Further Studies on the Interconversion of Large Ring and Cyclometallated Complexes of Rhodium, with the Diphosphines $Bu^t_2P(CH_2)_5PBu^t_2$† and $Bu^t_2PCH_2CH{=}CHCH_2PBu^t_2$‡

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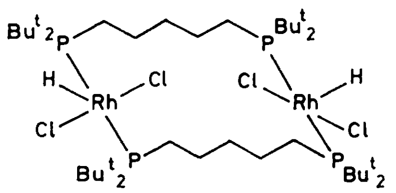
Improved routes to the fluxional cyclometallated hydride $[RhH(Cl)(Bu^t_2PCH_2CH_2CHCH_2CH_2PBu^t_2)]$ are reported. Treatment of this hydride with carbon monoxide and sodium tetraphenylborate in methanol gives the fluxional salt $[RhH(CO)(Bu^t_2PCH_2CH_2CHCH_2CH_2PBu^t_2)][BPh_4]$, together with a small amount of the 16-atom ring complex, *trans*-$[Rh_2Cl_2(CO)_2\{Bu^t_2P(CH_2)_5PBu^t_2\}_2]$, more readily prepared by treating $[Rh_2Cl_2(CO)_4]$ with the diphosphine. This 16-atom ring complex exists as two rotamers in solution at 25 °C. Although $[RhH(Cl)(Bu^t_2PCH_2CH_2CHCH_2CH_2PBu^t_2)]$ gives $[Rh(CO)(Bu^t_2PCH_2CH_2CHCH_2CH_2PBu^t_2)]$ with sodium propan-2-oxide and carbon monoxide on the other hand the corresponding complex $[RhH(Cl)(Bu^t_2PCH_2CH_2CMeCH_2CH_2PBu^t_2)]$ on similar treatment gives a complex mixture (probably containing rotamers of large-ring chelates). Treatment of $[RhH(Cl)(Bu^t_2PCH_2CH_2CHCH_2CH_2PBu^t_2)]$ with MeNC and sodium propan-2-oxide also gives mixtures, probably containing large-ring chelates. Treatment of $[RhH(Cl)(Bu^t_2PCH_2CH_2CHCH_2CH_2PBu^t_2)]$ with MeNC or Bu^tNC in the presence of sodium tetraphenylborate or ammonium hexafluorophosphate gives 16-atom ring chelate salts $[Rh_2(CNR)_4\{Bu^t_2P(CH_2)_5PBu^t_2\}_2][anion]_2$ which can also be made by treating $[Rh(CNR)_4][anion]$ with the diphosphine. Rotation of *trans*-MeNC–Rh–CNMe moieties around P–Rh–P bonds has been studied by variable-temperature n.m.r. spectroscopy. The complex $[Rh_2(CNBu^t)_4(Bu^t_2PCH_2CH{=}CHCH_2PBu^t_2)_2][PF_6]_2$ has also been prepared. Treatment of the cyclo-octene complex $[Rh_2Cl_2(C_8H_{14})_4]$ with $Bu^t_2P(CH_2)_5PBu^t_2$ and MeNC or Bu^tNC (1 mol per rhodium atom) gives 16-atom ring complexes of type $[Rh_2Cl_2(CNR)_2\{Bu^t_2P(CH_2)_5PBu^t_2\}_2]$. The complex $[Rh_2Cl_2(CNMe)_2\{Bu^t_2P(CH_2)_5PBu^t_2\}_2]$ gives only one rotamer in solution in which the two rhodiums are chemically non-equivalent. The diphosphine $Bu^t_2PCH_2CH{=}CHCH_2PBu^t_2$ reacts similarly with $[Rh_2Cl_2(C_8H_{14})_4]$ and MeNC but also gives a small amount of another (unidentified) product. Infrared and ^1H, ^{31}P, and ^{103}Rh n.m.r. data are given.

IN a preliminary communication [1] and a previous paper [2] we reported that the pentamethylene diphosphine $Bu^t_2P(CH_2)_5PBu^t_2$ reacted with $RhCl_3{\cdot}3H_2O$ in ethanol to give a mixture of the co-ordinatively unsaturated 16-atom ring dirhodium(III) dihydride $[Rh_2H_2Cl_4\{Bu^t_2P(CH_2)_5PBu^t_2\}_2]$, which exists in solution as the two rotamers (1) and (2) (see below), the fluxional cyclo-metallated rhodium(III) hydride complex $[RhH(Cl)(Bu^t_2PCH_2CH_2CHCH_2CH_2PBu^t_2)]$, *i.e.* (3a) and (3b), represented as $[RhH(Cl)(P{-}CH{-}P)]$, and an olefin–rhodium(I) complex, probably (4). We also showed that the 16-atom ring complex mixture of rotamers (1)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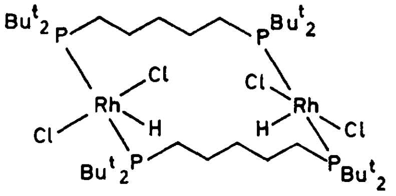
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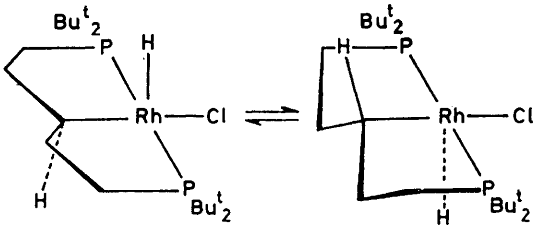
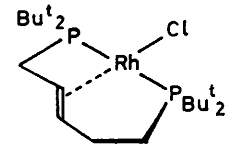

(3a) (3b)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† 1,5-Bis(di-t-butylphosphino)pentane.

‡ 1,4-Bis(di-t-butylphosphino)but-2-ene.

and (2), when treated with 2-methylpyridine, was converted by dehydrochlorination into the cyclometallated hydride [RhH(Cl)(P–CH–P)] (3a)/(3b), possibly *via* a three-co-ordinate, eight-atom ringed, intermediate [RhCl{$Bu^t_2P(CH_2)_5PBu^t_2$}] and a concerted oxidative addition of C–H to rhodium.[3] The interconversion of (3a) to (3b), rapid at room temperature, could go *via* the eight-atom ring complex [RhCl{$Bu^t_2P(CH_2)_5PBu^t_2$}], a process we now favour,[3] or by some other process.[2] In the present paper we have extended the chemistry of these cyclometallated and large-ring systems to complexes containing carbon monoxide or alkyl isonitrile (isocyanide) ligands.

RESULTS AND DISCUSSION

In our previous papers the methods of synthesizing the fluxional cyclometallated hydride (3) were time-consuming and the product was sometimes difficult to purify. We now report two much more convenient methods. One is to treat the cyclo-octene–rhodium(I) complex [$Rh_2Cl_2(C_8H_{14})_4$] with the diphosphine in toluene. Pure hydride (3a)/(3b) was readily isolated in 55% yield (details in the Experimental section). The second method is to treat $RhCl_3\cdot3H_2O$ with $Bu^t_2P(CH_2)_5PBu^t_2$ in tetrahydrofuran when the cyclometallated hydride (3a)/(3b) is obtained in 50% yield. We reported previously that [RhH(Cl)(P–CH–P)], (3a)/(3b), when treated with carbon monoxide and sodium methoxide in methanol gives the rhodium(I) carbonyl complex [Rh(CO)(P–CH–P)] in very good yield. We now find that in the absence of sodium methoxide different products are formed. Treatment of [RhH(Cl)(P–CH–P)] with carbon monoxide in ethanol or methanol, in the presence of sodium tetraphenylborate, readily gives a yellow crystalline tetraphenylborate salt, compound A, which we formulate as [RhH(CO)(P–CH–P)][BPh_4]. Microanalytical and conductivity data are in agreement with the formulation (Table 1) although it is possible that this product is [$RhH(CO)_2$(P–CH–P)][BPh_4], a dicarbonyl complex. The ^{31}P-{^1H} n.m.r. spectrum consisted of a well defined doublet, $\delta(P) = 101$ p.p.m., $^1J(Rh-P) = -107$ Hz. The proton n.m.r. spectrum (in $CDCl_3$) showed only *one* triplet due to Bu^t, $\delta(Bu^t) = 1.26$ p.p.m., $|^3J(PH) + {}^5J(PH)| = 14.6$ Hz, which suggests either that a rapid fluxional process is making both t-butyls on each phosphorus equivalent on the n.m.r. time scale or that they accidentally have the same chemical shift. In the i.r. spectrum there are two strong absorptions at 1 982 and 1 935 cm^{-1} (Nujol) of 1 990 and 1 944 cm^{-1} (chloroform solution) at least one of which is due to ν(CO) and the other, possibly, due to ν(Rh–H). We could not observe a hydride resonance in the ^1H n.m.r. spectrum between 30 and −90 °C indicating that if a fluxional process is occurring it is probably more rapid than with the hydride [RhH(Cl)(P–CH–P)], *i.e.* (3a) $\rightleftharpoons$ (3b), which ' freezes out ' at −62 °C.[2] A ^1H-{^{31}P,^{103}Rh} INDOR experiment on compound A in $CDCl_3$ at *ca.* 25 °C, observing the outer lines of the Bu^t triplet, determined the ^{103}Rh resonance at −716 p.p.m., as a triplet of triplets. Thus the rhodium is coupled to two phosphorus nuclei and *two*, apparently equivalent, hydrogens with a coupling constant, *J*(Rh–H), of 16 Hz. This is a similar result to that of the fluxional hydride (3a)/(3b) which also showed a triplet of triplets with $\frac{1}{2}[^1J(RhH) + {}^2J(RhH)] = 24$ Hz. We therefore suggest that in this hydrido(carbonyl)rhodium(III) cation the hydrogen on rhodium is rapidly interchanging with the hydrogen on carbon, *i.e.* (5a) and (5b) are rapidly interconverting, even at −76 °C, possibly *via* the eight-membered ring cation (6) (see Scheme 1). We also isolated from the methanolic mother-liquors, after filtering off [RhH(CO)(P–CH–P)][BPh_4], a small amount of a yellow neutral complex. This was identified by its i.r. and ^{31}P-{^1H} n.m.r. spectra as the neutral binuclear rhodium(I) complex *trans*-[$Rh_2Cl_2(CO)_2${$Bu^t_2P(CH_2)_5PBu^t_2$}$_2$] with a 16-atom ring (see below), contaminated by small amounts of other (unidentified) species.

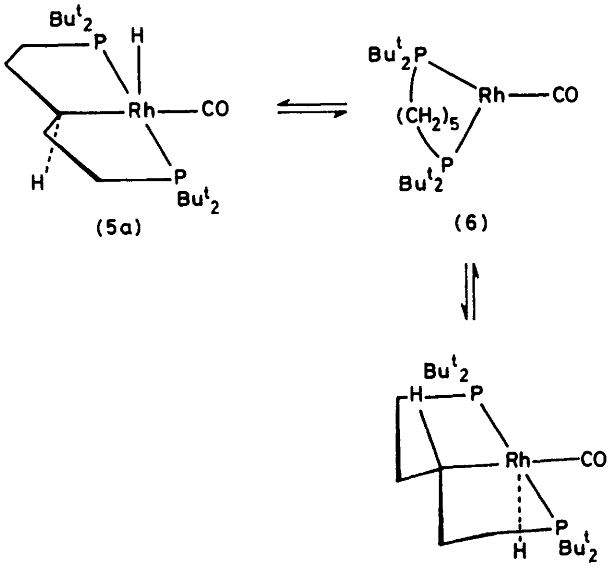
TABLE 1

Microanalytical,[a] molecular-weight,[a] and conductivity [a] data; the ligand $Bu^t_2P(CH_2)_5PBu^t_2$ is represented by P–C_5–P

Complex	Analysis (%) C	H	N	Halogen	*M*	Conductivity $\Lambda/\Omega^{-1}cm^2 mol^{-1}$
[RhH(CO)($Bu^t_2PCH_2CH_2CHCH_2CH_2PBu^t_2$)][$BPh_4$]	68.75(68.15)	8.25(8.2)		0.0(0.0)		16 [b]
[$Rh_2Cl_2(CO)_2$(P–C_5–P)$_2$]	49.9(50.15)	8.55(8.8)		6.8(6.7)	1 058(1 054) [c]	
[$Rh_2(CNMe)_4$(P–C_5–P)$_2$][BPh_4]$_2$	68.15(68.05)	8.25(8.40)	2.7(3.25)			174 [d]
[$Rh_2(CNMe)_4$(P–C_5–P)$_2$][PF_6]$_2$	43.5(43.5)	7.65(7.6)	4.2(4.05)	16.45(16.5)		78 [b]
[$Rh_2(CNBu^t)_4$(P–C_5–P)$_2$][PF_6]$_2$	47.8(48.05)	8.35(8.35)	3.75(3.6)	14.7(14.7)		66 [b]
[{RhCl(CO)($Bu^t_2PCH_2CH{=}CHCH_2PBu^t_2$)}$_n$]	49.35(49.35)	8.1(8.25)		6.8(6.95)	Too insoluble	
[$Rh_2Cl_2(CNMe)_2$(P–C_5–P)$_2$]	50.95(51.15)	8.95(9.15)	2.55(2.55)	6.85(6.55)	1 045(1 080) [e]	
[$Rh_2Cl_2(CNBu^t)_2$(P–C_5–P)$_2$]	54.1(53.65)	9.5(9.55)	2.25(2.4)	6.15(6.1)	1 152(1 164) [e]	
[$Rh_2(CNBu^t)_4$($Bu^t_2PCH_2CH{=}CHCH_2PBu^t_2$)$_2$][$PF_6$]$_2$	47.45(47.5)	7.85(8.00)	3.75(3.7)	14.7(15.0)		51 [b]

[a] Calculated values are given in parentheses. [b] Determined in nitrobenzene solution at 21 °C. [c] Determined in benzene solution. [d] Determined in chloroform solution. [e] Determined in acetone solution at 21 °C.

We have reported the preparation and crystal structure of the 26-atom ring rhodium(I) carbonyl chloride complex [$Rh_2Cl_2(CO)_2${$Bu^t_2P(CH_2)_{10}PBu^t_2$}$_2$] [4,5] and other large-ring diphosphine complexes of rhodium.[6] We have also reported that there are considerable energy barriers to the rotation of a *trans*-OC–Rh–Cl moiety around the rhodium–phosphorus bond when the phosphine is of the type PBu^t_2R (R = alkyl) so that in solution rotamers can be identified at low (and sometimes at room) temperature.[7,8] We thus anticipated that $Bu^t_2P(CH_2)_5PBu^t_2$ would give a 16-atom ring binuclear complex *trans,trans*-$[Rh_2Cl_2(CO)_2\{Bu^t_2P(CH_2)_5PBu^t_2\}_2]$ which would exist as rotamers. (We expected that because of restrictions imposed by the ring system the energy barrier to rotation of an OC–Rh–Cl moiety would be much higher than with mononuclear systems.) Treatment of $[Rh_2Cl_2(CO)_4]$ with $Bu^t_2P(CH_2)_5PBu^t_2$ readily gave $[Rh_2Cl_2(CO)_2\{Bu^t_2P(CH_2)_5PBu^t_2\}_2]$: see the Experimental section for preparative details, Table 1 for microanalytical and i.r. data, and Table 2 for ^{31}P and ^1H n.m.r. data. The ^{31}P-$\{^1H\}$ spectrum showed the presence of two rotamers at room temperature: one rotamer gives an A_2X and the other two A_2X patterns. The first, δ(P) = 44.1 p.p.m., we attribute to (7) or (8) and the other two resonances at δ(P) = 43.8 and 56.8 p.p.m. to rotamer (9), which has non-equivalent phosphorus nuclei.



SCHEME 1

We also treated $[Rh_2Cl_2(CO)_4]$ with the previously described unsaturated diphosphine $Bu^t_2PCH_2CH{=}CHCH_2PBu^t_2$.[2] This gave microcrystalline yellow prisms which analysed (C, H, Cl) for $[\{RhCl(CO)(Bu^t_2PCH_2CH{=}CHCH_2PBu^t_2)\}_n]$ (Table 1) but were too insoluble for molecular-weight or n.m.r. studies. The i.r. spectrum (Nujol) showed a strong band at 1 936 cm^{-1} with a shoulder at 1 940 cm^{-1}, due to ν(CO), medium-intensity bands at 988, 982, and 978 cm^{-1} in the region for out-of-plane deformations of *trans*-(–CH=CH–) and a band at 290 cm^{-1} which is typical of ν(Rh–Cl) with chlorine *trans* to a carbonyl ligand.

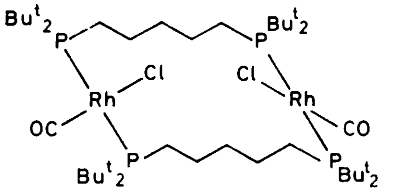
We have also studied the action of CO and sodium propan-2-oxide on the cyclometallated complex $[RhH(Cl)(Bu^t_2PCH_2CH_2CMeCH_2CH_2PBu^t_2)]$,[2] *viz.* [RhH(Cl)(P–CMe–P)]. As mentioned above we found that a similar treatment of [RhH(Cl)(P–CH–P)] (3a)/(3b)

TABLE 2

Infrared (cm^{-1})[a] and ^1H, ^{31}P, and ^{103}Rh n.m.r. data; the ligand $Bu^t_2P(CH_2)_5PBu^t_2$ is represented by P–C$_5$–P

	I.r.		N.m.r.				
Complex	ν(CO) or ν(CN)	ν(Rh–Cl)	^1H δ(*R*NC)[b]	^{31}P δ(P)[c]	^{31}P ^1J(RhP)	^{103}Rh δ(Rh)[d]	N.m.r. solvent
$[Rh_2Cl_2(CO)_2(P{-}C_5{-}P)_2]$	1 943s	290m		44.1	121		$CDCl_3$
	1 933s			56.8	120		
				43.8	121		
$[Rh_2(CNMe)_4(P{-}C_5{-}P)_2][BPh_4]_2$	2 180m[e]		3.6[f]	55.9	−119	−854	CD_3COCD_3
	2 135s		2.84	56.1	−119	−846	CH_2Cl_2–CD_2Cl_2
	2 184 (Raman)[g]						
$[Rh_2(CNMe)_4(P{-}C_5{-}P)_2][PF_6]_2$	2 180m[e]		3.63[h]	60.9	120		CD_3COCD_3
	2 130s		3.38				$CDCl_3$
$[Rh_2(CNBu^t)_4(P{-}C_5{-}P)_2][PF_6]_2$	2 140m		1.58(s)	55.1	120		CD_3COCD_3
	2 095s						
	2 050(sh)						
$[Rh_2Cl_2(CNMe)_2(P{-}C_5{-}P)_2]$	2 085s[e]	265m	3.01(s)	49.7	129	−205	$CDCl_3$
	1 975m		3.20(s)	41.4	130	−199	
$[Rh_2Cl_2(CNBu^t)_2(P{-}C_5{-}P)_2]$	2 072s[e]	232m	1.56	52.4	131		$CDCl_3$
	2 040(sh)		1.39	41.9	131		
	2 020s						
$[Rh_2(CNBu^t)_4(Bu^t_2PCH_2CH{=}CHCH_2PBu^t_2)_2][PF_6]_2$	2 205s		1.57	54.3	120		CD_3COCD_3
	2 150s						
	2 120s						

[a] As Nujol mulls, unless stated otherwise: s = strong, m = medium, sh = shoulder. [b] ±0.01 p.p.m. [c] In p.p.m. to high frequency of 85% H_3PO_4 taken as $\Xi(^{31}P)$ = 40 480 730 Hz, values ±0.1 p.p.m. [d] In p.p.m. to high frequency of $\Xi(^{103}Rh)$ = 3.16 MHz, values ±1 p.p.m. [e] As KBr discs. [f] At 25 °C. [g] As solid sample. When cooled to −40 °C or below, this resonance separated into two with δ(C*H*$_3$) = 3.64(dt) and 3.56 (dt) p.p.m. each coupled to phosphorus, ^5J(PH) *ca.* 1.6 Hz, and to rhodium, ^4J(RhH) *ca.* 0.6 Hz. dt = Doublet of triplets. [h] When the CD_3COCD_3 solution was cooled to −42 °C this single resonance at δ 3.63 was resolved into two peaks at δ(H) = 3.75 (dt) and 3.69 (dt) p.p.m. with estimated ^5J(PH) = 1.9 Hz and ^4J(RhH) = 0.5 Hz.



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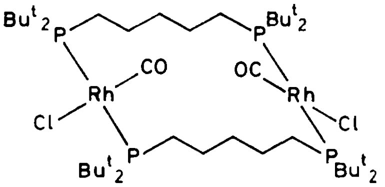

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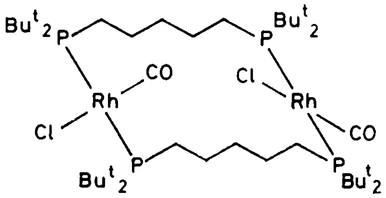


(9)

gave [Rh(CO)(P–CH–P)] in excellent yield. However, [RhH(Cl)(P–CMe–P)] with CO and sodium propan-2-oxide gave a yellow precipitate which was shown by ^{31}P-{^{1}H} n.m.r. spectroscopy to be a mixture of several species, none of which was the desired complex. The ^{31}P-{^{1}H} n.m.r. spectrum (CDCl$_3$) showed a 1 : 1 doublet at δ(P) = 43.3 p.p.m., ^{1}J(RhP) = 120 Hz, and at least two broad overlapping doublets at δ(P) = 56 and 52 p.p.m. with ^{1}J(Rh–P) = 129 and 125 Hz respectively. A yellow solid isolated from the mother-liquors showed these same doublets in its ^{31}P-{^{1}H} n.m.r. spectrum together with a species which showed δ(P) = 97.0 p.p.m., ^{1}J(Rh–P) = 152 Hz. These parameters are very similar to those of [Rh(CO)(P–CH–P)] *viz.* δ(P) = 103.7 p.p.m., ^{1}J(Rh–P) = 156 Hz and are probably therefore due to the desired complex [Rh(CO)(P–CMe–P)]. The i.r. spectrum of this mixture showed a strong broad band at 1 927 cm^{-1} with a medium-intensity shoulder at 1 895 cm^{-1}. This low-frequency band is probably due to [Rh(CO)(P–CMe–P)]. The higher-frequency i.r. band at 1 927 cm^{-1} and the ^{31}P-{^{1}H} resonances with δ values of 43.3, 52, and 56 p.p.m. and ^{1}J(RhP) of 120, 125, and 129 Hz respectively are possibly due to complexes of type *trans,trans*-[Rh$_2$Cl$_2$(CO)$_2$(Bu$^t_2$PCH$_2$CH$_2$CHMeCH$_2$CH$_2$PBu$^t_2$)$_2$], of which several isomers and rotamers are possible: these ^{31}P parameters are very similar to those found for the well characterized *trans*-[Rh$_2$Cl$_2$(CO)$_2${Bu$^t_2$P(CH$_2$)$_5$PBu$^t_2$}$_2$], discussed above. The difference in behaviour between [RhH(Cl)(P–CH–P)] and [RhH(Cl)(P–CMe–P)], when treated with CO and base possibly reflects the lower stability of the rhodium–tertiary alkyl moiety in the second complex compared with the rhodium–secondary alkyl moiety in the first complex.

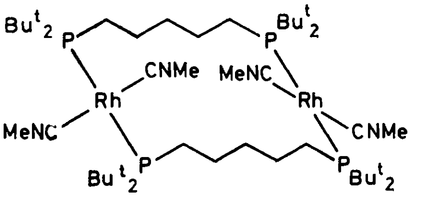
Complexes with Alkyl Isonitriles.—Alkyl isonitriles are in some respects similar to carbon monoxide as ligands, although isonitriles seem to be generally somewhat better donors and are more sterically demanding. We therefore anticipated some differences in behaviour between isonitriles and carbon monoxide as ligands to rhodium in cyclometallated or large-ring complexes.

Thus, although [RhH(Cl)(P–CH–P)] when treated with carbon monoxide and sodium methoxide or sodium propan-2-oxide gives [Rh(CO)(P–CH–P)], a volatile complex, similar treatment with methyl isonitrile and Na[OPr^i] gives a yellow microcrystalline solid which was shown by ^{31}P-{^{1}H} n.m.r. spectroscopy to be a mixture of four species with δ(P) = 56.0, 55.1, 53.7, and 45.1 p.p.m. and ^{1}J(RhP) = 119, 119, 127, and 130 Hz respectively. The solid showed i.r. absorption bands at 2 185w, 2 145s, and 1 940m cm^{-1}. A similar treatment using Bu^{t}NC also gave a complex mixture of products characterized by δ(P) values of 53—60 p.p.m. and coupling constants, ^{1}J(P–Rh), of *ca.* 120 Hz. We could not separate these mixtures and have not succeeded in isolating complexes of type [Rh(CNR)(P–CH–P)]. It is possible that some of the species in the four-component mixture obtained from MeNC are rotamers of large-ring compound(s) since they have similar δ(P) and ^{1}J(Rh–P) values to each other.

We also treated an ethanolic solution of complex [RhH(Cl)(P–CH–P)] with an excess of MeNC in the presence of sodium tetraphenylborate. This gave a yellow crystalline complex, the ^{31}P-{^{1}H} n.m.r. spectrum of which showed a single doublet δ(P) = 56.1 p.p.m., ^{1}J(Rh–P) = 119 Hz. Elemental analyses (Table 1), the conductivity value, and the extensive i.r. and ^{1}H n.m.r. studies discussed below indicated that this product was not a hydride and was almost certainly a salt [Rh$_2$(CNMe)$_4${Bu$^t_2$P(CH$_2$)$_5$PBu$^t_2$}$_2$][BPh$_4$]$_2$ with a 16-atom ring, *i.e.* on treatment with MeNC hydrogen has moved from rhodium to carbon with fission of the rhodium–carbon bond(s). The i.r. spectrum of this salt in a KBr disc gave peaks at 2 180m and 2 135s cm^{-1} due to ν(CN) whilst in acetone solution the values were 2 186w and 2 144s cm^{-1}. A Raman spectrum of a solid sample gave a peak at 2 184 cm^{-1}. These results suggested a mutually *trans* arrangement of MeNC ligands: see for example trends in i.r. and Raman spectra of compounds of the type *trans*-[MX$_2$(CNMe)$_2$] and *cis*-[MX$_2$(CNMe)$_2$] (M = Pd or Pt; X = Cl, Br, or I).[9] The ^{1}H n.m.r. spectrum of this salt in (CD$_3$)$_2$CO at 25 °C showed a single t-butyl triplet pattern at δ = 1.38 p.p.m., $|^3J(\text{PH}) + {}^5J(\text{PH})|$ = 13.1 Hz and one resonance due to the CH$_3$NC protons at δ 3.6 p.p.m. with evidence of coupling to phosphorus (*J ca.* 1.6 Hz). When this solution was cooled the single resonance due to CH$_3$NC split into two peaks, at or below −40 °C, with δ values of 3.64 and 3.56 p.p.m. (at −60 °C), each with ^5J(PH) *ca.* 2 Hz. In CDCl$_3$ solution at 25 °C the salt showed a t-butyl triplet but the resonance at *ca.* 2.5 p.p.m. due to CH_3NC was extremely broad. When cooled, this CH_3NC resonance shifted and separated into two (at δ 2.29 and 1.86 p.p.m. at −60 °C) and sharpened to one peak (at 2.57 p.p.m.) at 60 °C. However, although the solution of the salt in (CD$_3$)$_2$CO was stable, new peaks gradually appeared in the ^{1}H n.m.r. spectrum in CDCl$_3$ solution. Thus after storage at −25 °C for 3 d, two sharp singlets had appeared, one at δ 5.29 p.p.m. and the other at δ 2.17 p.p.m., together with a small broad peak at δ 0.88 p.p.m. We identified the peak at δ 5.29 p.p.m. as due to CH$_2$Cl$_2$ by adding more CH$_2$Cl$_2$ to the solution but did not identify the cause of the other new peaks. We could not identify a resonance due to hydride in the ^{1}H n.m.r. spectrum of the salt which we formulate as [Rh$_2$(CNMe)$_4${Bu$^t{}_2$P(CH$_2$)$_5$PBu$^t{}_2$}$_2$][BPh$_4$]$_2$ even at low temperatures, *e.g.* −90 °C. However, as described above, the fluxional hydride cation [RhH(CO)(P–CH–P)]$^+$ did not show a hydride resonance even at −74 °C. In order to confirm that the methyl isocyanide salt was not a hydride even though it was prepared from [RhH(Cl)(P–CH–P)] we determined the ^{103}Rh spectrum at *ca.* 25 °C by means of ^{1}H-{^{31}P, ^{103}Rh} INDOR experiments in both CD$_2$Cl$_2$ and (CD$_3$)$_2$CO solutions, observing the outer lines of the Bu^t triplet, as in other such INDOR experiments (see above). The rhodium resonance, at −846 p.p.m. (CD$_2$Cl$_2$) or −854 p.p.m. [(CD$_3$)$_2$CO], occurred as a 1 : 2 : 1 triplet due to coupling to phosphorus but there was no sign of coupling to hydrogen.

We also treated [RhH(Cl)(P–CH–P)] with methyl isocyanide in the presence of ammonium hexafluorophosphate, which gave a yellow crystalline solid from dichloromethane–cyclohexane. Elemental analytical data (Table 1) were in agreement with a PF$_6$ salt of composition C$_{25}$H$_{52}$N$_2$P$_2$Rh·PF$_6$. The i.r. spectrum showed a strong peak, at 2 130 cm^{-1}, with a medium-intensity shoulder at 2 180 cm^{-1} due to ν(CN) and a broad peak at 353m cm^{-1} which could be due to ν(Rh–C). Absorptions assigned to ν(M–C) have been observed for complexes of type *trans*-[MX$_2$(CNMe)$_2$] (M = Pd or Pt; X = Br or I).[9] The ^{31}P-{^{1}H} n.m.r. spectrum of this PF$_6$ salt in CDCl$_3$ showed a 1 : 1 doublet at δ(P) = 61.2 p.p.m., ^1J(Rh–P) = 120 Hz and a septet at δ −138.5, ^1J(PF) = 707 Hz due to PF$_6^-$. The ^{1}H n.m.r. spectrum of this PF$_6$ salt in (CD$_3$)$_2$CO was identical to that of the BPh$_4^-$ salt except for the resonances due to the BPh$_4^-$ ion. At 25 °C, the methyl resonances (CH_3NC) of the PF$_6^-$ salt were equivalent, δ(H) = 3.63 p.p.m., but when the (CD$_3$)$_2$CO solution was cooled the resonance broadened and split into two equally intense resonances, *e.g.* at −42 °C δ(H) = 3.75 and 3.69 p.p.m. with ^5J(PH) = 1.9 Hz and ^4J(RhH) = 0.5 Hz, in each case. In CDCl$_3$ solution this PF$_6^-$ salt showed a similar spectrum to the BPh$_4^-$ salt (except for resonances due to BPh$_4^-$) and, similarly, slowly attacked the solvent to give sharp singlets at δ(H) = 5.29 p.p.m. (due to CH$_2$Cl$_2$) and at 2.17 p.p.m. (not identified).

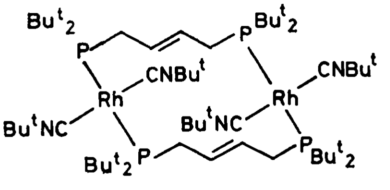
The results described above strongly suggested that the BPh$_4^-$ and PF$_6^-$ salts are of the binuclear dication *trans*-[Rh$_2$(CNMe)$_4${Bu$^t{}_2$P(CH$_2$)$_5$PBu$^t{}_2$}$_2$]$^{2+}$ with a 16-atom ring. One would expect the conformation of this ring to be analogous to the 16- or 20-atom rings of complexes of type *trans*-[M$_2$Cl$_4${Bu$^t{}_2$P(CH$_2$)$_n$PBu$^t{}_2$}$_2$] (M = Pd or Pt; *n* = 5 or 7)[10] or of the 26-atom ring [Rh$_2$Cl$_2$(CO)$_2${Bu$^t{}_2$P(CH$_2$)$_{10}$PBu$^t{}_2$}$_2$].[6] In order to get evidence in support of this formulation we attempted to prepare the PF$_6^-$ salt, formulated as [Rh$_2$(CNMe)$_4${Bu$^t{}_2$P(CH$_2$)$_5$PBu$^t{}_2$}$_2$][PF$_6$]$_2$, by an alternative route, namely by treating the salt [Rh(CNMe)$_4$][PF$_6$][11] with Bu$^t{}_2$P(CH$_2$)$_5$PBu$^t{}_2$ in acetone. When the mixture was heated under reflux a green solution formed, which changed through purple and red to brown over a period of 10 min. Isolation then gave the hoped for salt [Rh$_2$(CNMe)$_4${Bu$^t{}_2$P(CH$_2$)$_5$PBu$^t{}_2$}$_2$][PF$_6$]$_2$ as yellow needles in 36% yield. It was shown to be identical with the product obtained by treating the cyclometallated hydride complex [RhH(Cl)(Bu$^t{}_2$PCH$_2$CH$_2$CHCH$_2$CH$_2$PBu$^t{}_2$)] with MeNC and [NH$_4$][PF$_6$] by i.r. and n.m.r. spectroscopy (including spectra at different temperatures). We suggest that the complex has configuration (10) and that at room temperature the MeNC–Rh–CNMe moieties are rotating rapidly around the P–Rh–P axis but at lower temperatures this rotation is ‘ frozen out ’ and the MeNC ligands become non-equivalent.



(10)

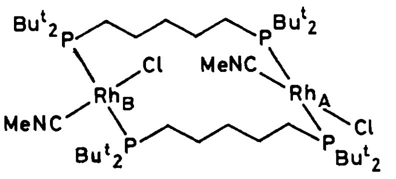
We obtained similar results with Bu^{t}NC. Treatment of [RhH(Cl)(P–CH–P)] with Bu^{t}NC in the presence of [NH$_4$][PF$_6$] gave a yellow crystalline product. However, ^{31}P-{^{1}H} n.m.r. spectroscopy showed it to be a mixture of two species, each showing a doublet resonance with δ(P) = 57.4 and 54.9 p.p.m. (major species) with ^1J(RhP) = 121 and 120 Hz respectively in the approximate proportions of 1 : 2. Recrystallization from dichloromethane–methanol gave the pure major species, which we formulate as the binuclear salt $[Rh_2(CNBu^t)_4\{Bu^t_2P(CH_2)_5PBu^t_2\}_2][PF_6]_2$ on the basis of microanalytical and conductivity data (Table 1) and i.r. and n.m.r. data (Table 2). The ^1H n.m.r. spectrum in $(CD_3)_2CO$ showed CN*Bu*^{t} resonances at $\delta(H) = 1.58$ p.p.m. as a singlet and at $\delta(H) = 1.44$ p.p.m. as a triplet with $|^3J(PH) + {}^5J(PH)| = 13$ Hz due to P*Bu*$^t_2$. When the deuterioacetone solution was cooled to -50 °C the *Bu*^{t}NC resonances resolved into two peaks at $\delta(H) = 1.62$ and 1.56 p.p.m. This behaviour is analogous to that of the methyl isocyanide analogues described above. We also treated $[Rh(CNBu^t)_4][PF_6]$ with $Bu^t_2P(CH_2)_5PBu^t_2$ in hot acetone. This gave $[Rh_2(CNBu^t)_4\{Bu^t_2P(CH_2)_5PBu^t_2\}_2][PF_6]_2$ in 72% yield. This product was identified by elemental analysis and by its i.r. and ^1H n.m.r. spectra and shown to be identical with that obtained by treating $[RhH(Cl)(Bu^t_2PCH_2CH_2CHCH_2CH_2PBu^t_2)]$ with $Bu^tNC–[NH_4][PF_6]$ and described above.

We also treated $[Rh(CNBu^t)_4][PF_6]$ with $Bu^t_2PCH_2CH{=}CHCH_2PBu^t_2$ and obtained a yellow solid, $[Rh_2(CNBu^t)_4(Bu^t_2PCH_2CH{=}CHCH_2PBu^t_2)_2][PF_6]_2$: microanalytical and conductivity data are in Table 1. The ^{31}P-$\{^1H\}$ n.m.r. spectrum of the product in CD_2Cl_2 showed a slightly broadened doublet at $\delta(P) = 54.5$ p.p.m., with $^1J(RhP) = 120$ Hz, parameters which are very similar to the PF_6^- salts formed from $Bu^t_2P(CH_2)_5PBu^t_2$ (see above). The ^1H n.m.r. spectrum contained broad bands at $\delta(H) = 5.84$ and 2.83 p.p.m. which are probably due to olefinic and P*CH*$_2$CH= protons respectively, but the t-butyl region was very complex and we could not assign peaks due to *Bu*$^t_2$P protons, even with ^{31}P decoupling. A peak at $\delta(H) = 1.57$ p.p.m. was probably due to Bu^{t}NC protons. The i.r. spectrum of this complex showed strong bands at 2 205, 2 150, and 2 120 cm^{-1} due to ν(CN) and a band at 978 cm^{-1} probably due to out-of-plane deformation of *trans*-(RCH=CHR). We tentatively assign the structure (11) to the cation $[Rh_2(CNBu^t)_4(Bu^t_2PCH_2CH{=}CHCH_2PBu^t_2)_2]^{2+}$.



(11)

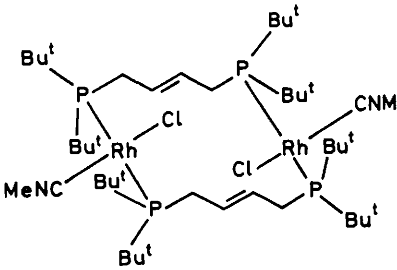
As described above $[Rh_2Cl_2(CO)_4]$, when treated with $Bu^t_2P(CH_2)_5PBu^t_2$, readily gave the 16-atom ring complex *trans*-$[Rh_2Cl_2(CO)_2\{Bu^t_2P(CH_2)_5PBu^t_2\}_2]$, which exists as two rotamers in solution. We hoped that isonitriles (RNC) would give analogous complexes, *trans*-$[Rh_2Cl_2(CNR)_2\{Bu^t_2P(CH_2)_5PBu^t_2\}_2]$, although we expected that the more sterically demanding CNR ligand would affect the rotamer populations. Treatment of a suspension of $[Rh_2Cl_2(C_8H_{14})_4]$ in benzene with $Bu^t_2P(CH_2)_5PBu^t_2$ and MeNC in the right proportions readily gave a yellow crystalline solid. This was shown to be the expected complex, *trans*-$[Rh_2Cl_2(CNMe)_2\{Bu^t_2P(CH_2)_5PBu^t_2\}_2]$, on the basis of elemental analytical and molecular-weight data (Table 1) and i.r. and n.m.r. spectroscopic results (Table 2). The i.r. spectrum (Nujol) showed two bands assigned to ν(CN) at 2 085s and 1 975m cm^{-1} and a broad band at 265s cm^{-1} due to ν(Rh–Cl). The ^{31}P-$\{^1H\}$ n.m.r. spectrum at room temperature was particularly well defined consisting of two equally intense and very sharp 1 : 1 doublets of $\delta(P) = 49.7$ p.p.m., $^1J(RhP) = 129$ Hz and $\delta(P) = 41.4$ p.p.m., $^1J(RhP) = 130$ Hz. The ^1H n.m.r. spectrum showed two equally intense peaks due to C*H*$_3$NC at $\delta(H) = 3.20$ and 3.01 p.p.m. and a complex pattern of overlapping triplets in the t-butyl region, which simplified to three singlets in the ^1H-$\{^{31}P\}$ spectrum at $\delta(H) = 1.50$, 1.40, and 1.37 p.p.m., in intensity ratio 1 : 2 : 1. A ^1H-$\{^{31}P, ^{103}Rh\}$ INDOR experiment gave two rhodium resonances at $\delta(Rh) = -205$ and -199 p.p.m. and together with ^1H-$\{^{31}P\}$ selective-decoupling experiments it was shown that the rhodium resonance at -205 p.p.m. was associated with the ^{31}P resonance at $\delta(P) = 49.7$ p.p.m., the CH_3NC resonance at $\delta(H) = 3.01$ p.p.m., and two t-butyl resonances at $\delta(H) = 1.40$ and 1.37 p.p.m. Thus the rhodium resonance of -199 p.p.m. must be associated with the other resonances due to *P*Bu$^t_2$, C*H*$_3$NC, and P*Bu*$^t_2$ (Table 2). These n.m.r. data indicate that this 16-atom ring complex $[Rh_2Cl_2(CNMe)_2\{Bu^t_2P(CH_2)_5PBu^t_2\}_2]$ is present in solution as only one rotamer, to which we assign the structure (12). We made a similar complex, *trans*-$[Rh_2Cl_2(CNBu^t)_2\{Bu^t_2P(CH_2)_5PBu^t_2\}_2]$, by treating $[Rh_2Cl_2(C_8H_{14})_4]$ with $CNBu^t$ and $Bu^t_2P(CH_2)_5PBu^t_2$ in benzene. The resultant orange prisms readily lost benzene of solvation in air and crumbled to a yellow solid. Microanalytical and molecular-weight data (Table 1) are in agreement with the formulation and the ^{31}P-$\{^1H\}$ n.m.r. pattern, as with the CNMe complexes, consisted of two equally intense doublets $\delta(P) \pm 52.4$ p.p.m., $^1J(RhP) = 131$ Hz and $\delta(P) = 41.9$ p.p.m., $^1J(RhP) = 131$ Hz. These data are in agreement with structure (12) with CNBu^t in place of CNMe. The ^1H n.m.r. spectrum showed a complex set of t-butyl resonances but by carrying out an ^1H-$\{^{31}P\}$ experiment we could assign the peaks at $\delta(H) = 1.50$, 1.41, 1.40, and 1.37 p.p.m. to P*Bu*^{t} and at 1.56 and 1.39 p.p.m. to CN*Bu*^{t}. The i.r. spectrum (Nujol) showed strong bands at 2 072 and 2 020 cm^{-1} with a shoulder at 2 040 cm^{-1} due to ν(CN) and a strong band at 232 cm^{-1} due to ν(RhCl).



(12)

As described above, the complex $[\{RhCl(CO)(Bu^t_2$-

$\mathrm{PCH_2CH{=}CHCH_2PBu^t_2)\}_n]}$ was too insoluble to study by n.m.r. techniques. We thought it possible, however, that an analogous complex would be formed with methyl isocyanide, *i.e.* $[\{\mathrm{RhCl(CNMe)(Bu^t_2PCH_2CH{=}CHCH_2PBu^t_2)}\}_n]$, which might be more soluble. When we treated $[\mathrm{Rh_2Cl_2(C_8H_{14})_4}]$ with 2 mole equivalents of $\mathrm{Bu^t_2PCH_2CH{=}CHCH_2PBu^t_2}$ and methyl isocyanide, a very dark suspension was formed which on stirring became green. The major product from this reaction was a yellow solid whose $^{31}\mathrm{P}$ n.m.r. spectrum showed it to be a mixture with a main resonance of $\delta(\mathrm{P}) =$ *ca.* 46 p.p.m. and $^1J(\mathrm{RhP}) =$ *ca.* 117 Hz as a broad doublet. There was also a small amount of a complex showing a low-frequency doublet at $\delta(\mathrm{P}) = -96.5$ p.p.m. with $^1J(\mathrm{RhP}) = 98$ Hz. This would seem to be a very strained mononuclear olefinic rhodium(I) complex since the phosphorus chemical shift is much lower than even that of $[\mathrm{RhCl(Bu^t_2PCH_2CH{=}CHCH_2PBu^t_2)}]$ (−41.0 p.p.m.) or $[\mathrm{Rh(CO)(Bu^t_2PCH_2CH{=}CHCH_2PBu^t_2)}][\mathrm{BPh_4}]$ (−39.2 p.p.m.).[2] When the $\mathrm{CDCl_3}$ solution of this mixture was cooled the broad resonance sharpened into a doublet with $\delta(\mathrm{P}) = 48.1$ p.p.m. and $^1J(\mathrm{RhP}) = 131$ Hz at −20 °C, and at −30 °C other sharp resonances at $\delta(\mathrm{P}) = 48.6$ and 41.7 p.p.m., with $^1J(\mathrm{RhP}) = 124$ and 127 Hz respectively were visible. This could be due to the 'freezing out' of rotamers of the 16-atom ring complex $[\mathrm{Rh_2Cl_2(CNMe)_2(Bu^t_2PCH_2CH{=}CHCH_2BPu^t_2)_2}]$. The $^1\mathrm{H}$ n.m.r. spectrum of this mixture showed a broad peak at $\delta(\mathrm{H}) =$ *ca.* 1.4 p.p.m. for t-butyl protons. There was also an olefinic resonance at $\delta(\mathrm{H}) = 6.04$ p.p.m. and a peak at $\delta(\mathrm{H}) = 2.94$ p.p.m. which is due to a methyl isocyanide ligand. A broad resonance at $\delta(\mathrm{H}) = 2.82$ p.p.m. is probably due to the $\mathrm{C}H_2\mathrm{CH{=}}$ protons. The i.r. spectrum of this product contained a broad, strong band due to ν(CN) at 2 085 $\mathrm{cm^{-1}}$ and a weaker broad band at 1 980 $\mathrm{cm^{-1}}$. There was also a band at 980 $\mathrm{cm^{-1}}$, probably due to out-of-plane deformations of *trans*-(RCH=CHR). A broad weak band at 275 $\mathrm{cm^{-1}}$ could be due to ν(Rh–Cl). Extraction of this product with benzene gave a yellow crystalline product in exceedingly low yield (5 mg, 2%). However, the $^{31}\mathrm{P}$-$\{^1\mathrm{H}\}$ spectrum of this product was well defined consisting of a doublet $\delta(\mathrm{P}) = 49.0$ p.p.m., $^1J(\mathrm{Rh{-}P}) = 131$ Hz with shoulders on the resonances. These are undoubtedly due to $^5J(\mathrm{PP})$ and analysis of the spectrum as an $[\mathrm{A[X]_2}]_2$ system[12] assuming $J(\mathrm{RhRh}) = {}^7J(\mathrm{PP}) = 0$ gave a value for $^5J(\mathrm{PP})$ of 3.4 ± 0.5 Hz, which is comparable to the value of $^5J(\mathrm{PP})$ for the free phosphine. The $^1\mathrm{H}$ n.m.r. spectrum contained broad resonances at $\delta(\mathrm{H}) = 6.1$ and 2.7 p.p.m. due to olefinic and $\mathrm{PC}H_2\mathrm{CH{=}}$ protons respectively. The *Me*NC resonance occurred at $\delta(\mathrm{H}) = 3.54$ p.p.m. The t-butyl resonance occurred as overlapping triplets at $\delta(\mathrm{H}) = 1.5$ p.p.m. with $|^3J(\mathrm{PH}) + {}^5J(\mathrm{PH})|$ *ca.* 12 Hz. We recovered the sample from the n.m.r. solution and elemental analytical data were quite close to the values expected for $[\mathrm{Rh_2Cl_2(CNMe)_2(Bu^t_2PCH_2CH{=}CHCH_2PBu^t_2)_2}]$ (Table 1). Unfortunately we could not repeat the preparation. However, the n.m.r. and microanalytical data (above) strongly suggest that the material was the hoped for complex $[\mathrm{Rh_2Cl_2(CNMe)_2(Bu^t_2PCH_2CH{=}CHCH_2PBu^t_2)_2}]$ for which we suggest configuration (13).



(13)

EXPERIMENTAL

The general techniques used were the same as in other recent papers from this laboratory.[13] The $^1\mathrm{H}$ and $^{31}\mathrm{P}$-$\{^1\mathrm{H}\}$ n.m.r. spectra were recorded with a JEOL FX100Q spectrometer using an internal deuterium lock. Except where stated otherwise, measurements were made at ambient temperatures (*ca.* 296 K). $^{103}\mathrm{Rh}$ INDOR spectra were obtained by $^1\mathrm{H}$-$\{^{31}\mathrm{P}, {}^{103}\mathrm{Rh}\}$ triple resonance as described previously.[2] Values of $^2J(\mathrm{PP})$ in complexes containing chemically equivalent phosphines were obtained by $^1\mathrm{H}$-$\{^{31}\mathrm{P}\}$ INDOR by observing the outside lines of the t-butyl triplets, as described previously:[2] values ±5 Hz.

Preparation of $[\mathrm{RhH(Cl)\{Bu^t_2PCH_2CH_2CHCH_2CH_2PBu^t_2\}}]$.—*From* $\mathrm{RhCl_3{\cdot}3H_2O}$ *and* $\mathrm{Bu^t_2P(CH_2)_5PBu^t_2}$ *in tetrahydrofuran.* A solution of the diphosphine (2.9 g, 8.04 mmol) in tetrahydrofuran (thf) (15 $\mathrm{cm^3}$) was added to a solution of $\mathrm{RhCl_3{\cdot}3H_2O}$ (0.87 g, 3.46 mmol) in thf (25 $\mathrm{cm^3}$)–water (1 $\mathrm{cm^3}$). A pink precipitate was produced which dissolved on refluxing over a period of 5.5 d to give a clear orange solution. The solvent was then evaporated under reduced pressure and the residue recrystallized from benzene. The required product was obtained as orange prisms (0.89 g, 50%) and identified by its i.r. and $^1\mathrm{H}$ and $^{31}\mathrm{P}$ n.m.r. spectra.

From $[\mathrm{Rh_2Cl_2(C_8H_{14})_4}]$ *and* $\mathrm{Bu^t_2P(CH_2)_5PBu^t_2}$ *in toluene.* A solution of the diphosphine (0.69 g, 1.90 mmol) in toluene (4 $\mathrm{cm^3}$) was added to a suspension of $[\mathrm{Rh_2Cl_2(C_8H_{14})_4}]$ (0.62 g, 0.86 mmol) in toluene (20 $\mathrm{cm^3}$) and the mixture refluxed for 30 min. The solvent was then removed under reduced pressure and the residue recrystallized from dichloromethane–hexane to give the required complex (0.47 g, 55%), identified as above.

Preparation of $[\mathrm{RhH(Cl)\{Bu^t_2PCH_2CH_2CMeCH_2CH_2PBu^t_2\}}]$ *from* $[\mathrm{Rh_2Cl_2(C_8H_{14})_4}]$ *and* $\mathrm{Bu^t_2PCH_2CH_2CHMeCH_2CH_2PBu^t_2}$.—A solution of the diphosphine (0.44 g, 1.16 mmol) in benzene (8 $\mathrm{cm^3}$) was added to a suspension of $[\mathrm{Rh_2Cl_2(C_8H_{14})_4}]$ (0.40 g, 0.55 mmol) in benzene (6 $\mathrm{cm^3}$). The mixture was refluxed for 2.5 h after which some insoluble brown material was filtered off and the filtrate evaporated. The residue formed orange-yellow prisms of the desired product from pentane. Yield 0.28 g, 51%. It was identified by i.r. and n.m.r. ($^1\mathrm{H}$ and $^{31}\mathrm{P}$) spectroscopy.

Treatment of $[\mathrm{RhH(Cl)\{Bu^t_2PCH_2CH_2CHCH_2CH_2PBu^t_2\}}]$ *with* CO *and* $\mathrm{Na[BPh_4]}$.—Carbon monoxide was bubbled through a solution of the cyclometallated hydride (0.040 g, 0.08 mmol) and sodium tetraphenylborate (0.14 g, 0.40 mmol) in ethanol (5 cm^3) for 5 min. The lemon-yellow plates which had precipitated were filtered off, washed with water and cold ethanol, and dried. Yield 0.023 g. They were identified as $[RhH(CO)\{Bu^t_2PCH_2CH_2CHCH_2CH_2PBu^t_2\}]$-$[BPh_4]$, see Results and Discussion section.

Preparation of $[Rh_2Cl_2(CO)_2\{Bu^t_2P(CH_2)_5PBu^t_2\}_2]$.—A solution of rhodium trichloride trihydrate (0.42 g, 41.5% Rh, 1.68 mmol) in ethanol (12 cm^3) was treated with carbon monoxide under reflux for 3 h. The resultant yellow solution was cooled to room temperature and treated with $Bu^t_2P(CH_2)_5PBu^t_2$ (0.69 g, 1.85 mmol) and the mixture left for 1 h. The required product separated as yellow microcrystals. Yield 0.60 g, 1.13 mmol, 67%.

Preparation of $[\{Rh_2Cl_2(CO)_2(Bu^t_2PCH_2CH{=}CHCH_2PBu^t_2)_2\}_n]$.—A solution of the diphosphine (0.56 g, 1.64 mmol) in benzene (15 cm^3) was added to a solution of $[Rh_2Cl_2(CO)_4]$ (0.30 g, 0.78 mmol) in benzene (50 cm^3). This caused effervescence and the solution became paler. The solution was refluxed during which a pale yellow precipitate formed. After 12 h reflux this was filtered off, washed with light petroleum (b.p. 60—80 °C), and dried to give the product in quantitative yield.

Reactions of $[RhH(Cl)\{Bu^t_2PCH_2\mathit{CH}_2CHCH_2\mathit{CH}_2PBu^t_2\}]$.—*With* Bu^tNC *and* $[NH_4][PF_6]$. A solution of Bu^tCN (48 µl, 0.54 mmol) in methanol (1.5 cm^3) and ammonium hexafluorophosphate (0.22 g, 1.36 mmol) in methanol (8 cm^3) were added to a solution of the cyclometallated hydride (0.13 g, 0.25 mmol) in methanol (5 cm^3). The mixture was stirred for 1 h, the yellow crystalline precipitate was then filtered off and recrystallized from dichloromethane–methanol. The product formed yellow needles and was identified as $[Rh_2(CNBu^t)_4\{Bu^t_2P(CH_2)_5PBu^t_2\}_2][BPh_4]_2$, see Results and Discussion section. Yield 0.19 g.

With MeNC *and* $Na[BPh_4]$. Methyl isonitrile (9.5 µl, 0.18 mmol) was added to a solution of the cyclometallated hydride (3) (0.040 g, 0.08 mmol) and sodium tetraphenylborate (0.14 g, 0.40 mmol) in ethanol (5 cm^3). The yellow precipitate produced was filtered off, washed with water and cold ethanol, and dried. This product was obtained as yellow microcrystals (0.05 g) and identified as $[Rh(CNMe)_4$-$\{Bu^t_2P(CH_2)_5PBu^t_2\}_2][BPh_4]_2$, see Results and Discussion section and the alternative method of preparation below.

With MeNC *and* $[NH_4][PF_6]$. A solution of methyl isonitrile (16.5 µl, 0.31 mmol) in methanol (0.8 cm^3) and a solution of ammonium hexafluorophosphate (0.12 g, 0.72 mmol) in methanol (5 cm^3) were added to a stirred solution of the cyclometallated hydride (0.070 g, 0.14 mmol) in methanol (8 cm^3). After 10 min the resultant greenish yellow precipitate was filtered off *etc.* and recrystallized from dichloromethane–cyclohexane. The product formed yellow microcrystals (0.070 g) and was identified as $[Rh_2(CNMe)_4$-$\{Bu^t_2P(CH_2)_5PBu^t_2\}_2][BPh_4]_2$, see Results and Discussion section.

Action of $Bu^t_2P(CH_2)_5PBu^t_2$ *on* $[Rh(CNMe)_4][PF_6]$.—A solution of $Bu^t_2P(CH_2)_5PBu^t_2$ (0.19 g, 0.54 mmol) in acetone (7 cm^3) was added to a suspension of $[Rh(CNMe)_4][PF_6]$ (0.20 g, 0.49 mmol) in acetone (10 cm^3). The resultant mixture was heated under reflux for 35 min to give a dark brown solution which was evaporated to dryness under reduced pressure. The resultant grey-green solid was extracted with hot methanol to give a yellow solution. This was slowly evaporated under reduced pressure to low bulk giving a greenish yellow crystalline precipitate, identified as $[Rh_2(CNMe)_4\{Bu^t_2P(CH_2)_5PBu^t_2\}_2][PF_6]_2$. It formed yellow microcrystals from dichloromethane–cyclohexane. Yield 0.12 g, 36%.

Action of $Bu^t_2P(CH_2)_5PBu^t_2$ *on* $[Rh(CNBu^t)_4][PF_6]$.—A solution of the diphosphine (0.17 g, 0.48 mmol) in acetone (10 cm^3) was added to a solution of the salt (0.27 g, 0.46 mmol) in acetone (10 cm^3). The mixture was heated under reflux for 2 min and then stirred at *ca.* 25 °C for a further 8 min. A small amount of solid was filtered off and propan-2-ol added to the yellow filtrate. Most of the acetone was then slowly evaporated under reduced pressure. This gave $[Rh_2(CNBu^t)_4\{Bu^t_2P(CH_2)_5PBu^t_2\}_2][PF_6]_2$ as yellow microcrystals. Yield 0.25 g, 72%.

Action of $Bu^t_2PCH_2CH{=}CHCH_2PBu^t_2$ *on* $[Rh(CNBu^t)_4]$-$[PF_6]$.—A solution of the olefinic diphosphine (0.23 g, 0.65 mmol) in acetone (15 cm^3) was added to a solution of $[Rh(CNBu^t)_4][PF_6]$ (0.35 g, 0.60 mmol) in acetone (15 cm^3) and the mixture heated under reflux for 30 min. Addition of propan-2-ol and evaporation of most of the acetone under reduced pressure gave a yellow microcrystalline solid which was filtered off, washed with n-pentane, and dried. Yield 0.43 g.

Action of MeNC *and* $Bu^t_2P(CH_2)_5PBu^t_2$ *on* $[Rh_2Cl_2$-$(C_8H_{14})_4]$.—A stirred suspension of the cyclo-octene complex (0.40 g, 0.56 mmol) in benzene (15 cm^3) was treated with a solution of the diphosphine (0.43 g, 1.19 mmol) in benzene (10 cm^3) and MeNC (64 µl, 1.19 mmol) in benzene (5 cm^3). A dark green suspension formed which was filtered off after 15 min to give a green solid and a yellow solution. The solid was extracted with hot benzene to give a black solid (not identified) and a yellow solution. The combined yellow solutions were evaporated to low bulk under reduced pressure and n-pentane added. This gave $[Rh_2Cl_2(CNMe)_2$-$\{Bu^t_2P(CH_2)_5PBu^t_2\}_2]$ as a yellow, microcrystalline solid. Yield 0.34 g, 56%.

Action of Bu^tNC *and* $Bu^t_2P(CH_2)_5PBu^t_2$ *on* $[Rh_2Cl_2$-$(C_8H_{14})_4]$.—A stirred suspension of the cyclo-octene complex (0.54 g, 0.75 mmol) in benzene (25 cm^3) was treated with a solution of the diphosphine (0.58 g, 1.60 mmol) in benzene (3 cm^3) and a solution of Bu^tNC (0.13 g, 1.60 mmol) in benzene (2 cm^3). A yellow solution with a small amount of insoluble material was produced. After 30 min, the product mixture was evaporated to dryness under reduced pressure and the residue extracted with dichloromethane. The dichloromethane was evaporated and the residue recrystallized from benzene. This gave $[Rh_2Cl_2(CNBu^t)_2$-$\{Bu^t_2P(CH_2)_5PBu^t_2\}_2]$ as yellow prisms. Yield 0.61 g, 69%.

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