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Platinum(II) complexes of the tridentate ligand 1,1,1-tris(diphenylphosphinomethyl)ethane. *Trans* influence studies and detection of linkage isomers of thiocyanate by ^{31}P NMR in $[PtX_2(triphos)]$ complexes

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Abstract

Two series of complexes $[PtX_2(triphos)]$ (X = Cl, Br, I, CH_3, C_6H_5, CN, thiocyanate; triphos = 1,1,1-tris(diphenylphosphinomethyl)ethane) and $[PtX_2(dpp)]$ (X = Cl, CN, thiocyanate; dpp = 1,3-bis(diphenylphosphino)propane) have been prepared, and their structures have been established on the basis of ^{31}P NMR spectroscopy. A definitive *trans* influence order is found: $CH_3 > C_6H_5 > CN > SCN > I > NCS > Br > Cl$. For the thiocyanate complexes, all three possible linkage isomers are observed and assigned from ^{31}P NMR spectroscopy. The [Pt(thiocyanate)$_2$(triphos)] complex is fluxional at room temperature. Isomerization is believed to occur by a non-dissociative process.

Keywords: *Trans* influence; Linkage isomerism; Platinum complexes; Tridentate phosphorus ligand complexes; Thiocyanate complexes

1. Introduction

We have recently reported how the tripodal ligand 1,1,1-tris(diphenylphosphinomethyl)ethane (triphos) can react with $[PtX_2COD]$ (X = Cl, I, CH_3) to form complexes of the type $[PtX_2(triphos)]$ wherein two of the three phosphorus atoms of the ligand are coordinated to Pt. These complexes were shown to further react with $[PtX_2COD]$ to form trimetallic complexes of the type $[(PtX_2\text{-}\eta\text{-}(triphos))_2PtX_2]$ [1]. In this paper, we would like to report some additional complexes of the type $[PtX_2(triphos)]$ (X = Br, CN, CH_3, C_6H_5, NCS) and for comparison purposes $[PtX_2(dpp)]$ (X = CN, NCS; dpp = 1,3-bis(diphenylphosphino)propane).

For [Pt(thiocyanate)$_2$(triphos)] and [Pt(thiocyanate)$_2$-(dpp)], three linkage isomers are possible, since the thiocyanate ion can coordinate to a transition metal either through nitrogen or sulfur. These isomers will be assigned by ^{31}P NMR spectroscopy.

2. Experimental

^{31}P NMR spectra were recorded on Bruker HX-90, WM-300 and AM-500 spectrometers operating at 36.43, 121.51 and 202.40 MHz, respectively. Spectra were run in CH_2Cl_2 solutions at ambient temperature unless otherwise indicated, and are referenced to external 85% phosphoric acid with downfield shifts defined as positive. IR spectra were recorded in nujol on a Perkin-Elmer grating spectrophotometer, and were calibrated with polystyrene film. Elemental analyses were performed by M-H-W Laboratories, Phoenix, AZ.

All reactions were performed under dry high purity argon. Solvents were purged with argon prior to use. The ligand 1,1,1-tris(diphenylphosphinomethyl)ethane (triphos) was purchased from Organometallics. Potassium cyanide and potassium bromide were purchased from Fisher Scientific while sodium thiocyanate was purchased from J.T. Baker. The compounds 1,5-cy-

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clooctadiene and 1,3-bis(diphenylphosphino)propane were purchased from Aldrich. Benzene was distilled from sodium benzophenone ketal under dry nitrogen. The compounds [PtX_2COD] (X = Cl, I, CH_3, C_6H_5) [2] and [$Pt(CH_3)_2$(triphos)] [3] were prepared by literature methods.

2.1. [$PtCl_2$(triphos)]

To a solution of triphos (1.073 g, 1.718 mmol) in benzene (20 ml), solid [$PtCl_2COD$] (0.643 g, 1.72 mmol) was added. Immediately a white precipitate formed. The suspension was refluxed for 3 h. The solvent was then removed under reduced pressure. The resultant solid was dissolved in dichloromethane (20 ml) and the solution was filtered. Addition of light petroleum ether (40 ml) to the filtrate produced white crystals. These crystals were collected on a Schlenk frit, washed with petroleum ether, and dried under vacuum (88% yield). The complex [$PtCl_2$(dpp)] was prepared analogously, except that light petroleum ether was added to the benzene suspension after refluxing (85% yield).

2.2. [PtI_2(triphos)]

To a hot suspension of [PtI_2COD] (0.80 g, 1.4 mmol) in benzene (30 ml) was added triphos (0.897 g, 1.44 mmol). Immediately an orange–yellow precipitate formed. The suspension was refluxed for 3 h. The volume of solvent was reduced to 20 ml. Addition of light petroleum ether produced a bright yellow precipitate. After filtering the mixture, the precipitate was dried under vacuum (95% yield). Recrystallization from CH_2Cl_2/OEt_2 gave bright yellow crystals. M.p. 164 °C. *Anal.* Found: C, 46.07; H, 3.74; P, 8.43. Calc. for [PtI_2(triphos)]: C, 45.87; H, 3.67; P, 8.65%.

2.3. [$Pt(C_6H_5)_2$(triphos)]

To a solution of [$Pt(C_6H_5)_2COD$] (0.0611 g, 0.133 mmol) in benzene was added triphos (0.0834 g, 0.133 mmol). The solution was refluxed for 3 h. After cooling to room temperature, diethyl ether was added. The solution was then cooled to −10 °C for 24 h which resulted in the precipitation of a bright-yellow crystalline solid which was collected on a frit and dried under vacuum (78% yield). M.p. 188–190 °C. *Anal.* Found: C, 66.13; H, 5.20. Calc. for [$Pt(C_6H_5)_2$(triphos)]: C, 65.35; H, 5.08%.

2.4. [$Pt(CN)_2$(triphos)] and [$Pt(CN)_2$(dpp)]

To a suspension of [$PtCl_2$(triphos)] (0.50 g, 0.56 mmol) in acetone (30 ml) and dichloromethane (5 ml) was added a solution of KCN (0.081 g, 1.24 mmol) in methanol (10 ml). The suspension, which turned turbid after 30 min, was stirred for 2½ h at room temperature. The solvent was evaporated under vacuum, and the resultant greenish-yellow residue was extracted with dichloromethane (20 ml). A white precipitate formed upon the addition of light petroleum ether (30 ml). The precipitate was filtered, washed with light petroleum ether, and dried under vacuum (yield 80%). M.p. 350 °C. *Anal.* Found: C, 59.23: H, 4.08. Calc. for [$Pt(CN)_2$(triphos)]: C, 59.23; H, 4.51%. The compound [$Pt(CN)_2$(dpp)] was obtained similarly from [$PtCl_2$(dpp)] and KCN in 70% yield.

2.5. [Pt(thiocyanate)$_2$(triphos)] and [Pt(thiocyanate)$_2$(dpp)]

To a suspension of [$PtCl_2$(triphos)] (0.50 g, 0.56 mmol) in acetone (15 ml) and methanol (8 ml) was added NaSCN (0.136 g, 1.68 mmol). The suspension was stirred for 6 h at room temperature. The solvent was then removed under reduced pressure, and the resulting white residue was extracted with dichloromethane (20 ml). The volume was reduced to 5 ml. Addition of light petroleum ether (10 ml) produced a white precipitate which was filtered and dried under vacuum (87%). M.p. 282–285 °C. *Anal.* Found: C, 55.01; H, 4.40; P, 10.09. Calc. for [Pt(thiocyanate)$_2$(triphos)]: C, 55.18; H, 4.21; P, 9.93%. [Pt(thiocyanate)$_2$(dpp)] was prepared from [$PtCl_2$(dpp)] and NaSCN in 60% yield in a similar manner with the exception that more dichloromethane (40 ml) was needed to extract the product. M.p. 282–285 °C. *Anal.* Found: C, 47.36; H, 4.98; P, 8.35. Calc. for [Pt(thiocyanate)$_2$(dpp)]: C, 46.15; H, 3.48; P, 8.49%.

2.6. [$PtBr_2$(triphos)]

A suspension of [$PtCl_2$(triphos)] (0.174 g, 0.195 mmol) and KBr (0.30 g, 2.5 mmol) in acetone (20 ml) and methanol (10 ml) was refluxed for 1½ h. The solvent was then removed under vacuum. The resulting residue was extracted with dichloromethane (20 ml). After reducing the volume of the solvent to 5 ml, the addition of light petroleum ether gave a white precipitate which was filtered and dried under vacuum (75% yield).

2.7. [$PtCl_2$(triphosmonoxide)]

A mixture of [$PtCl_2$(triphos)] (0.040 g, 0.045 mmol), acetone (5 ml), dichloromethane (3 ml) and 3% hydrogen peroxide (8 ml) was heated under reflux for 1 h. The solvent was then removed under vacuum. The residue was dissolved in dichloromethane (6 ml), and reprecipitated by adding light petroleum ether (10 ml). The precipitate was collected and dried under vacuum (70% yield).

3. Results and discussion

The ligands 1,1,1-tris(diphenylphosphinomethyl)-ethane (triphos) and 1,3-bis(diphenylphosphino)-propane (dpp) easily displace 1,5-cyclooctadiene from [PtX_2COD] (X=Cl, I, CH_3, C_6H_5) to form [$PtCl_2$(triphos)] and [PtX_2(dpp)] complexes. When X=CN, NCS or Br, metathesis reactions could be carried out by adding potassium cyanide or potassium thiocyanate to solutions of [$PtCl_2$(triphos)] or [PtX_2(dpp)] in molar ratios of 2.2 to 1. In the case of bromide, refluxing in a solution of acetone/methanol is required.

In all the triphos complexes studied, two of the three phosphorus atoms of the ligand are coordinated to Pt while the third is uncoordinated. The ^{31}P NMR spectrum of [$PtBr_2$(triphos)] is shown in Fig. 1. The resonance at low-field with platinum satellites (^{195}Pt natural abundance 33.7%) can be assigned to the two phosphorus atoms bound to the platinum atom while the high-field resonance is assigned to the dangling phosphorus. The stereochemical rigidity of the triphos ligand in these complexes is similar to what we have previously observed in [$Pt(CH_3)_2$(triphos)] [3]. Fluxional behavior of the triphos ligand in [Pt(SR)(H)(triphos)] (R=H or Ph) has recently been reported where the uncoordinated phosphorus exchanges with the phosphorus atom coordinated in the *cis* position with respect to the hydride ligand. The fluctional behavior was attributed to the high *cis* effect of the hydride ligands [4]. The fact that the triphos ligands in the complexes reported herein, none of which contain a hydride ligand coordinated to Pt, are all rigid at ambient temperature, is in agreement with this explanation. The ^{31}P NMR parameters for the triphos and dpp complexes are given in Table 1.

It is seen that there is a consistent upfield shift in the dangling phosphorus ligand of 3–5 ppm in the [PtX_2(triphos)] complexes with respect to the free ligand. This may be due to interaction of the phosphorus with the metal center.

Oxidizing the dangling phosphorus in [$PtCl_2$(triphos)] had little effect on the chemical shift of the previously coordinated phosphorus atoms. The ^{31}P NMR chemical shifts in the [PtX_2(dpp)] complexes parallel those observed for the triphos complexes in that the chemical shift of the cyanide complex lies upfield of the chloride and that the chemical shifts of the thiocyanate complex lie in increasing order of downfield shifts N,N < N,S < S,S.

Well resolved spectra are observed for all complexes at room temperature except where X=CN and NCS. It is possible that the π-acceptor ability of these anions renders the metal center more electrophilic and thus increases interaction with the dangling phosphorus atom. It can be noted that the dangling phosphorus atoms in these two complexes are shifted furthest upfield. Room-temperature fluxional behavior was previously noted in the (diphosphine)Pd(thiocyanate)$_2$ and (diphosphine)$_2Pd_2$(thiocyanate)$_2$ complexes [5] but not in the $(PR_3)_2$Pt(thiocyanate)$_2$ complexes [6].

For the [PtX_2(triphos)] complexes the ^1J(Pt–P) values decrease in the order Cl > Br > N-bound thiocyanate > I > S-bound thiocyanate > CN > C_6H_5 > CH_3. This

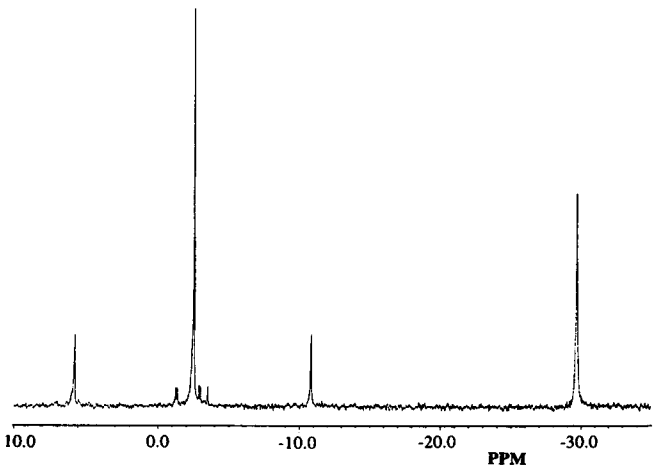

Fig. 1. ^{31}P NMR of [$PtBr_2$(triphos)] measured at ambient temperature in CH_2Cl_2.

Table 1
^{31}P NMR and IR data for the [PtX_2(triphos)] and [PtX_2(dpp)] complexes

	δ(P1) [a]	δ(P2) [b]	^1J(Pt–P)	ν(C≡N
triphos		−26.3		
dpp		−25.4		
[$PtCl_2$(triphos)]	−1.7 [c]	−29.6	3425	
[$PtBr_2$(triphos)]	−2.5 [c]	−29.8	3372	
[PtI_2(triphos)]	−6.4 [c]	−30.0	3222	
[$Pt(CN)_2$(triphos)]	−7.8	−33.0	2369	2157
[$Pt(CH_3)_2$(triphos)]	4.7 [c]	−28.7	1821	
[$Pt(C_6H_5)_2$(triphos)]	8.2 [c]	−28.9	1922	
[$PtCl_2$(triphosmonoxide)]	−2.7	+26.6	3425	
[Pt(thiocyanate)$_2$(triphos)]	2.7 (S, S)	−32.6	2993	2132
	1.3 (*S*, N) [d,f]	−32.6	2884	2093
	−7.5 (S, *N*) [e,f]	−32.6	3299	
	−8.6 (N, N) [g]	−32.6	3271	
[$PtCl_2$(dpp)]	−5.5		3409	
[$Pt(CN)_2$(dpp)]	−11.0		2369	2157
[Pt(thiocyanate)$_2$(dpp)]	−2.1 (S, S)		2975	2132
	−6.8 (*S*, N) [d,h]		2866	2095
	−11.7 (S, *N*) [e,h]		3299	
	−13.5 (N, N) [i]		3271	

[a] Chemical shift of phosphorus atoms bound to Pt.
[b] Chemical shift of uncoordinated phosphorus.
[c] ^4J(P–P) = 2 Hz,
[d] Chemical shift of phosphorus *trans* to sulfur bound thiocyanate.
[e] Chemical shift of phosphorus *trans* to nitrogen bound thiocyanate.
[f] ^2J(P–P) = 27 Hz.
[g] ^2J(P–^{14}N) = 30 Hz.
[h] ^2J(P–P) = 29 Hz.
[i] ^2J(P–^{14}N) = 38 Hz.

order parallels what was previously reported for ^1J(Pt–P) couplings *trans* to X in [Pt(ttp)X] [7] and PtXR(dppe) [8] complexes (ttp = $_2(Ph_2CH_2CH_2CH_2)PPh$; dppe = $Ph_2PCH_2CH_2PPh_2$) except the *trans* influence of CH_3 is greater than that of C_6H_5. This order observed here is to be expected on the basis of the former ligand being a better sigma donor. In agreement, the ^1J(Pt–P) value of 1492 Hz reported for [Pt$(C_6H_5)_2$dpm] (dpm = bis(diphenylphosphino)methane) [9a] is greater than that of 1434 Hz reported for [Pt$(CH_3)_2$dpm] [9b].

The ^{31}P NMR spectra of [Pt(thiocyanate)$_2$(triphos)] and [Pt(thiocyanate)$_2$(dpp)] indicate that all three isomers (N,N-, N,S- and S,S-bonded) are present in dichloromethane solution. In the triphos complex, the chemical shift for the dangling phosphorus is identical for the three isomers. The *trans* influence of S-bound thiocyanate was found to be larger than N-bound thiocyanate in a series of [Pt(thiocyanate)$_2(PR_3)_2$] complexes [6a]. By analogy, the low-field resonances with smaller values of ^1J(Pt–P) are assigned to the S,S-bonded isomers in [Pt(thiocyanate)$_2$(triphos)] and [Pt(thiocyanate)$_2$(dpp)]. For the geminite S,N-bonded isomers, the two coordinated phosphorus atoms are chemically non-equivalent; thus, two doublets (along with their platinum satellites) are observed with ^2J(P–P) = 27 (triphos complex) and 29 (dpp complex) Hz. It should be noted that the phosphorus atoms *trans* to sulfur are at lower field. This does not seem to be a general trend, however [6a]. The N,N-bonded isomer occurs upfield with a J(Pt–P) value of 3271. Support for these assignments comes from the fact that the resonances of the phosphorus atoms *trans* to N-bound thiocyanate tend to be broadened. This broadening is attributed to scalar interaction with the quadrupolar ^{14}N nucleus [5,7,10]. Furthermore, at room temperature the ^{31}P{^{1}H} NMR spectra clearly show the coupling between ^{14}N and phosphorus nuclei of 30 and 38 Hz for triphos and dpp complexes, respectively, which is similar to the *trans* ^2J(Pt–^{14}N) coupling of 34 Hz reported in Pt(ttp)NCS [7].

Peak integration of the triphos complex shows that the S,S-bound isomer is the least abundant (5%), the N,N-bound isomer being intermediate (22%) while the S,N-bound isomer is predominant (73%). On the basis of the SHAB principle, one would expect a high proportion of S,S-bonded isomers, since Pt(II) is a soft metal. Conversely a crowded metal center, such as would be expected in [Pt(thiocyanate)$_2$(triphos)], should favor N-bound thiocyanate [6a, 11]. Recently, Burmeister has argued that there is a conjunctive response of two thiocyanate groups to steric hindrance wherein the N,S-geminite configuration minimizes both interaction with bulky substituents on other ligands and with each other [12]. The predominance of the geminite isomers in [Pt(thiocyanate)$_2$(triphos)] and [Pd(thiocyanate)$_2$(diphosphine)] complexes [5] in low temperature solutions supports this conclusion. Geminite complexes were also observed for Pt(thiocyanate)$_2(PR_3)_2$, but in these complexes the N,N-bound isomers were always predominant [6a]. The predominance of N,N-bound isomers in these complexes may be due to greater steric demands of the monodentate phosphine ligands. In *trans*-[Pt(thiocyanate)$_2(PEt_3)_2$], where the thiocyanates would be expected to be especially crowded due to two phosphines being in *cis* positions, only the N,N-bound isomer was reported [6a].

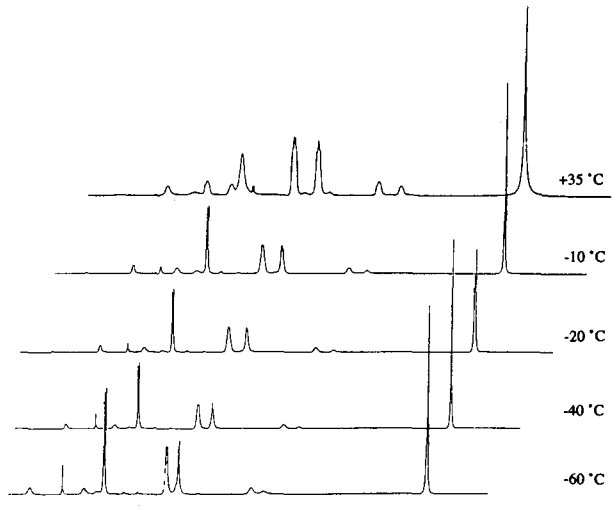

Fig. 2. Variable temperature ^{31}P NMR of [Pt(thiocyanate)$_2$(triphos)] in CH_2Cl_2.

The ^{31}P NMR spectra of the triphos and dpp thiocyanate complexes indicate that the triphos complex is fluxional above −60 °C, whereas the dpp analogue is rigid. Upon raising the temperature above −60 °C, the proportion of S,S-bound isomer in [Pd(thiocyanate)$_2$-(triphos)] is seen to diminish (Fig. 2). Previously, Hunt and Balch argued that thiocyanate isomerism in [Pd(thiocyanate)$_2$(diphosphine)] (diphosphine = $(C_6H_5)_2P(CH_2)_nP(C_6H_5)_2$, n = 1–3) was an intramolecular process on the basis that the spectra obtained for two different concentrations were identical [5]. The fact that platinum–phosphorus coupling is maintained during the isomerization of [Pt(thiocyanate)$_2$(triphos)] also supports a non-dissociative process. In order to determine if the process is thermodynamically or kinetically controlled, the ^{31}P NMR of the same solution was run again after two days at −60 °C. The appearance of an identical spectrum indicates that it is a thermodynamically controlled process.

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