The Synthesis and Reactivity of Some 2-Ethyltetraphenoxydiphosphazane Derivatives of Rhodium

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Treatment of [$\{Rh(diene)Cl\}_2$] (diene = C_8H_{12} or C_7H_8) with the ditertiary phosphite $(PhO)_2PN(Et)P(OPh)_2$ (etdp) in benzene leads to successive replacement of the diene ligands and the formation of [Rh_2(diene)(etdp)Cl_2] and [$\{Rh(etdp)Cl\}_2$]. The corresponding bromo- and iodo- derivatives [$\{Rh(etdp)X\}_2$] (X = Br or I) are produced analogously. Reactions of [$\{Rh(C_8H_{12})Cl\}_2$] with excess of etdp in ethanol or methanol in the presence of a suitable counter ion effects not only the displacement of the diene ligands but also the halogens as halide ions to afford [$Rh(etdp)_2$][A] (A = BPh_4 or SbF_6). Carbon monoxide reacts reversibly with [$Rh(etdp)_2$]$^+$ and [$Rh(C_8H_{12})(etdp)$]$^+$, obtained by treatment of [$Rh(C_8H_{12})(solvent)_x$]$^+$ with etdp, to yield [$Rh(etdp)_2(CO)$]$^+$ and [$Rh(C_8H_{12})(etdp)(CO)$]$^+$ respectively. Reaction of [$Rh(etdp)_2$]$^+$ with HBr and Br_2 gives *trans*-[$Rh(etdp)_2H(Br)$]$^+$ and [$Rh(etdp)_2Br_2$]$^+$ respectively, although the former degrades to [$Rh(etdp)_2$]$^+$ in solution.

PREVIOUS studies have indicated that cationic rhodium(I) species of the type [$Rh(diene)L_2$]$^+$ (diene = C_8H_{12} or C_7H_8; L = tertiary phosphine or phosphite) react with dihydrogen in weakly co-ordinating solvents such as acetone or tetrahydrofuran to afford reaction mixtures which are very active catalytically for the hydrogenation of olefins to alkanes, of alkynes to *cis*-olefins, and of dienes, but not butadienes, to monoenes.[1-3] Catalytic systems derived from [Rh(diene)(L–L)]$^+$ (L–L = ditertiary phosphine or arsine) on the other hand effect the selective and rapid hydrogenation of butadiene derivatives to their corresponding butenes.[3]

Because the activity of catalysts derived from [$Rh(diene)L_2$]$^+$ is very dependent on the basicity of the phosphorus ligand L and also on whether the catalyst contains unidentate or chelating phosphine ligands,[1-3] a number of ditertiary phosphite complexes of rhodium have been synthesised and their reactivity towards dihydrogen and carbon monoxide investigated. This study forms part of a much larger one investigating the co-ordination behaviour of ditertiary phosphites, an area that has been little explored.

RESULTS AND DISCUSSION

It is well established that treatment of [$\{Rh(diene)X\}_2$] (X = Cl, Br, or I) with tertiary phosphines, L, in benzene leads to cleavage of the halide bridges and the formation of [Rh(diene)L(X)].[4-9] In contrast, $P(OPh)_3$ has been shown to preferentially displace the diene groups from this dimeric species in this solvent to afford successively [$Rh_2(diene)\{P(OPh)_3\}_2X_2$], [$\{Rh[P(OPh)_3]_2X\}_2$], and [$Rh\{P(OPh)_3\}_3X$] (diene = C_8H_{12} or C_7H_8).[10] It has now been found that the ditertiary phosphite $(PhO)_2PN(Et)P(OPh)_2$ (2-ethyltetraphenoxydiphosphazane, etdp) behaves similarly to $P(OPh)_3$ on reaction with [$\{Rh(C_8H_{12})Cl\}_2$] in benzene affording [$Rh_2(C_8H_{12})(etdp)Cl_2$] or [$\{Rh(etdp)Cl\}_2$] depending on the molar ratios employed [equation (1)]. The experimentally obtained molecular weights for these complexes were somewhat low for dimeric formulations but this is interpreted in terms of dissociation occurring in solution. Similar treatment of [$\{Rh(C_8H_{12})Br\}_2$] and [$\{Rh(C_8H_{12})I\}_2$] with a 2 : 1 mol ratio of etdp and of [$\{Rh(C_7H_8)Cl\}_2$] with 1 : 1 and 2 : 1 mol ratios of this ligand gave [$\{Rh(etdp)Br\}_2$], [$\{Rh(etdp)I\}_2$], [$Rh_2(C_7H_8)(etdp)Cl_2$], and [$\{Rh(etdp)Cl\}_2$] respectively. The complex [$Rh_2(C_7H_8)(etdp)Cl_2$] could not be isolated analytically pure and was characterised by means of spectroscopic evidence only (Tables 1—3).

$$[\{Rh(C_8H_{12})Cl\}_2] \xrightarrow[-C_8H_{12}]{\text{etdp}} [Rh_2(C_8H_{12})(etdp)Cl_2] \xrightarrow[-C_8H_{12}]{\text{etdp}} [\{Rh(etdp)Cl\}_2] \quad (1)$$

Reaction of [$\{Rh(C_8H_{12})Cl\}_2$] with a 4 : 1 mol ratio of etdp in ethanol or methanol in the presence of Na[BPh_4] or K[SbF_6] led not only to the replacement of the cyclo-octadiene ligands but also to the displacement of the halogens as halide ions to afford in high yield [$Rh(etdp)_2$][A] (A = BPh_4 or SbF_6). To establish whether this reaction occurs *via* the path represented in equation (1) or that outlined in (2), as found for a similar reaction involving PBu^n_3,[10] the reaction was carried out with a 2 : 1 mol ratio of etdp. The product which separated from the alcoholic solution was characterised as the neutral species [$\{Rh(etdp)Cl\}_2$].

$$[\{Rh(C_8H_{12})Cl\}_2] \xrightarrow{\text{etdp}} 2[Rh(C_8H_{12})(etdp)]^+ + 2Cl^- \xrightarrow[-C_8H_{12}]{\text{etdp}} 2[Rh(etdp)_2]^+ \quad (2)$$

The synthesis of [$Rh(C_8H_{12})(etdp)$]$^+$ was readily achieved by addition of etdp to an equimolar quantity of [$Rh(C_8H_{12})(solvent)_x$]$^+$, produced by treatment of [$\{Rh(C_8H_{12})Cl\}_2$] with silver ions in a weakly co-ordinating solvent such as acetone or tetrahydrofuran (thf). An alternative method of synthesis involved the addition of cyclo-octadiene to [$Rh(etdp)(solvent)_x$]$^+$. These reactions were found to also afford [$Rh(etdp)_2$]$^+$ and [$Rh(C_8H_{12})_2$]$^+$ in low yield.

Passage of carbon monoxide through a dichloromethane solution of [$Rh(etdp)_2$][BPh_4] gave the monocarbonyl derivative [$Rh(etdp)_2(CO)$][BPh_4], isolated as a yellow crystalline salt. A frequency of 2 050 cm^{-1} (Nujol mull) for the C–O stretching mode is indicative of a weakly bound carbonyl group and, consistent with this, the complex was found to slowly degrade to [$Rh(etdp)_2$][BPh_4] in both solution and the solid state.

Slow passage of a stream of carbon monoxide through a dichloromethane solution of [$Rh(C_8H_{12})(etdp)$]$^+$ for

TABLE 1

Conductivity, analytical, and molecular-weight data

Complex	Colour	Λ [a] / S cm^2 mol^{-1}	Analysis (%) Found C	Found H	Found Others	Calc. C	Calc. H	Calc. Others	M [b]
$[Rh_2(C_8H_{12})(etdp)Cl_2]$	Orange	0.68	47.2	4.35	N 1.70 Cl 8.45	47.35	4.30	N 1.60 Cl 8.20	761 (862)
$[\{Rh(etdp)Cl\}_2]$	Yellow	0.55	50.8	4.15	Cl 5.95	50.7	4.10	Cl 5.75	909 [c] (1 232)
$[\{Rh(etdp)Br\}_2]$	Yellow	1.26	46.95	3.55	N 2.05 Br 12.55	47.3	3.80	N 2.10 Br 12.1	854 (1 320)
$[\{Rh(etdp)I\}_2]$	Yellow	1.48	44.5	3.60	N 2.02 I 18.4	44.15	3.55	N 2.00 I 17.95	1 074 (1 415)
$[Rh(etdp)_2][BPh_4]$	Yellow	107	66.0	5.20	P 8.70	66.3	5.10	P 9.00	
$[Rh(etdp)_2][SbF_6]$	Yellow	152	48.65	3.90	N 2.10	48.3	3.90	N 2.15	
$[Rh(C_8H_{12})(etdp)][SbF_6]$	Orange	112	44.1	4.05	N 1.45 P 6.25	44.2	4.05	N 1.50 P 6.70	
$[Rh(etdp)_2(CO)][BPh_4]$	Yellow	103	65.85	5.20		65.8	5.05		
$[Rh(etdp)_2H(Br)][SbF_6]$	Off-white	133	45.35	3.60	N 2.10 Br 6.45	44.45	3.75	N 2.05 Br 5.80	
$[Rh(etdp)_2Br_2][SbF_6]$	Pale yellow	138	43.15	3.25	N 1.75 Br 11.45	43.0	3.45	N 1.95 Br 11.0	
$[Rh(C_8H_{12})(etdp)(CO)]$-$[SbF_6]$	Yellow	146	44.05	4.00		44.15	3.90		

[a] 1 × 10^{-4}—1 × 10^{-3} mol dm^{-3} in acetone. [b] Measured in benzene; calculated values are given in parentheses. [c] Two separate determinations gave values of 799 and 863.

TABLE 2

N.m.r. spectroscopic data (p.p.m.) and assignments [a]

Complex	Diene protons Olefinic	Diene protons Aliphatic	Ligand protons Aromatic	Ligand protons N–CH$_2$	Ligand protons CH$_3$
$[Rh_2(C_8H_{12})(etdp)Cl_2]$ [b]	3.91 (br s)	2.21 (br)	7.20 (m)	3.25 (m)	1.40 (t)
$[Rh_2(C_7H_8)(etdp)Cl_2]$ [b]	3.75 (br s)	1.06 (br s)	7.26 (m)	3.00 (m)	1.28 (t)
$[\{Rh(etdp)Cl\}_2]$ [b]			7.23 (m)	3.20 (m)	1.27 (t)
$[\{Rh(etdp)Br\}_2]$ [b]			7.23 (m)	3.13 (m)	1.28 (t)
$[\{Rh(etdp)I\}_2]$ [b]			7.20 (m)	3.15 (m)	1.27 (t)
$[Rh(etdp)_2][BPh_4]$ [b]			7.16 (m)	2.96 (m)	0.96 (t)
$[Rh(etdp)_2][SbF_6]$ [b]			7.30 (m)	3.03 (m)	1.0 (t)
$[Rh(C_8H_{12})(etdp)][SbF_6]$ [c]	4.96 (br s)	2.03 (br m)	7.53 (m)	3.63 (m)	1.53 (t)
$[Rh(C_8H_{12})_2][SbF_6]$ [c]	5.33 (br s)	2.56 (br s)			
$[Rh(etdp)_2(CO)][BPh_4]$ [b]			7.10 (m)	3.08 (m)	1.0 (t)
$[Rh(C_8H_{12})(etdp)(CO)][SbF_6]$ [b]	4.76 (br s)	1.86 (br)	7.23 (m)	3.50 (m)	1.26 (t)
$[Rh(etdp)_2Br_2][SbF_6]$ [b]			7.23 (m)	3.11 (m)	1.07 (t)

[a] br = Broad, m = multiplet, s = singlet, t = triplet. [b] Measured in CDCl$_3$ at 34 °C. [c] Measured in CD$_2$Cl$_2$ at 34 °C.

several minutes followed by slow addition of diethyl ether while continuing this passage led to the separation of a microcrystalline compound containing the cation $[Rh(C_8H_{12})(etdp)(CO)]^+$. More rigorous addition of CO over a longer period of time afforded a reaction mixture which from i.r. spectroscopic evidence contained a number of products including one containing bridging carbonyl groups. The ready rearrangement of these species prevented their separation and characterisation. Similar to $[Rh(etdp)_2(CO)]^+$, $[Rh(C_8H_{12})(etdp)(CO)]^+$ was found to readily lose CO, slowly in the solid state but rapidly in solution, to afford $[Rh(C_8H_{12})(etdp)]^+$.

Attempts to obtain $[Rh(etdp)_2H_2]^+$ by direct reaction of $[Rh(etdp)_2]^+$ with dihydrogen were unsuccessful irrespective of the method employed. Various solvents such as thf, alcohol, CH_2Cl_2, and diethyl ether, as well as high pressures of H_2 and high and ambient temperatures, were utilised but in all cases the starting material $[Rh(etdp)_2]^+$ was isolated intact. An earlier study [10] revealed a decrease in the stability of the dihydrides $[RhL_4H_2][BPh_4]$ along the series L = $PBu^n_3 > P(OMe)_3 > P(OPh)_3$ paralleling the decrease in the (δ–π) donor properties of these ligands but, although unstable to degradation, $[Rh\{P(OPh)_3\}_4H_2]$, unlike $[Rh(etdp)_2H_2]^+$, can be isolated.[11] In contrast to $[Rh(C_8H_{12})L_2]^+$ (L = tertiary phosphine or phosphite) and $[Rh(C_8H_{12})(L\text{–}L)]^+$ (L–L = ditertiary phosphine) which afford $[RhL_2(solvent)_2H_2]^+$ and $[Rh(L\text{–}L)(solvent)_2H_2]^+$ respectively on reaction with dihydrogen in weakly co-ordinating solvents such as acetone,[1] $[Rh(C_8H_{12})(etdp)]^+$ gave no evidence for the formation of $[Rh(etdp)(solvent)_2H_2]^+$ in an analogous reaction.

TABLE 3

Infrared spectroscopic data (cm^{-1})

Complex	Band	Assignment
$[Rh(etdp)_2(CO)][BPh_4]$	2 050 (Nujol mull)	ν(C–O)
	2 045 (in CH$_2$Cl$_2$)	ν(C–O)
$[Rh(C_8H_{12})(etdp)(CO)][SbF_6]$ *	2 059 (Nujol mull)	ν(C–O)
$[Rh(etdp)_2H(Br)][SbF_6]$ *	2 025 (Nujol mull)	ν(Rh–H)

* Decomposed too rapidly in solution for a spectrum to be obtained.

Treatment of $[Rh(etdp)_2]^+$ with HBr in solution also failed to afford an oxidative-addition product; work-up of the reaction mixture gave $[Rh(etdp)_2]^+$. However, dropwise addition of a diethyl ether solution of hydrobromic acid to a suspension of $[Rh(etdp)_2][SbF_6]$ in ether produced a new off-white complex, also insoluble in diethyl ether, which was characterised as $[Rh(etdp)_2H(Br)][SbF_6]$. The complex is stable in the solid state but decomposes readily in solution to $[Rh(etdp)_2][SbF_6]$ which accounts for the initial synthesis being unsuccessful. A Rh–H stretching frequency of 2 025 cm^{-1} is interpreted in terms of the complex adopting a *trans* configuration.[12,13]

Bromination of $[Rh(etdp)_2]^+$ in CH_2Cl_2 readily gave rise to the formation of the dibromide, $[Rh(etdp)_2Br_2]^+$, stable in both solution and the solid state.

EXPERIMENTAL

The complexes $[\{Rh(C_8H_{12})X\}_2]$ (X = Cl, Br, or I) and $[\{Rh(C_7H_8)Cl\}_2]$ were synthesised by established methods.[4,14] 2-Ethyltetraphenoxydiphosphazane was obtained by reaction of $Cl_2PN(Et)PCl_2$ [15] with phenol in diethyl ether in the presence of the base pyridine. All the experiments were carried out at room temperature under nitrogen. Yields of products varied from 60 to 80%.

The i.r. and ^{1}H n.m.r. spectra were recorded on a Perkin-Elmer model 457 grating spectrophotometer and on a Varian T-60 instrument respectively. Conductivities were determined using an Autobalance Universal Bridge conductometer. The elemental analyses and the molecular-weight determinations were performed by the Alfred Bernhardt Microanalytical Laboratory, Elbach-über-Engelskirchen, West Germany, by Mr. H. H. Lachmann of the National Chemical Research Laboratory, C.S.I.R., Pretoria, and by Mr. I. Antonowitz, Department of Chemistry, University of Natal, Pietermaritzburg.

(*a*) *Di-μ-chloro-cyclo-octa-*1,5-*diene*(2-*ethyltetraphenoxydiphosphazane*)*dirhodium*(I).—A solution of etdp (0.48 g, 1.0 mmol) in benzene (*ca.* 3 cm^3) was added dropwise to a stirred solution of $[\{Rh(C_8H_{12})Cl\}_2]$ (0.49 g, 1.0 mmol) in benzene (*ca.* 10 cm^3) and the stirring continued for 10 min. The solvent was removed under reduced pressure and the resulting oil washed with diethyl ether and crystallised from CH_2Cl_2–OEt_2.

(*b*) *Di-μ-chloro-bicyclo*[2.2.1]*hepta-*2,5-*diene*(2-*ethyltetraphenoxydiphosphazane*)*dirhodium*(I).—This complex was obtained by treating etdp (0.48 g, 1.0 mmol) with $[\{Rh(C_7H_8)Cl\}_2]$ (0.46 g, 1.0 mmol) according to the method outlined in (*a*). Crystallisation from CH_2Cl_2–OEt_2 gave an impure product.

(*c*) *Di-μ-chloro-bis*[(2-*ethyltetraphenoxydiphosphazane*)*rhodium*(I)].—A solution of etdp (0.95 g, 2.0 mmol) in benzene (*ca.* 5 cm^3) was added dropwise to a stirred solution of $[\{Rh(C_8H_{12})Cl\}_2]$ (0.49 g, 1.0 mmol) in benzene (*ca.* 15 cm^3) and the stirring continued for another 5 min. The solvent was removed under reduced pressure and the oily residue washed with ethanol and crystallised from CH_2Cl_2–EtOH or from benzene–light petroleum.

(*d*) *Di-μ-bromo- and Di-μ-iodo-*[*bis*(2-*ethyltetraphenoxydiphosphazane*)*rhodium*(I)].—The complexes were obtained by treating etdp (0.95 g, 2.0 mmol) with $[\{Rh(C_8H_{12})Br\}_2]$ (0.58 g, 1.0 mmol) or $[\{Rh(C_8H_{12})I\}_2]$ (0.68 g, 1.0 mmol) according to the method outlined in (*c*). In both cases crystallisation was effected from CH_2Cl_2–EtOH.

(*e*) *Bis*(2-*ethyltetraphenoxydiphosphazane*)*rhodium*(I) *Tetraphenylborate.*—A solution of etdp (0.6 g, 1.3 mmol) in methanol (*ca.* 5 cm^3) was added dropwise to a stirred suspension of $[\{Rh(C_8H_{12})Cl\}_2]$ (0.3 g, 0.3 mmol) in methanol (*ca.* 15 cm^3) and stirring continued until complete dissolution of $[\{Rh(C_8H_{12})Cl\}_2]$ had occurred. Dropwise addition of $Na[BPh_4]$ (0.26 g, 0.7 mmol) in methanol (*ca.* 5 cm^3) resulted in the precipitation of the complex, which was crystallised from CH_2Cl_2–MeOH.

(*f*) *Bis*(2-*ethyltetraphenoxydiphosphazane*)*rhodium*(I) *Hexafluoroantimonate.*—The complex was obtained by treating etdp (0.3 g, 0.6 mmol) with $[\{Rh(C_8H_{12})Cl\}_2]$ (0.06 g, 0.13 mmol) followed by the addition of $K[SbF_6]$ (0.21 g, 0.7 mmol) according to the method outlined in (*e*). Crystallisation was effected from CH_2Cl_2–EtOH.

(*g*) *Cyclo-octa-*1,5-*diene*(2-*ethyltetraphenoxydiphosphazane*)*rhodium*(I) *Hexafluoroantimonate.*—*Method* (*A*). A solution of $Ag[SbF_6]$ (0.27 g, 0.8 mmol) in acetone (*ca.* 10 cm^3) was added dropwise to a stirred solution of $[\{Rh(C_8H_{12})Cl\}_2]$ (0.20 g, 0.4 mmol) in acetone (*ca.* 20 cm^3) and the solution stirred for another 20 min. The AgCl which precipitated was filtered off. A solution of etdp (0.38 g, 0.8 mmol) in acetone (*ca.* 10 cm^3) was then added dropwise to the filtrate and stirring continued for another 10 min. The solvent was removed under reduced pressure and the oily residue washed with light petroleum and crystallised from CH_2Cl_2–light petroleum.

Method (*B*). A solution of $Ag[SbF_6]$ (0.14 g, 0.4 mmol) in acetone (*ca.* 10 cm^3) was added dropwise to a stirred solution of $[\{Rh(etdp)Cl\}_2]$ (0.26 g, 0.2 mmol) in acetone (*ca.* 10 cm^3) and the solution stirred for another 20 min. The AgCl which precipitated was filtered off. A solution of C_8H_{12} (0.04 g, 0.4 mmol) in acetone (*ca.* 5 cm^3) was then added dropwise to the filtrate and stirring continued for another 10 min. The product was isolated and purified as described in (*A*).

(*h*) *Carbonylbis*(2-*ethyltetraphenoxydiphosphazane*)*rhodium*(I) *Tetraphenylborate.*—A stream of CO was passed through a solution of $[Rh(etdp)_2][BPh_4]$ (0.3 g, 0.2 mmol) in CH_2Cl_2 (*ca.* 5 cm^3) for 5 min. Methanol (*ca.* 10 cm^3) was added to the solution and the CH_2Cl_2 removed under a stream of CO. The pale yellow microcrystalline complex which separated from solution was not purified further.

(*i*) *Carbonyl*(*cyclo-octa-*1,5-*diene*)(2-*ethyltetraphenoxydiphosphazane*)*rhodium*(I) *Hexafluoroantimonate.*—A stream of CO was passed through a solution of $[Rh(C_8H_{12})(etdp)][SbF_6]$ (0.43 g, 0.5 mmol) in CH_2Cl_2 (*ca.* 10 cm^3) at a slow rate for 10 min. Diethyl ether (*ca.* 50 cm^3) was added and the passage of carbon monoxide continued until a yellow microcrystalline product separated. This was not purified further.

(*j*) *Bromobis*(2-*ethyltetraphenoxydiphosphazane*)*hydridorhodium*(III) *Hexafluoroantimonate.*—Dropwise addition of diethyl ether solution (*ca.* 5 cm^3) of hydrobromic acid (0.9 mmol) to a stirred suspension of $[Rh(etdp)_2][SbF_6]$ (0.5 g, 0.4 mmol) in diethyl ether (*ca.* 10 cm^2) led to the formation of a new off-white microcrystalline solid which remained suspended in the ether. The solid was isolated, washed with cold diethyl ether, and dried thoroughly.

(*k*) *Dibromobis*(2-*ethyltetraphenoxydiphosphazane*)*rhodium*(III) *Hexafluoroantimonate.*—A solution of Br_2 (0.07 g, 0.42 mmol) in CH_2Cl_2 (*ca.* 5 cm^3) was added dropwise to a stirred solution of $[Rh(etdp)_2][SbF_6]$ (0.52 g, 0.4 mmol) in CH_2Cl_2 (*ca.* 10 cm^3) and the solution stirred for another 10 min. The solvent was removed under reduced pressure and the oily residue washed with cold ethanol and crystallised from CH_2Cl_2–OEt_2.

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