5)(CO)_2}]$ (0.5 g, 2.23 mmol) to vigorously stirred sodium amalgam (1.5 g of Na, 10 cm^3 of Hg), a colour change from orange to yellow-black occurred over 1—2 h (specified for particular reactions below). Excess of amalgam was decanted from the reaction vessel, and after brief stirring with clean mercury, which was also removed, reagents were added as described below.

(b) *From* $[\mathrm{Rh(\eta\text{-}C_5H_5)(CO)I_2}]$. The complex $[\mathrm{Rh(\eta\text{-}C_5H_5)(CO)I_2}]$ (0.5 g, 1.11 mmol) in tetrahydrofuran (*ca.* 50 cm^3) was treated with sodium amalgam as in (a), but with a contact time of only 10—15 min.

Reactions of $[\mathrm{Rh(\eta\text{-}C_5H_5)(CO)H}]^-$.—*Prepared* via (*a*). (i) *With* $\mathrm{GeBrMe_3}$. A tetrahydrofuran (30 cm^3) solution of $\mathrm{GeBrMe_3}$ (0.88 g, 4.44 mmol) was added dropwise to a quantity of the anion prepared over 75 min as in (a) and the whole stirred for 30 min. Removal of solvent left an orange-black residue which on alumina chromatography yielded (I; M = Ge) (0.2 g, 20%) and unchanged $[\mathrm{Rh(\eta\text{-}C_5H_5)(CO)_2}]$ in turn, identified by their i.r. spectra.

(ii) *With* $\mathrm{SnMe_3Cl}$. A similar reaction of the anion (1 h reduction) with $\mathrm{SnMe_3Cl}$ (0.9 g, 4.53 mmol) in tetrahydrofuran (60 cm^3) gave, after chromatography on alumina and sublimation, (I; M = Sn) (0.07 g, 7%) and a trace amount of very air-sensitive liquid $[\mathrm{Rh(\eta\text{-}C_5H_5)(CO)H(SnMe_3)}]$. The formation of the latter was inferred from i.r. (1 999 cm^{-1}) and mass spectra $\{[M - n\mathrm{CO} - \mathrm{H}]^+$ (n = 0 or 1) and $[M - n\mathrm{CO} - \mathrm{H} - \mathrm{Me}]^+$ (n = 0 or 1)$\}$ and from its slightly greater volatility than (I; M = Sn).

(iii) *With* $\mathrm{PbMe_3Cl}$. An anion solution prepared over 95 min was treated with $\mathrm{PbMe_3Cl}$ (1.3 g, 4.51 mmol) in tetrahydrofuran (*ca.* 50 cm^3) and, after stirring for 30 min, chromatography on alumina gave a broad yellow band which was removed as three fractions. Sublimation [25 °C(10^{-2}Torr)] of each of these gave small quantities of a very air-sensitive mixture of variable composition which was tentatively identified by i.r. and mass spectra as containing (I; M = Pb) [ν(CO) at 1 979 cm^{-1}] (Found: *M* 702. $\mathrm{C_{12}H_{23}OPb_2Rh}$ requires *M* 702), $[\mathrm{Rh(\eta\text{-}C_5H_5)(CO)H(PbMe_3)}]$, [ν(CO) at 1 995 cm^{-1}], and $[\mathrm{RhMe(\eta\text{-}C_5H_5)(CO)(PbMe_3)}]$ [ν(CO) at 2 018 cm^{-1}].

(iv) *With* $\mathrm{SnMe_2Cl_2}$. Addition of a tetrahydrofuran (30 cm^3) solution of $\mathrm{SnMe_2Cl_2}$ (0.55 g, 2.50 mmol) to an anion solution prepared over 70 min, with subsequent stirring for 25 min, followed by chromatography on alumina, gave three yellow bands. The first two contained (I; M = Sn) and $[\mathrm{Rh(\eta\text{-}C_5H_5)(CO)_2}]$ in small quantities, identified by i.r. spectra, while the third yielded 0.02 g (3%) of the known [5] $[\{\mathrm{Rh(\eta\text{-}C_5H_5)(CO)(\mu\text{-}SnMe_2)}\}_2]$, identified by i.r. [ν(CO) at 1 989m, 1 984m, 1 972s, and 1 961s cm^{-1}] and mass spectra (Found: *M* 690. $\mathrm{C_{16}H_{22}O_2Rh_2Sn_2}$ requires *M* 690).

Prepared via (*b*). (i) *With* $\mathrm{GeBrMe_3}$. A tetrahydrofuran (30 cm^3) solution of $\mathrm{GeBrMe_3}$ (0.44 g, 2.22 mmol) was added dropwise to a solution of the anion prepared as in (b) above. After stirring for 30 min, removal of solvent and chromatography of the residue on silica gel gave (I; M = Ge) (0.24 g, 50%) after sublimation, identified by its i.r. spectrum.

(ii) *With* $\mathrm{SnMe_3Cl}$. A tetrahydrofuran (30 cm^3) solution of $\mathrm{SnMe_3Cl}$ (0.45 g, 2.28 mmol) similarly gave (I; M = Sn) (0.25 g, 43%) and a trace amount of $[\mathrm{Rh(\eta\text{-}C_5H_5)(CO)H(SnMe_3)}]$ on chromatography, the latter being identified by i.r. [ν(CO) at 1 999 cm^{-1}] and mass spectra $\{[M - \mathrm{H} - n\mathrm{CO}]^+$ (n = 0 or 1)$\}$.

Reactions of $[\mathrm{Rh(\eta\text{-}C_5H_5)(CO)(GeMe_3)_2}]$, (I; M = Ge). (i) *With iodine*. A hexane (50 cm^3) solution of excess of iodine (0.5 g, 1.97 mmol) was added dropwise at room temperature to a hexane (300 cm^3) solution of (I; M = Ge) (0.5 g, 1.16 mmol). Monitoring by i.r. spectroscopy showed the reaction to be complete within 1 h, leaving a dark red solution after filtering. Removal of solvent gave a dark red solid which was recrystallised from dichloromethane–hexane to yield dark red-purple *crystals* of $[\mathrm{Rh(\eta\text{-}C_5H_5)(CO)(GeMe_3)I}]$ (0.3 g, 53%) (Found: C, 24.8; H, 3.3%; *M* 442. $\mathrm{C_9H_{14}GeIORh}$ requires C, 24.5; H, 3.2%; *M* 442). In a similar reaction, $[\mathrm{Rh(\eta\text{-}C_5H_5)(CO)(GeMe_3)(SnMe_3)}]$ gave $[\mathrm{Rh(\eta\text{-}C_5H_5)(CO)(GeMe_3)I}]$ exclusively on treatment with iodine and was identified by i.r. spectroscopy.

(ii) *With* $\mathrm{SnMe_3H}$. Irradiation of a mixture of (I; M = Ge) (0.27 g, 0.63 mmol) and $\mathrm{SnMe_3H}$ (0.5 g, 3.1 mmol) in hexane (20 cm^3) for 3 d gave a pale yellow solution showing ν(CO) bands at 1 995, 1 989, and 1 984 cm^{-1}, consistent with a mixture of (I; M = Ge), $[\mathrm{Rh(\eta\text{-}C_5H_5)(CO)(GeMe_3)(SnMe_3)}]$ (see below), and (I; M = Sn) as products.

Reactions of $[\mathrm{Rh(\eta\text{-}C_5H_5)(CO)(GeMe_3)I}]$.—(a) *With sodium amalgam*. A tetrahydrofuran (30 cm^3) solution of the iodide (0.2 g, 0.45 mmol) was stirred vigorously with sodium amalgam (0.3 g of Na, 10 cm^3 of Hg) for 15 min giving a dark brown solution. Excess of analgam was decanted off and after brief stirring with clean mercury the solution was treated with reagents as below.

(i) *With* $\mathrm{SnMe_3Cl}$. A tetrahydrofuran (10 cm^3) solution of $\mathrm{SnMe_3Cl}$ (0.1 g, 0.5 mmol) was added dropwise to the anion solution, and the mixture stirred for 30 min. Removal of solvent and chromatography of the residue on silica gel gave in turn, on hexane elution, a small amount of (I; M = Ge), $[\mathrm{Rh(\eta\text{-}C_5H_5)(CO)(GeMe_3)(SnMe_3)}]$ (0.09 g, 41%), obtained as a pale yellow *liquid* on sublimation [50 °C(10^{-2}Torr)] (Found: C, 30.3; H, 4.9%; *M* 478. $\mathrm{C_{12}H_{23}GeORhSn}$ requires C, 30.1; H, 4.8%; *M* 478), and (I; M = Sn) in trace amount.

(ii) *With* $\mathrm{SnPh_3Cl}$. In an analogous manner $\mathrm{SnPh_3Cl}$ (0.18 g, 0.47 mmol) in tetrahydrofuran (30 cm^3) was added to the anion, and after recrystallisation from dichloromethane–hexane colourless *crystals* of $[\mathrm{Rh(\eta\text{-}C_5H_5)(CO)(GeMe_3)(SnPh_3)}]$ were obtained (0.063 g, 21%) (Found:

M 664. $C_{27}H_{29}GeORhSn$ requires *M* 664), slightly contaminated with $SnPh_3Cl$.

(b) *With* $Sn(\sigma\text{-}C_5H_5)Ph_3$. A mixture of $[Rh(\eta\text{-}C_5H_5)(CO)(GeMe_3)I]$ (0.1 g, 0.2 mmol) and $Sn(\sigma\text{-}C_5H_5)Ph_3$ (0.08 g, 0.2 mmol) was heated under reflux in tetrahydrofuran (60 cm^3) for 40 min. Chromatography on alumina, after solvent removal, yielded a red band on elution with 50% dichloromethane–hexane, which in turn gave rise to a red solid. Recrystallisation from dichloromethane–hexane gave red *crystals* of $[Rh(\eta\text{-}C_5H_5)(CO)I(SnPh_3)]$ (0.06 g, 44%) (Found: C, 43.0; H, 3.1%; *M* 674. $C_{24}H_{20}IORhSn$ requires C, 42.8; H, 3.0%; *M* 674).

(c) *With* $Na[BH_4]$. The iodide (0.1 g, 0.2 mmol) and excess of $Na[BH_4]$ were stirred in diethyl ether (30 cm^3) until (3 h) evolution of hydrogen ceased when a dark brown air-sensitive solution remained. Removal of solvent *in vacuo* and extraction with hexane (5 cm^3) gave a colourless solution exhibiting a single strong ν(CO) band at 2 013 cm^{-1}, consistent with the expected formation of $[Rh(\eta\text{-}C_5H_5)(CO)(GeMe_3)H]$.

Preparation of μ-*Carbonyl*-ae-*dicarbonylbis*(η-*cyclopentadienyl*)*dirhodium*, $[Rh_2(\eta\text{-}C_5H_5)_2(CO)_3]$ (IV).—A hexane (30 cm^3) solution of $[Rh(\eta\text{-}C_5H_5)(CO)_2]$ (0.5 g, 2.23 mmol) was irradiated in a Pyrex vessel for 168 h, and the red solution so formed was chromatographed on alumina. Elution with hexane resulted in four bands, yellow, red, green, and pink in turn. The first gave rise to unchanged $[Rh(\eta\text{-}C_5H_5)(CO)_2]$, and the second, eluted with 30% dichloromethane–hexane, gave dark red *crystals* of $[Rh_2(\eta\text{-}C_5H_5)_2(CO)_3]$ (0.3 g, 32%) (Found: C, 37.6; H, 2.5%; *M* 420. $C_{13}H_{10}O_3Rh_2$ requires C, 37.2; H, 2.4%; *M* 420). The third, green, band eluted with dichloromethane gave a small amount of dark green solid, identified by mass spectroscopy as one (or both) of the known isomers of $[\{Rh(\eta\text{-}C_5H_5)(CO)\}_3]$. The pink band decomposed on the column.

Reactions of Complex (IV).—Reactions (a)—(c) were made on a small scale in sealed evacuated tubes with heating until the red colour due to (IV) was discharged. Products were identified by i.r. spectroscopy.

(a) *With* $SiMe_3H$. Complex (IV) (0.05 g, 0.12 mmol) and $SiMe_3H$ (0.5 g, 6.75 mmol) on heating in hexane (10 cm^3) at 80 °C for 2 h gave $[Rh(\eta\text{-}C_5H_5)(CO)_2]$ and a species with a strong ν(CO) band at 2 016 cm^{-1}, typical of $[Rh(\eta\text{-}C_5H_5)(CO)H(SiMe_3)]$.

(b) *With* $GeMe_3H$. Trimethylgermane (0.5 g, 4.2 mmol) and (IV) (0.05 g, 0.12 mmol) in hexane (10 cm^3) at 80 °C for 1 h gave $[Rh(\eta\text{-}C_5H_5)(CO)_2]$, (I; M = Ge), and $[Rh(\eta\text{-}C_5H_5)(CO)(GeMe_3)H]$.

(c) *With* $SnMe_3H$. Trimethylstannane (0.4 g, 2.43 mmol) and (IV) (0.1 g, 0.24 mmol) in hexane (20 cm^3) gave a clear yellow solution within 10 min at room temperature, shown to contain $[Rh(\eta\text{-}C_5H_5)(CO)_2]$, (I; M = Sn), and $[Rh(\eta\text{-}C_5H_5)(CO)H(SnMe_3)]$ by i.r. spectroscopy.

(d) *With* $P(OMe)_3$. (i) A hexane solution of $P(OMe)_3$ of known concentration was added dropwise to a refluxing hexane (50 cm^3) solution of (IV) (0.2 g, 0.48 mmol), and reaction monitored by i.r. spectroscopy. After addition of $P(OMe)_3$ (0.04 g, 0.32 mmol) all (IV) had been consumed, and after removal of solvent and recrystallisation from dichloromethane–hexane dark red crystalline $[Rh_2(\eta\text{-}C_5H_5)_2(CO)_2\{P(OMe)_3\}]$, (V) (0.105 g, 40%) (Found: C, 35.0; H, 3.7%; *M* 516. $C_{15}H_{19}O_5PRh_2$ requires C, 34.9; H, 3.7%; *M* 516) was obtained.

(ii) In a similar reaction, with a heating period of 75 min, (IV) (0.15 g, 0.36 mmol) and $P(OMe)_3$ (0.50 g, 0.40 mmol) yielded, on chromatography on alumina with hexane elution, two yellow bands. The first gave rise to $[Rh(\eta\text{-}C_5H_5)(CO)_2]$, identified by i.r. spectroscopy, and the second to a yellow *liquid*, $[Rh(\eta\text{-}C_5H_5)(CO)\{P(OMe)_3\}]$ (0.058 g, 51%) (Found: C, 33.2; H, 4.6%; *M* 320. $C_9H_{14}O_4PRh$ requires C, 33.6; H, 4.4%; *M* 320), purified by distillation [50 °C(10^{-2}Torr)] to a water-cooled probe.

Reactions of $[Rh(CO)_3(SnMe_3)_3]$, (II).—(a) *With cyclopentadiene*. Excess of cyclopentadiene (*ca*. 0.5 g) was heated under reflux in heptane (100 cm^3) with (II) (0.8 g, 1.18 mmol) for 4 h. Chromatography on silica gel then gave, on elution with hexane, pale yellow and red bands. The first band gave a small amount of unchanged (II), and the second *ca*. 0.01 g of a red liquid with ν(CO) bands at 2 011m and 2 002 cm^{-1} which was not identified. Following this band a colourless solution of (I; M = Sn) (0.23 g, 36%) was eluted and the complex was identified by i.r. spectroscopy.

(b) *With* $P(OMe)_3$. To a refluxing solution of (II) (0.5 g, 0.74 mmol) in hexane (100 cm^3), a hexane solution of $P(OMe)_3$ was added dropwise over 1.5 h until the i.r. spectra showed all of (II) had been consumed and a new species with ν(CO) at 1 972 cm^{-1} formed. Removal of solvent gave a small amount of a yellow *liquid*, $[Rh(CO)_2\{P(OMe)_3\}(SnMe_3)_3]$ (Found: *M* 774. $C_{14}H_{36}OPRhSn_3$ requires *M* 774).

(c) *With* PPh_3. In a reaction similar to (b), (II) and PPh_3 in hexane gave after 70 min a colourless solution exhibiting a single ν(CO) band at 1 975 cm^{-1}, but no species was isolated on attempted crystallisation.

We thank the British Petroleum Company Ltd. for the award of a research studentship (to R.H.) and Johnson, Matthey & Co. Ltd. for a loan of rhodium trichloride.

[5/1116 *Received*, 9*th June*, 1975]