

Facile P-C Bond Cleavage in Bis(diphenylphosphino)methane with the Formation of New Pt(II) P, S-Chelates Containing a P-N Bond

Seichi OKEYA,* Hiroshi SHIMOMURA,[†] and Yoshihiko KUSHI[†]

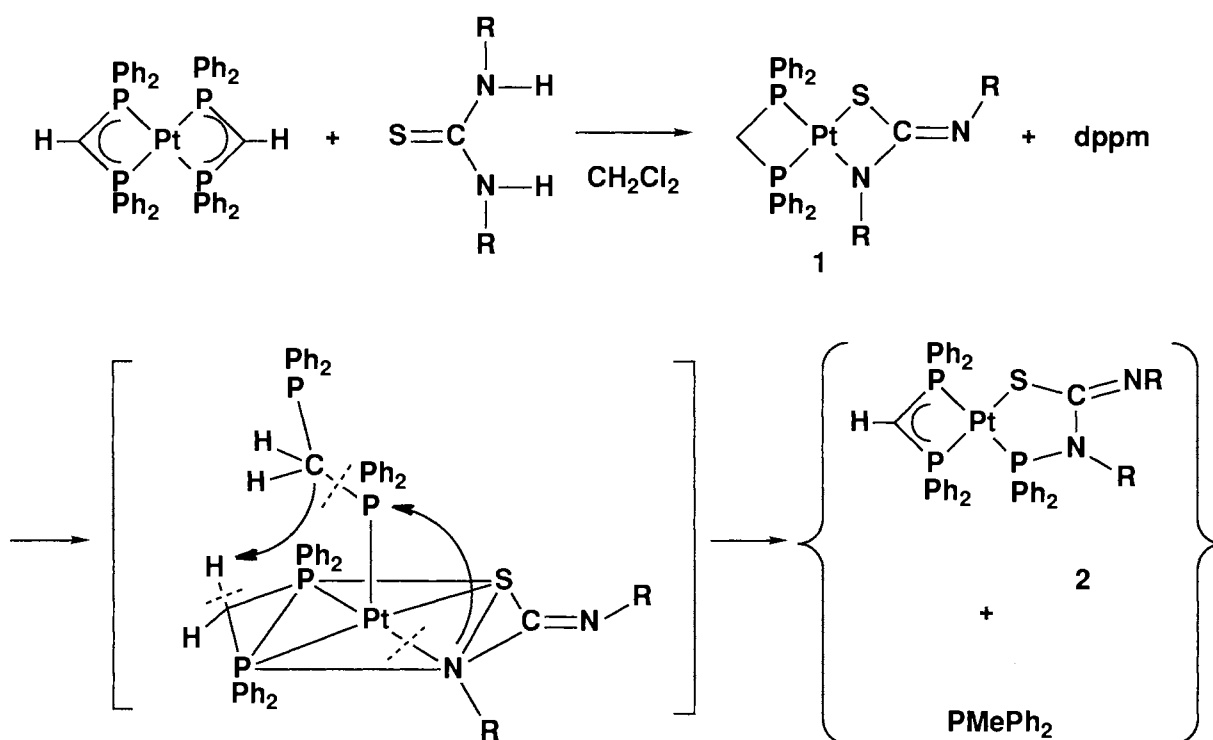
Faculty of Education, Wakayama University, Sakaedani, Wakayama 640

[†]Coordination Chemistry Laboratory, Institute for Molecular Science, Myodaiji, Okazaki 444

New platinum(II) P, S-chelates, $[(\text{dppm-H})\text{PtP}(\text{Ph})_2\text{N}(\text{R})\text{C}(=\text{NR})\text{S}]$ ($\text{R}=\text{o-tolyl}$ or Et (**2b**)), were prepared by a reaction of $[\text{Pt}(\text{dppm-H})_2]$ with 1,3-disubstituted thioureas. A reaction intermediate, $[(\text{dppm})\text{PtN}(\text{R})\text{C}(=\text{NR})\text{S}]$ ($\text{R}=\text{o-tol}$), was isolated. Crystallographic X-ray analysis for **2b** revealed a P, S-chelated structure containing a P-N bond.

As tertiary phosphines are very versatile ligands for stabilizing M-H and M-R bonds for a wide variety of metals and their oxidation states, they have been widely used in catalytic systems. They are usually thermally stable but under some reaction conditions P-C bond cleavage has been found.¹⁾ For bis-(diphenylphosphino)methane (dppm) as a useful chelating or bridging ligand, there have been few reports of P-Ph²⁾ or P-CH₂³⁻⁷⁾ bond cleavage in coordinated dppm. In this letter, we report a first example of facile P-CH₂ bond cleavage in non-coordinating dppm with new P-N bond formation under mild reaction conditions (Scheme 1).

1,3-Di(*o*-tolyl)thiourea (tol₂TU) was added to an equimolar suspension of bis[bis(diphenylphosphino)-methanido]platinum(II), $[\text{Pt}(\text{dppm-H})_2]$,⁸⁾ in dichloromethane and the reaction mixture was stirred for several minutes at room temperature to form a clear yellow solution that contained $[(\text{dppm})\text{PtN}(\text{o-tol})\text{C}(=\text{N}(\text{o-tol}))\text{S}]$ (**1**)⁹⁾ and dppm in 100% ³¹P NMR yields. In this reaction two protons of tol₂TU were abstracted by dppm-H ligands. Pentane was added to the solution, and this was allowed to stand at -5 °C to afford pale yellow plates of **1** (one molecule of CH₂Cl₂ was solvated) in an 85% yield. When the reaction was allowed to continue for 2 hours without isolating **1**, $[(\text{dppm-H})\text{PtP}(\text{Ph})_2\text{N}(\text{o-tol})\text{C}(=\text{N}(\text{o-tol}))\text{S}]$ (**2a**)¹⁰⁾ was deposited as yellow crystals in a 33% yield on addition of pentane. 1,3-Diethylthiourea (Et₂TU) also reacted with $[\text{Pt}(\text{dppm-H})_2]$ to afford **2b**¹¹⁾ (one molecule of CH₂Cl₂ was solvated) as yellow plates in a 50% yield, but no intermediate was detected by ³¹P NMR. In each case, the ³¹P NMR signals of PMePh₂ (δ -27.1) and **2** (an ABX pattern with ¹⁹⁵Pt satellite) were observed in the reaction mixture within 2 hours after start of the reaction, together with the signals of unreacted dppm and a small amount of unidentified by-products. Figure 1 shows an X-ray molecular structure¹²⁾ of **2b** and selected bond distances and angles. The coordination geometry around the platinum atom is almost planar, and two phosphorous atoms from dppm-H, a sulphur atom and a phosphorous atom of the P,S-chelate coordinate to the platinum. The significant distortions from an ideal square arrangement of the ligand atoms are apparently due to the small bite angle of the chelating dppm. Because of the difference between the four and five-membered chelate rings, the bond angle of P1-Pt-P2 is



Scheme 1.

rather smaller than that of P3-Pt-S. The angle of P2-Pt-P3 is significantly larger than that of S-Pt-P1, and this suggests the occurrence of large steric repulsion between the P2 and P3 diphenylphosphine moieties. The Pt-P1 and Pt-P2 bond lengths are the same within the limits of error. Deprotonation of the $\text{Ph}_2\text{PCH}_2\text{PPh}_2$ methylene group to form a delocalized P-C-P system is indicated mainly by the P-C1 bond lengths (1.705(7), 1.716(7) Å), which are significantly shorter than the P-C(phenyl) distances (1.807(7)-1.831(7) Å). The geometry of the Pt-P1-C1-P2 ring is similar to that of the coordinated dppm-H ligand reported in the related platinum(II) complexes.¹³ In the present complex, one of the nitrogen atoms (N1) of the diethylthiourea is bonded to the phosphorus atom (P3) which is thought to originate from free dppm, and forms a five-membered P,S-chelate ring of minus one charge. The P3-N1 bond length has quite normal value for a P-N(sp²) bond.¹⁴ The geometry of the thiourea moiety is quite different from that of the coordinated neutral thiourea derivatives.¹⁵ The P3-N1-C2-S plane in this chelate is almost coplanar with the Pt(II) coordination plane. The Pt-S-C2 angle suggests that the sulphur atom is sp³ hybridized as reported in tetrakis(1,3-dimethylthiourea)platinum(II) chloride.¹⁶ The bond distance of S-C2 is significantly longer than those reported in coordinated neutral thiourea derivatives.^{15,16} The bond angles around C2, N1, and N2 indicate that these atoms have an sp² hybridized character. In the monodentate neutral thiourea derivatives, the two C-N bond distances are almost equal.^{15,16} In the present complex, on the other hand, the C2-N2 bond distance is much shorter than that of C2-N1, and this indicates C2-N2 double bond character.

Although complex **1** was stable in CH_2Cl_2 for a long time in the absence of dppm, a smooth reaction was caused by the addition of equimolar dppm, giving **2** and PMePh_2 . This implies that the P-C bond in free dppm was cleaved with the assistance of **1**. Conversely, in all other reported cases P-C bond cleavage occurred only in the coordinated dppm. Nucleophilic attack by the coordinated N-donor in **1** on a P atom of

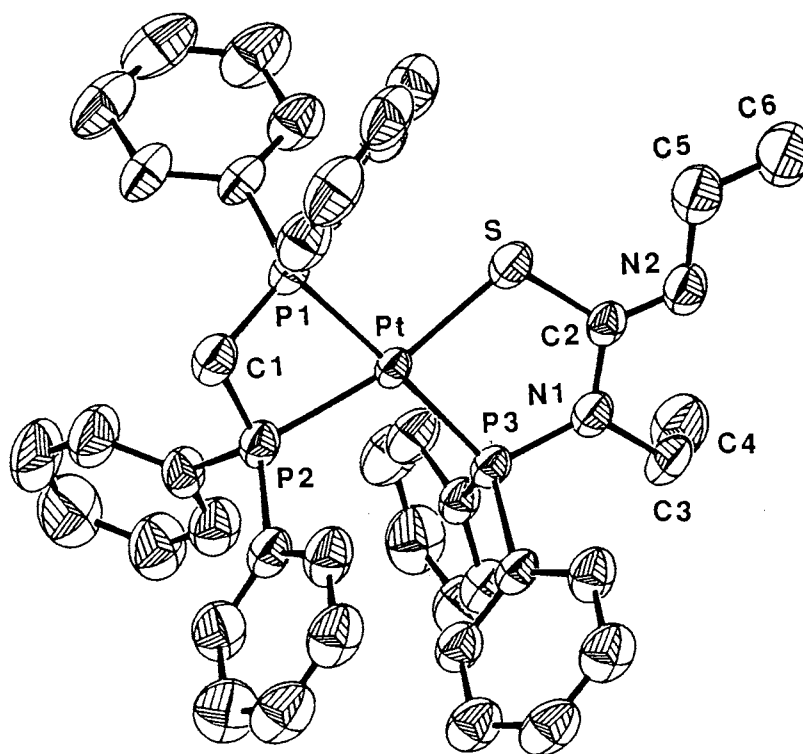


Fig. 1. A view of the structure of **2b**. Selected bond lengths(Å); Pt-P1 2.308(2), Pt-P2 2.303(2), Pt-P3 2.269(2), Pt-S 2.291(2), P3-N1 1.683(6), N1-C2 1.418(8), N1-C3 1.468(9), S-C2 1.771(6), C2-N2 1.267(8), N2-C5 1.48(1), Selected bond angles(deg.); P1-Pt-P2 108.60(6), P1-Pt-S 96.86(6), P1-Pt-P3 177.17(6), P2-Pt-S 164.86(6), P2-Pt-P3 108.60(6), S-Pt-P3 85.72(6), Pt-P3-N1 108.6(2), Pt-S-C2 107.1(2), P3-N1-C2 121.3(4), P3-N1-C3 121.0(5), C2-N1-C3 117.7(5), N1-C2-S 117.0(4), N1-C2-N2 118.6(6), S-C2-N2 124.4(5), C2-N2-C5 116.8(6).

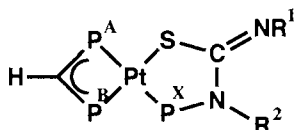
the free dppe, which probably interacts with Pt(II) in the transition state, might be an initiating step. It is followed by proton transfer from the coordinated dppe to the Ph_2PCH_2 moiety (see Scheme 1). ^{31}P NMR showed that **1** reacted with 1,2-bis(diphenylphosphino)ethane to afford $[\text{Pt}(\text{dppe})(\text{tol}_2\text{TU}-2\text{H})]$ and dppe, but P-C bond cleavage in dppe or dppe did not occur. This implies that the driving force of this novel P-C bond cleavage reaction originates from the total strain energy of the coordinated dppe and thioureido dianion.

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- 9) An X-ray analysis of a similar complex, [Pt(PPh₃)₂(Et₂TU-2H)], will be published: S. Okeya, Y. Fujiwara, S. Kawashima, Y. Nakamura, Y. Hayashi, K. Isobe, H. Shimomura, Y. Kushi, *Chem. Lett.*, in press. **1**: ¹H NMR(CD₂Cl₂) δ 2.16(3H, tol-CH₃), 2.30(3H, tol-CH₃), 4.52(2H, t, ²J(P-H)=11 Hz, ³J(Pt-H)=4 Hz, dppm-CH₂), 6.7-6.9(Ph); ¹³C NMR (CD₂Cl₂) δ 18.8, 19.0(tol-CH₃), 45.9(t, ¹J(P-C)=31 Hz, dppm-CH₂), 121-151(Ph), 166.6(t, ³J(P-C)=3 Hz, CS); ³¹P NMR (CD₂Cl₂) δ -53.4 (AB, ²J(P-P)=66 Hz, ¹J(Pt-P)=2602 Hz), -51.6(AB, ¹J(Pt-P)=2630 Hz).

10)



- 2a**: ¹H NMR(CD₂Cl₂) δ 1.23(3H, tol-CH₃), 2.06(3H, tol-CH₃), 6.9-7.4(Ph); ¹³C NMR(CD₂Cl₂) δ 17.4, 18.3(tol-CH₃), 120-140(Ph), 150.8(CS); ³¹P NMR(CD₂Cl₂) δ -45.0(ABX, ²J(P^A-P^B)=40 Hz, ²J(P^A-P^X)=377 Hz, ¹J(Pt-P^A)=2217 Hz, P^A), -44.2(ABX, ¹J(Pt-P^B)=1935 Hz, P^B), 76.5 (ABX, ¹J(Pt-P^X)=2514 Hz, P^X); ¹⁹⁵Pt NMR (CD₂Cl₂) δ -3019 from ext. K₂PtCl₄ (ddd, ¹J(Pt-P)=1943, 2203, 2515 Hz)
- 11) 2b**: ¹H NMR(CDCl₃) δ 0.37(3H, t, ³J(H-H)=7 Hz, R¹-CH₃), 1.24(3H, t, ³J(H-H)=7 Hz, R¹-CH₃), 13.33(2H, quintet, ³J(H-H)=³J(P-H)=7 Hz, R²-CH₂), 3.60(2H, q, ³J(H-H)=7 Hz, R¹-CH₂), 6.9-7.2(Ph); ¹³C NMR(CDCl₃) δ 12.4(R²-CH₃), 16.4(R¹-CH₃), 27.0(t, br, ¹J(P-C)=68 Hz, dppm-CH), 42.8(³J(Pt-C)=27 Hz, R²-CH₂), 47.6(d, ⁴J(P-C)=3 Hz, ⁴J(Pt-C)=16 Hz, R¹-CH₂), 128-140(Ph), 159.7(dd, J(P-C)=11, 36 Hz, CS); ³¹P NMR(CD₂Cl₂) δ -44.00(ABX, ²J(P^A-P^B)=39 Hz, ²J(P^A-P^X)=382 Hz, ¹J(Pt-P^A)=2229 Hz, P^A), -44.02(ABX, ¹J(Pt-P^B)=1932 Hz, P^B), 75.0(ABX, ¹J(Pt-P^X)=2525 Hz, P^X); ¹⁹⁵Pt NMR(CD₂Cl₂) δ -3056 (ddd, ¹J(Pt-P)=1942, 2227, 2526 Hz); MS, (m/e) 894 (M⁺); M.w. (CH₂Cl₂) 964(calcd. 979).
- 12)** Crystal data of **2b**: F.W.=978.84, triclinic, $P\bar{1}$, $a=12.811(3)$, $b=15.718(2)$, $c=12.343(3)$ Å, $\alpha=92.43(2)$, $\beta=116.76(2)$, $\gamma=105.97(2)^\circ$, $U=2093(1)$ Å³, $Z=2$, $D_c=1.55$, $D_m=1.53$ g cm⁻³, $\mu(\text{Mo } K\alpha)=37.1$ cm⁻¹. $R=0.042$, $R_w=0.046$. Total 8420 independent reflections with $|F_o| > 3\sigma |F_o|$ (2σ max=60°) were used.
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