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A RHODIUM(I) DERIVATIVE OF DIETHYL(DIPHENYLPHOSPHINOMETHYL)AMINE AS A LIGAND FOR THE SYNTHESIS OF HOMO- AND HETERO-DINUCLEAR COMPLEXES

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Summary

The reaction of $[Rh(\mu\text{-}Cl)(CO)(C_2H_4)]_2$ with diethyl(diphenylphosphinomethyl)amine (ddpa) (1 : 4) yields $RhCl(CO)(ddpa)_2$, a mononuclear complex able to act as ligand towards a second metal through its uncoordinated nitrogen atom. Two examples are described, namely the reaction with $[Rh(\mu\text{-}Cl)(CO)_2]_2$ leading to $Rh_2(\mu\text{-}Cl)Cl(\mu\text{-}CO)(CO)(\mu\text{-}ddpa)_2$ and that with $PdCl_2(COD)$ (COD = 1,5-cyclooctadiene) to $PdRh(\mu\text{-}Cl)Cl_2(CO)(\mu\text{-}dppa)_2$. In both homo- and hetero-dinuclear complexes, the ligand is thought to retain a head-to-head arrangement.

Introduction

In the last decade the availability of bridging ligands such as bis(diphenylphosphino)methane (dppm) [1,2], 2-(diphenylphosphino)pyridine (Ph_2Ppy) [3,4], 2-(bis(diphenylphosphino)methyl)pyridine (PNP) [5] and bis(diphenylphosphino)amine [6] that can hold two metal atoms in close proximity has led to the synthesis of new dinuclear complexes showing specific reactivities. In this context we have examined the potential of diethyl(diphenylphosphinomethyl)amine (ddpa), a bridging ligand which contains soft and hard base centres, namely phosphorus and nitrogen donor atoms, and we have recently reported the preparation and properties of homobinuclear platinum and palladium derivatives [7]. Like 2-(diphenylphosphino)pyridine, this ligand can act primarily as a phosphorus monodentate ligand whose uncoordinated nitrogen atom can bond to a second metal centre. We describe here the stepwise construction of binuclear Rh–Rh and Rh–Pd transition metal complexes.

The use of a bidentate ligand with different donor sites to form binuclear metal complexes creates new types of structural variation which are not possible with a symmetrical ligand such as dppm. For homobinuclear complexes, two structural

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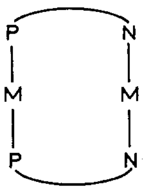
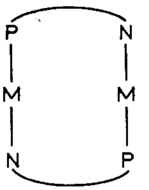
types are expected, namely head-to-head (**a**) and head-to-tail (**b**) structures:



(a)



(b)

If the two metals are different then the head-to-head complex can exist as two isomers (**a** and **a′**), differing in the location of the two metal ions in the coordination sites.

Results

Mononuclear complex of rhodium

Reaction of di-μ-chlorodicarbonyldiethylene dirhodium with ddpa in a 1 : 4 mol ratio in dichloromethane yields a solution showing only a terminal CO band (1970 cm^{-1}) and a low frequency band at 380 cm^{-1} assigned to ν(Rh–Cl). The $^{31}P\{^1H\}$ NMR spectra (solvent CH_2Cl_2/CD_2Cl_2) show a doublet centred at 17.6 ppm with ^1J(P–Rh) 125 Hz. The ^1H NMR spectrum (solvent CD_2Cl_2) consists of a triplet centred at 0.86 ppm (J 7.1 Hz), a quadruplet centred at 2.80 ppm (J 7.1 Hz), a singlet at 3.76 ppm, and two signals centred at 7.39 and 7.81 ppm. The integrated signals from the CH_3, CH_2, and (N)CH_2(P) protons were in the correct ratio (3 : 2 : 1). The appearance of a singlet for the protons of CH_2 coordinated to N and P was surprising.

The $^{31}P\{^1H\}$ (for data, see Table 1) and ^1H (for data, see Table 2) spectra show no obvious change when the temperature is lowered from 295 to 173 K. Although the $^{31}P\{^1H\}$ NMR spectrum of RhCl(CO)(ddpa)$_2$ in the presence of excess ddpa shows no obvious change when the temperature is lowered from 293 to 183 K, significant changes are observed in the ^1H NMR spectrum, arguing in favor of an exchange between the free ligand and the complex. As shown in Fig. 1, at 294 K the signals of RhCl(CO)(dppa)$_2$ and ddpa are superimposed, whereas at 188 K these signals are separated, but they are not well resolved and doublets are not observed.

TABLE 1

SPECTROSCOPIC DATA

Compound	$^{31}P\{^1H\}$ NMR		IR	
	δ (ppm)	J(Rh–P) (Hz)	ν(CO) (cm^{-1})	ν(M–Cl) (cm^{-1})
RhCl(CO)(ddpa)$_2$	17.6 [a]	125 [a]	1970 [b]	380 [c]
$Rh_2(\mu$-Cl)Cl(μ-CO)(CO)(μ-ddpa)$_2$	37.8 [a]	140 [a]	1760,1990 [c]	240,285 [c]
(species **2**)	38.4 [d]	143 [d]	1760,1990 [b]	
			1760,1990 [e]	
PdRhCl$_3$(CO)(μ-ddpa)$_2$	39.8 [a]	107 [a]	2070 [b]	250,275,320 [c]

[a] External ref. H_3PO_4 in D_2O; solvent CH_2Cl/CD_2Cl_2. [b] In CH_2Cl_2 solution. [c] Solid state CsBr. [d] Solvent $C_6D_5CD_3$. [e] Solvent $C_6H_5CH_3$.

TABLE 2

^1H NMR DATA

Compound	Solvent	Ethyl group		PCH$_2$N $\delta(CH_2)$ (ppm)	^2J(PCH) (Hz)
		$\delta(CH_3)$ (ppm)	$\delta(CH_2)$ (ppm)		
$(C_6H_5)_2PCH_2N(CH_2CH_3)_2$ (= ddpa)	CD_2Cl_2	0.98(t)	2.69(q)	3.29(d)	4
$(C_6H_5)_2P(O)CH_2N(CH_2CH_3)_2$	CD_2Cl_2	0.90(t)	2.66(q)	3.29(d)	6
	$CDCl_3$	0.868(14)	2.63(14)	3.286(d)(14)	6.5(14)
RhCl(CO)(ddpa)$_2$	CD_2Cl_2	0.86(t)	2.80(q)	3.76(s)	
Rh$_2$(μ-Cl)Cl(μ-CO)(CO)(μ-ddpa)$_2$ (species **2**)	CD_2Cl_2	1.34(t)	2.98(q)	3.55 or 3.64(d)	6

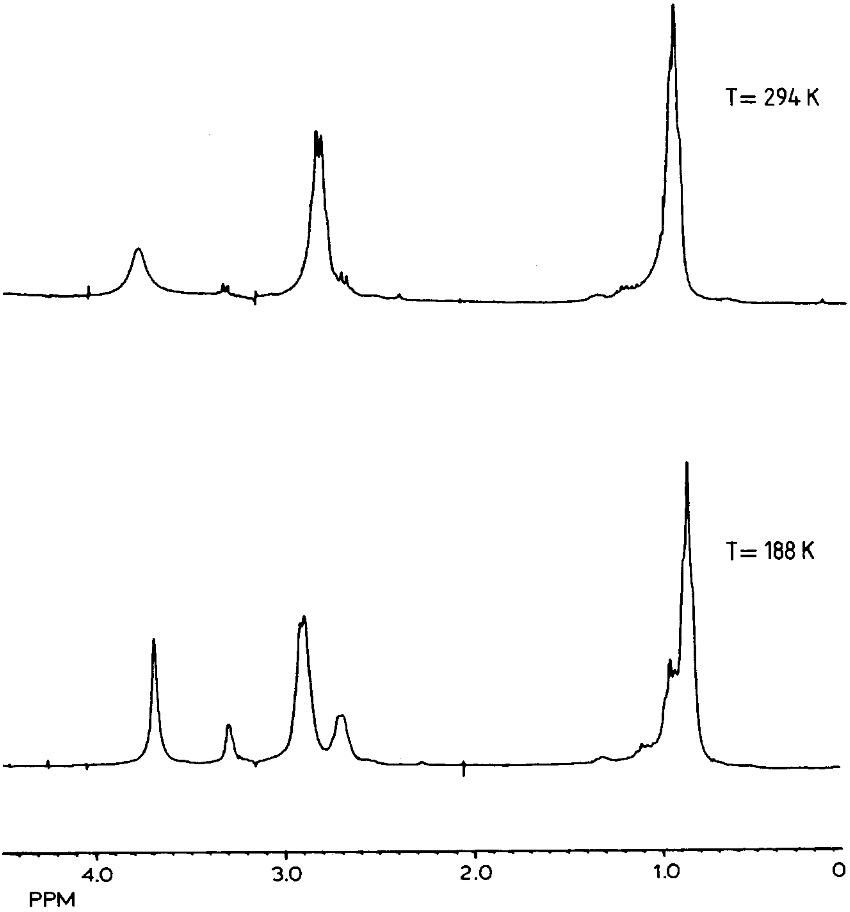


Fig. 1. ^1H NMR spectra of a mixture of RhCl(CO)(ddpa)$_2$ and ddpa in CD_2Cl_2 at selected temperatures.

The complex is stable in solution but decomposes when crystallization is attempted. Nevertheless, in these solutions, in which no free phosphine can be detected, we assume the reaction to be analogous to that of $[Rh(\mu\text{-}Cl)(CO)_2]_2$ with Ph_2Ppy, which produces $RhCl(CO)(Ph_2Ppy)_2$ [8] (ν(CO) 1969 cm^{-1}, ν(Rh–Cl) 304 cm^{-1}; $^{31}P\{^1H\}$ in chloroform: δ 30.13 ppm, ^1J(Rh–P) 127.8 Hz) and we identify the product complex as $RhCl(CO)[Ph_2PCH_2N(C_2H_5)_2]_2$ (**1**).

Thus, like Ph_2Ppy, ddpa retains a free end for coordination to another centre.

Dinuclear complex of rhodium

Addition of di-μ-chlorotetracarbonyl dirhodium to ddpa in a 1 : 2 mol ratio in dichloromethane yields many products.

The $^{31}P\{^1H\}$ NMR spectra in dichloromethane solution contain numerous signals: a doublet at 37.8 ppm (J 140 Hz) (species **2**), a singlet at 28.4 ppm (phosphine oxide) and a broad signal at 17 ppm in the region associated with the

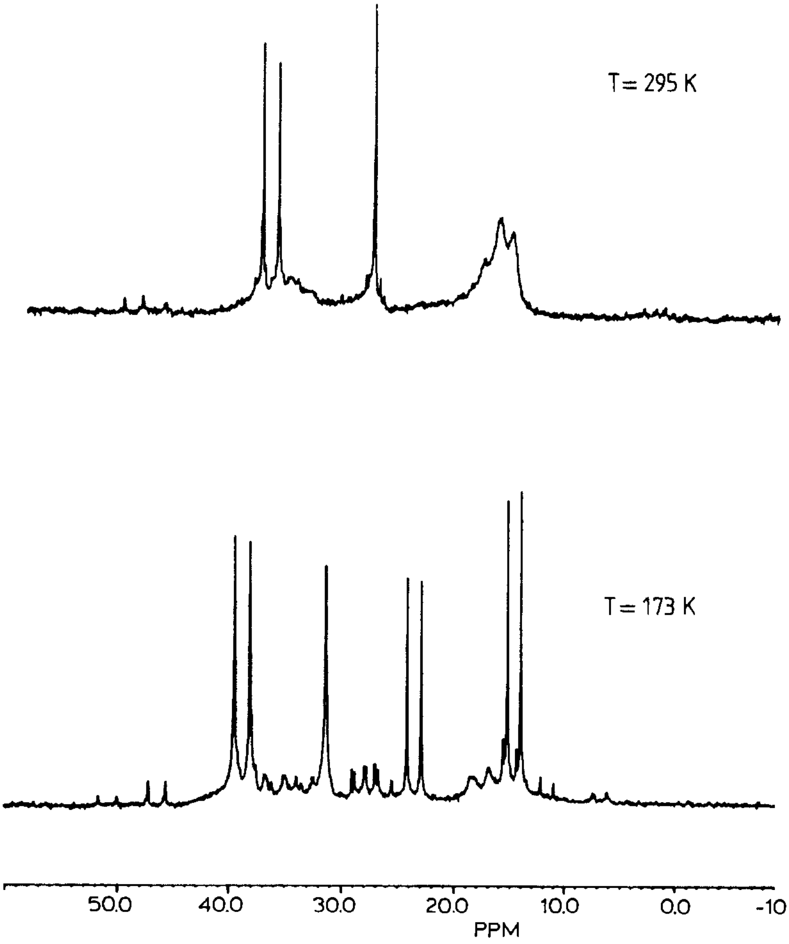


Fig. 2. $^{31}P\{^1H\}$ NMR spectra of species in CD_2Cl_2 at selected temperatures.

mononuclear species. The results of a variable temperature study (Fig. 2) still show the presence of a doublet at 38.8 ppm, and in addition an exchange between the mononuclear species and a species at 23.5 ppm (*J* 127 Hz) (species **3**).

The IR spectra in dichloromethane show a CO band at 1970 cm^{-1} characteristic

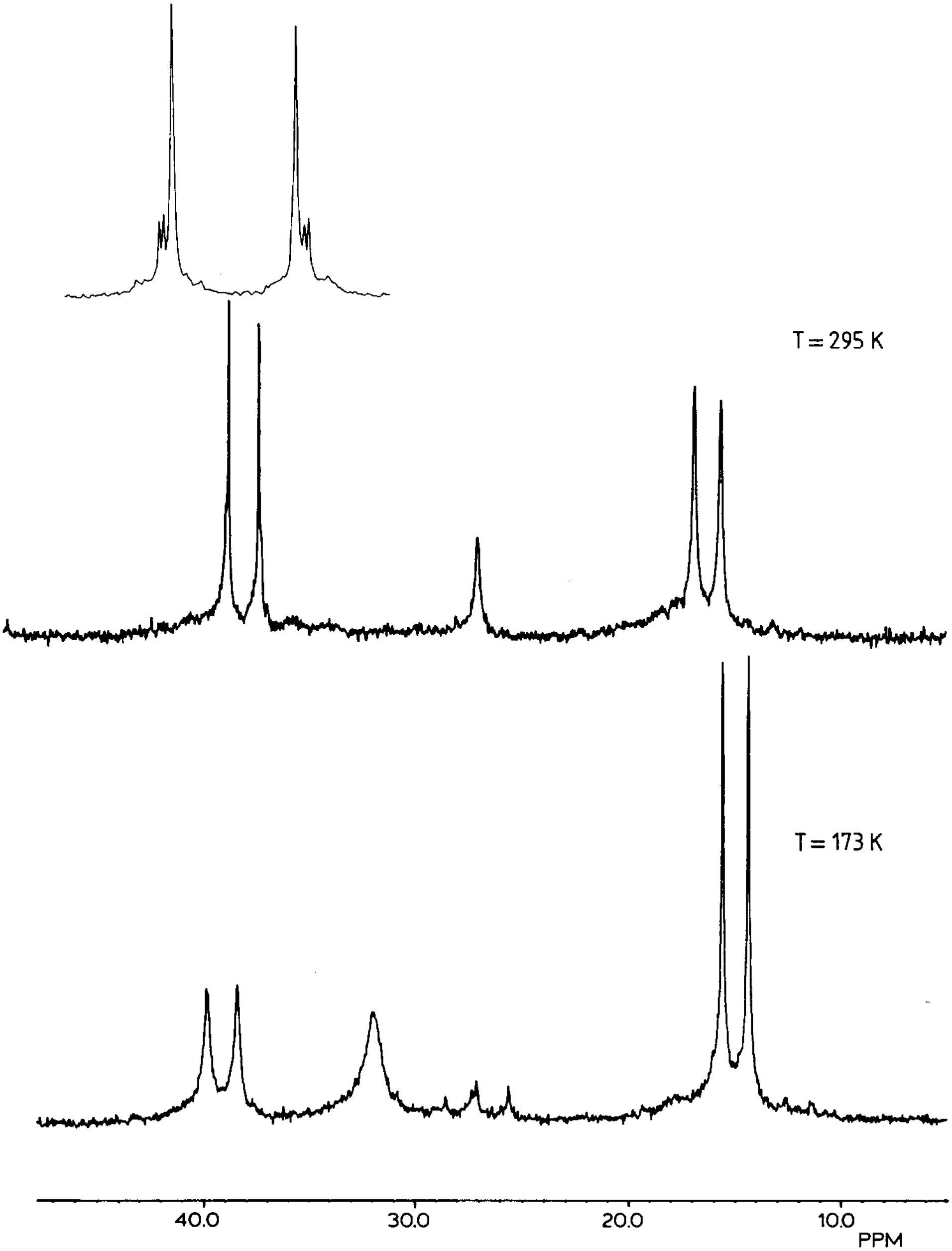


Fig. 3. $^{31}P\{^1H\}$ NMR spectra of species in $C_6D_5CD_3$ at selected temperatures.

of a mononuclear species but also four CO bands at 1760, 1850, 1990 and 2070 cm^{-1}.

It was possible to crystallize species **2** from toluene. The $^{31}P\{^1H\}$ NMR spectrum in deuterated toluene mainly consists of a doublet at 38.4 ppm (*J* 143 Hz) together with signals from the mononuclear species and a minor amount of the phosphine oxide.

Cooling to 173 K caused no change in the $^{31}P\{^1H\}$ NMR spectrum (Fig. 3) except in the ratio of the mononuclear species to species **2**. The IR spectrum in toluene contains the usual CO band at 1970 cm^{-1} but only two additional CO bands, at 1760 and 1990 cm^{-1}.

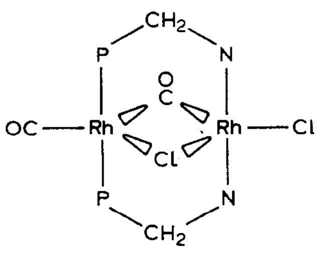
The ^1H NMR spectrum in deuterated toluene shows in the ddpa methylene region a triplet at 1.06 ppm (NCH_2CH_3), a quadruplet at 2.85 ppm (NCH_2CH_3), a doublet at 3.29 ppm (*J* 6Hz) and a singlet at 4.55 ppm. The last two signals for the protons of the (NCH_2P) group cannot be attributed specifically to any of the species present in solution, namely dinuclear **2**, phosphine oxide **4**, or mononuclear **1**. ^{31}P spectroscopy involving selective irradiation of **1**, **2** or **4** reveals exchange reactions. The low exchange rate spectrum cannot be obtained by lowering the temperature.

The various signals in the ^1H NMR spectrum in deuterated dichloromethane can be attributed to the several species present in solution. The two doublets at 3.55 and 3.64 ppm can be attributed to the protons of the (NCH_2P) group of **2** (^{31}P NMR 37.8 ppm) and **3** (^{31}P NMR 23.5 ppm).

A complex may be isolated by evaporation of the dichloromethane solution then recrystallized from toluene as brown crystals analysing for $Rh_2Cl_2(CO)_2(ddpa)_2$. The conductivity (16.2 Ω^{-1} cm^2 mol^{-1}) in acetone is consistent with a molecular species. The IR spectrum in the solid state shows one terminal CO band at 1990 cm^{-1}, one bridging CO band at 1760 cm^{-1}, and two Rh–Cl bands at 240 and 285 cm^{-1}. This spectrum is similar to that in toluene. The species isolated as solids have been identified by NMR as species **2**.

The conductivity data precluding an ionic structure, the discussion can be limited to molecular structures. A structure of type **2** or **2′** is in agreement with the presence of two equivalent phosphorus, one terminal CO band, one bridging CO band, and also of nonequivalent protons if a fast exchange is assumed. Structure **2** is supported by the increase of the CO frequency on going from the mononuclear to the dinuclear species.

Species **3**, which was only present in dichloromethane and was characterized by a ^{31}P signal at 23.5 ppm (*J* 127 Hz) and CO bands at 1850 and 2070 cm^{-1} could not be identified.



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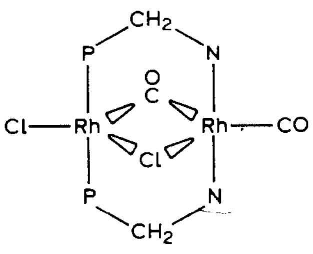

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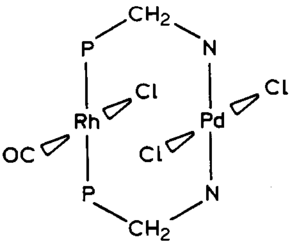
Rhodium–palladium dinuclear complex

The complex $RhCl(CO)[Ph_2PCH_2N(C_2H_5)_2]_2$ (**1**) can likewise act as a ligand toward $PdCl_2(COD)$ (**5**) (COD = 1,5-cyclooctadiene). Reaction of the palladium complex with an equimolar quantity of **1** in dichloromethane gives a solution showing one terminal CO frequency (2070 cm^{-1}). The proton-decoupled ^{31}P NMR spectrum primarily consists of a doublet centred at 39.8 ppm (solvent: CH_2Cl_2/CD_2Cl_2) with $^1J(P\text{–}Rh)$ 107 Hz (together with other minor species).

Orange crystals can be precipitated then separated and dried under vacuum. From the analytical data they are identified as $PdRhCl_3(CO)[Ph_2PCH_2\text{-}N(CH_2CH_3)_2]_2$. The conductivity (8.6 Ω^{-1} cm^2 mol^{-1} in nitromethane) is consistent with a molecular species. The IR spectrum of the solid shows one band at 320 cm^{-1} and two overlapping bands at 275 and 250 cm^{-1}.

The most acceptable structures consistent with the presence of two equivalent phosphorus atoms and one terminal CO band are shown below.



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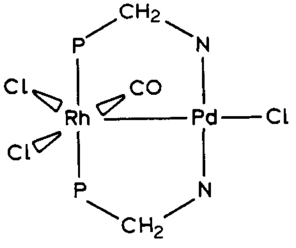
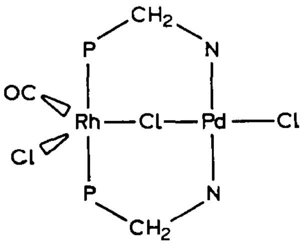


7 and isomer



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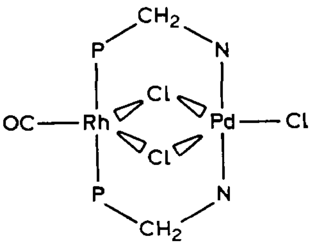

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If the shoulder at 250 cm^{-1} is attributed to a bridged Rh–Cl bond, structures **6** and **7** with only terminal chlorine ligands must be rejected. As previously observed [8,9], the coupling constant $^1J(Rh\text{–}P)$ is sensitive to oxidation state and coordination geometry. The rather low value observed for compounds **1** and **2** suggests a structure such as **8** and **9**. If the band at 275 cm^{-1} is attributed to a terminal chlorine ligand, then structure **8** is preferable. Crystallographic confirmation of this is desirable.

Experimental

The ^1H and $^{31}P\{^1H\}$ NMR spectra were recorded on a Bruker 250 (250.13 MHz). Proton chemical shifts are positive downfield relative to external tetramethylsilane.

Positive phosphorus chemical shifts are downfield relative to H_3PO_4. Infrared spectra were recorded on a Perkin-Elmer 225 spectrometer.

The preparations of diethyl(diphenylphosphinomethyl)amine (ddpa) [10], $Rh_2(\mu\text{-}Cl_2)(C_2H_4)_4$ [11], $Rh_2(\mu\text{-}Cl_2)(CO)_2(C_2H_4)_2$ [12], and $PdCl_2$(1,5-COD) [13] (1,5-COD = cyclooctadiene) have been described previously. All reactions were carried out under argon with deoxygenated solvents.

$RhCl(CO)Ph_2PCH_2N(C_2H_5)_2]_2$

A solution of $Rh_2(\mu\text{-}Cl_2)(CO)_2(C_2H_4)_2$ (216 mg, 0.51 mmol) in 4 cm^3 of dichloromethane was rapidly added to a solution of ddpa (603 mg, 2.22 mmol) in dichloromethane (1 cm^3). Gas was evolved for 10 min, and the mixture was stirred for 2 h. Addition of ether precipitated white crystals of $RhCl(CO)[Ph_2PCH_2N(C_2H_5)_2]_2$, which decomposes rapidly to give a syrupy liquid.

Addition of $Rh_2(\mu\text{-}Cl_2)(CO)_4$ to $Ph_2PCH_2N(C_2H_5)_2$ (1 : 4) also yields $RhCl(CO)[Ph_2PCH_2N(C_2H_5)_2]_2$.

$Rh_2Cl_2(CO)_2[Ph_2PCH_2N(C_2H_5)_2]_2$

A solution of $Rh_2(\mu\text{-}Cl_2)(CO)_4$ (218 mg, 0.56 mmol) in dichloromethane was added to a solution of ddpa (305 mg, 1.12 mmol) in dichloromethane. The mixture was stirred at 50°C for 2 h. When toluene was used as solvent the reaction was slower.

The complex was isolated by evaporation of the dichloromethane and recrystallized from toluene solution as brown crystals.

Anal. Found: C, 48.79, H, 4.96, N, 3.13, P, 6.88, Cl, 8.17, Rh, 23,62. $C_{36}H_{44}N_2Cl_2O_2P_2Rh_2$ calc: C, 49.39, H, 5.07, N, 3.20, P, 7.08, Cl, 8.10, Rh, 23.51%.

$PdRhCl_3(CO)[Ph_2PCH_2N(C_2H_5)_2]_2$

A solution of $Rh_2(\mu\text{-}Cl_2)(CO)_2(C_2H_4)_2$ (392 mg, 1.01 mmol) in dichloromethane (10 cm^3) was added to a solution of ddpa (1093 mg, 4.03 mmol) in 5 cm^3 of dichloromethane. The mixture was stirred for 4 h, then a solution of $PdCl_2$(1,5-COD) (580 mg) in 2 cm^3 of dichloromethane was added with stirring. After 3 h the IR and NMR spectra were recorded. The product separated out slowly as orange crystals, and was filtered off and vacuum dried.

Anal. Found: C, 45.87, H, 4.86. $C_{35}H_{44}N_2Cl_3OP_2PdRh$ calc: C, 47.43, H, 5.00%.

Conclusion

The rhodium complexes involving the ddpa ligand can be compared with those involving the dppm and Ph_2Ppy ligands. Like the Ph_2Ppy ligand [3], ddpa gives mononuclear species able to act as ligand toward a second identical or different metal atom. Both dppm [2] and ddpa form binuclear species of the type $Rh_2Cl_2(CO)_2(ligand)_2$, and we suggest that the complex $Rh_2(\mu\text{-}Cl)Cl(\mu\text{-}CO)(CO)(\mu\text{-}ddpa)_2$ is a head-to-head dimer, in contrast with $Rh_2Cl_2(\mu\text{-}CO)(\mu\text{-}Ph_2Ppy)_2$ which is a head-to-tail species [3]. The heterobinuclear Rh–Pd complex formed by the ddpa ligand is also a head-to-head dimer (with Rh coordination through phosphorus and Pd coordination through nitrogen) in contrast to the heterobinuclear Rh–Pd complex formed by the Ph_2Ppy ligand, which is a head-to-tail dimer. Thus the formation of homo (Rh–Rh) and hetero (Rh–Pd) compounds using

$RhCl(CO)(ddpa)_2$ as ligand does not require self-reorientation of the ddpa ligand. Use of the unsymmetrical ddpa ligand to form binuclear complexes does not lead to metal–phosphorus bond breaking assumed for Ph_2Ppy by Balch et al. [3], probably because the ddpa ligand is less labile and more flexible than the Ph_2Ppy ligand.

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