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PREPARATION AND PROPERTIES OF NOVEL PALLADIUM COMPOUNDS CONTAINING A THIOMETHOXYMETHYL GROUP

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Summary

Oxidative addition of chloromethyl methyl sulfide to $Pd(Ph_3P)_4$ provided a good yield of $Pd(Ph_3P)_2(CH_2SCH_3)Cl$ (I) whose ^1H NMR and molecular weight data showed that dissociation of either the phosphine or the chloride ligand occurs in CH_2Cl_2 solution. In accord with such equilibria, repeated crystallization of I from CH_2Cl_2 and Et_2O gradually removed the triphenylphosphine set free in these solvents to give the monomeric complex, $Pd(Ph_3P)(CH_2SCH_3)Cl$ (III), while treatment of I with NH_4PF_6 in CH_2Cl_2 and acetone gave the cationic complex $[Pd(Ph_3P)_2(CH_2SCH_3)]PF_6$ (II). ^1H NMR spectra of II and III are discussed in terms of a three-membered chelate structure arising from coordination of sulfur with palladium.

Introduction

The study of transition-metal compounds containing the thiomethoxymethyl group is of interest in that this ligand may behave in either a mono- or a bi-dentate fashion [1], resulting in novel structural and chemical features. We have started work on palladium and platinum derivatives containing this ligand mainly because these systems may find application as new homogeneous catalysts.

In our previous communication [2], we reported briefly the novel behavior of the bidentate thiomethoxymethyl ligand in some palladium complexes. This paper presents details on the preparation, configuration and properties of such palladium complexes.

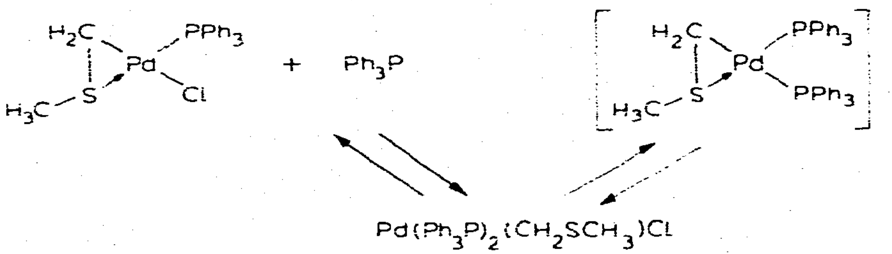
Results and discussion

New palladium complexes of the type $Pd(L)_2(CH_2SCH_3)Cl$ were isolated in good yield as yellow crystals by reaction of the corresponding zerovalent palladium complexes with chloromethyl methyl sulfide;

$$Pd(L)_4 + ClCH_2SCH_3 \rightarrow Pd(L)_2(CH_2SCH_3)Cl + 2L$$

(I) $L = Ph_3P$,
(Ia) $L = MePh_2P$

$Pd(MePh_2P)_2(CH_2SCH_3)Cl$ (Ia) was treated with KBr in aqueous THF solution to give $Pd(MePh_2P)_2(CH_2SCH_3)Br$. Osmometric molecular weight studies indicated that the partial dissociation of either the phosphine or the halogen ligand occurs in solution. We suggest that the equilibria shown in eq. 1 occur rapidly in solution on the basis of the observations discussed below.



(1)

(I)

Repeated crystallization of I from CH_2Cl_2 and Et_2O gradually removed the triphenylphosphine set free in the solvents to give monomeric $Pd(Ph_3P)(CH_2SCH_3)Cl$. However, the ^1H NMR spectrum of I showed the resonances due to the methylene and methyl protons at lower and higher magnetic fields, respectively, than those of $Pd(Ph_3P)(CH_2SCH_3)Cl$ (Table 2). Moreover, addition of one mole of Ph_3P to I resulted in a further downfield shift (ca. 0.16 ppm) of the methylene and an upfield shift (ca. 0.05 ppm) of the methyl protons. On the other hand, the isolation of $[Pd(Ph_3P)_2(CH_2SCH_3)]PF_6$ on treatment of I with NH_4PF_6 indicated the existence of $[Pd(Ph_3P)_2(CH_2SCH_3)]Cl$ as the other equilibrium species. The somewhat small value of the molar conductivity of I (7 cm^2 Ω^{-1} mol^{-1} at 1.08×10^{-3} mol l^{-1}) in CH_2Cl_2 at 25°C would be due to an ion-pairing effect *. However, a quantitative estimation of the equilibrium constant was not possible, since in the spectrum of I each of the methylene and methyl signals was observed as only one singlet even at −30°C. This suggests a still rapid equilibration process on the NMR time scale, although the downfield shift (0.14 ppm) of the methylene and the upfield shift (0.17 ppm) of the methyl protons may be attributed to the enhanced extent of the formation of the ionic species at the lower temperatures. Similarly, it is difficult to determine whether a neutral species, $Pd(Ph_3P)_2(CH_2SCH_3)Cl$, also takes part in the equilibrium to any significant extent, or whether it is better regarded as only a transient complex. In the solid state, I was shown to contain the monodentate CH_3SCH_2 ligand, with the remaining coordination site being occupied by the chloride and two mutually *trans*-phosphine ligands by a single crystal X-ray crystallographic study by Kasai et al. [3].

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* Such an ion-pairing effect could also account for the fact that the methyl and methylene proton resonances of I in $CDCl_3$ in the presence of benzyltriphenylphosphonium chloride (phosphonium salt/Pd = 2.8) showed no significant change in chemical shifts.

$[Pd(Ph_3P)_2(CH_2SCH_3)]PF_6$ (II)

This complex exhibited only very low molar conductivity (1.14 cm^2 Ω^{-1} mol^{-1} at 5.26 × 10^{-3} mol l^{-1}) in $CHCl_3$ at 25°C. The fact that the experimental molecular weight (791 at 8.78 × 10^{-3} mol l^{-1}) in $CHCl_3$ at 25°C is nearly the calculated value (837) might be attributed to the formation of ion pairs in the solution.

In the ^{1}H NMR spectrum of $[Pd(Ph_3P)_2(CH_2SCH_3)]PF_6$ (Fig. 1), the methyl resonance appeared as a doublet due to coupling with a ^{31}P nucleus, suggesting coordination of the sulfur to the palladium atom. The two methylene protons appeared as magnetically non-equivalent even at 50°C, owing to the adjacent asymmetric sulfur atom in the bidentate thiomethoxymethyl group. A preliminary single crystal X-ray structural determination has shown that $[Pd(Ph_3P)_2(CH_2SCH_3)]PF_6$ contains the three-membered ring with one methylene group, one sulfur and one palladium atom [3].

Attempts to isolate pure $[Pd(MePh_2P)_2(CH_2SCH_3)]PF_6$ on treatment of $Pd(MePh_2P)_2(CH_2SCH_3)Br$ or $Pd(MePh_2P)_2(CH_2SCH_3)Cl$ with NH_4PF_6 were unsuccessful. However, in $CDCl_3$ solution the ^{1}H NMR spectrum of the product, a yellow oil (prepared in situ), is consistent with the formation of $[Pd(MePh_2P)_2(CH_2SCH_3)]PF_6$ (Table 2).

$Pd(Ph_3P)(CH_2SCH_3)Cl$ (III)

A preliminary X-ray structural determination showed III to be an approximately square-planar complex as depicted in eq. 1 with the $(H_2)C—S$ bond length (1.76 Å) [3] practically the same as that found in the complex $Mo(\pi\text{-}C_5H_5)(CO)_2(\pi\text{-}CH_2SCH_3)$ (1.78 Å) [4]. In the ^{1}H NMR spectrum * of III in $CDCl_3$ at −30°C the methyl and methylene protons appear as doublets at δ 2.34 (J(HP) 4 Hz) and 2.68 ppm (J(HP) 2 Hz), respectively. However, each signal coalesces to a singlet at elevated (~ 40°C) temperatures. Both coalescenses may arise from rapid phosphine exchange at higher temperatures. The fact that the methylene protons are magnetically equivalent even at −30°C is best attributed to rapid inversion at the sulfur atom without cleavage of the Pd—S bond, since we observe

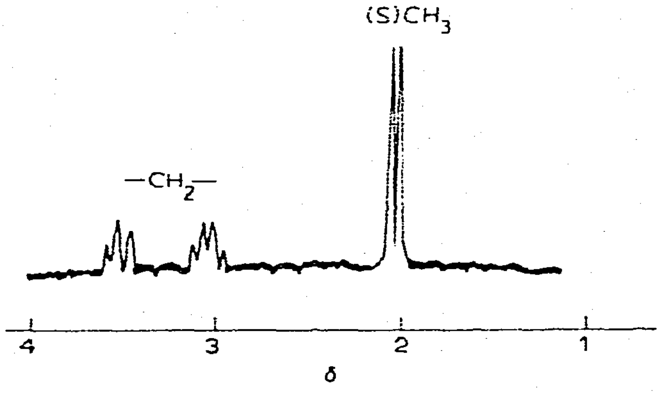

Fig. 1. ^{1}H NMR resonance pattern of $[Pd(Ph_3P)_2(CH_2SCH_3)]PF_6$ in $CDCl_3$.

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* The spectra were recorded at both 60 and 100 MHz.

TABLE 1

ANALYTICAL DATA AND MELTING POINTS OF THE THIOMETHOXYMETHYLPALLADIUM COMPLEXES (R = CH_2SCH_3, (L) = Ph_3P, (L$'$) = $MePh_2P$)

Compounds	M.p. (°C)	Analysis found (calcd.) (%)	
		C	H
$Pd(L)_2(R)Cl \cdot CH_2Cl_2$ [a]	144(dec.)	57.30 (57.65)	4.47 (4.59)
$[Pd(L)_2(R)]PF_6$	205(dec.)	54.39 (54.53)	4.32 (4.22)
$Pd(L)(R)Cl$	210(dec.)	51.68 (51.63)	4.33 (4.33)
$Pd(L')_2(R)Cl$	167(dec.)	55.09 (55.73)	5.12 (5.17)
$Pd(L')_2(R)Br$	170(dec.)	51.71 (51.91)	4.96 (4.82)

[a] The presence of one mole of CH_2Cl_2 was also confirmed by the ^1H NMR spectrum in $CDCl_3$ and an X-ray crystallographic study [3].

TABLE 2

^1H NMR [a] AND IR [b] DATA FOR THIOMETHOXYMETHYLPALLADIUM COMPOUNDS (R = CH_2SCH_3, L = Ph_3P, L$'$ = $MePh_2P$)

Compounds	δ(SCH_3)	δ(CH_2)	δ(PCH_3)	ν(Pd—Cl) (cm^{-1})
$Pd(L)_2(R)Cl \cdot CH_2Cl_2$	2.29(s)	3.26(s)	—	275
$[Pd(L)_2(R)]PF_6$	2.00(d, J(PH)5)	3.52(m)	—	—
		3.04(m)		
$Pd(L)(R)Cl$	2.34(d, J(PH)5)	2.68(s)	—	273
$Pd(L')_2(R)Br$	2.34(s)	2.97(s)	1.96(d, J(PH)9)	—
$[Pd(L')_2(R)]PF_6$ [c]	2.14(d, J(PH)4)	3.26(b)	1.60(d, J(PH)7)	—
		3.06(b)	1.99(d, J(PH)10)	—

[a] In $CDCl_3$ at room temperature: (s) singlet; (d) doublet; (m) multiplet; (b) broad. [b] Nujol mulls. [c] Prepared in situ.

no loss of coupling between (S)CH_3 protons and ^{31}P nucleus at this temperature. A similar inversion at sulfur in some dialkyl sulfide complexes of platinum [5] has been discussed in terms of the internal displacement of one sulfur lone-pair by another. However, we cannot interpret the different pattern of the methylene proton resonances of II and III precisely.

Experimental

General comments. The reactions of the zerovalent palladium complexes with chloromethyl methyl sulfide were carried out under a dry nitrogen atmosphere, and nitrogen was bubbled into solvents before use. The anion exchange reactions were carried out in air.

Starting materials: $Pd(Ph_3P)_4$ was prepared according to directions in the literature [6]. $Pd(MePh_2P)_4$ was prepared in the same manner as $Pd(Ph_3P)_4$. 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 a Hitachi EPI-2G spectrophotometer (700—200 cm^{-1}).

Preparation of chloro(thiomethoxymethyl)bis(triphenylphosphine)palladium (I) and chloro(thiomethoxymethyl)bis(methyldiphenylphosphine)palladium (Ia)

Tetrakis(triphenylphosphine)palladium (1.10 g, 0.95 mmol) was suspended in benzene (20 ml) and a solution of chloromethyl methyl sulfide (0.46 g, 4.75 mmol) in benzene (5 ml) was added dropwise. After stirring for 4 h at room temperature, the solvent volume was reduced to 5 ml and dry n-hexane (40 ml) was added to precipitate the complex. The resulting yellow solid was recrystallized from CH_2Cl_2/n-hexane to give yellow crystals of $Pd(Ph_3P)_2(CH_2SCH_3)Cl \cdot CH_2Cl_2$ in 95% yield. $Pd(MePh_2P)_2(CH_2SCH_3)Cl$ was obtained in 98% yield. Osmometric molecular weights of $Pd(Ph_3P)_2(CH_2SCH_3)Cl \cdot CH_2Cl_2$ in CH_2Cl_2 at 25°C were 435, 466 and 537 at concentrations (wt.%) of 0.356, 0.663 and 1.325, respectively, whereas the calculated molecular weight was 728.

Bromo(thiomethoxymethyl)bis(methyldiphenylphosphine)palladium

A solution of potassium bromide (0.06 g, 0.5 mmol) in 3 ml of water was added to a solution of $Pd(MePh_2P)_2(CH_2SCH_3)Cl$ (0.15 g, 0.25 mmol) in 20 ml of THF. After 30 min the solvents were removed under reduced pressure and the resulting solid was recrystallized from CH_2Cl_2/n-hexane as yellow crystals (yield, 65%).

Osmometric molecular weights of this complex in $CHCl_3$ at 37°C were 481, 533, 540 and 544 at concentrations (wt.%) of 0.133, 0.277, 0.421 and 0.562, respectively, whereas the calculated molecular weight was 648.

Thiomethoxymethylbis(triphenylphosphine)palladium hexafluorophosphate (II)

Ammonium hexafluorophosphate (0.167 g, 1.02 mmol) in 5 ml of acetone was added to a solution of $Pd(Ph_3P)_2(CH_2SCH_3)Cl \cdot CH_2Cl_2$ (0.37 g, 0.51 mmol) in 20 ml of CH_2Cl_2. After 15 min, the white precipitate 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 II in 79% yield.

Chloro(thiomethoxymethyl)(triphenylphosphine)palladium (III)

$Pd(Ph_3P)_2(CH_2SCH_3)Cl \cdot CH_2Cl_2$ (1.10 g) was dissolved in a minimum amount of CH_2Cl_2. Diethyl ether was added until the solution became turbid, and it was let stand overnight in a refrigerator. Filtration gave a mixture of $Pd(Ph_3P)_2(CH_2SCH_3)Cl \cdot CH_2Cl_2$ and $Pd(Ph_3P)(CH_2SCH_3)Cl$. Repeating the procedure, pure $Pd(Ph_3P)(CH_2SCH_3)Cl$ (0.55 g) was obtained in 87% yield.

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