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Note

Trimetallic complexes of the tripod ligand 1,1,1-tris(diphenylphosphinomethyl)ethane
Part I. Homotrimetallic *cis,cis,cis* and *cis,trans,cis* complexes of the type $[(PtX_2\text{-}\eta\text{-tripod})_2PtX_2]$ ($X=Cl$, I and CH_3)

A. Rauf Khan*,**, Steven M. Socol*,† and Devon W. Meek††

Department of Chemistry, The Ohio State University, Columbus, OH 43210 (USA)

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Abstract

Complexes of types *cis,cis,cis*- and *cis,trans,cis*-$[(PtX_2\text{-}\eta\text{-tripod})_2PtX_2]$ ($X=Cl$, I and CH_3; tripod = 1,1,1-tris(diphenylphosphinomethyl)ethane) have been isolated and have been shown by both ^{31}P and ^{195}Pt NMR spectroscopy to possess phosphino-bridged trimetallic structures. The assignment of these structures is established on the basis of ^1J(Pt–P) couplings and the coordination chemical shift, ΔP, of the dangling phosphino group of the monometallic complexes upon coordination. In both *cis,cis,cis* and *cis,trans,cis* geometries, the ^{31}P NMR chemical shift of the chelating phosphorus atoms and the ^{195}Pt NMR chemical shift for the $[PtX_2(\text{tripod})]$ complexes remain unperturbed upon coordination of the previously non-coordinated phosphorus. For the monomeric complexes of tripod, trends in the ^{31}P and ^{195}Pt NMR chemical shifts as a function of X parallel those which have previously been reported for analogous complexes which contain monodentate ligands.

Key words: Platinum complexes; Polydentate ligand complexes; Trimetallic complexes

Introduction

Metal complexes of tripodal polyphosphines have attracted much recent attention in regard to their potential as catalysts in a number of homogeneous reactions [1–5]. The most widely investigated tripodal polyphosphine, 1,1,1,-tris(phenylphosphinomethyl)ethane ('tripod'), has been shown to form complexes with most d-block metals in a wide variety of stereochemistries, wherein the tripod liquid tends to occupy three facial sites in a coordination polyhedron [1]. Recently, intermediates have been proposed in a number of catalytic reactions in which one of the arms of the tripod ligand dissociates [1, 5].

In this paper we would like to report some platinum(II) complexes of the type $[PtX_2(\text{tripod})]$ where two of the three arms of the tripod ligand are coordinated to the metal, while the third remains dangling. These $[PtX_2(\text{tripod})]$ complexes are shown to further react with $[PtX_2COD]$ to form homotrimetallic complexes of the type $[(PtX_2\text{-}\eta\text{-tripod})_2PtX_2]$.

Experimental

^{31}P NMR spectra were recorded in CH_2Cl_2 on Bruker HX-90 (36.43 MHz) and WM-300 (127.47 MHz) spectrometers and are referenced to 85% H_3PO_4 with downfield shifts being defined as positive. ^{195}Pt NMR spectra were recorded in CH_2Cl_2/CD_2Cl_2 solutions at 305 K on a Bruker WM-300 (64.4 MHz) spectrometer, and are referenced to aqueous H_2PtCl_6 with downfield shifts being defined as positive. Elemental analysis were carried out by MHW Laboratories, Phoenix, AZ. All reactions were performed under an atmosphere of high purity argon. The complexes $[PtX_2COD]$ ($X=Cl$, I and CH_3) were prepared as previously described [6]. The complexes $[PtX_2(\text{tripod})]$ ($X=Cl$, I and CH_3) were prepared as was previously described for $[Pt(CH_3)_2(\text{tripod})]$ [7].

Cis,cis,cis-$[(PtCl_2\text{-}\eta\text{-tripod})_2PtCl_2]$

(a) A solution containing $[PtCl_2(\text{tripod})]$ (0.150 g, 0.168 mmol) and $[PtCl_2COD]$ (0.0135 g, 0.084 mmol) was refluxed in benzene (10 ml) for 2 h. The volume of solvent was reduced to 5 ml. A white precipitate formed overnight which was filtered, washed with light petroleum ether (10 ml), and dried under vacuum. Yield 0.155 g, 90%.

(b) A solution of $[PtCl_2(\text{tripod})]$ (0.5169 g, 0.5804 mmol) and $Pt(CH_3)_3Cl$ (0.080 g, 0.29 mmol) in chloroform was refluxed for 5 h. A white precipitate formed after the solvent was reduced to 10 ml. The precipitate was filtered, washed with light petroleum ether, and

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*Authors to whom correspondence should be addressed.

**Present address: Principal, Government Graduate College-I, Dara Ismail Khan (NWFP), Pakistan.

†Present address: Southern Utah University, Department of Physical Sciences, Cedar City, UT 84720, USA.

††Deceased.

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dried under vacuum. Yield 0.32 g, 55%. *Anal.* Found: C, 54.84; H, 5.16; P, 9.79. Calc. for [$(PtCl_2$-η-tripod$)_2PtCl_2$]: C, 54.91; H, 5.03; P, 9.66%.

Cis,cis,cis-[(Pt(CH$_3$)$_2$-η-tripod)$_2$Pt(CH$_3$)$_2$]

A solution of [$Pt(CH_3)_2COD$] (0.10 g, 0.30 mmol) and tripod (0.125 g, 0.199 mmol) in benzene (10 ml) was refluxed for 3 h. The volume of the solvent was reduced to 2 ml after which light petroleum ether (10 ml) was added. A white solid precipitated which was filtered and dried under vacuum. Yield 0.153 g, 80%. *Anal.* Found: C, 48.76; H, 4.33; P, 9.68. Calc. for [$(Pt(CH_3)_2$-η-tripod$)_2Pt(CH_3)_2$]: C, 48.11; H, 3.84; P, 10.39%.

Cis,trans,cis-[(PtI$_2$-η-tripod)$_2$PtI$_2$]

(a) A solution of [PtI_2COD] (0.0159 g, 0.0931 mmol) and [PtI_2(tripod)] (0.20 g, 0.18 mmol) in chloroform (10 ml) was refluxed for 3 h. After reducing the solvent volume to 4 ml, light petroleum ether was added. An orange–yellow precipitate formed which was filtered, washed with light petroleum ether, and dried under vacuum. Yield 0.373 g, 80%.

(b) A solution of [PtI_2COD] (0.150 g, 0.269 mmol) and tripod (0.112 g, 0.179 mmol) in benzene (10 ml) was refluxed for 2 h. After reducing the solvent volume to 3 ml, light petroleum ether (15 ml) was added. The orange–yellow precipitate which formed was filtered, washed with light petroleum ether (10 ml), and then dried under vacuum. Yield 0.209 g, 90%. *Anal.* Found: C, 38.10; H, 3.02; P, 7.31. Calc. for [$(PtI_2$-η-tripod$)_2PtI_2$]: C, 37.96; H, 3.02; P, 7.16%.

Results and discussion

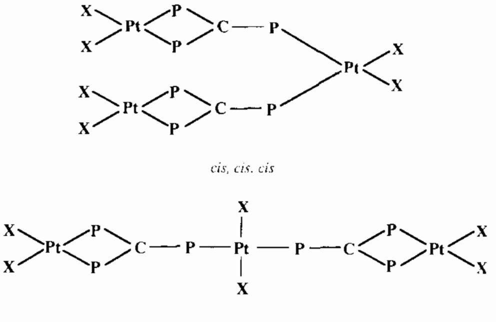
Complexes of the type [PtX_2(tripod)] react analogous to a monodentate phosphine ligand with [PtX_2COD] in molar ratio of 2:1 to form homotrimetallic complexes according to eqn. (1).

$$2[PtX_2(\text{tripod})] + [PtX_2COD] \longrightarrow [(PtX_2\text{-}\eta\text{-tripod})_2PtX_2] + COD \quad (1)$$

These trimetallic complexes can also be prepared in high yield by refluxing [PtX_2COD] and tripod in a 3:2 molar ratio in benzene. A third, and less obvious route for the synthesis of [$(PtCl_2$-η-tripod$)_2PtCl_2$], involves reaction between [$PtCl_2$(tripod)] and [$Pt(CH_3)_3Cl]_4$. The less soluble trimetallic compound can be removed by filtration, while the more soluble monometallic complex(s) remain in the mother liquor.

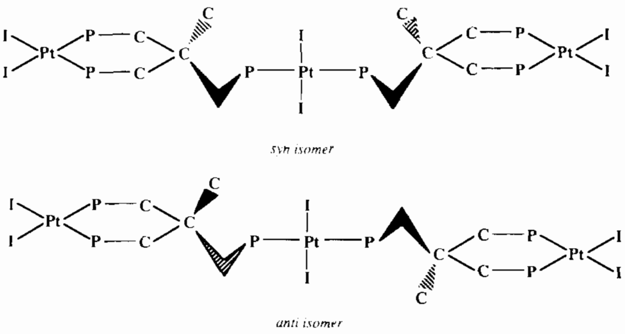
The trimetallic complexes [$(PtX_2$-η-tripod$)_2PtX_2$] can possess either a *cis,cis,cis* or a *cis,trans,cis* geometry depending on the arrangement around the central platinum metal (Fig. 1). Distinction between the two geometries can be made by comparison of ^1J(Pt–P) couplings. In [$(PtCl_2$-η-tripod$)_2PtCl_2$], the ^1J(Pt–P) coupling constants are 3425 and 3045 Hz. These couplings can be assigned to phosphorus atoms *trans* to chlorine [8, 9]; hence the complex has a *cis,cis,cis* geometry. Similarly in [$(Pt(CH_3)_2$-η-tripod$)_2Pt(CH_3)_2$], the ^1J(Pt–P) coupling constants of 1812 and 1810 Hz are assigned to phosphorus atoms *trans* to methyl [8, 9]. For [$(PtI_2$-η-tripod$)_2PtI_2$], the ^1J(Pt–P) values of 3218 and 2400 Hz are assigned to phosphorus atoms *trans* to iodine and phosphorus respectively, since the ^1J(Pt–P) coupling constants of phosphorus atoms *trans* to phosphorus in Pt(II)–phosphine complexes lie between 1950 and 2600 Hz [8, 10–12], and those *trans* to iodine lie from 3000 to 3500 Hz [12]. Hence, the complex is assigned a *cis,trans,cis* geometry.

If the Pt–P bonds on the central phosphorus do not rotate on the NMR time scale, at least two rotamers, *syn* and *anti*, are possible for the complexes (Fig. 2). Each rotamer in the *cis,cis,cis* or *cis,trans,cis* geometry contains two chemically different phosphorus and platinum environments. Thus, for a *syn* or *anti* isomer of either geometry, two signals in a 2:1 intensity ratio are expected in both the ^{31}P and ^{195}Pt NMR spectra. Therefore, a mixture of *syn* and *anti* rotamers will show a maximum of four peaks in the ^{31}P and ^{195}Pt NMR spectra. For [$(PtI_2$-η-tripod$)_2PtI_2$] we observe three resonances in the ^{31}P and four in the ^{195}Pt NMR spectra


cis, cis, cis

cis, trans, cis

Fig. 1. *Cis,cis,cis*- and *cis,trans,cis*-[$(PtX_2$-η-tripod$)_2PtX_2$].


syn isomer

anti isomer

Fig. 2. *Syn* and *anti* rotamers of *trans*-[$(PtI_2$-η-tripod$)_2PtI_2$].

TABLE 1. ^{31}P and ^{195}Pt NMR spectral parameters

Compound	δ(P1)[a]	δ(P2)[b]	J(Pt–P)[c]	δ(Pt1)[d]	δ(Pt2)[e]	J(Pt–P)[f]
[Pt(CH$_3$)$_2$(tripod)]	4.7	−28.7	1818	−4744		1818
[PtCl$_2$(tripod)]	−1.7	−29.6	3425	−4614		3425
[PtI$_2$(tripod)]	−6.4	−29.8	3222	−5398		3223
cis-[Pt(CH$_3$)$_2$(PCH$_3$(C$_6$H$_5$)$_2$)$_2$][g]	−5.3		1852 ± 10	−4649		
cis-[PtCl$_2$(PCH$_3$(C$_6$H$_5$)$_2$)$_2$][g]	−2.2		3622 ± 15	−4437		
cis-[PtI$_2$(PCH$_3$(C$_6$H$_5$)$_2$)$_2$][g]	−5.1		3394 ± 30	−5226		
cis,cis,cis-[(Pt(CH$_3$)$_2$-η-tripod)$_2$Pt(CH$_3$)$_2$]	4.4		1812	not sufficiently soluble		
		4.5	1810			
cis,cis,cis-[(PtCl$_2$-η-tripod)$_2$PtCl$_2$]	−1.7		3425	−4607		3425
		11.7	3046		−4571	3045
cis,cis,cis-[(PtI$_2$-η-tripod)$_2$PtI$_2$]	−6.6		3218	−5385		3218
				−5581		3212
		−6.7	2406		−5552	2415
		−4.0	2400		−5550	2404
[Pt(CH$_3$)$_2$(C$_6$H$_5$)$_2$P(CH$_2$)$_3$P(C$_6$H$_5$)$_2$][h]	3.2		1767	−4589		
[PtCl$_2$(C$_6$H$_5$)$_2$P(CH$_2$)$_3$P(C$_6$H$_5$)$_2$]	−5.6[h]		3410[h]	−4514[i]		

[a] Chemical shift of coordinated phosphorus in monometallic complex, or phosphorus bound to a peripheral platinum in a trimetallic complex. [b] Uncoordinated phosphorus in monometallic complex or phosphorus bound to central platinum in trimetallic complex. [c] Coupling constant obtained from ^{31}P NMR. [d] Peripheral platinum in trimetallic complex. [e] Central platinum in trimetallic complex. [f] Coupling constant obtained from ^{195}Pt NMR. [g] Ref. 8. [h] Ref. 13. [i] Ref. 14.

(Table 1). The observation of only three phosphorus signals may be due to fortuitous overlap. It is difficult to assign these resonances due to similar ^1J(Pt–P) coupling constants and chemical shift values (Table 1). However, for *cis,cis,cis*-[(PtCl$_2$-η-tripod)$_2$PtCl$_2$] and *cis,cis,cis*-[Pt(CH$_3$)$_2$-η-tripod)$_2$Pt(CH$_3$)$_2$] only two resonances are observed in both the ^{31}P and ^{195}Pt NMR spectra which indicates the presence of only one rotamer (Table 1). We believe that these complexes possess the *anti* configuration which is sterically less crowded than the corresponding *syn* isomer.

In all three trimetallic complexes, the ^{31}P NMR chemical shifts, ^{195}Pt NMR chemical shifts, and ^1J(Pt–P) coupling constants of the chelating phosphorus atoms of the [PtX$_2$(tripod)] complexes remain unperturbed upon complex formation (Table 1) which is indicative of little interaction between metal centers. A similar phenomenon was observed by Balch *et al.* in the reactions of monometallic Pt(II) and Pd(II) complexes of the dpmp ligand (bis(diphenylphosphino)methyl)phenylphosphine, wherein one of the phosphorus atoms is uncoordinated. The ^{31}P NMR chemical shifts of the previously coordinated phosphorus change little upon reaction of the uncoordinated phosphorus atom [15]. In our complexes we would expect even less metal–metal interaction than in the complexes reported by Balch *et al.*, since the dangling phosphorus is expected to be further away from the metal center. In the solid state structure of [Pt(CH$_3$)$_2$(tripod)] the distance, between the dangling phosphorus and the platinum atom is 6.29 Å [7].

For monometallic complexes, [PtX$_2$(tripod)], the ^{195}Pt NMR chemical shifts move upfield in the order $Cl < CH_3 < I$, whereas for ^{31}P chemical shifts the trend is $CH_3 > Cl > I$. As expected, these parallel the trends previously observed for platinum(II) bis(phosphine) complexes [8]. In both the mono- and trimetallic complexes reported herein, the ^{195}Pt NMR chemical shifts of chloride complexes lie downfield of the analogous iodine complexes. This general trend has also been reported earlier [16, 17]. The chemical shift of the dangling phosphine moves downfield more than 30 ppm upon formation of *cis,cis,cis* complexes, but less than 30 ppm in *cis,trans,cis* complexes. A similar trend can be derived from the data on trimetallic complexes reported by Balch *et al.* [15].

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