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Preliminary communication

PALLADIUM(II) COMPLEXES WITH SULFUR YLIDES: A NEW COMPLEX CONTAINING METHYLSULFOXONIUM DIMETHYLIDE AS A CHELATING LIGAND

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Summary

The complex $[CH_3SO(CH_2)_2 \cdot PdI]_2$ which contains the new methylsulfoxonium dimethylide as a chelating ligand, is described.

In the last ten years ylides have been shown to be versatile ligands. We recently reported that weakly basic ylides of sulfur, phosphorus, arsenic, and nitrogen (pyridinium) react with $PdCl_2$ or its simple complexes to give a new series of *trans*-square-planar complexes of palladium(II) containing two ylide molecules bound to the metal through the ylidic carbon [1—3]. Even the more reactive dimethylsulfonium methylide gives, in our hands a palladium(II) complex with a monodentate ylide ligand [2]. On the other hand, the corresponding trimethylphosphonium methylide formed complexes with several transition metals in which the ylide acted as a bidentate ligand (dimethylsulphonium dimethylide), and so formed a bridge between two metal atoms or acted as a chelating agent with a single atom [4].

We now report the synthesis of a new complex (I), which shows that, in the sulfur series also, bis-ylides can act as ligands to transition metals.

Complex I is made by mixing a solution of dimethylsulfoxonium methylide, prepared from trimethylsulfoxonium iodide [5] (5 mmol in 8 ml DMSO) with a solution of the palladium chloride—styrene complex [6] (2 mmol in 10 ml DMSO). The mixture is set aside overnight, diluted with an equal volume of water, extracted with ether to remove the liberated styrene, and again set aside. Product I slowly deposits as a microcrystalline yellow solid. After a few days the product is collected, dissolved in a small amount of warm DMSO, and recovered by dilution with water : 0.77 g, 60% yields; m.p. ≈200°C (dec.) Anal. Found: C, 11.4; H, 2.3; I, 39.0; Pd, 32.7; S, 9.8; $C_6H_{14}I_2O_2Pd_2S_2$ calcd.: C, 11.1; H, 2.2; I, 39.1; Pd, 32.8; S, 9.9%. IR

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(nujol): 2860, 2820, 1450, 1400, 1370, 1310, 1175 (very strong), 1055, 1025, 965, 940, 920, 805, 708, 700 cm^{-1}.

The same complex can also be prepared from the palladium chloride—benzonitrile complex by the above procedure*.

The structure shown in Fig. 1 is the most consistent with analytic and spectroscopic data, especially NMR.

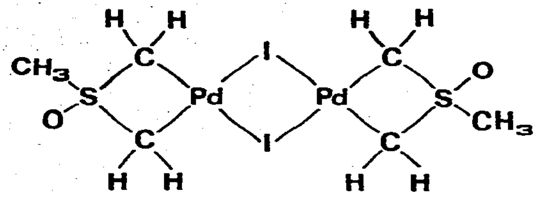


Fig.1.

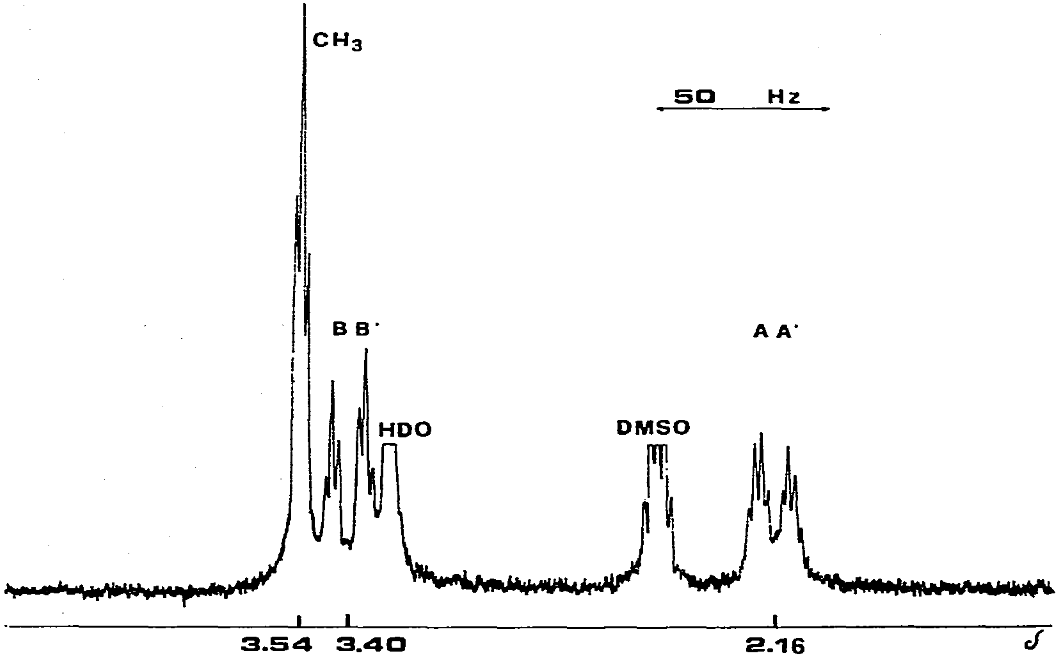
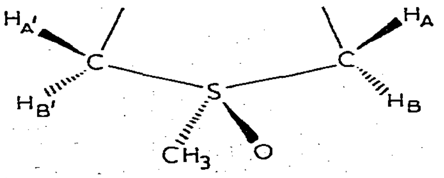


Fig.2. ^{1}H NMR spectrum (DMSO) of complex I.

The ^{1}H NMR spectrum (Fig. 2) is in good agreement with the symmetric fragment:



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[*] Occasionally I precipitates along with other complexes; these are probably cross-complexes still containing benzonitrile, as suggested by the NMR spectra of the crude product.

The AA′BB′ system consists of two multiplets at δ 2.16 (AA′) and 3.40 ppm (BB′). Protons A and A′ are also coupled with CH_3 at δ 3.54 ppm ($J(H_A,CH_3) = J(H_{A'},CH_3) = 1.75$ Hz), while the easily recognisable B,B′ protons exhibit no further coupling*. They form a six line signal, thus confirming the general case for an AA′BB′ spectrum in which K = M [7]. The coupling constants are 9.15 and 0.35 Hz for $^2J_{AB}$ and $^4J_{AB'}$, respectively, and 3.50 and 0.0 Hz for $^4J_{AA'}$ and $^4J_{BB'}$. Since the larger constant (9.15 Hz) must be geminal, the assignment of the $^2J_{AB}$ relative to $^4J_{AB'}$ is straightforward. However, for the assignment of $^4J_{AA'}$ and $^4J_{BB'}$, one must look to the $CH_2SO(CH_3)CH_2$ fragment. A structure with a four-membered ring can most reasonably explain the large value (3.5 Hz) of a four bond coupling in a saturated system of this type [8].

The formation of I can be explained as follows. The ylide $CH_2{=}SO(CH_3)_2$ readily displaces benzonitrile and stryrene from their complexes, while the iodide ions in solution replace the chloride. Because of their greater bridging capacity, these lead to a dimeric complex: $[(CH_3)_2SOCH_2]_2Pd_2I_4$. A transylidation between the free ylide in solution and one of the methyl groups of the bound ylide yields a bis-ylide ($\geqslant PdCH_2\overset{+}{S}O(CH_3)CH_2^-$), which displaces a halogen atom from the same palladium atom to become a chelating ligand, and so form the four-membered ring.

Two further conclusions can be drawn from the NMR spectrum of I, viz. that the ring must be folded in some way and that the methyl must be in an axial position (and the oxygen equatorial). The first conclusion stems from the difference in the $J_{AA'}$ and $J_{BB'}$ couplings; it is known that this can occur in four-membered rings of this type if they are folded [8]. Since $^4J_{eq,eq}$ than becomes larger than $^4J_{ax,ax}$, we can thus assign J 3.5 Hz to $^4J_{BB'}$ (pseudo-equatorial) and 0.0 Hz to $^4J_{AA'}$ (pseudo-axial).

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*This assignment is confirmed by double resonance experiments: irradiation of A,A′ at δ 2.16 ppm causes the collapse of both the methyl at δ 3.54 ppm and B,B′ at δ 3.40 ppm. Conversely, simultaneous irradiation of the methyl and B,B′ protons causes the collapse of A,A′ to a singlet at δ 2.16 ppm.