

Preliminary Communication

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

Chongfu Xu, Gordon K. Anderson *

Department of Chemistry, University of Missouri-St. Louis, 8001 Natural Bridge Road, St. Louis, MO 63121, USA

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Abstract

The organoplatinum compounds $[\text{PtR}(\text{dppm-PP})(\text{dppm-P})]\text{PF}_6$ ($\text{R} = \text{Me, Et, Ph}$) react with $[\text{Rh}_2(\mu\text{-Cl})_2(\text{cod})_2]$ in the presence of carbon monoxide to yield the double A-frame complexes $[\text{RPt}(\mu\text{-Cl})(\mu\text{-CO})(\mu\text{-dppm})_2\text{Rh}(\text{CO})]\text{PF}_6$. These lose CO reversibly to give the corresponding A-frame species $[\text{RPt}(\mu\text{-Cl})(\mu\text{-dppm})_2\text{Rh}(\text{CO})]\text{PF}_6$. 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 $\nu(\text{CO})$ bands in the range $1855\text{--}1864\text{ cm}^{-1}$, typical of bridging carbonyls.

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

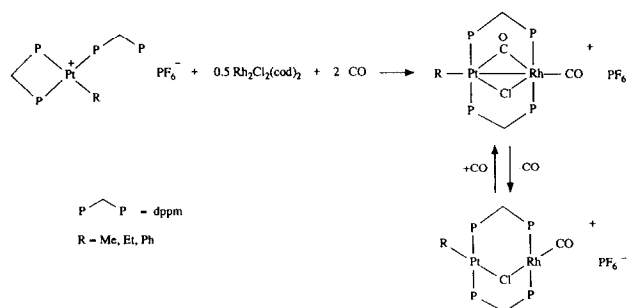
The bis(diphenylphosphino)methane (dppm) ligand has been used to support a wide variety of diplatinum and dirhodium complexes [1–3]. The diplatinum species generally adopt *trans–trans* or A-frame structures, whereas with rhodium *trans–trans*, A-frame, and doubly-bridged, or ‘double A-frame’, structures 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 $[\text{PtR}(\text{dppm-PP})(\text{dppm-P})]\text{PF}_6$, 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 $[\text{PtR}(\text{dppm-PP})(\text{dppm-P})]\text{PF}_6$ ($\text{R} = \text{Me, Et, Ph}$) is added dropwise to a solution of $[\text{Rh}_2(\mu\text{-Cl})_2(\text{cod})_2]$, which has been saturated previously with carbon monoxide, the solution becomes clear yellow, and the double A-frame complex $[\text{RPt}(\mu\text{-Cl})(\mu\text{-CO})(\mu\text{-dppm})_2\text{Rh}(\text{CO})]\text{PF}_6$ is formed quantitatively, as indicated by $^{31}\text{P}\{^1\text{H}\}$ 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 $[\text{RPt}(\mu\text{-Cl})(\mu\text{-dppm})_2\text{Rh}(\text{CO})]\text{PF}_6$ 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 $[\text{RPt}(\mu\text{-Cl})(\mu\text{-dppm})_2\text{Rh}(\text{CO})]\text{PF}_6$ for a few minutes, however, regenerates the double A-frame complex (Scheme 1).

The double A-frames exhibit very broad features in their $^{31}\text{P}\{^1\text{H}\}$ 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.

* Corresponding author.

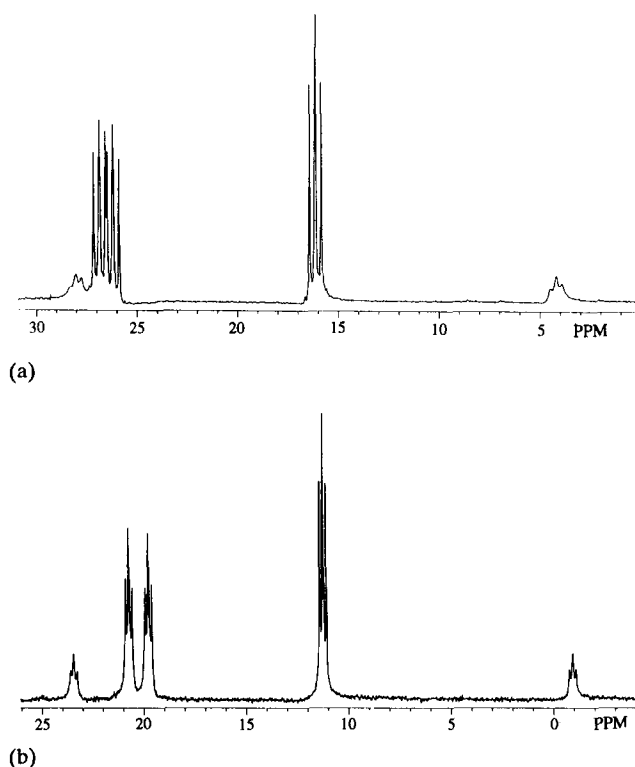


Fig. 1. $^{31}\text{P}\{^1\text{H}\}$ NMR spectra of (a) $[\text{PhPt}(\mu\text{-Cl})(\mu\text{-CO})(\mu\text{-dppm})_2\text{Rh}(\text{CO})]\text{PF}_6$ at -60°C , (b) $[\text{PhPt}(\mu\text{-Cl})(\mu\text{-dppm})_2\text{Rh}(\text{CO})]\text{PF}_6$ at 25°C , recorded in CDCl_3 solution.

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 $^{13}\text{C}\{^1\text{H}\}$ NMR spectra of $[\text{RPt}(\mu\text{-Cl})(\mu\text{-CO})(\mu\text{-dppm})_2\text{Rh}(\text{CO})]\text{PF}_6$, 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 $^1J(\text{Rh},\text{C})$ 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 $[\text{Rh}_2(\mu\text{-Cl})(\mu\text{-CO})(\mu\text{-dppm})_2(\text{CO})_2]$ [11]. In $[\text{RPt}(\mu\text{-Cl})(\mu\text{-CO})(\mu\text{-dppm})_2\text{Rh}(\text{CO})]\text{PF}_6$ ($\text{R}=\text{Me}, \text{Et}$) the bridging CO ligands exhibit $^1J(\text{Pt},\text{C})$ 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 $^{13}\text{C}\{^1\text{H}\}$ 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 $[\text{RPt}(\mu\text{-Cl})(\mu\text{-CO})(\mu\text{-dppm})_2\text{Rh}(\text{CO})]\text{PF}_6$ 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, $[\text{RPt}(\mu\text{-Cl})(\mu\text{-dppm})_2\text{Rh}(\text{CO})]\text{PF}_6$, exhibit sharp $^{31}\text{P}\{^1\text{H}\}$ 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 $^1J(\text{Rh},\text{P})$ values increase to 116 Hz (typical of other platinum–rhodium A-frames [7,8]), and the P–P couplings are reduced. The $^{13}\text{C}\{^1\text{H}\}$ NMR spectra of $[\text{RPt}(\mu\text{-Cl})(\mu\text{-dppm})_2\text{Rh}(\text{CO})]\text{PF}_6$ 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 $\nu(\text{CO})$ absorption at 1991–1994 cm^{-1} , typical of a terminal carbonyl ligand.

Table 1

Spectroscopic data for complexes of the type $[\text{RPt}(\mu\text{-Cl})(\mu\text{-CO})_n(\mu\text{-dppm})_2\text{Rh}(\text{CO})]\text{PF}_6$ ($n=0, 1$)^a

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

^a Chemical shifts are in ppm relative to external H_3PO_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 $J(\text{P},\text{P}) = [^2J(\text{P}_\text{A},\text{P}_\text{B}) + ^4J(\text{P}_\text{A},\text{P}_\text{B})]$.

^c $^2J(\text{P},\text{C}) = 15$ Hz.

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

Acknowledgements

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