CHEMISTRY LETTERS, pp. 375-378, 1979. Published by the Chemical Society of Japan

PLATINUM(II) COMPLEXES OF S,S-DIMETHYLSULFONIUM 2-PICOLINYLMETHYLIDE AND X-RAY MOLECULAR STRUCTURE OF CHLORO(DIMETHYLSULFIDE)(2-PICOLINYLCHLOROMETHYL)PLATINUM(II)

Gen-etsu MATSUBAYASHI,* Yasuo KONDO,* Toshio TANAKA,* Satoshi NISHIGAKI,** and Kazumi NAKATSU**

*Department of Applied Chemistry, Faculty of Engineering, Osaka University, Yamadakami, Suita, Osaka 565, and

**Department of Chemistry, Faculty of Science, Kwansei Gakuin University, Uegahara, Nishinomiya, Hyogo 662

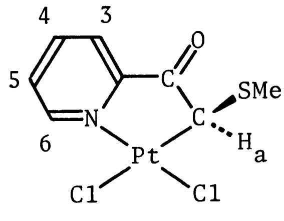
S,S-Dimethylsulfonium 2-picolinylmethylide ($PyC(O)\overset{-}{C}H\overset{+}{S}Me_2$, Y_{dms}) reacts with $PtCl_2(SMe_2)_2$ to give $PtCl_2Y_{dms}$ and $PtCl(SMe_2)(PyC(O)CHCl)$; the former involves the coordination of both the pyridine nitrogen and ylide carbon atoms, and the latter is a complex with the 2-picolinylchloromethyl ligand which is formed by the fission of the ylide carbon to sulfur bond. An X-ray structure of the latter complex is determined.

Ylide molecules are known to react with platinum(II) ions to form stable complexes, in which the ylide carbon atom coordinates to the metal ion.$^{1-6)}$ In the course of studies on metal complexes of chelate ylides containing a pyridine ring,$^{7)}$ we have found that the reaction of $PtCl_2(SMe_2)_2$ with S,S-dimethylsulfonium 2-picolinylmethylide (Y_{dms}) gives not only a ylide complex but also a complex with the 2-picolinylchloromethyl ligand which is formed by the fission of the ylide carbon to sulfur bond.

A dichloromethane (4 ml) solution of Y_{dms} (0.16 g, 0.90 mmol) was added to $PtCl_2(SMe_2)_2$ (0.53 g, 0.89 mmol) in dichloromethane (5 ml). After stirred for 4 h at room temperature, the mixture was allowed to stand overnight. The solution was evaporated to dryness under reduced pressure to give an oily residue. The addition of dichloromethane (3 ml) to it separated out a precipitate, which was collected by filtration and recrystallized from acetonitrile to give yellow microcrystals of $PtCl_2Y_{dms}$ (**1**), mp. 144°C (dec.) (0.064 g, 17 % yield). Anal. Calcd for $C_9H_{11}NOSCl_2Pt$: C, 24.17; H, 2.48; N, 3.13 %. Found: C, 24.05; H, 2.45; N, 3.44 %. To the filtrate was added diethyl ether (30 ml). The solution was allowed to stand at room temperature for 4 days to liberate orange crystals of $PtCl(SMe_2)(PyC(O)CHCl)$ (**2**), mp. 90-95°C (dec.) (0.14 g, 37 % yield). Anal. Calcd for $C_9H_{11}NOSCl_2Pt$: C, 24.17; H, 2.48; N, 3.13 %. Found: C, 24.06; H, 2.38; N, 3.16 %.

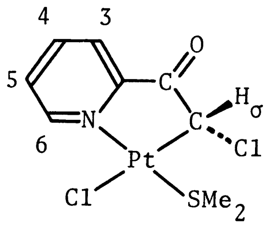
The infrared spectrum of **1** showed a $\nu(C=O)$ band at 1689 cm^{-1} which is 167 cm^{-1} higher than the $\nu(C=O)$ frequency of free ylide, suggesting the coordination of Y_{dms} to platinum through the ylide carbon, as described previously.$^{1)}$ The ^1H NMR spectrum of **1** in liquid sulfur dioxide at room temperature showed satellites due to the spin-spin coupling with the ^{195}Pt nucleus at the signals of the proton (H_6)

attached to carbon adjacent to the pyridine nitrogen atom (9.30 δ, $^{3}J(^{195}Pt\text{-}H)$ = 50 Hz) and the ylide proton (H_a) (4.69 δ, $^{2}J(^{195}Pt\text{-}H)$ = 106 Hz). This is an evidence for the coordination of Y_{dms} through pyridine nitrogen as well as ylide carbon. In addition, two S-methyl signals were observed at 3.14 δ ($^{4}J(^{195}Pt\text{-}H)$ = 4 Hz) and 2.98 δ. This may be due to asymmetry of the coordinating ylide carbon atom. Complex **1** is therefore suggested to assume the configuration **A**, which is consistent with the occurrence of two ν(Pt-Cl) bands at 290 and 334 cm^{-1} in the infrared spectrum.



A

Elemental analyses confirm that **2** has the same chemical formula as **1**. Molecular weight determination in chloroform and electric conductivity measurement in acetonitrile indicated that **2** is essentially monomeric (Found 477, Calcd 447) and a non-electrolyte (2.6 $ohm^{-1}cm^{2}mol^{-1}$, 2.0×10^{-3} M at 25°C) in solution. Complex **2** exhibited the ν(C=O) band at 1687 cm^{-1}. The ^{1}H NMR spectrum shows two S-methyl signals accompanied with satellites due to spin-spin coupling with the ^{195}Pt nucleus (Figure 1). The coupling constants (54 Hz) are close to those of cis-$PtCl_2(SMe_2)_2$-(p-Cl-$C_6H_4C(O)\bar{C}H\overset{+}{S}MePh$) (52.4, 54.5 Hz) and cis-$PtCl_2(SMe_2)_2$ (50.9 Hz),1) suggesting the coordination of sulfur to platinum in **2**. The signals at 9.64 δ and 5.19 δ which are assigned to H_6 and the proton attached to the ylide carbon atom are also accompanied with the coupling satellites with the ^{195}Pt nucleus ($J(^{195}Pt\text{-}H)$ = 45 and 76 Hz, respectively). This confirms the coordination of both the pyridine nitrogen and ylide carbon atoms to platinum. In accordance with these results, an X-ray crystallographic analysis has demonstrated the structure **B** for **2**. Thus, the reaction of $PtCl_2(SMe_2)_2$ with Y_{dms} is suggested to involve the cleavage of the ylide carbon to sulfur bond, followed by migration of the chloride ion to the ylide carbon.



B

Crystal data for **2**: Triclinic, space group P$\bar{1}$; a = 8.855(3), b = 9.213(2), c = 8.284(2) Å; α = 90.16(2), β = 108.37(2), γ = 101.61(2)°; U = 626.7(3) $Å^3$; D_m(flota-

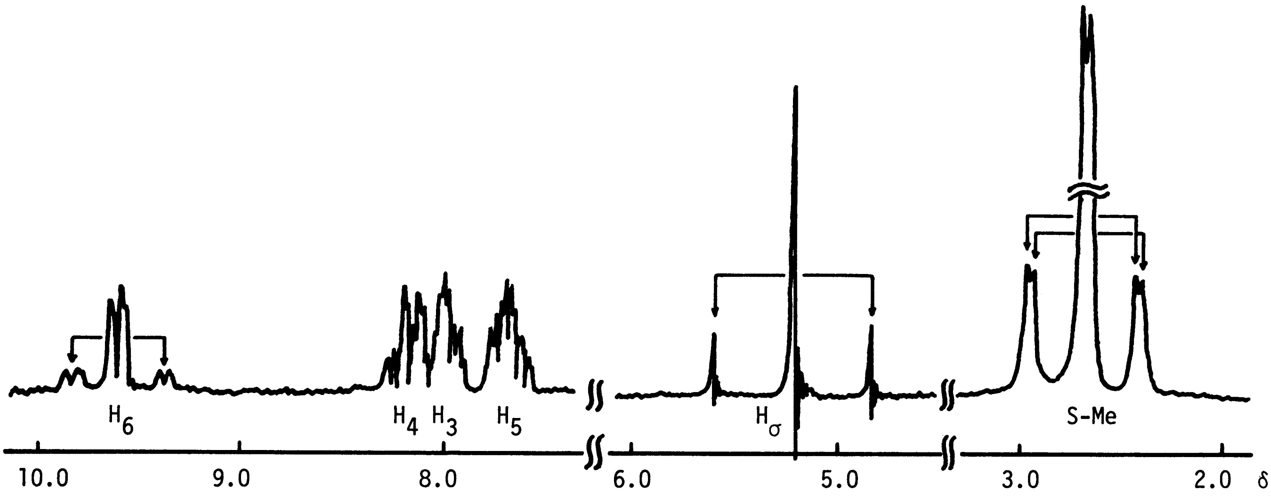


Figure 1. The ^{1}H NMR spectrum of $PtCl(SMe_2)(PyC(O)CHCl)$ in chloroform-d_1 at 24°C.

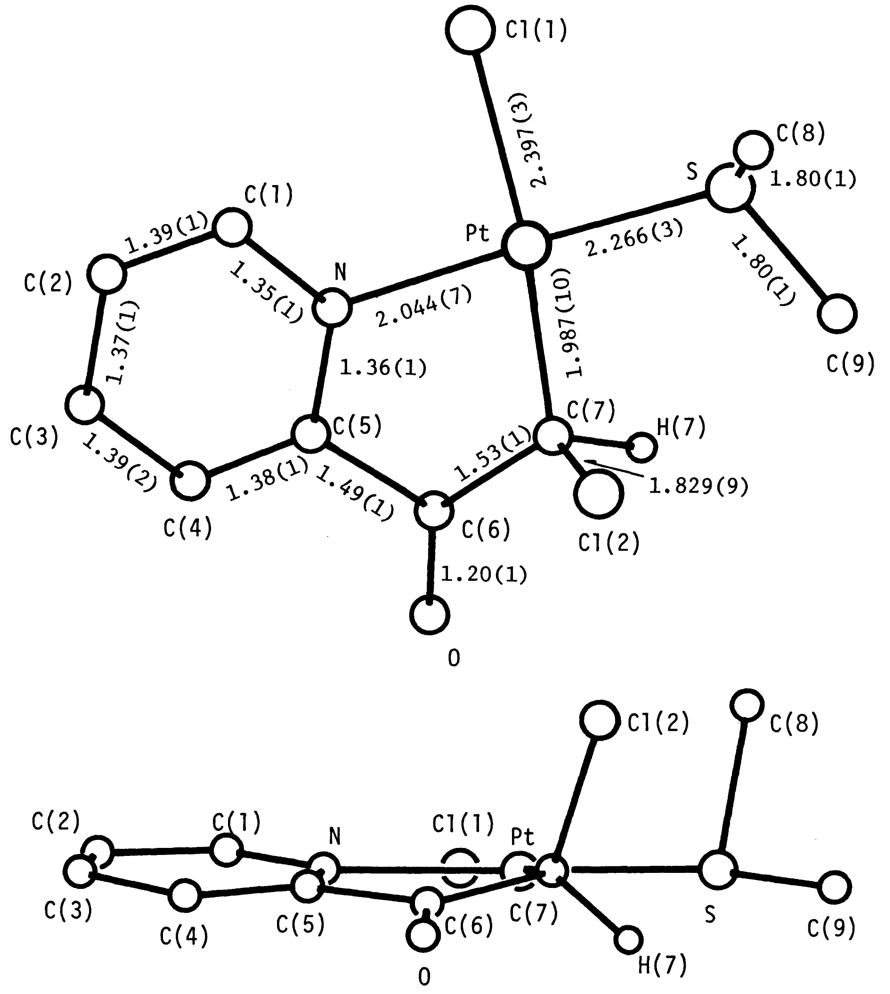


Figure 2. Molecular structure of PtCl(SMe$_2$)(PyC(O)CHCl) and important bond lengths (in Å) together with a view parallel to the Pt-N-S-Cl(1)-C(7) plane. All the hydrogen atoms except for H(7) are omitted. Relevant bond angles (in degrees) are: N-Pt-Cl(1), 94.4(2); N-Pt-C(7), 83.1(3); S-Pt-Cl(1), 85.36(9); S-Pt-C(7), 97.1(3); Pt-N-C(1), 125.5(7); Pt-N-C(5), 115.6(6); Pt-S-C(8), 103.0(4); Pt-S-C(9), 112.7(4); Pt-C(7)-C(6), 110.9(6); Pt-C(7)-Cl(2), 112.4(6); N-C(5)-C(6), 114.5(8); Cl(2)-C(7)-C(6), 103.3(6); C(5)-C(6)-C(7), 113.4(9).

tion) = 2.37 g cm^{-3}, Z = 2, D_x = 2.37 g cm^{-3}. A specimen, approximately 0.035 × 0.055 × 0.075 mm, was used for analysis. The intensity data were collected on an automated diffractometer with graphite-monochromatized Mo-Kα radiation. The structure was solved by the standard heavy-atom method and refined by the block-diagonal least-squares procedure. Anisotropic thermal vibrations were assumed for all the non-hydrogen atoms. All the hydrogen atoms were revealed from a difference Fourier map and refined isotropically. At convergence the conventional R value was 4.1 % for 2489 independent reflections with $|F_o| > 3\sigma(F)$.

The crystal structure consists of two discrete molecules per unit cell. The molecular structure is illustrated in Figure 2, which shows that in the complex the ylide carbon to sulfur bond is broken, the C(7)-Pt σ-bond being formed. N, S, Cl(1), and C(7) form a square-planar coordination around the platinum atom. However, C(6), O, and the pyridine ring considerably deviate from this plane. The Pt-C(7) bond distance of 1.987(10) Å is considerably shorter than the Pt-C(sp^3) distance of 2.08 Å predicted by assuming the covalent radii (1.31 Å for Pt and 0.772 Å for C(sp^3)$^{8)}$), and is rather close to the Pt-C(sp^2 and carbenoid) (2.03 – 1.96 Å)$^{9-11)}$ or Pt-C(sp) bonds (1.98 Å).$^{12)}$ The strengthened Pt-C(7) bond may be partly due to the increasing s-character caused by the electronegative chlorine atom and carbonyl group attached to C(7).$^{13)}$ The Pt-Cl(1) distance of 2.397(3) Å is significantly lengthened by the *trans*-influence of the C(7)HCl moiety. The similar Pt-Cl lengthening was observed in *trans*-$PtCl(CH{=}CH_2)(PPhEt_2)_2$ (2.398(4) Å) and *trans*-$PtCl(C{\equiv}CPh)(PPhEt_2)_2$ (2.407(6) Å).$^{12)}$ The Pt-N and Pt-S distances are close to those reported for such bonds in other compounds.$^{14-16)}$

References

1) H. Koezuka, G. Matsubayashi, and T. Tanaka, Inorg. Chem., 13, 443 (1974); 15, 417 (1976).
2) E. T. Weleski, Jr., J. L. Silver, M. D. Jansson, and J. L. Burmeister, J. Organomet. Chem., 102, 365 (1975).
3) Y. Oosawa, T. Miyamoto, T. Saito, and Y. Sasaki, Chem. Lett., 33 (1975).
4) M. Kato, H. Urabe, Y. Oosawa, T. Saito, and Y. Sasaki, J. Organomet. Chem., 121, 81 (1976).
5) Y. Oosawa, H. Urabe, T. Saito, and Y. Sasaki, ibid., 122, 113 (1976).
6) M. Seno and S. Tsuchiya, J. Chem. Soc. Dalton, 751 (1977).
7) G. Matsubayashi, Y. Kondo, and T. Tanaka, to be published.
8) L. Pauling, "The Nature of the Chemical Bond", 3rd ed., Cornell University Press, Ithaca N. Y. (1960).
9) D. J. Cardin, B. Cetinkaya, E. Cetinkaya, M. F. Lappert, L. J. Manojlovic-Muir, and K. W. Muir, J. Organomet. Chem., 44, C59 (1972).
10) E. M. Badley, J. Chatt, R. L. Richards, and G. A. Sim, Chem. Comm., 1322 (1969).
11) E. M. Badley, K. W. Muir, and G. A. Sim, J. Chem. Soc. Dalton, 1930 (1976).
12) C. J. Cardin, D. J. Cardin, M. F. Lappert, and K. W. Muir, J. Organomet. Chem., 60, C70 (1973).
13) C. A. Coulson, "Valence", 2nd ed., The Clarendon Press, Oxford (1961).
14) R. S. Osborn and D. Rogers, J. Chem. Soc. Dalton, 1002 (1974).
15) K. W. Nordquest, D. W. Phelps, W. F. Little, and D. J. Hodgson, J. Am. Chem. Soc., 98, 1104 (1976).
16) K. W. Jennette, J. T. Gill, J. A. Sadownick, and S. J. Lippard, ibid., 98, 6159 (1976).

(Received February 13, 1979)