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PREPARATION, PROPERTIES AND REACTIVITIES OF NOVEL PLATINUM COMPOUNDS CONTAINING A THIOMETHOXYMETHYL GROUP

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Summary

Oxidative addition of $ClCH_2SCH_3$ to PtL_4 afforded *trans*-$PtL_2(CH_2SCH_3)Cl$ (Ia, L = Ph_3P; Ib, L = $MePh_2P$). Treatment of I with NH_4PF_6 or Et_3OBF_4 in CH_2Cl_2 gave ionic species, $[PtL_2(CH_2SCH_3)]X$ (II, L = Ph_3P, $MePh_2P$, X = BF_4, PF_6), while similar treatment with $MeSO_3F$ in benzene yielded a new type of stable dimethylsulfonium methylide—platinum complex, *trans*-$[PtL_2(CH_2SMe_2)Cl]SO_3F$ (IIIa, L = Ph_3P; IIIb, L = $MePh_2P$). Action of H_2O_2 on Ia gave $[Pt(Ph_3P)(\mu\text{-}CH_2SCH_3)Cl]_2$ (IV) and its triphenylarsine analog, $[Pt(Ph_3As)(\mu\text{-}CH_2SCH_3)Cl]_2$ (V) was prepared in one step by oxidative addition of $ClCH_2SCH_3$ to $Pt(AsPh_3)_4$. The structural difference between $[Pt(Ph_3P)(\mu\text{-}CH_2SCH_3)Cl]_2$ and $Pd(Ph_3P)(CH_2SCH_3)Cl$ is discussed in terms of the difference in the ionization potential from d^{10} to d^8 electronic state of metals.

Introduction

We have reported previously novel thiomethoxymethyl—palladium complexes which involve intramolecular coordination of sulfur with palladium [1]. However, it has remained unclear why the thiomethoxymethyl group in these complexes acts as an intramolecular bidentate ligand in spite of the high strain energy believed to be induced by the three-membered Pd—C—S ring. In order to shed some light on this problem and to extend further our understanding of the reactivity of the thiomethoxymethyl—metal complexes, we have prepared such compounds of platinum(II), and have studied their structures and reactions.

Discussion

Oxidative addition of chloromethyl methyl sulfide to PtL_4 provided a good yield of *trans*-$PtL_2(CH_2SCH_3)Cl$.

$$PtL_4 + ClCH_2SCH_3 \rightarrow trans\text{-}PtL_2(CH_2SCH_3)Cl + 2\,L$$

$$(Ia,\ L = Ph_3P;\ Ib,\ L = MePh_2P)$$

TABLE 1

^{1}H NMR [a] AND IR [b] DATA FOR SOME PLATINUM AND PALLADIUM COMPOUNDS

Compounds	δ(—SCH$_3$) (ppm)	δ(—CH$_2$—) (ppm)	δ(—PCH$_3$) (ppm)	δ(—NCH$_3$) (ppm)	ν(Pt—Cl) (cm^{-1})
Ia [c]	1.09 (s)	1.36 (t) J(PH) 8 J(PtH) 82			272
Ib [c]	1.24 (s)	1.47 (t) J(PH) 8 J(PtH) 82	2.21 (t) J(PH) 7 J(PtH) 31		282
IIa [c]	1.85 (d) J(PH) 5 J(PtH) 31	2.7 (m)			
IIIa	1.92 (s)	2.09 (t) J(PH) 6.5 J(PtH) 80			294
IIIb	1.94 (s)	2.00 (t) J(PH) 7 J(PtH) 78	2.33 (t) J(PH) 7 J(PtH) 27		303
IV	2.14 (d) J(PH) 4 J(PtH) 32	[d]			290
V	2.22 (s) J(PtH) 42	[d]			285
PtL(R)(dtc) [e]	1.94 (s)	2.30 (d) J(PH) 5 J(PtH) 70		3.16 (s) 3.30 (s)	
PdL(R)(dtc) [e,f]	1.96 (s)	2.22 (d) J(PH) 6		3.27 (s) 3.38 (s)	

[a] In CDCl$_3$ at 23°C except as noted. (s) singlet; (d) doublet; (t) triplet; (m) unresolved multiplet. [b] In Nujol mulls. [c] In CH$_2$Cl$_2$. [d] Overlapped with the S—CH$_3$ resonances. [e] Abbreviations are noted in Table 2. [f] At −50°C.

As shown in Table 1, the triplet pattern of both the methylene proton (in Ia and Ib) and the P—CH$_3$ proton resonances (in Ib) in the ^{1}H NMR spectra indicated that these complexes have *trans*-configuration. These spectral patterns did not change on raising the temperature up to 50°C. Thus, Ia and Ib have a rigid structure on the NMR time scale, with the sulfur atom uncoordinated in the ground state, which is in marked contrast to the corresponding palladium analogs [1].

However, the thiomethoxymethyl group in I does induce three reactions as shown in Scheme 1 as a result of the Lewis base character of the sulfur atom.

[PtL$_2$(CH$_2$SCH$_3$)]PF$_6$ complexes (II) were obtained on treatment of I with NH$_4$PF$_6$. Similar treatment with Et$_3$OBF$_4$ in CH$_2$Cl$_2$ also gave [PtL$_2$-(CH$_2$SCH$_3$)]BF$_4$, in contrast to the inertness of *trans*-Pt(Ph$_3$P)$_2$MeCl toward Et$_3$OBF$_4$ [2]. In the ^{1}H NMR spectra *, the S—CH$_3$ protons of IIa were coupled with the ^{195}Pt and ^{31}P nuclei, indicating coordination of sulfur with platinum. The IR spectrum of IIa exhibited a very strong band at 549 cm^{-1}, suggesting *cis*-configuration [3]. At present we cannot distinguish between two possible structures for II, i.e. one involving intramolecular coordination of sulfur to platinum, as in [Pd(Ph$_3$P)$_2$(CH$_2$SCH$_3$)]PF$_6$ [1], and the other in-

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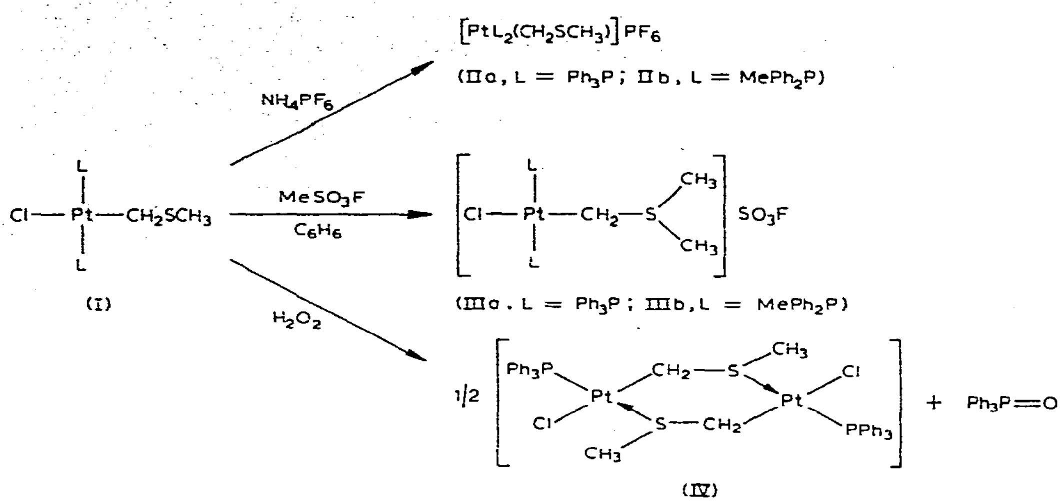
* The ^{1}H NMR spectrum of IIb was too complex to resolve.

SCHEME 1



volving intermolecular bridging by sulfur as in $[Pt(Ph_3P)(\mu\text{-}CH_2SCH_3)Cl]_2$ (see later).

The ylide complexes (III) were obtained in good yield by the reaction of I with $MeSO_3F$ in benzene. Similar treatment of I with $MeSO_3F$ in CH_2Cl_2 afforded a mixture of $[PtL_2(CH_2SCH_3)]SO_3F$ and III in 7 to 1 ratio. Interestingly, once formed, III is very stable even in CH_2Cl_2 and showed no sign of forming the former complex. Although the dimethylsulfonium methylide complex of palladium was obtained from $[Pd(styrene)Cl_2]_2$ and the free ylide prepared in situ [4], it seems notable that this ligand was formed on the platinum atom without difficulty, for it is well known that the ylide cannot be isolated as a stable species because of its thermolability [5].

The reaction of Ia with an equimolar quantity of H_2O_2 gave the corresponding mono-phosphine platinum complex IV and triphenylphosphine oxide. However, we found that *trans*-$Pt(Ph_3P)_2MeCl$ does not react with H_2O_2 under the same conditions, suggesting that the coordination of sulfur to platinum plays an important role in the above reaction to form IV. A triphenylarsine analog, $[Pt(AsPh_3)(\mu\text{-}CH_2SCH_3)Cl]_2$ (V) was prepared in one step from $ClCH_2SCH_3$ and $Pt(AsPh_3)_4$. As shown in Tables 1 and 2, molecular weight measurements and ^1H NMR data of IV and V indicate that the sulfur atom in the thiomethoxymethyl group coordinates to another platinum atom. The fact that the value of J(Pt—Me) in IV is close to that in IIa but much smaller than that in *cis*-$Pt(Me_2S)_2Cl_2$ (49.5 Hz) [6] leads us to assign triphenylphosphine as the ligand *trans* to the sulfur atom according to the trends in NMR *trans*-influence. Similarly, though on a little less direct ground, V would have the configuration in which the arsine and the sulfur atom are *trans* to each other. Unfortunately, because of extreme broadness of the diastereotopic methylene proton resonances, it was impossible to determine the J(Pt—CH_2) values in IV and V which also are expected to depend on the *trans* ligand. The ^1H NMR pattern of V in the presence of triphenylarsine in increasing quantities did not show any change, indicating the stability of the sulfur—platinum bond.

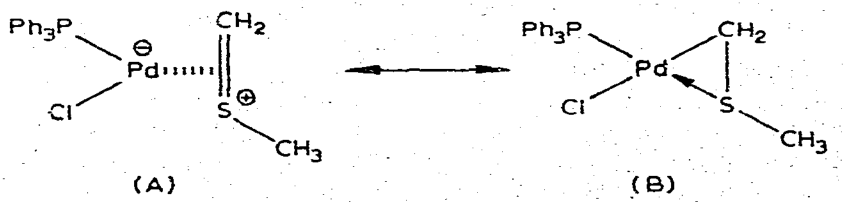
TABLE 2

ANALYTICAL DATA AND MELTING POINTS OF THE THIOMETHOXYMETHYL AND DIMETHYLSULFONIUM METHYLIDE METAL COMPLEXES ($R = CH_2SCH_3$, $R' = CH_2S(CH_3)_2$, $L = Ph_3P$, $L' = MePh_2P$, $L'' = Ph_3As$, $dtc = SSCN(CH_3)_2$)

Compounds	M.p. (°C)	Analysis found (calcd.) (%)			Mol. wt. (calcd.)
		C	H	N	
$PtL_2(R)Cl$ (Ia)	209	55.74	4.32		819 [a]
	(dec.)	(55.92)	(4.32)		(817)
$PtL'_2(R)Cl$ (Ib)	184	48.36	4.74		694 [b]
	(dec.)	(48.59)	(4.52)		(693)
$[PtL_2(R)]PF_6$ (IIa)	242	49.19	3.92		
	(dec.)	(49.30)	(3.81)		
$[PtL'_2(R)]PF_6$ (IIb)	109	41.66	3.78		
	(dec.)	(41.95)	(3.90)		
$[PtL_2(R')Cl]SO_3F.3/2\,CH_2Cl_2$ (IIIa) [d]	207	46.06	3.86		
	(dec.)	(45.99)	(3.91)		
$[PtL'_2(R')Cl]SO_3F.CH_2Cl_2$ (IIIb) [d]	88	40.71	4.03		
	(dec.)	(40.44)	(4.07)		
$[PtL(R)Cl]_2$ (IV)	238	42.98	3.60		1106 [a]
	(dec.)	(43.36)	(3.64)		(1108)
$[PtL''(R)Cl]_2$ (V)	224	39.97	3.50		1192 [a]
	(dec.)	(40.18)	(3.37)		(1196)
PtL(R)(dtc)	182—	43.26	4.08	2.24	684 [c]
	184	(43.25)	(4.10)	(2.19)	(639)
PdL(R)(dtc)	161	50.22	4.88	2.64	511 [a]
	(dec.)	(50.32)	(4.59)	(2.55)	(513)

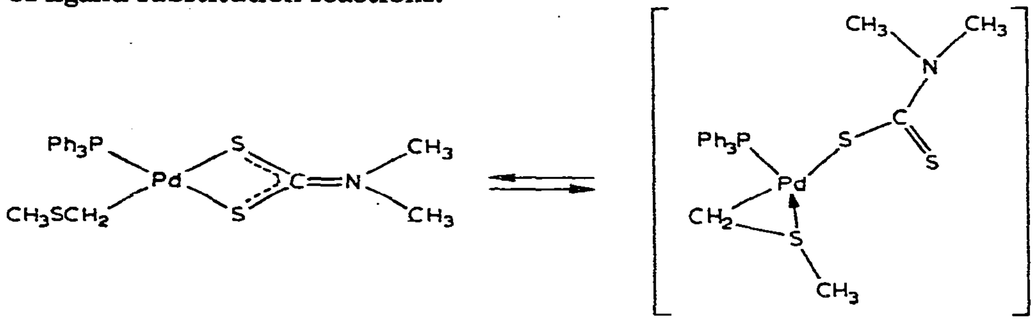
[a] In $CHCl_3$ at 37°C. [b] In $CHCl_3$ at 25°C. [c] In CH_2Cl_2 at 25°C. [d] The presence of the indicated moles of CH_2Cl_2 was confirmed by the ^1H NMR spectrum in $CDCl_3$.

It is of particular interest to note that the thiomethoxymethyl group acts as an intermolecular bridging ligand in IV, but as an intramolecular chelating ligand in the palladium analog, $Pd(Ph_3P)(CH_2SCH_3)Cl$ [1]. As numerous X-ray crystallographic structural determinations indicate that the covalent radii in platinum(II) and palladium(II) complexes are comparable, the reason for such structural differences would probably be electronic in origin. We propose that the resonance hybrid A ↔ B plays some role in stabilizing the mononuclear structure in the palladium compound.



Structure B involves the electron-pair σ bonds within the three-membered Pd—C—S ring, while in A the thiomethoxymethyl cation donates two π electrons [7] to the palladium atom in formally zero oxidation state. On the other hand, dimerization in IV may be a result of the smaller resonance energy gained in the form analogous to A which cannot compensate for the steric repulsion involved. This argument is consistent with the different ionization potential from the d^{10} to d^8 electronic state between two metals; the ionization potentials of palladium and platinum from d^{10} to d^9 were 8.33 and 8.20 eV and those from d^9 to d^8 19.42 and 18.56 eV, respectively [8,9].

Finally, we note another example of different behavior exhibited by the thiomethoxymethyl complexes of palladium and platinum. In complexes of type $M(Ph_3P)(CH_2SCH_3)(dtc)$ (dtc = *N,N*-dimethyldithiocarbamate) where the CH_3SCH_2 group is monodentate in the ground state both in M = Pd and Pt, the N—CH_3 proton resonances in the palladium complex appear as a singlet at room temperature and as a magnetically non-equivalent pair at lower temperatures [10], while those in the platinum complex remain doublets up to 50° C. The process leading to exchange of the N—CH_3 groups in the former is clearly monomolecular (see Experimental), and such *N*-methyl exchange could occur readily in intermediate C which has a greater stability in the palladium than in the platinum system. The activation energy for going to C would also be much smaller in the palladium system in view of the general trend in the rate of ligand substitution reactions.



(C)

Experimental

General comments

The reactions of the zerovalent platinum complexes with chloromethyl methyl sulfide were carried out under a dry nitrogen atmosphere, and nitrogen was bubbled into solvents before use. Starting materials: PtL_4 (L = Ph_3P [11], $MePh_2P$ [12], Ph_3As [11]) were prepared according to directions in the literature. Chloromethyl methyl sulfide was distilled before use. ^1H NMR spectra were measured on a Japan Electron Optics JNM-PS-100 spectrometer. Infrared spectra were recorded on JASCO IR-G (4000—700 cm^{-1}) and Hitachi EPI-2G spectrophotometers (700—200 cm^{-1}).

Chloro(thiomethoxymethyl)bis(triphenylphosphine)platinum (Ia)

Chloromethyl methyl sulfide (0.94 ml, 11.2 mmol) was added to a suspension of tetrakis(triphenylphosphine)platinum (3.48 g, 2.8 mmol) in dry benzene (40 ml) and the mixture was refluxed until the solution became colorless (1.0—1.5 h). The volume of the solution was reduced to 5 ml and dry n-hexane was added to precipitate the complex. The latter was recrystallized from $CHCl_3$/n-hexane to give colorless crystals of *trans*-$Pt(Ph_3P)_2(CH_2SCH_3)Cl$ in 92% yield.

Chloro(thiomethoxymethyl)bis(methyldiphenylphosphine)platinum (Ib)

This compound was prepared in a manner similar to that used for Ia, except that the reaction mixture was maintained at room temperature for 24 h. Recrystallization from CH_2Cl_2/n-hexane gave colorless prisms of Ib (97% yield).

(Thiomethoxymethyl)bis(triphenylphosphine)platinum hexafluorophosphate (IIa) and (thiomethoxymethyl)bis(methyldiphenylphosphine)platinum hexafluorophosphate (IIb)

Ammonium hexafluorophosphate (0.19 g, 1.17 mmol) in 5 ml of acetone was added to a solution of Ia (0.31 g, 0.38 mmol) in 20 ml of $CHCl_3$. After 20 h, the white precipitate which had formed was removed by filtration and the solvents were removed under reduced pressure. The solid residue was recrystallized from CH_2Cl_2/n-hexane to give colorless crystals of $[Pt(Ph_3P)_2(CH_2SCH_3)]PF_6$ in 48% yield. $[Pt(MePh_2P)_2(CH_2SCH_3)]PF_6$ was obtained in 44% yield.

Reaction of Ia with triethyloxonium tetrafluoroborate

Et_3OBF_4 (0.09 g, 0.47 mmol) in 5 ml of CH_2Cl_2 was added to a solution of Ia (0.38 g, 0.47 mmol) in 15 ml of CH_2Cl_2. After stirring for 2 h at room temperature, the solvent was removed under reduced pressure. The resulting solid was recrystallized from CH_2Cl_2/n-hexane to give colorless crystals of $[Pt(Ph_3P)_2(CH_2SCH_3)]BF_4$ in 45% yield. The IR and ^1H NMR spectra of this complex were almost identical with those of IIa except for the bands due to the BF_4^- and PF_6^- anions.

Chloro(dimethylsulfonium methyl)bis(triphenylphosphine)platinum fluorosulfonate (IIIa) and chloro(dimethylsulfonium methyl)bis(methyldiphenylphosphine)platinum fluorosulfonate (IIIb)

Methyl fluorosulfonate (0.44 ml, 3.8 mmol) in dry benzene (5 ml) was added dropwise under nitrogen to a benzene solution (20 ml) of Ia (1.0 g, 1.23 mmol). A white precipitate began to separate out immediately. After 2 h the solution was concentrated and dry n-hexane was added. The resulting solid was recrystallized from CH_2Cl_2/Et_2O to give colorless crystals of *trans*-$[Pt(Ph_3P)_2(CH_2SMe_2)Cl]SO_3F$ (IIIa) in 71% yield. *trans*-$[Pt(MePh_2P)_2(CH_2SMe_2)Cl]SO_3F$ (IIIb) was obtained in a similar manner in 52% yield. Both IIIa and IIIb showed a very strong band at 1270 cm^{-1} ($\nu_{asym}(SO_3)$) and a strong band at 580 cm^{-1} ($\delta_{asym}(SO_3)$), which are the characteristic absorption bands of free $[SO_3F]^-$ ion [12]. A similar treatment of Ia with $MeSO_3F$ in CH_2Cl_2 gave $[Pt(Ph_3P)_2(CH_2SCH_3)]SO_3F$ and IIIa in 7 to 1 ratio. The former complex was identified on the basis of IR and ^1H NMR data of the $[Pt(Ph_3P)_2(CH_2SCH_3)]^+$ moiety, which are quite similar to those of IIa.

Dichloro-di-μ-thiomethoxymethylbis(triphenylphosphine)diplatinum (IV)

Hydrogen peroxide (0.16 ml, 1.4 mmol) in 30% aqueous solution was added to a suspension of Ia (1.14 g, 1.4 mmol) in 20 ml of acetone. The reaction mixture was stirred at room temperature for 20 h. The volume of the solvents was reduced to 7 ml under vacuum, and n-hexane (40 ml) was added to precipitate the complex. This was dried under vacuum and recrystallized from

CH_2Cl_2/n-hexane to give colorless crystals of $[Pt(Ph_3P)(\mu\text{-}CH_2SCH_3)Cl]_2$ (IV) in 68% yield.

Dichloro-di-μ-thiomethoxymethylbis(triphenylarsine)diplatinum (V)

Chloromethyl methyl sulfide (0.25 ml, 3.0 mmol) was added to a suspension of tetrakis(triphenylarsine)platinum (1.41 g, 1.0 mmol) in dry benzene (20 ml) and the mixture was vigorously stirred overnight at room temperature. The volume of the solvent then was reduced to 5 ml and dry n-hexane (40 ml) was added to precipitate the complex. This was recrystallized from CH_2Cl_2/n-hexane to give light yellow crystals of $[Pt(Ph_3As)(\mu\text{-}CH_2SCH_3)Cl]_2$ (V) in 42% yield.

Thiomethoxymethyl(triphenylphosphine)platinum dimethyldithiocarbamate

To a CH_2Cl_2 solution (10 ml) of Ia (0.27 g, 0.33 mmol) was added dropwise a solution of Na(dtc) (0.1 g, 0.7 mmol) in EtOH (5 ml). The solution was filtered and the filtrate evaporated to dryness under reduced pressure. The solid residue was recrystallized from CH_2Cl_2/light petroleum (b.p. 30—60°C) to give pale yellow prisms in 30% yield.

Thiomethoxymethyl(triphenylphosphine)palladium dimethyldithiocarbamate

This complex was prepared similarly from $Pd(Ph_3P)(CH_2SCH_3)Cl$ and Tl(dtc) in CH_2Cl_2. Recrystallization from CH_2Cl_2/n-hexane gave orange yellow prisms (54% yield). ^1H NMR measurements were carried out in CH_2Cl_2 at concentrations of 0.0637, 0.0783 and 0.1372 mol/l. The $N—CH_3$ proton resonance appeared magnetically non-equivalent at —50°C (see Table 1), but on warming the solution, the resonance coalesced to a singlet at —9°C irrespective of the concentration of the solution.

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