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Inorganica Chimica Acta 228 (1995) 73–75

Inorganica Chimica Acta

Preliminary Communication

Platinum–rhodium A-frame and double A-frame complexes bridged by bis(diphenylphosphino)methane ligands

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Received 1 July 1994; revised 28 September 1994

Abstract

The organoplatinum compounds [PtR(dppm-*PP*))(dppm-*P*)]PF_6 (R = Me, Et, Ph) react with [$Rh_2(\mu\text{-}Cl)_2(cod)_2$] in the presence of carbon monoxide to yield the double A-frame complexes [RPt(μ-Cl)(μ-CO)(μ-dppm)$_2$Rh(CO)]PF_6. These lose CO reversibly to give the corresponding A-frame species [RPt(μ-Cl)(μ-dppm)$_2$Rh(CO)]PF_6. The products have been characterized by NMR and IR spectroscopies, the double A-frames exhibiting ^{13}C resonances around 200 ppm, which show couplings to both platinum and rhodium, and ν(CO) bands in the range 1855–1864 cm^{-1}, typical of bridging carbonyls.

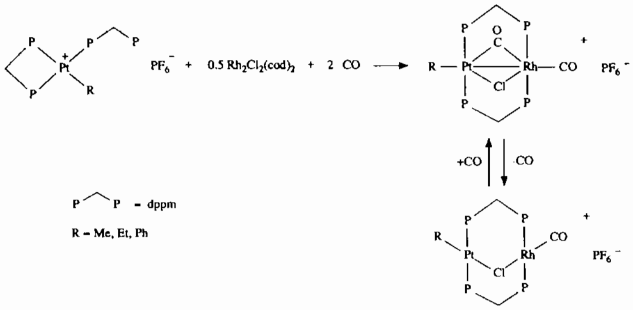
Keywords: Platinum complexes; Rhodium complexes; A-frame complexes

The bis(diphenylphosphino)methane (dppm) ligand has been used to support a wide variety of diplatinum and dirhodium complexes [1–3]. The diplatinum species generally adopt *trans–trans* or A-frame structures, whereas with rhodium *trans–trans*, A-frame, and doubly-bridged, or 'double A-frame', structures are known. A few examples of mixed platinum–rhodium species have been prepared [2,4–8], and these adopt A-frame, *trans–trans* or *cis–trans* structures.

We have prepared the organoplatinum compounds [PtR(dppm-*PP*)(dppm-*P*)]PF_6, which contain one chelated and one monodentate dppm ligand, and employed these successfully in the synthesis of unsymmetrical diplatinum and platinum–palladium chloride-bridged [9] or hydride-bridged [10] A-frame complexes. In this paper, we report an extension of this work to platinum–rhodium species including, to our knowledge, the first double A-frame complexes incorporating platinum.

When a dichloromethane solution of [PtR(dppm-*PP*)(dppm-*P*)]PF_6 (R = Me, Et, Ph) is added dropwise to a solution of [$Rh_2(\mu\text{-}Cl)_2(cod)_2$], which has been saturated previously with carbon monoxide, the solution becomes clear yellow, and the double A-frame complex [RPt(μ-Cl)(μ-CO)(μ-dppm)$_2$Rh(CO)]PF_6 is formed quantitatively, as indicated by $^{31}P\{^1H\}$ NMR spectroscopy. These doubly-bridged complexes are stable in solution under a CO atmosphere, or at low temperatures, but they lose CO at ambient temperature. The loss of CO may be enhanced by sweeping argon gas through the solution, in which case the chloride-bridged, A-frame complex [RPt(μ-Cl)(μ-dppm)$_2$Rh(CO)]PF_6 is formed quantitatively within a few minutes. The singly-bridged species have been isolated as yellow, analytically pure solids, which are stable to air and moisture. Bubbling carbon monoxide through a dichloromethane solution of [RPt(μ-Cl)(μ-dppm)$_2$Rh(CO)]PF_6 for a few minutes, however, regenerates the double A-frame complex (Scheme 1).

The double A-frames exhibit very broad features in their $^{31}P\{^1H\}$ NMR spectra at ambient temperature, but at −60 °C two sharp resonances are observed (Fig. 1(a)). The lower frequency signal is a deceptively simple



Scheme 1.

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SSDI 0020-1693(94)04315-M

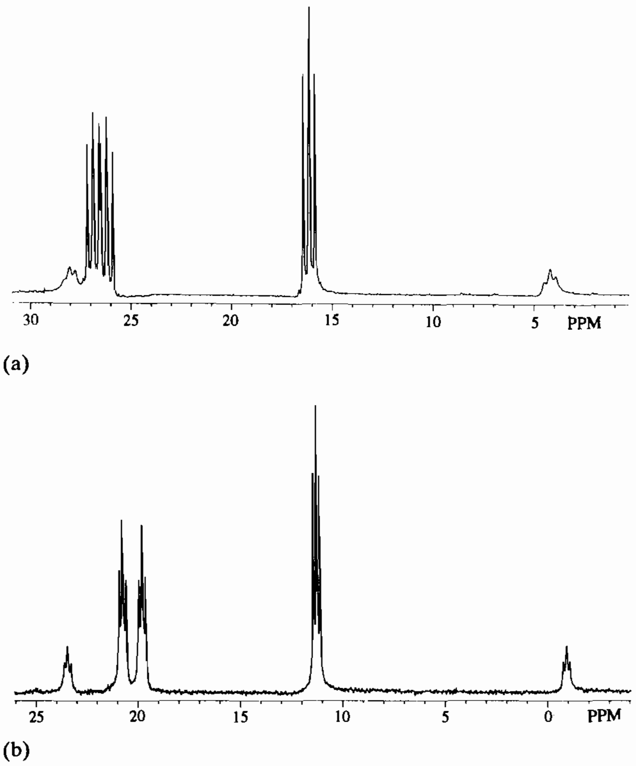

Fig. 1. $^{31}P\{^1H\}$ NMR spectra of (a) [PhPt(μ-Cl)(μ-CO)(μ-dppm)$_2$Rh(CO)]PF$_6$ at −60 °C, (b) [PhPt(μ-Cl)(μ-dppm)$_2$Rh(CO)]PF$_6$ at 25 °C, recorded in CDCl$_3$ solution.

triplet with ^{195}Pt satellites, due to the two phosphorus atoms attached to platinum, and the higher frequency resonance is a doublet of triplets. The latter exhibits a one-bond rhodium–phosphorus coupling of 82 Hz (Table 1) in each case, smaller than those found previously in platinum–rhodium A-frame complexes [7,8]. The low temperature $^{13}C\{^1H\}$ NMR spectra of [RPt(μ-Cl)(μ-CO)(μ-dppm)$_2$Rh(CO)]PF$_6$, prepared by using 99% ^{13}CO, each display two resonances in the carbonyl region. A broad doublet is observed in the range 183–186 ppm, due to the terminal carbonyl, with a ^1J(Rh,C) value of 80–85 Hz. A second broad doublet, due to the bridging CO, is found around 200 ppm, which exhibits a smaller one-bond coupling to rhodium (50–53 Hz). These parameters are similar to those found for the dirhodium double A-frame complex [Rh$_2$(μ-Cl)(μ-CO)(μ-dppm)$_2$(CO)$_2$] [11]. In [RPt(μ-Cl)(μ-CO)(μ-dppm)$_2$Rh(CO)]PF$_6$ (R = Me, Et) the bridging CO ligands exhibit ^1J(Pt,C) values of ~470 Hz, the value in the phenyl derivative being slightly smaller. These are significantly smaller than those found for terminal carbonyl complexes of platinum [12]. The $^{13}C\{^1H\}$ NMR spectra are also broad at ambient temperature, due to dissociative exchange of carbon monoxide, as found for the dirhodium system [11]. The solution IR spectra of [RPt(μ-Cl)(μ-CO)(μ-dppm)$_2$Rh(CO)]PF$_6$ are also consistent with this formulation, exhibiting strong absorptions around 1860 and 2015 cm^{-1}, due to the bridging and terminal carbonyl ligands, respectively.

The chloride-bridged, A-frame complexes, [RPt(μ-Cl)(μ-dppm)$_2$Rh(CO)]PF$_6$, exhibit sharp $^{31}P\{^1H\}$ NMR spectra at 25 °C (Fig. 1(b)), which are qualitatively similar to those of the double A-frames. Each resonance is shifted to lower frequency; the ^1J(Rh,P) values increase to 116 Hz (typical of other platinum–rhodium A-frames [7,8]), and the P–P couplings are reduced. The $^{13}C\{^1H\}$ NMR spectra of [RPt(μ-Cl)(μ-dppm)$_2$Rh(^{13}CO)]PF$_6$ each contain one, well-resolved doublet of triplets around 186 ppm due to the terminal CO, with a one-bond rhodium–carbon coupling of 81 Hz (somewhat larger than that found in the double A-frame complex). The solution IR spectra also exhibit only one ν(CO) absorption at 1991–1994 cm^{-1}, typical of a terminal carbonyl ligand.

Table 1
Spectroscopic data for complexes of the type [RPt(μ-Cl)(μ-CO)$_n$(μ-dppm)$_2$Rh(CO)]PF$_6$ (n = 0, 1) [a]

R, n	δP	^1J(M,P)	J(P,P) [b]	δC	^1J(M,C)	ν(CO) (cm^{-1})
Me, 1	23.3 t	^1J(Pt,P) 2865	70	186.2 br d	^1J(Rh,C) 84	2015
	27.9 dt	^1J(Rh,P) 82		201.9 br d	^1J(Rh,C) 53, ^1J(Pt,C) 475	1860
Et, 1	22.5 t	^1J(Pt,P) 3115	74	183.0 br d	^1J(Rh,C) 81	2014
	27.6 dt	^1J(Rh,P) 82		198.6 br d	^1J(Rh,C) 50, ^1J(Pt,C) 465	1855
Ph, 1	16.1 t	^1J(Pt,P) 2893	70	185.6 br d	^1J(Rh,C) 80	2016
	26.5 dt	^1J(Rh,P) 82		200.1 br d	^1J(Rh,C) 53, ^1J(Pt,C) 426	1864
Me, 0	16.2 t	^1J(Pt,P) 2924	40	186.1 dt [c]	^1J(Rh,C) 81	1993
	19.4 dt	^1J(Rh,P) 116				
Et, 0	16.4 t	^1J(Pt,P) 3167	40	185.7 dt [c]	^1J(Rh,C) 81	1991
	20.5 dt	^1J(Rh,P) 116				
Ph, 0	11.2 t	^1J(Pt,P) 2962	40	185.5 dt [c]	^1J(Rh,C) 81	1994
	20.3 dt	^1J(Rh,P) 116				

[a] Chemical shifts are in ppm relative to external H$_3$PO$_4$ or TMS. Coupling constants are in Hertz. NMR spectra were recorded for CDCl$_3$ solutions, at −60 °C where n = 1, and at 25 °C where n = 0.

[b] $J(P,P) = |^2J(P_A,P_B) + {}^4J(P_A,P_{B'})|$.

[c] ^2J(P,C) = 15 Hz.

Studies of the reactions of these platinum–rhodium A-frame and double A-frame complexes are in progress.

Acknowledgements

Thanks are expressed to the National Science Foundation (Grant No. CHE-9101834) and the University of Missouri Weldon Spring Fund for support of this work, and to Johnson Matthey for generous loans of platinum salts.

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