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^{31}P NMR Studies of *cis*-[RhCl(CO)(bis-phosphine)] Complexes

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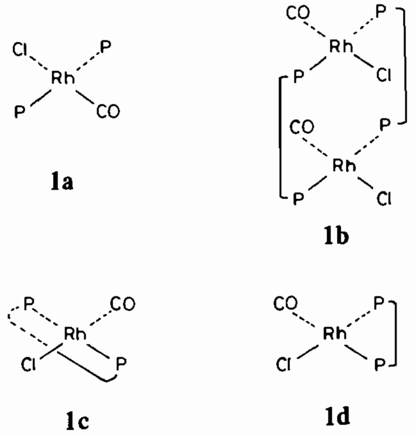
Abstract

Further examples of complexes with the previously unique *cis*-chelated [RhCl(CO)(bis-phosphine)] structure are reported where bis-phosphine = $R_2P(C_2B_{10}H_{10})PR'_2$ with R and R′ = C_6H_5 or NMe_2. In the unsymmetrical R ≠ R′ example only the isomer with PPh_2 *trans* to Cl is formed. These complexes as well as the analogous dppe complex show interesting fluxional behavior under CO implying the existence of a five-coordinate $[RhCl(CO)_2(\text{bis-phosphine})]$ species. The compound *trans*-[RhCl(CO){$Ph_2P(C_2B_{10}H_{10})H$}$_2$] is also described.

Introduction

Rhodium carbonyl chloride complexes with either two monodentate phosphine ligands or one bidentate phosphine ligand are probably the most readily characterized class of rhodium(I) complexes with tertiary phosphine ligands. They are of great interest because of their catalytic activity, e.g. hydroformylation. With monodentate phosphines, *trans* monomeric complexes (Fig. 1, **1a**) are formed exclusively; they are readily recognized by their ν(CO) stretching frequency of 1950–1975 cm^{-1} characteristic of CO *trans* to Cl, and by their ^{31}P NMR spectra indicating two magnetically equivalent phosphorus atoms with $^1J(RhP)$ of approximately 120 Hz [1]. The chloro ligand may easily be exchanged by metathesis for a wide range of other anionic ligands [2]. With bidentate phosphines, three structural types of complex have been well established; *trans*-bridged, *trans*-chelated and *cis*-chelated (Fig. 1, **1b**, **1c**, **1d** respectively). *Trans*-bridged dimeric complexes with bidentate phosphines (**1b**) are formed most commonly, e.g. with $Ph_2P(CH_2)_nPPh_2$ (n = 1, 3, 4), with *cis*-$Ph_2PCH{=}CHPPh_2$, with (+) – diop [3], with $(t\text{-}Bu)_2P(CH_2)_{10}P(Bu\text{-}t)_2$ [4] and with many other bis-phosphine ligands [5]. *Trans*-chelated monomeric complexes (**1c**) have been reported for the rigid backbone ligand 2,11-bis(diphenylphosphinomethyl)-benzo[c]phenanthrene [6], $Ph_2P(CH_2CH_2O)_mCH_2CH_2PPh_2$ (m = 1, 2, 3) [7] and $Ph_2P(o\text{-}C_6H_4)(CH_2)_2(o\text{-}C_6H_4)PPh_2$ [8]. The only *cis*-chelated complex previously reported is *cis*-[Rh(Cl)(CO)($Ph_2P(CH_2)_2PPh_2$)] [3]. This unique example is easily distinguished from the *trans* analogs by the higher ν(CO) stretching frequency (2010 cm^{-1}, CO *trans* to P) and by the ^{31}P NMR spectrum which exhibits a doublet of doublets for each non-equivalent phosphorus (Table I).



1a

1b

1c

1d

Fig. 1. Structures observed for rhodium(I) carbonyl chlorides with phosphines.

We now wish to report further examples of the *cis*-chelated structure and NMR studies of their fluxional behavior under a CO atmosphere. We have also noted remarkable fluxional behavior of the $Ph_2P(CH_2)_2PPh_2$(dppe) complex in a CO atmosphere.

Results and Discussion

The complex [RhCl(CO){$Ph_2P(C_2B_{10}H_{10})PPh_2$}] readily separates in high yield as a bright yellow microcrystalline powder from a solution of $[Rh(cod)Cl]_2$ and $Ph_2P(C_2B_{10}H_{10})PPh_2$ in benzene upon saturation with CO gas. The compound is stable in air, very soluble in chloroform and dichloromethane but sparingly soluble in benzene, toluene, methanol,

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TABLE I. $^{31}P\{^1H\}$ NMR and Infrared Spectra of the Complexes

Complex	ν(CO) (cm^{-1})	δ_P (ppm)^a	^1J(RhP) (Hz)	^2J(PP) (Hz)	$\Delta\delta$ (ppm)^b
cis-[RhCl(CO)dppe]	2010^c	+48.8^e +70.3^f	124 158	34	+64.0 +85.8
cis-[RhCl(CO){$Ph_2P(C_2B_{10}H_{10})PPh_2$}]	2031^c	+76.0^e +90.1^f	139 171	41	+67.8 +81.9
cis-[RhCl(CO){$Ph_2P(C_2B_{10}H_{10})P(NMe_2)_2$}]	2030^d	+75.9^{e,g} +123.4^{f,g}	148 197	40	+58.6 +19.7
cis-[RhCl(CO){$(Me_2N)_2P(C_2B_{10}H_{10})P(NMe_2)_2$}]	2045^d	+139.2^e +151.4^f	178 211	43	+32.7 +44.4
trans-[RhCl(CO){$Ph_2P(C_2B_{10}H_{10})H$}$_2$]	1996^c	+49.1	140		+23.9

^{a}Relative to 85% H_3PO_4 in $CDCl_3$ solution unless otherwise stated. ^{b}Coordination shift $\Delta\delta = \delta$ (complex) $- \delta$ (free ligand). ^{c}Nujol mull. ^{d}$CDCl_3$ solution. ^{e}P *trans* to Cl. ^{f}P *trans* to CO. ^{g}CD_2Cl_2 solution.

or ethanol. The infrared spectrum of the solid shows a strong sharp band at 2031 cm^{-1} (ν(CO)); in chloroform solution a broader band appears at *ca.* 2045 cm^{-1}. This relatively high stretching frequency is indicative of CO *trans* to P (*i.e. cis* geometry). The higher value, compared to that for the dppe complex, reflects the higher electronegativity of the carboranyl ligand backbone. Under a nitrogen atmosphere the $^{31}P\{^1H\}$ NMR spectrum of a $CDCl_3$ solution of the complex shows the expected doublet of doublets for each non-equivalent phosphorus atom (Table I, Fig. 1, **1d**). The doublet of doublets centered at +76.0 ppm (^1J(RhP) = 139 Hz) is assigned to the PPh_2 group *trans* to the π-acceptor CO ligand. The pattern is qualitatively similar to that observed for the dppe complex, the larger ^1J(RhP) values suggesting shorter Rh–P bond lengths, consistent with the greater electronegativity of the carboranyl ligand backbone [10]. The very large coordination chemical shifts are consistent with the values generally found when five-membered chelate rings are formed [11]. Conductivity of a 10^{-3} M solution of the complex in nitromethane is 1.1 ohm^{-1} cm^2 mol^{-1} indicating negligible ionization.

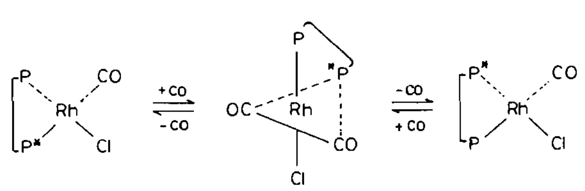

Fig. 2. Fluxional behavior of *cis*-complexes under CO.

Under one atmosphere of CO the $^{31}P\{^1H\}$ NMR spectrum in $CDCl_3$ solution collapses to one very broad signal (*ca.* 1000 Hz or 30 ppm width) centered at +83 ppm – the average of the original ($\delta^{31}P$) values. Upon cooling the solution to about –50 °C the very broad signal begins to resolve into two broad signals, and in a similar CD_2Cl_2 solution at –90 °C further resolution occurs into the same eight lines observed under a nitrogen atmosphere. Increasing the CO concentration by bubbling CO into the solution at –78 °C makes it impossible to resolve the broad signal even at –100 °C. Decreasing the CO concentration by purging the solution with nitrogen restores the original eight-line spectrum. These observations suggest that the process shown in Fig. 2 is occurring at a rate comparable to the NMR time scale. Of course, if CO enters into the equatorial site of the trigonal bipyramidal intermediate and departs from the same site, there is no equilibration of the two phosphorus donors without invoking pseudorotation of the five-coordinate intermediate. The equilibrium concentration of the five-coordinate species must be extremely small since it is spectroscopically undetectable. Conductivity of a 10^{-3} M solution of the complex in nitromethane under a CO atmosphere is 3.74 ohm^{-1} cm^2 mol^{-1} again indicating negligible ionization.

In view of these results, we have studied the behavior of the analogous dppe complex in $CDCl_3$ solution under a CO atmosphere and indeed observed fluxional behavior. The characteristic eight-line spectrum collapses to a sharp doublet under one atmosphere of CO (δ = +59.6 ppm, ^1J(RhP) = 141 Hz). These values are the average of those observed for the two non-equivalent P nuclei under nitrogen. Therefore, the P *trans* to Cl and P *trans* to CO are in fast exchange presumably by the formation of the five-coordinate intermediate as described above for the $Ph_2P(C_2B_{10}H_{10})PPh_2$ case. The fluxional process must be intramolecular since rhodium–phosphorus coupling is never lost. Again the equilibrium concentration of the five-coordinate species must be very low since the chemical shift and coupling constant observed in the fast exchange case are very near the average of the value under nitrogen where no exchange occurs. Interestingly corresponding fluxional five-coordinate iridium analogs, [$IrX(CO)_2$(dppe)] (X = Br, I), have been reported [12].

In the dppe case, bubbling nitrogen through the solution for one minute reduced the CO concentration thereby slowing the rate of the fluxional process (Fig. 2). This is evidenced by the disappearance of the sharp doublet and the appearance of two broad humps. Complete removal of CO by prolonged nitrogen purging restores the characteristic eight-line spectrum. These observations are consistent with a faster exchange process for dppe compared to the $Ph_2P(C_2B_{10}H_{10})PPh_2$ complex.

With the unsymmetrical ligand, $Ph_2P(C_2B_{10}H_{10})P(NMe_2)_2$, the complex *cis*-[RhCl(CO){$Ph_2P(C_2B_{10}H_{10})P(NMe_2)_2$}] could not be isolated in the solid state. Evaporation of the solution produced by the reaction of $[Rh(cod)Cl]_2$ with bis-phosphine under CO gives an orange–red oil which solidifies on scratching. This product contains no CO (infrared). However *in situ* preparation (see 'Experimental') in $CDCl_3$ under CO gives a poorly resolved ^{31}P NMR spectrum containing four broad peaks. Upon purging the solution for a few seconds with nitrogen, the spectrum resolves into eight sharp lines (Table I), the δ and J values are convincing evidence for the formation of a *cis*-chelated complex. The infrared spectrum of the solution showed the expected ν(CO) at 2030 cm^{-1}.

With this unsymmetrical ligand, two isomers of *cis*-[RhCl(CO){$Ph_2P(C_2B_{10}H_{10})P(NMe_2)_2$}] are possible. The $^{31}P\{^1H\}$ NMR spectrum clearly shows that the only isomer formed contains PPh_2 *trans* to Cl. The signal centered at +75.9 ppm is assigned to the PPh_2 group by analogy with *cis*-RhCl(CO){$Ph_2P(C_2B_{10}H_{10})PPh_2$}] ($\delta$ = +76.0). The signal at +123.4 ppm is therefore assigned to the $P(NMe_2)_2$ group and the larger ^1J(RhP) value is consistent with this being *trans* to CO. The two magnetically non-equivalent phosphorus atoms show a ^2J(PRhP) of 40 Hz. Interestingly the free ligand, $Ph_2P(C_2B_{10}H_{10})P(NMe_2)_2$, has a ^3J(PCCP) of 120 Hz. Thus ^2J(PRhP) and ^3J(PCCP) must have different signs. Different signs for J(PP) coupling via ligand backbone and via metal have also been noted for complexes of platinum(II) [13] and of chromium(0), molybdenum(0) and tungsten(0) [11c].

Further confirmation of these assignments is provided by the analogous *in situ* preparation of *cis*-[RhCl(CO){$(Me_2N)_2P(C_2B_{10}H_{10})P(NMe_2)_2$}]. The two $P(NMe_2)_2$ groups show NMR behavior analogous to that observed for two PPh_2 groups attached to a carboranyl backbone (Table I).

We have also prepared *trans*-[RhCl(CO){$Ph_2P(C_2B_{10}H_{10})H$}$_2$] (**1a**). Under a nitrogen atmosphere the $^{31}P\{^1H\}$ NMR spectrum consists of a sharp doublet (δ = +49.1 ppm, ^1J(RhP) = 140 Hz). Under a CO atmosphere the two lines broaden considerably. However, this broadening under CO is not a general phenomenon for all rhodium carbonyl chloride complexes: the *trans*-bridged dimers (**1c**) with $Ph_2P(CH_2)_nPPh_2$ (n = 4, 6, 10, 12) in $CDCl_3$ under one atmosphere of CO at room temperature exhibit sharp lines [14].

Experimental

$[Rh(cod)Cl]_2$ and [RhCl(CO)(dppe)] and ligands were prepared as previously described [9, 15, 16]. Infrared spectra were recorded as nujol mulls or in $CDCl_3$ solutions on a Perkin-Elmer Model 580 Spectrophotometer. $^{31}P\{^1H\}$ NMR spectra were measured on a Varian CFT 20 spectrometer operating at 32.1 MHz. Conductivity measurements were made in nitromethane solutions.

cis-[RhCl(CO){$Ph_2P(C_2B_{10}H_{10})PPh_2$}]

$[Rh(cod)Cl]_2$ (0.369 g, 0.75 mmol) and $Ph_2P(C_2B_{10}H_{10})PPh_2$ (0.768 g, 1.5 mmol) were dissolved under CO (1 atm.) in C_6H_6 (25 ml). Carbon monoxide was bubbled through the solution for 0.5 h and then the solution was stirred for 4 h during which time the yellow product separated. Low boiling petroleum ether (25 ml) was added and the mixture was cooled to 0 °C and stirred for a further 0.5 h. The bright yellow microcrystalline product was collected by filtration. Yield 0.92 g, 90%. *Anal.* Calc. for $C_{27}H_{30}B_{10}C_{10}P_2Rh$: C, 47.8; H, 4.42. Found: C, 47.3; H, 4.52%.

trans-[RhCl(CO){$Ph_2P(C_2B_{10}H_{10})H$}$_2$]

By use of a similar procedure with $[Rh(cod)Cl]_2$ (0.246 g, 0.5 mmol) and $Ph_2P(C_2B_{10}H_{10}H)$ (0.657 g, 2.0 mmol) in C_6H_6 (20 ml) under CO a clear orange–yellow solution resulted. The product was isolated by concentrating the solution to 7 ml, adding low boiling petroleum ether (50 ml) and filtering. Yield 0.41 g, 50%. A second crop of identical material may be obtained by adding more petroleum ether to the filtrate. *Anal.* Calc. for $C_{29}H_{42}B_{10}ClOP_2Rh$: C, 42.3; H, 5.1; Cl, 4.3. Found: C, 42.7; H, 4.8; Cl, 4.6%.

cis-[RhCl(CO){$Ph_2P(C_2B_{10}H_{10})P(NMe_2)_2$}] and cis-[RhCl(CO){$(Me_2N)_2P(C_2B_{10}H_{10})P(NMe_2)_2$}]

Attempts to isolate these complexes by the above procedure gave materials containing no CO (infrared). However *in situ* preparations in an 8 mm NMR tube using $[Rh(cod)Cl]_2$ (0.1 mmol) and ligand (0.2 mmol) in either C_6D_6, CD_2Cl_2 or $CDCl_3$ under CO (1 atm.) gave clear orange–yellow solutions used for NMR and infrared studies. Excess CO is removed by a nitrogen purge.

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