Synthesis and NMR Studies of Palladium(II) and Platinum(II) Complexes with Hybrid Bidentate Ligands $Ph_2P(CH_2)_2SR$

ALESSANDRO DEL ZOTTO, ANTONIO MEZZETTI, PIERLUIGI RIGO*

Istituto di Chimica, Università di Udine, viale Ungheria 43, 33100 Udine, Italy

MARIO BRESSAN, FRANCO MORANDINI and ANTONINO MORVILLO

Dipartimento di Chimica Inorganica, Università di Padova, via Marzolo 1, 35131 Padua, Italy

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Abstract

The reactions of a series of hybrid, potentially bidentate ligands $Ph_2P(CH_2)_2SR$ (P-SR; R = Me, Et, Ph) with palladium(II) and platinum(II) salts are described, together with the syntheses and characterization of a variety of cationic and neutral square-planar complexes of the types [MCl$_2$(*P-S*R)], *cis-* or *trans-*[MX$_2$(*P-S*R)$_2$] (X = Cl, CN), [MCl(*P-S*R)(*P-*SR)]$^+$ and [M(*P-S*R)$_2$]$^{2+}$, in which the P-SR molecules can act either as chelating (*P-S*R) or monodentate, P-bound ligands (*P-*SR). In solution, the various species are interconverted among each other by equilibria which show a marked dependence on solvent polarity, presence of excess ligand, temperature, nature of X and R groups.

Introduction

Many complexes of the platinum-group metals have been found to catalyze important chemical reactions involving unsaturated organic molecules. The existence of a vacant coordination site is an essential property of homogeneous catalysts, since it allows organic substrates to enter the coordination sphere of the metal atom [1]. In this context, we are currently investigating the chemistry of transition metal complexes containing various phosphorus—sulfur bidentate ligands [2]. A general feature of these compounds is that the sulfur end of the chelate can be easily displaced from the metal atom by a molecule of a substrate, generating potential catalytically-active systems.

In this paper, we describe a series of palladium(II) and platinum(II) complexes with the ligands Ph_2P-$(CH_2)_2SR$ (R = Me, P-SMe; R = Et; P-SEt; R = Ph, P-SPh). A few palladium(II) and platinum(II) derivatives with P-SPh have been previously reported by Sanger [3], who prepared complexes of the type *cis*-[M(*P-S*Ph)$_2$](BPh$_4$)$_2$, [MCl(*P-S*Ph)(*P-*SPh)]BPh$_4$ and MCl$_2$(P-SPh)$_n$ (M = Pd, Pt; *n* = 1, 2). Moreover, Anderson and Kumar [4] reported on the reaction of the P-SMe ligand with chloroform solutions of [PtX$_2$-(cod)] (X = Cl, I). With the aim to have a complete scope of the topic, we have extended the study to the previously unexplored P-SEt ligand, systematically investigating the complexes formed by palladium(II) and platinum(II) with all three P-SR ligands. The structures of the adducts [MCl$_2$(*P-S*R)], MX$_2$(P-SR)$_2$ (X = Cl, CN), [MCl(*P-S*R)(*P-*SR)]BPh$_4$ and *cis*-[M(*P-S*R)$_2$](ClO$_4$)$_2$ have been determined by $^{31}P\{^1H\}$ NMR as well as by UV–Vis, IR and ^1H NMR spectroscopy.

The solution behaviour of these adducts is quite complex, since equilibria are established between different species, depending on both temperature and solvent polarity, as found for other hybrid ligands containing P (or As) and O (or N) as donor atoms [5]. The stereochemistry of the compounds appears to be related to the nature of both the anionic ligand and the organic substituent at the sulfur atom. Moreover, in the 2:1 ligand-to-metal complexes, each P-SR can act as either a bidentate (indicated in the present work as *P-S*R), or a monodentate ligand bonding only through the phosphorus atom (*P-*SR). These flexible P-SR ligands appear to be more versatile than diphenyl(*o*-methylthiophenyl)phosphine which has the same donor atom set but a rather rigid aryl framework [6]. A preliminary communication on the electrochemical behaviour of some of the complexes described herein has appeared previously [7].

Experimental

General Procedures and Materials

IR and UV–Vis spectra were recorded on Perkin-Elmer 457 and 576 spectrophotometers; solid-state spectra were obtained by use of nujol mulls sup-

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ported on filter paper. ^{31}P NMR spectra were recorded at 24.28 and 32.44 MHz on Bruker WP 60 and WP 80 spectrometers, respectively, with ^{1}H complete decoupling. Chemical shifts are referenced to external 85% H_3PO_4 with downfield positive shifts. Conductance measurements were performed on a Radiometer CDM-3 conductivity bridge using nitromethane solutions. The ligands 1-(thiomethyl)-2-(diphenylphosphino)ethane (P-SMe), 1-(thioethyl)-2-(diphenylphosphino)ethane (P-SEt) and 1-(thiophenyl)-2-(diphenylphosphino)ethane (P-SPh) were prepared as described previously [2a]. The starting materials $(NH_4)_2[PdCl_4]$, $K_2[PtCl_4]$, $[PdCl_2(CH_3-CN)_2]$ and $[PtCl_2(PhCN)_2]$ were either commercially available or synthesized by standard procedures. The compounds $[MCl(P\text{-}SPh)(P\text{-}SPh)]BPh_4$ (M = Pd, Pt) were obtained as described previously [3]. The preparations of the complexes were performed under a nitrogen atmosphere. Yields were in the range 65–90%. All compounds were analyzed for carbon, hydrogen, chlorine or nitrogen, and gave results within acceptable limits. Microanalyses were performed by the Microanalytical Laboratories of the Istituto di Chimica (Udine) and the Dipartimento di Chimica Inorganica (Padova).

cis-[M(P-SR)₂](ClO₄)₂ (M = Pd, Pt, R = Et, Ph)

A hot ethanol solution of the P-SR ligand (2 mmol) was added under stirring to a hot concentrated aqueous solution of $(NH_4)_2[PdCl_4]$ or $K_2[PtCl_4]$ (1 mmol). The resulting mixture was heated until a clear solution was obtained. An ethanolic solution of $NaClO_4 \cdot H_2O$ (2.5 mmol) was added, and the solution allowed to cool. The white precipitate was filtered off and recrystallized from dichloromethane–ethanol.

cis-[M(P-SMe)₂](ClO₄)₂ (M = Pd, Pt)

The ligand P-SMe (2 mmol) and the complex $[MCl_2(RCN)_2]$ (M = Pd, R = Me; M = Pt, R = Ph) (1 mmol) were suspended in methanol, and the resulting mixture stirred until dissolution occurred. The compound was precipitated by addition of $NaClO_4 \cdot H_2O$ (2.5 mmol), and recrystallized from dichloromethane–ethanol.

trans-[M(CN)₂(P-SR)₂] (M = Pd, Pt; R = Et, Ph)

To a suspension of $[M(P\text{-}SR)_2](ClO_4)_2$ (1 mmol) in ethanol, an aqueous solution of NaCN (2 mmol) was slowly added. The mixture was refluxed with continuous stirring until a clear solution formed. The product separated by addition of hexane, and was recrystallized from dichloromethane–hexane.

trans-[M(CN)₂(P-SMe)₂] (M = Pd, Pt)

The complex $[MCl_2(RCN)_2]$ (M = Pd, R = Me; M = Pt, R = Ph) (1 mmol) and the ligand (2 mmol) were suspended in methanol until a clear solution

formed. KCN (2 mmol), dissolved in ethanol–water (10:1), was added. The complex separated by addition of hexane, and was recrystallized from dichloromethane–hexane.

[MCl₂(P-SR)] (M = Pd, Pt; R = Et, Ph)

A hot ethanolic solution of P-SR (1 mmol) was added to an aqueous solution of $(NH_4)_2[PdCl_4]$ or $K_2[PtCl_4]$ (1 mmol). After refluxing for 2 h, the mixture was cooled to room temperature, yielding the product, which was recrystallized from dichloromethane–ethanol.

[MCl₂(P-SMe)] (M = Pd, Pt)

The ligand P-SMe (1 mmol) and the complex $[MCl_2(RCN)_2]$ (M = Pd, R = Me; M = Pt, R = Ph) (1 mmol) were dissolved in benzene, wherefrom the compound separated upon addition of hexane. Recrystallization from dichloromethane–hexane.

cis-[M(P-SMe)₂]Cl₂ (M = Pd, Pt)

The ligand P-SMe (2 mmol) and the complex $[MCl_2(RCN_2)]$ (M = Pd, R = Me; M = Pt, R = Ph) (1 mmol) were suspended in benzene, wherefrom the product precipitated. Recrystallization from dichloromethane–hexane.

[MCl₂(P-SR)₂] (M = Pd, Pt; R = Et, Ph)

Aqueous solutions of $(NH_4)_2[PdCl_4]$ or $K_2[PtCl_4]$ (1 mmol) and ethanolic solutions of the ligand P-SR (2 mmol) were mixed together and refluxed for 2 h. The resulting clear solution was cooled and diethyl ether added. The crude precipitate was recrystallized from dichloromethane–diethyl ether.

cis-[MCl(P-SR)₂]BPh₄ (M = Pd, Pt; R = Me, Et, Ph)

The ligand P-SR (2 mmol) and the complex $[MCl_2-(R'CN)_2]$ (M = Pd, R' = Me; M = Pt, R' = Ph) (1 mmol) were dissolved in dichloromethane, and $NaBPh_4$ (1 mmol), dissolved in tetrahydrofurane, was added. The compound separated upon addition of hexane, and was recrystallized from dichloromethane–hexane.

Results and Discussion

Perchlorate Derivatives

The white $[M(P\text{-}SR)_2](ClO_4)_2$ complexes can be prepared directly by reacting the P-SR ligands (R = Et, Ph) with either $(NH_4)_2[PdCl_4]$ or $K_2[PtCl_4]$ in boiling aqueous ethanol (molar ratio 2:1). In the case of the P-SMe derivatives, a milder route can be followed, in order to avoid S-demethylation reactions [8], *i.e.* starting from $[MCl_2(RCN)_2]$ complexes, in which the chelating ligand easily displaces the two nitrile molecules. In agreement with a four-coordinate

planar structure, the IR spectra of the diamagnetic solids show no evidence for the coordination of the perchlorate groups, and their nitromethane solutions (1 mM) have molar conductances which are close to the values expected for 2:1 electrolytes. Conductivities were measured also at various concentrations, the plot Λ_e *versus* $N^{1/2}$ being linear over the concentration range 10–0.1 mM. A and Λ_o values (330–345 ohm^{-1} cm^2 equiv^{-1} $N^{-1/2}$ and 102–108 ohm^{-1} cm^2 equiv^{-1}, respectively) from the Onsanger equation $\Lambda_o = \Lambda_e + AN^{1/2}$ agree with those reported for 2:1 electrolytes [9]. The $^{31}P\{^1H\}$ NMR spectra of the $[Pt(P\text{-}SR)_2]^{2+}$ cations exhibit a single sharp resonance with ^{195}Pt satellites [$^1J(Pt-P) = ca.$ 3100 Hz], thus suggesting structure **I** (Scheme 1), in which the phosphorus atoms are in mutually *cis* positions [10].

The palladium derivatives are likely to have a similar structure, although direct evidence has been obtained only in the case of the P-SMe derivative. The ^1H NMR spectrum of $[Pd(P\text{-}SMe)_2](ClO_4)_2$ shows that the resonance of the methyl protons (which appears as a singlet both in the free ligand and when P-SMe acts as monodentate) consists of a sharp doublet due to coupling to the phosphorus atom in the *trans* position [$^4J(P-H) = 4.5$ Hz]. In the case of the $[Pt(P\text{-}SMe)_2](ClO_4)_2$ complex, the thiomethyl proton resonance also appears as a doublet [$^4J(P-H) = 3.3$ Hz], accompanied by satellites due to coupling to ^{195}Pt ($^3J(Pt-H) = 16.1$ Hz). The methyl resonances of the coordinated thiomethyl group show characteristic downfield shifts with respect to the free ligand (about 0.7 ppm).

The downfield shift of phosphorus resonances upon coordination $\Delta_{obs} = \delta_{coordinated} - \delta_{free\ ligand}$ is remarkably large, as expected for phosphorus donors involved in five-membered chelate rings [11]. The observed values are given in Tables 1 and 2, and are similar to those reported for other palladium(II) and

platinum(II) complexes containing five-membered chelating diphosphines [11]*.

Cyano Derivatives

The *cis*-$[M(P\text{-}SR)_2](ClO_4)_2$ complexes readily react with CN$^-$ (1:2 molar ratio) to give diamagnetic products of composition $M(CN)_2(P\text{-}SR)_2$. When the reaction is carried out in a 1:1 molar ratio, only a mixture of *trans*-$[M(CN)_2(P\text{-}SR)_2]$ and *cis*-$[M(P\text{-}SR)_2](ClO_4)_2$ is recovered. The dicyano complexes are monomeric and non-electrolytes in 1,2-dichloroethane and nitromethane. Their IR spectra in nujol mull exhibit a single sharp peak in the 2120–2130 cm^{-1} region, which is consistent with a *trans* arrangement of the two cyano groups. The ^{31}P NMR spectra consist of a single resonance, accompanied in the case of the platinum derivatives by satellites due to coupling to ^{195}Pt, and are invariant over the temperature range 190–310 K. Coordination chemical shifts are similar to those found for analogous complexes with monodentate phosphines [11], and also the $^1J(Pt-P)$ values agree with those of the *trans*-$[Pt(CN)_2(PR_3)_2]$ adducts (Tables 1, 2). Moreover, in the ^1H NMR spectra of the P-SMe and P-SEt derivatives, the spectral patterns of the thiomethyl and thioethyl groups are nearly the same as in the free ligands. Structure **II** is therefore proposed for the $[M(CN)_2(P\text{-}SR)_2]$ complexes, in which both P-SR ligands are bonded to the metal through the phosphorus atom only.

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*The observed Δ values can be regarded as being made up of a 'normal' coordination shift Δ_N, measured from an equivalent phosphorus atom in a non-chelate analogue, and a 'ring contribution' Δ_R, *i.e.* $\Delta = \Delta_N + \Delta_R$. A qualitative estimation of Δ_R is obtained assuming for Δ_N the data found for the series of *trans*-$[M(CN)_2(P\text{-}SR)_2]$ (differences would be caused by the different *trans* ligands), and gives 44.8–50.1 and 31.7–37.8 ppm for Pd(II) and Pt(II), respectively.
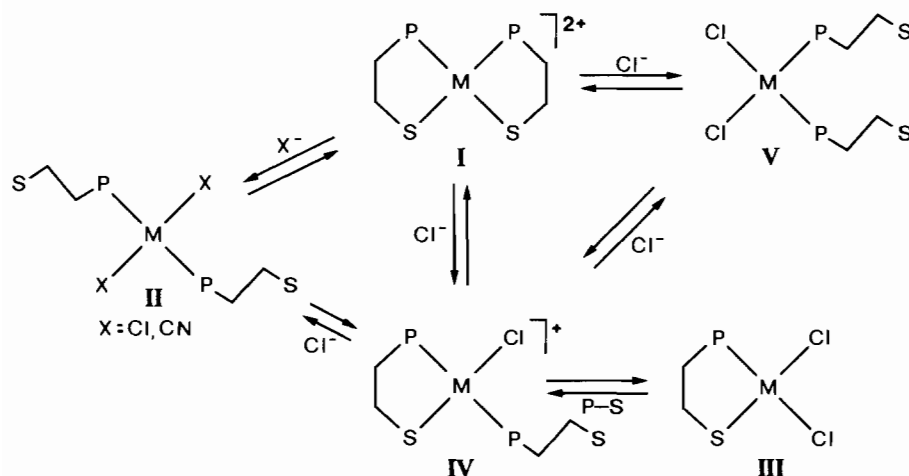
Scheme 1.

TABLE 1. Spectroscopic and Physical Data for Palladium Complexes

Compound	Colour	^{31}P NMR[a, b] $\delta(\Delta)$ (ppm)[f]	Dominant species	UV–Vis[c] λ_{max} (nm)	IR[d] (cm^{-1})	Λ_M[e] (S cm^2 mol^{-1})
cis-[Pd(P-SMe)$_2$](ClO$_4$)$_2$	white	61.3 (78.2)	I			178
cis-[Pd(P-SEt)$_2$](ClO$_4$)$_2$	white	61.2 (78.0)	I			181
cis-[Pd(P-SPh)$_2$](ClO$_4$)$_2$	white	62.1 (79.1)	I			195
trans-[Pd(CN)$_2$(P-SMe)$_2$]	white	16.2 (33.2)	II		2119[g]	
trans-[Pd(CN)$_2$(P-SEt)$_2$]	white	16.4 (33.2)	II		2120[g]	
trans-[Pd(CN)$_2$(P-SPh)$_2$]	pale yellow	16.6 (33.6)	II		2118[g]	
[PdCl$_2$(P-SMe)]	yellow	63.4 (80.4)	III	361	334, 287[h]	
[PdCl$_2$(P-SEt)]	yellow	66.5 (83.3)	III	358	330, 291[h]	
[PdCl$_2$(P-SPh)]	yellow	64.3 (81.3)	III	364	320, 284[h]	
cis-[PdCl(P-SMe)(P-SMe)]BPh$_4$	yellow	43.8 (60.8) 58.2 (75.2)[i]	IV I	335(sh)	316[h]	79
cis-[PdCl(P-SEt)(P-SEt)]BPh$_4$	yellow	46.5 (63.3) 58.5 (75.3)[i]	IV I	335(sh)	315[h]	64
cis-[PdCl(P-SPh)(P-SPh)]BPh$_4$	yellow	43.4 (60.4) 64.4 (81.4), 21.5 (38.5)[i]	IV IV	340(sh)	311[h]	48
cis-[Pd(P-SMe)$_2$]Cl$_2$	white	44.1 (61.1) 59.4 (76.4)[j] 57.1 (74.1)[k]	IV I I	335(sh)		75
trans-[PdCl$_2$(P-SPh)$_2$]	yellow	15.5 (32.5) 43.9 (60.1)[l] 64.9 (81.9), 20.5 (37.5)[i]	II IV IV	342	325[h]	75
[PdCl$_2$(P-SEt)] + P-SEt		45.7 (62.5) 57.4 (74.2)[l] 59.7 (76.5)[m]	IV I I			81
[PdCl$_2$(P-SEt)] + PEtPh$_2$[n]		63.1 (79.9), 28.0 (40.5)[o, p]	IV			
[PdCl$_2$(P-SPh)] + PEtPh$_2$[n]		16.5, 18.5[q] 62.9 (79.9), 29.9 (42.4)[o, r]	II IV			

[a]In CH$_2$Cl$_2$ solution at room temperature, unless otherwise stated. [b]Positive values downfield from 85% H$_3$PO$_4$. [c]In CH$_2$Cl$_2$ solution. [d]In nujol mull. [e]In CH$_3$NO$_2$ solution (10^{-3} M). [f]$\Delta = \delta_{coord} - \delta_{free\ ligand}$; δ values (ppm) for free ligands in CH$_2$Cl$_2$ at room temperature: −17.0 (P-SMe), −16.8 (P-SEt), −17.0 (P-SPh) and −12.5 (PEtPh$_2$). [g]ν(CN). [h]ν(Pd–Cl). [i]In CD$_2$Cl$_2$–CHF$_2$Cl solution, $t = -90$ °C. [j]In CD$_2$Cl$_2$–CHF$_2$Cl solution, $t = -120$ °C. [k]In CH$_3$OH–CH$_3$NO$_2$ (1:1) solution, at room temperature. [l]$t = -60$ °C. [m]In CH$_3$OH solution, at room temperature. [n]In 1:1 molar ratio. [o]In CH$_2$Cl$_2$–CH$_3$OH (9:1) solution, at room temperature. [p]^2J(P–P') = 5.5 Hz. [q]^2J(P–P') = 52.0 Hz. [r]^2J(P–P') = 5.5 Hz.

TABLE 2. Spectroscopic and Physical Data for Platinum Complexes

Compound	^{31}P NMR[a, b] $\delta(\Delta)$ (ppm)[e]	^1J(Pt–P) (Hz)	Dominant species	IR[c] (cm^{-1})	Λ_M[d] (S cm^2 mol^{-1})
cis-[Pt(P-SMe)$_2$](ClO$_4$)$_2$	45.3 (62.3)	3089	I		179
cis-[Pt(P-SEt)$_2$](ClO$_4$)$_2$	45.2 (62.0)	3112	I		197
cis-[Pt(P-SPh)$_2$](ClO$_4$)$_2$	45.2 (62.2)	3142	I		179
trans-[Pt(CN)$_2$(P-SMe)$_2$]	7.5 (24.5)	2310	II	2132[f, g]	
trans-[Pt(CN)$_2$(P-SEt)$_2$]	7.6 (24.4)	2304	II	2120[f]	
trans-[Pt(CN)$_2$(P-SPh)$_2$]	7.9 (24.9)	2300	II	2118[f]	
[PtCl$_2$(P-SMe)]	39.2 (56.2)	3662	III	291, 323[h]	
[PtCl$_2$(P-SEt)]	39.5 (56.3)	3660	III	298, 320[h]	
[PtCl$_2$(P-SPh)]	39.7 (56.7)	3584	III	293, 325[h]	
cis-[PtCl(P-SMe)(P-SMe)]BPh$_4$	27.0 (44.0) 43.9 (60.9)[i]	3331 3130	IV I	315[h]	60
cis-[PtCl(P-SEt)(P-SEt)]BPh$_4$	26.8 (43.6) 43.7 (60.5)[i]	3324 3127	IV I	314[h]	65

(continued)

TABLE 2. *(continued)*

Compound	^{31}P NMR[a, b]		Dominant species	IR[c] (cm^{-1})	Λ_M[d] ($S\ cm^2\ mol^{-1}$)
	$\delta(\Delta)$ (ppm)[e]	^1J(Pt–P) (Hz)			
cis-[PtCl(*P-S*Ph)(*P*-SPh)]BPh$_4$	43.9 (60.9), 6.3 (23.3)[j]	3495, 3142[k]	IV	314[h]	50
	44.7 (61.7)[l]	3079	I		
cis-[Pt(*P-S*Me)$_2$]Cl$_2$	27.5 (44.5)	3333	IV		81
	44.6 (61.6)[i]	3150	I		
	45.1 (62.1)[m]	3070	I		
cis-[PtCl$_2$(*P*-SEt)$_2$]	28.9 (45.7)	3320	V	308, 312[h]	86
	44.2 (61.0)[n]	3194	I		
	45.6 (62.4)[m]	3201	I		
cis-[PtCl$_2$(*P*-SPh)$_2$]	13.4 (30.4)	3512	V	303, 316[h]	78
	44.3 (61.3), 7.3 (24.3)[i]	3497, 3142[o]	IV		
	5.4 (22.4)[p]	3586	V		
	31.4 (48.4)[n]	3296	IV		
	46.3 (63.3)[q]	3121	I		
[PtCl$_2$(*P*-SEt)] + PEtPh$_2$ [r]	43.7 (60.5), 11.9 (24.4)[s]	3538, 3140[t]	IV		

[a]In CH$_2$Cl$_2$ solution at room temperature, unless otherwise stated. [b]Positive values downfield from 85% H$_3$PO$_4$. [c]In nujol mull. [d]In CH$_3$NO$_2$ solution (10^{-3} M). [e]$\Delta = \delta_{coord} - \delta_{free\ ligand}$; δ values (ppm) for free ligands in CH$_2$Cl$_2$ at room temperature: −17.0 (P-SMe), −16.8 (P-SEt), −17.0 (P-SPh), and −12.5 (PEtPh$_2$). [f]ν(CN). [g]In CH$_2$Cl$_2$ solution; 2134, 2128 cm^{-1} in nujol mull. [h]ν(Pt–Cl). [i]In CD$_2$Cl$_2$–CHF$_2$Cl solution, t = −90 °C. [j]t = −60 °C. [k]^2J(P–P') = 15.8 Hz. [l]In CH$_2$Cl$_2$–CH$_3$OH (1:3) solution, t = −90 °C. [m]In CH$_3$OH at room temperature. [n]t = −70 °C. [o]^2J(P–P') = 14.6 Hz. [p]In CH$_2$Cl$_2$–C$_6$H$_6$ (1:1) solution, at room temperature. [q]In CH$_3$OH, t = −70 °C. [r]In 1:1 molar ratio. [s]In CH$_2$Cl$_2$–CH$_3$OH (9:1) solution, at room temperature. [t] ^2J(P–P') = 4.0 Hz.

It should be noted that, while in the starting bis-chelate complexes the phosphorus atoms of the two P-SR ligands are in mutually *cis* positions, in the dicyano derivatives a *trans* arrangement is present. It is interesting to recall here that the stereochemistry of the related Ni(CN)$_2$(P-SR)$_2$ complexes depends on the nature of R: when the substituent is a phenyl group, a complex with structure **II** is obtained, whereas with P-SMe and P-SEt the five-coordinate complexes [Ni(CN)$_2$(P-SR)(P-SR)], containing both mono- and bidentate P-SR ligands, are formed [2a].

Chloro Derivatives

The reactions between ammonium tetrachloropalladate(II) or potassium tetrachloroplatinate(II) and the ligands P-SR (R = Ph, Et) in ethanol (1:1 molar ratio) lead to [MCl$_2$(*P-S*R)] species. The P-SMe derivatives are more conveniently prepared from [MCl$_2$(RCN)$_2$] in non-polar solvents. The IR spectra of these monomeric, non-electrolyte compounds exhibit two bands in the 280–335 cm^{-1} region, attributable to M–Cl vibrations (Tables 1, 2). Their ^{31}P{^{1}H} NMR spectra show sharp singlets, with coordination chemical shift values typical of five-membered chelate rings (Tables 1, 2). The ^1J(Pt–P) values of the platinum adducts (around 3600 Hz) are typical for a phosphorus atom *trans* to chlorine (structure **III**) [10].

The reactions of [MCl$_4$]$^{2-}$ or [MCl$_2$(RCN)$_2$] with an excess of P-SR yield the 1:2 adducts MCl$_2$(P-SR)$_2$, whose solid state structures and solution behaviour

appear to be dependent on the nature of the thioether arm. The PdCl$_2$(P-SEt)$_2$ complex can be obtained only in an impure form, since one P-SEt molecule is lost upon recrystallization.

In low polarity solvents, the reactions of the MCl$_2$(P-SR)$_2$ adducts with equimolar amounts of NaBPh$_4$ give the corresponding [MCl(*P-S*R)(*P*-SR)]-BPh$_4$ complexes, which are attributed structure **IV** on the basis of the following evidences. The complexes [MCl(*P-S*R)(*P*-SR)]BPh$_4$ behave as 1:1 electrolytes both in dichloromethane and nitromethane, though the P-SMe and P-SEt derivatives exhibit slightly higher Λ_M values (Tables 1, 2), possibly due to the formation of the dicationic species **I** in 10^{-3} M solutions (*vide infra*). In these solvents the compounds are stereochemically non-rigid on the NMR time scale, as their room temperature ^{31}P NMR spectra exhibit a broad resonance with a coordination chemical shift which is intermediate between the values expected for chelating and phosphorus-bound, monodentate P-SR ligands. It is apparent that the two inequivalent P atoms give rise to a single broad resonance owing to the rapid exchange between the bi- and monodentate P-SR ligands.

In the case of [PdCl(*P-S*Ph)(*P*-SPh)]BPh$_4$, the single resonance splits into two broad signals of intensity ratio 1:1, when a dichloromethane–difluorochloromethane solution of the complex is cooled to −90 °C. The lower field signal (64.4 ppm) can be assigned to the P atom of a chelate P-SPh ligand, while the high-field one (21.5 ppm) is attributed to a

P-SPh molecule acting as monodentate. No fine structure is observed, thus suggesting a low $^2J(P-P')$ value, which is indicative of a mutually *cis* position of the two phosphorus atoms (structure **IV**). In the case of [PtCl(*P-S*Ph)(*P*-SPh)]BPh$_4$, as previously reported by Sanger [3], the exchange can be frozen already at -60 °C, the single resonance at *ca.* 26 ppm (with ^{195}Pt satellites) being replaced by a pair of doublets at 43.9 and 6.3 ppm, with a $^2J(P-P')$ value typical of mutually *cis*-phosphines.

On the contrary, when the solutions of [MCl(*P-SR*)(*P*-SR)]BPh$_4$ (R = Me, Et) are cooled below room temperature, the ^{31}P NMR signals undergo marked downfield shifts (from *ca.* 45 to *ca.* 58 ppm, and from *ca.* 27 to *ca.* 44 ppm for M = Pd and Pt, respectively), to positions typical of the bis-chelate derivatives **I**. It is concluded that in this case a temperature-dependent equilibrium takes place between species **IV** and **I**, the latter being favoured at low temperature.

Due to the non-rigid nature of the P-SMe and P-SEt derivatives of type **IV**, we were not able to determine the mutual positions of the two phosphorus atoms. However, as far as the palladium derivatives are concerned, it should be noted that the UV−Vis spectra of the three complexes [PdCl(*P-SR*)(*P*-SR)]BPh$_4$ have similar patterns both in the solid state and in dichloromethane solution at room temperature, and are consistent with identical square-planar structures. In the case of the analogous platinum(II) derivatives, the $^1J(Pt-P)$ coupling constants at room temperature (*ca.* 3330 Hz) are intermediate between the characteristic values found for a phosphorus *trans* to a chlorine [$^1J(Pt-P) = ca.$ 3600 Hz] and a phosphorus *trans* to a thioether function [$^1J(Pt-P) = ca.$ 3130 Hz] (Table 2).

At low temperature, the yellow colours of the dichloromethane solutions of the [PdCl(*P-SR*)(*P*-SR)]BPh$_4$ (R = Me, Et) complexes fade, thus ruling out the formation of five-coordinate species of the type [PdCl(*P-SR*)$_2$]$^+$, which are expected to be more intensely coloured than the square-planar analogues [6].

The yellow [PdCl$_2$(*P*-SPh)$_2$] derivative is assigned *trans* configuration **II** with two dangling ligands in the solid state on the basis of the single Pd−Cl absorption in its IR spectrum, and of the UV−Vis spectrum ($\lambda_{max} = 340$ nm in nujol mull), which is practically coincident with that of *trans*-[PdCl$_2$-(PPh$_2$Et)$_2$]. The dichloromethane solutions are only slightly conducting, being the UV−Vis spectra substantially coincident with those observed for the solid state. Significantly, the ^{31}P NMR spectrum consists of a single signal at 15.5 ppm, indicating the presence of two monodentate P-SPh ligands. However, on cooling this signal broadens and shifts downfield to the typical position of the [PdCl(*P-S*Ph)-(*P*-SPh)]$^+$ species. Addition of excess chloride rapidly

restores the original signal at 15.5 ppm; thus, in agreement with the suggestions already made by Sanger [3], it is concluded that a temperature-dependent equilibrium takes place between species **II** and the monocationic species [PdCl(*P-S*Ph)-(*P*-SPh)]$^+$ (**IV**). If the temperature is lowered below -90 °C (CH$_2$Cl$_2$−CHF$_2$Cl solution), a static, resolved NMR spectrum is obtained, with ^{31}P signals at *ca.* 65 and 21 ppm, as found for [PdCl(*P-S*Ph)(*P*-SPh)]$^+$.

In more polar media (nitromethane, methanol) [PdCl$_2$(*P*-SPh)$_2$] behaves as a 1:1 electrolyte already at room temperature. Conductometric titrations in nitromethane of either [PdCl$_2$(*P*-SPh)] with P-SPh or [Pd(*P-S*Ph)$_2$](ClO$_4$)$_2$ with [AsPh$_4$]Cl exhibit sharp equivalent points at 1:1 molar ratios. The ^{31}P NMR spectra of the equivalent point mixtures, or more directly of [PdCl$_2$(*P*-SPh)$_2$] in nitromethane, all exhibit the single resonance at *ca.* 43 ppm, diagnostic of the monocationic species **IV**, whose presence is also confirmed by UV−Vis measurements.

In this context, we have examined the reactions between [PdCl$_2$(*P-S*Ph)] and the tertiary phosphine PPh$_2$Et, which is the closest monodentate analogue of P-SPh. In dichloromethane solution, the reaction leads to the neutral *trans*-[PdCl$_2$(*P*-SPh)(PPh$_2$Et)] species, which contains a monodentate P-SPh ligand (structure **II**); the two inequivalent phosphorus atoms give rise to a ^{31}P NMR AB pattern, with a $^2J(P-P')$ of 52.0 Hz. When the reaction is carried out in more polar media, the spectral pattern is entirely different, and fully consistent with the presence of the mono-cationic *cis*-[PdCl(*P-S*Ph)(PPh$_2$Et)]$^+$ derivative [$^2J(P-P') = 5.5$ Hz], with a chelating P-SPh ligand (structure **IV**). It is noteworthy that the equilibrium between the species **II** and **IV** involves a *cis−trans* isomerization reaction, which appears to be dependent on both temperature and medium polarity.

As noted above, the yellow PdCl$_2$(P-SEt)$_2$ complex cannot be obtained in a pure form. Therefore, the behaviour of 1:1 mixtures of [PdCl$_2$(*P-S*Et)] and PSEt have been studied. Conductometric titrations, UV−Vis spectra, and ^{31}P NMR data suggest the formation of the monocationic derivative **IV** in nitromethane solution. Accordingly, [PdCl(*P-SEt*)-(*P*-SEt)]BPh$_4$ shows the same NMR features as the above mixtures. It should be noted that, in contrast with the P-SPh derivative, species **IV** predominates also in dichloromethane solution. Even when an excess of chloride is added, there is no evidence for the presence of **II**; instead, elimination of a P-SEt molecule occurs and [PdCl$_2$(*P-S*Et)] is formed. The same differences are observed for the model system [PdCl$_2$(*P-S*Et)]/PPh$_2$Et (1:1 molar ratio), which quantitatively yields the *cis* [PdCl(*P-SEt*)(PPh$_2$Et)]$^+$ cation in both dichloromethane and methanol solution [$^2J(P-P') = 5.5$ Hz].

If a dichloromethane solution containing [PdCl$_2$-(*P-S*Et)] and free P-SEt is cooled to low temperature,

the ^{31}P NMR signal shifts downfield from *ca.* 46 to *ca.* 57 ppm ($t = -60$ °C), in agreement with a temperature-dependent equilibrium between **IV** and **I**. It should be noted that, if [PdCl$_2$(*P-S*Et)] and PSEt are dissolved in methanol, the bis-chelate species (**I**) is formed already at room temperature, even in the presence of excess [AsPh$_4$]Cl.

At contrast with the yellow P-SPh and P-SEt derivatives, the 2:1 adduct PdCl$_2$(P-SMe)$_2$ is white. Since no bands attributable to Pd—Cl stretchings are observed in the 300 cm^{-1} region, this complex is presumed to have the dicationic structure I with ionic chlorines in the solid state. Dissolution of [Pd(*P-SMe*)$_2$]Cl$_2$ in dichloromethane or nitromethane gives yellow solutions, whose UV—Vis and ^{31}P NMR features are very similar to those of [PdCl(*P-SMe*)-(*P-SMe*)]BPh$_4$. Moreover, the solution behaviour of [Pd(*P-SMe*)$_2$]Cl$_2$ suggests a temperature and medium polarity dependent equilibrium between species **IV** and I (Table 1), as found for the analogous system with P-SEt.

The solid-state structures of the colourless PtCl$_2$-(P-SR)$_2$ are tentatively assigned on the basis of their far-infrared spectra. In the 325—295 cm^{-1} region, the thiophenyl and thioethyl derivatives exhibit two bands which can be attributed to Pt—Cl stretching modes, in agreement with *cis*-structure V, in which the ligands act as monodentate. By contrast, no Pt—Cl bands are observed in the spectrum of the P—SMe derivative, which is assumed to have structure I, with ionic chlorines in the solid state.

Dissolution of the three complexes in dichloromethane is accompanied by the formation of species **IV**, which can be in equilibrium with **I** and V, depending on the nature of P—SR, the polarity of solvent, and the temperature. Again, a somewhat different behaviour is observed with the phenyl substituted thioether. At room temperature in dichloromethane solution, the ^{31}P{^{1}H} NMR spectrum of *cis*-[PtCl$_2$(P-SPh)$_2$] exhibits a broad signal at 13.4 ppm, which suggests an equilibrium between species V and **IV**. If benzene (1:1) is added, the signal shifts to 5.4 ppm, in a position typical for monodentate P-SR ligands. Moreover, cooling of the dichloromethane solution causes the signal to shift downfield and broaden; as previously observed for [PtCl(*P-SPh*)(*P-SPh*)]$^+$, this broad resonance resolves at −60 °C, in agreement with the dominant presence of species **IV**. In methanol solution, an equilibrium between **IV** and **I** is observed, with the dication dominating at low temperature (Table 2).

In the case of *cis*-[PtCl$_2$(P-SEt)$_2$] and *cis*-[Pt(*P-SMe*)$_2$]Cl$_2$, species **IV** predominate in dichloromethane solution at room temperature, while at low temperature, or in more polar solvents such as methanol, almost quantitative conversion to dication **I** is observed (Table 2). In neither of the two solvents there is any evidence for the formation of ion-paired

species, as previously reported by Anderson and Kumar for chloroform solutions of the [PtCl$_2$(cod)]/P-SMe system [4]. Indeed, [Pt(*P-SMe*)$_2$]Cl$_2$ is completely insoluble in chloroform, and this prevents direct NMR measurements to be performed.

Conclusions

The reactions and interconversions of palladium-(II) and platinum(II) complexes with the P-SR ligands, which are summarized in Scheme 1, indicate that the dications **I** are formed with non-coordinating anions, whereas in the presence of a strong σ-donor such as cyanide the thioether functions are readily displaced, yielding the neutral species **II**, in which the phosphorus atoms are in mutually *trans* positions. The reactions in the presence of chloride ions have proved to be much more complicated, since equilibria among several products are established. The position of these equilibria depend on the polarity of media and the temperature, but also on the nature of the P-SR ligands. With the more basic (or less hindered) thioalkyl ligands, the coordination of the sulfur moiety appears to be favoured: in fact, with P-SPh the monocationic species **IV** are stabilized in dichloromethane solution even at low temperature, whereas with the other P-SR ligands the chloride ligand is readily displaced on lowering the temperature, with formation of bis-chelate species **I**. It is apparent that in dichloromethane the thioether function is a sufficiently good nucleophile as to displace chloride when R is an alkyl, but not when R is a phenyl group.

In more polar solvents such as methanol, which definitely stabilize ionic species, the equilibria are shifted in favour of the dication **I** also at room temperature. No reaction occurs upon introduction of a large excess of chloride ions, indicating that in these conditions the chloride does not compete effectively with the thioether moiety for the coordination at the metal. The present results also indicate that the nature of the solvent plays a crucial role in determining different reaction pathways, and therefore may greatly influence the possible applications of these complexes in homogeneous catalysis.

Supplementary Material

Tables of elemental analyses are available on request from the authors at the Udine address.

Acknowledgements

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