Journal of Organometallic Chemistry, 342 (1988) 263–268
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

Platinum and rhodium complexes in which diphenylphosphino(methylthio)methane acts as a monodentate, chelated or bridging ligand

Gordon K. Anderson* and **Ravi Kumar**

Department of Chemistry, University of Missouri-St. Louis, St. Louis, Missouri 63121 (U.S.A.)

(Received April 3rd, 1987)

Abstract

Reaction of $[PtCl_2(cod)]$ with $Ph_2PCH_2SCH_3$ yields *cis*-$[PtCl_2(Ph_2PCH_2SCH_3)_2]$ which, on treatment with $AgBF_4$, is converted to $[PtCl(Ph_2PCH_2SCH_3)_2]BF_4$, in which one of the ligands is chelated. With $[Pt(dba)_2]$, *cis*-$[PtCl_2(Ph_2PCH_2SCH_3)_2]$ reacts to give the platinum(I) complex $[Pt_2Cl_2(\mu\text{-}Ph_2PCH_2SCH_3)_2]$, which contains a platinum–platinum bond. The terminal chlorides may be replaced by iodide, but the complex is cleaved by carbon monoxide. $[Rh_2(\mu\text{-}Cl)_2(CO)_4]$ reacts with $Ph_2PCH_2SCH_3$ to produce $[Rh_2Cl_2(CO)_2(\mu\text{-}Ph_2PCH_2SCH_3)_2]$, whereas with $Ph_2PCH_2CH_2SCH_3$ it yields $[RhCl(CO)(Ph_2PCH_2CH_2SCH_3)]$. A ligand exchange reaction occurs between *cis*-$[PtCl_2(Ph_2PCH_2SCH_3)_2]$ and $[Rh_2(\mu\text{-}Cl)_2(CO)_4]$ to give *cis*-$[PtCl_2(CO)(Ph_2PCH_2SCH_3)]$ and $[Rh_2Cl_2(CO)_2(\mu\text{-}Ph_2PCH_2SCH_3)_2]$.

Introduction

Bimetallic complexes containing bridging bis(diphenylphosphino)methane (dppm) ligands have been known for some time, and the extensive chemistry of such compounds has recently been reviewed [1,2]. There has been recent interest, however, in the use of unsymmetrical, small-bite, bidentate ligands to prepare bimetallic complexes with similar or dissimilar metal centers. Balch, in particular, has made effective use of (diphenylarsino)(diphenylphosphino)methane (dapm) and 2-(diphenylphosphino)pyridine (Ph_2Ppy) to this end [2,3]. We report here the use of diphenylphosphino(methylthio)methane as a bridging ligand in the preparation of diplatinum and dirhodium complexes. A preliminary report has appeared [4].

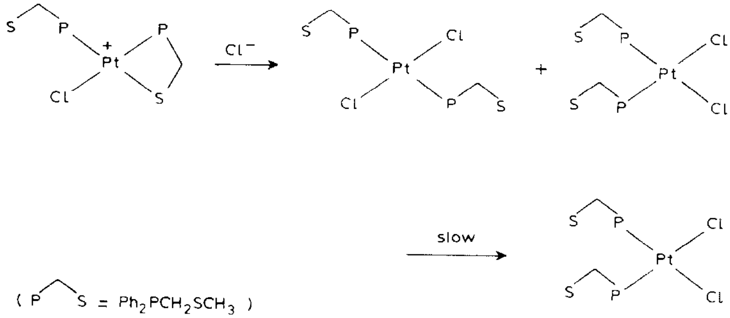
Results and discussion

Diphenylphosphino(methylthio)methane, $Ph_2PCH_2SCH_3$, is prepared in a manner similar to that previously reported for other unsymmetrical, bidentate

0022-328X/88/$03.50

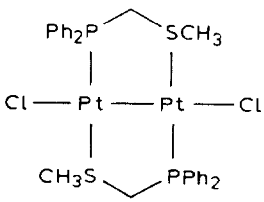
ligands [5]. Reaction of $[PtCl_2(cod)]$ with 2 mol equiv. of $Ph_2PCH_2SCH_3$ yields *cis*-$[PtCl_2(Ph_2PCH_2SCH_3)_2]$, in which the ligands are coordinated to platinum through phosphorus only. (With 1 mol equiv. of $Ph_2PCH_2SCH_3$ a 1/1 mixture of $[PtCl_2(cod)]$ and *cis*-$[PtCl_2(Ph_2PCH_2SCH_3)_2]$ is obtained.) The $^{31}P\{^1H\}$ NMR spectrum of *cis*-$[PtCl_2(Ph_2PCH_2SCH_3)_2]$ exhibits a single resonance, with ^{195}Pt satellites, and a $^1J(Pt,P)$ value of 3680 Hz, typical of a complex of the type *cis*-$[PtCl_2(PR_3)_2]$. Addition of $AgBF_4$ to a $CDCl_3$ solution of *cis*-$[PtCl_2(Ph_2PCH_2SCH_3)_2]$ produces a white precipitate of AgCl and a solution containing $[PtCl(Ph_2PCH_2SCH_3)_2]BF_4$. The $^{31}P\{^1H\}$ NMR spectrum of the latter consists of two singlets ($^2J(P,P) < 2$ Hz), each with ^{195}Pt satellites ($\delta(P)$ 9.2, $^1J(Pt,P)$ 3280 Hz and $\delta(P)$ -58.7, $^1J(Pt,P)$ 3050 Hz). The high field signal is typical of a phosphorus atom which is part of a four-membered chelate ring [6], indicating that one ligand is chelating whereas the other is not. Addition of excess $AgBF_4$ does not cause removal of the second chloride.

When a $CDCl_3$ solution of $[PtCl(Ph_2PCH_2SCH_3)_2]BF_4$ is treated with Et_4NCl a broad ^{31}P resonance is observed at ambient temperature. Cooling to $-50\,°C$, however, allows observation of resonances due to *cis*- and *trans*-$[PtCl_2(Ph_2PCH_2SCH_3)_2]$. The latter appears at $\delta(P)$ 16.0, with a one-bond coupling constant of 2450 Hz. When the solution is allowed to stand at ambient temperature for several hours, complete conversion to the *cis*-isomer occurs (eq. 1).



(1)

The complexes *cis*-$[PtCl_2(Ph_2Ppy)_2]$ [7,8] and *cis*-$[PtCl_2(dapm)_2]$ [3,9], both of which contain P-coordinated ligands only, have been employed in the preparation of binuclear metal complexes. Similarly, when *cis*-$[PtCl_2(Ph_2PCH_2SCH_3)_2]$ is allowed to react with $[Pt(dba)_2]$ (dba = dibenzylideneacetone) in CH_2Cl_2 solution the binuclear complex, $[Pt_2Cl_2(\mu\text{-}Ph_2PCH_2SCH_3)_2]$, is obtained. Its $^{31}P\{^1H\}$ NMR spectrum in $CDCl_3$ solution demonstrates its dimeric nature. In particular, the observation of $^2J(Pt,P)$ and $^3J(P,P)$ reveals this, and the large value of $^1J(Pt,Pt)$ [10] is indicative of a platinum–platinum bond. The magnitude of $^1J(Pt,P)$ shows that the complex exists as the head-to-tail isomer, **1** [8]. Reaction with Bu^n_4NI yields the

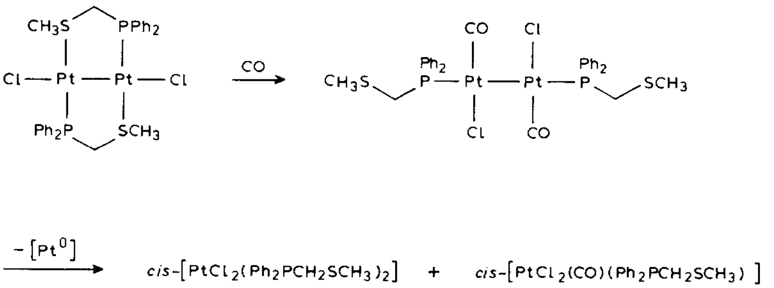


(**1**)

corresponding iodo complex, which has been characterized by $^{31}P\{^1H\}$ NMR spectroscopy (δ(P) 3.0, ^1J(Pt,P) 3980 Hz, ^2J(Pt,P) 110 Hz, ^3J(P,P) 7.5 Hz, ^1J(Pt,Pt) not observed). It also exists as the head-to-tail isomer exclusively.

Complex **1** does not undergo insertion of carbon monoxide into the Pt–Pt bond. When a $CDCl_3$ solution of **1** is treated with ^{13}CO (90% enriched) at $-50\,°C$, a single carbonyl resonance is observed in the ^{13}C NMR spectrum at 167.9 ppm (^1J(Pt,C) 1860 Hz). The magnitude of ^1J(Pt,C) is typical of a terminal carbonyl ligand lying *trans* to a ligand of low *trans*-influence, such as chloride [11]. After standing at ambient temperature for several days this resonance disappears, and is replaced by a weaker resonance at 156.0 ppm (^1J(Pt,C) not observed). The $^{31}P\{^1H\}$ NMR spectrum at this stage indicates the major phosphorus-containing species in solution to be *cis*-$[PtCl_2(Ph_2PCH_2SCH_3)_2]$. A minor species with parameters δ(P) 7.6, ^1J(Pt,P) 2985 Hz is also detected. An infrared study of the reaction of **1** with CO in chloroform solution reveals ν(CO) absorptions at 2005 and 2030 cm^{-1} which, on standing, are replaced by a weaker band at 2100 cm^{-1}. The minor, carbonyl-containing product is identified as *cis*-$[PtCl_2(CO)(Ph_2PCH_2SCH_3)]$ by comparison of its NMR and infrared spectra with those of an authentic sample prepared by an established method [12].

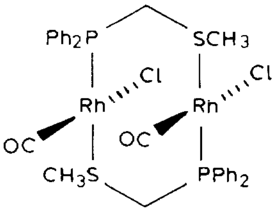
We suggest the reaction occurs by initial cleavage of the Pt–S bonds in **1** by carbon monoxide, followed by disproportionation of the binuclear platinum(I) complex to give platinum(II) and platinum(0) products (although **1** also reacts slowly in $CDCl_3$ solution to give *cis*-$[PtCl_2(Ph_2PCH_2SCH_3)_2]$ and platinum metal). These steps are summarized in equation 2. The initial product of the analogous reaction of $[Pd_2Cl_2(\mu\text{-}Ph_2Ppy)_2]$ with CO was suggested to be $[Pd_2Cl_2(CO)_2(Ph_2Ppy)_2]$ in which the phosphine ligands were believed to occupy the axial positions in order to minimize steric crowding [13].



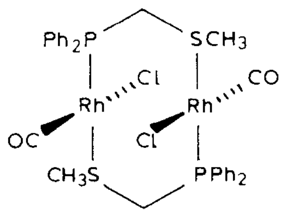
(2)

When *cis*-$[PtCl_2(CO)(Ph_2PCH_2SCH_3)]$ is refluxed in $CDCl_3$ solution carbon monoxide is evolved and $[PtCl_2(Ph_2PCH_2SCH_3)]$, in which the $Ph_2PCH_2SCH_3$ is chelated, is formed. It is characterized by a high field ^{31}P resonance (-59.5 ppm), typical of a four-membered chelate ring [6], and a ^1J(Pt,P) value of 3030 Hz, which is similar to that found in $[PtCl_2(dppm)]$ [14]. It has not been isolated in pure form, however, owing to the presence of several minor, unidentified products. The formation of $[PtCl_2(Ph_2PCH_2SCH_3)]$ is somewhat surprising, since the reaction of $[PtCl_2(cod)]$ with 1 mol equiv. of $Ph_2PCH_2SCH_3$ results in 50% conversion to *cis*-$[PtCl_2(Ph_2PCH_2SCH_3)_2]$ (vide supra).

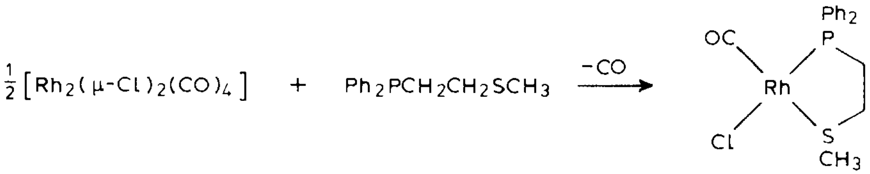
Addition of 2 mol equiv. of $Ph_2PCH_2SCH_3$ to an acetone solution of $[Rh_2(\mu\text{-}Cl)_2(CO)_4]$ results in evolution of carbon monoxide, and $[Rh_2Cl_2(CO)_2(\mu\text{-}Ph_2PCH_2SCH_3)_2]$ is formed. The magnitude of ^1J(Rh,P) is indicative of phosphine *trans* to a thioether, rather than *trans* to a second phosphine [7,15], suggesting that this complex also exists as the head-to-tail isomer. The infrared spectrum exhibits a broad band at 1965 cm^{-1}. The complex may exist as either **2a** or **2b**, or as a mixture of these two. By way of contrast, $[Rh_2(\mu\text{-}Cl)_2(CO)_4]$ reacts with $Ph_2PCH_2CH_2SCH_3$ [5] to give a monomeric complex with a chelated ligand (eq. 3).



(2a)

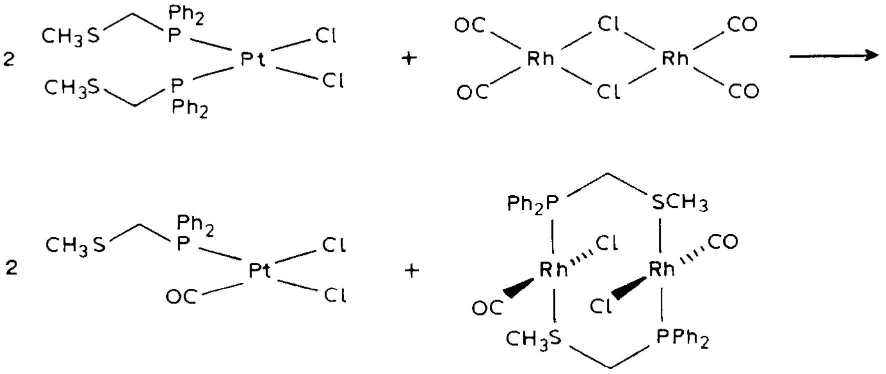


(2b)



(3)

A heterometallic complex with Ph_2Ppy bridges has been generated by reaction of *cis*-$[PtCl_2(Ph_2Ppy)_2]$ with $[Rh_2(\mu\text{-}Cl)_2(CO)_4]$ [7]. It seemed reasonable that *cis*-$[PtCl_2(Ph_2PCH_2SCH_3)_2]$ should react similarly with $[Rh_2(\mu\text{-}Cl)_2(CO)_4]$. However, when these two complexes are allowed to react in $CDCl_3$ solution a ligand exchange reaction takes place, but no heterometallic species are obtained (eq. 4). The reaction is very clean, as monitored by $^{31}P\{^1H\}$ NMR spectroscopy, but its mechanism has not been investigated.



(4)

Experimental

All reactions were carried out under nitrogen or argon, unless otherwise stated. $Ph_2PCH_2CH_2SCH_3$ was prepared as described previously [5]. The complexes

$[PtCl_2(cod)]$, $[Pt(dba)_2]$ and $[Rh_2(\mu\text{-}Cl)_2(CO)_4]$ were prepared by established procedures [16–18]. Microanalyses were performed by Galbraith Microanalytical Laboratories, Knoxville, Tennessee. ^1H, $^{13}C\{^1H\}$ and $^{31}P\{^1H\}$ NMR spectra (δ, ppm) were recorded for $CDCl_3$ solutions on a JEOL FX-100 spectrometer, operating in the FT mode, at 100.0, 25.1 and 40.3 MHz respectively. Chemical shifts are reported in ppm relative to TMS or external 85% H_3PO_4, positive shifts representing deshielding. Infrared spectra were recorded on a Perkin–Elmer 783 spectrophotometer.

Preparation of $Ph_2PCH_2SCH_3$

Chlorodiphenylphosphine (12.0 g, 0.054 mol) was dissolved in dry THF (150 ml) and finely-divided lithium metal (0.76 g, 0.11 mol) was introduced. When all the lithium had reacted, the deep red solution was cooled to 0 ° C, then $ClCH_2SCH_3$ (5.3 g, 0.055 mol) was added over 30 min. The mixture was stirred overnight, the THF was evaporated, and degassed water (50 ml) was added to the residue. The oily organic layer was separated and distilled under reduced pressure (b.p. 180 ° C at 0.5 torr) to give $Ph_2PCH_2SCH_3$ as a colorless oil; yield 9.4 g (71%). ^1H NMR: δ 2.20 (s, 3H, CH_3), 3.10 (d, J(P,H) 3.3 Hz, 2H, CH_2), 7.3–7.5 (m, 10H, C_6H_5); $^{13}C\{^1H\}$ NMR: δ 17.4 (d, J(P,C) 9 Hz, CH_3), 32.5 (d, J(P,C) 22 Hz, CH_2), 128.5 (d, J(P,C) 7 Hz), 128.9 (s), 132.8 (d, J(P,C) 19 Hz); $^{31}P\{^1H\}$ NMR: δ −20.3.

Preparation of cis-$[PtCl_2(Ph_2PCH_2SCH_3)_2]$

$[PtCl_2(cod)]$ (2.00 g, 5.36 mmol) was dissolved in dichloromethane (200 ml). A CH_2Cl_2 solution (50 ml) of $Ph_2PCH_2SCH_3$ (2.61 g, 10.7 mmol) was added, and the mixture was stirred for 15 minutes. The solution was concentrated to 100 ml, and diethyl ether was slowly added to initiate crystallization. The precipitate was filtered, and washed with ether, to give the product as a white powder (2.92 g, 72%). $^{31}P\{^1H\}$ NMR: δ 7.0, ^1J(Pt,P) 3680 Hz. Found: C, 44.38; H, 4.07. $C_{28}H_{30}Cl_2P_2PtS_2$ calcd.: C, 44.33; H, 3.99%.

Preparation of cis-$[PtCl_2(CO)(Ph_2PCH_2SCH_3)]$

Carbon monoxide was bubbled through a CH_2Cl_2 solution (100 ml) of $[PtCl_2(cod)]$ (1.00 g, 2.67 mmol) for 30 min. $Ph_2PCH_2SCH_3$ (0.66 g, 2.68 mmol), dissolved in CH_2Cl_2 (10 ml), was added slowly, and the mixture was stirred for 30 min. The solution was reduced in volume, and addition of ether produced a white precipitate, which was filtered and air-dried (0.90 g, 62%), ν(CO) 2110 cm^{-1} (KBr pellet). $^{31}P\{^1H\}$ NMR: δ 7.6, ^1J(Pt,P) 2985 Hz. Found: C, 32.80; H, 3.23. $C_{15}H_{15}Cl_2OPPtS$ calcd.: C, 33.34; H, 2.80%.

Preparation of $[Pt_2Cl_2(\mu\text{-}Ph_2PCH_2SCH_3)_2]$

A CH_2Cl_2 solution (50 ml) of $[Pt(dba)_2]$ (1.20 g, 1.80 mmol) was added to a solution of *cis*-$[PtCl_2(Ph_2PCH_2SCH_3)_2]$ (1.37 g, 1.80 mmol) in dichloromethane (200 ml). The mixture became dark and it was stirred for 10 h. After filtration to remove the black residue formed, the filtrate was concentrated and addition of ether gave a yellow precipitate. This was purified by several crystallizations from CH_2Cl_2 by slow addition of ether, to give $[Pt_2Cl_2(\mu\text{-}Ph_2PCH_2SCH_3)_2]$ as yellow crystals (0.56 g, 33%). $^{31}P\{^1H\}$ NMR: δ 4.8, ^1J(Pt,P) 4080 Hz, ^2J(Pt,P) 140 Hz, ^3J(P,P) 12 Hz, ^1J(Pt,Pt) 7750 Hz. Found: C, 35.37; H, 3.29. $C_{28}H_{30}Cl_2P_2Pt_2S_2$ calcd.: C, 35.26; H, 3.17%.

Preparation of $[Rh_2Cl_2(CO)_2(\mu\text{-}Ph_2PCH_2SCH_3)_2]$

$Ph_2PCH_2SCH_3$ (0.16 g, 0.66 mmol) was dissolved in acetone (20 ml) under argon, and $[Rh_2(\mu\text{-}Cl)_2(CO)_4]$ (0.13 g, 0.34 mmol) was added as a solid. The solid dissolved and, after a few minutes, an orange precipitate began to form. The mixture was heated to reflux for 10 min, then allowed to cool. The orange product was filtered (0.18 g, 66%). This was recrystallized from acetone to give $[Rh_2Cl_2(CO)_2(\mu\text{-}Ph_2PCH_2SCH_3)_2]$ as orange-red crystals, ν(CO) 1965 (br) cm^{-1} (Nujol). $^{31}P\{^1H\}$ NMR: δ 32.2 d, ^1J(Rh,P) 144 Hz. Found: C, 43.66; H, 3.81. $C_{30}H_{30}Cl_2O_2P_2Rh_2S_2$ calcd.: C, 43.66; H, 3.66%.

Preparation of $[RhCl(CO)(Ph_2PCH_2CH_2SCH_3)]$

A 100-ml three-necked flask was charged with $[Rh_2(\mu\text{-}Cl)_2(CO)_4]$ (0.10 g, 0.25 mmol) and $Ph_2PCH_2CH_2SCH_3$ (0.13 g, 0.51 mmol). The flask was purged with argon, then acetone (20 ml) was introduced. The reactants dissolved and carbon monoxide was evolved. After 15 min the solvent was removed. The residue was washed with ether and filtration gave the product as an orange powder (0.13 g, 59%), ν(CO) 1990 cm^{-1} (KBr pellet). $^{31}P\{^1H\}$ NMR: δ 70.2, ^1J(Rh,P) 155 Hz. Found: C, 44.65; H, 3.98. $C_{16}H_{17}ClOPRhS$ calcd.: C, 45.03; H, 4.02%.

Acknowledgements

Thanks are expressed to the donors of the Petroleum Research Fund, administered by the American Chemical Society, Research Corporation and the University of Missouri Weldon Spring Fund for support of this work. The authors are grateful to Johnson Matthey for a generous loan of K_2PtCl_4.

References

1 R.J. Puddephatt, Chem. Soc. Rev., 12 (1983) 99.
2 A.L. Balch in L.H. Pignolet (Ed.), Homogeneous Catalysis Using Metal Phosphine Complexes, Plenum Press, New York, 1983, p. 167.
3 A.L. Balch, R.R. Guimerans, J. Linehan and F.E. Wood, Inorg. Chem., 24 (1985) 2021, and refs. therein.
4 G.K. Anderson and R. Kumar, Inorg. Chim. Acta, 97 (1985) L21.
5 G.K. Anderson and R. Kumar, Inorg. Chem., 23 (1984) 4064.
6 P.E. Garrou, Chem. Rev., 81 (1981) 229.
7 J.P. Farr, M.M. Olmstead, F.E. Wood and A.L. Balch, J. Am. Chem. Soc., 105 (1983) 792.
8 J.P. Farr, F.E. Wood and A.L. Balch, Inorg. Chem., 22 (1983) 3387.
9 R.R. Guimerans and A.L. Balch, Inorg. Chim. Acta, 77 (1983) L177.
10 F.A. Bovey, Nuclear Magnetic Resonance Spectroscopy, Academic Press, New York, 1969, p. 116–118.
11 G.K. Anderson, R.J. Cross and D.S. Rycroft, J. Chem. Res. (M), (1979) 1601.
12 G.K. Anderson, H.C. Clark and J.A. Davies, Inorg. Chem., 20 (1981) 1636.
13 A. Maisonnet, J.P. Farr and A.L. Balch, Inorg. Chim. Acta, 53 (1981) L217.
14 G.K. Anderson, H.C. Clark and J.A. Davies, Inorg. Chem., 20 (1981) 3607.
15 A.R. Sanger, J. Chem. Soc., Dalton Trans. (1977) 120; A.R. Sanger, Can. J. Chem., 61 (1983) 2214; A.R. Sanger, Can. J. Chem., 63 (1985) 571.
16 J.X. McDermott, J.F. White and G.M. Whitesides, J. Am. Chem. Soc., 98 (1976) 6521.
17 K. Moseley and P.M. Maitlis, J. Chem. Soc., Dalton Trans., (1974) 169.
18 J. Chatt and L.M. Venanzi, J. Chem. Soc., (1957) 4735.