C=S Bond Fission in Coordinated Thioureas and Formation of a Sulfide-bridged Dinuclear Pd(II) Complex

Seichi Okeya,* Hidemi Kameda, Hiromu Kawashima, Hiroshi Shimomura,† Takanori Nishioka,† and Kiyoshi Isobe†
Faculty of Education, Wakayama University, Sakaedani, Wakayama 640
†*Institute for Molecular Science, Myodaiji, Okazaki 444*

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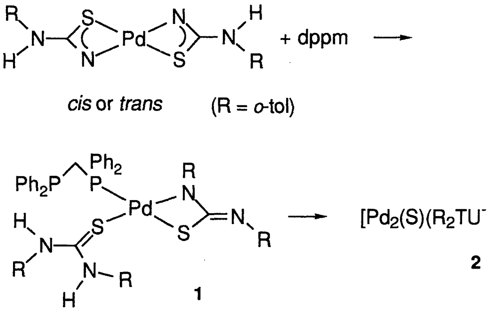
A reaction of [Pd(tol$_2$TU^{-1}-*N,S*)$_2$] (tol$_2$TU=1,3-di(*o*-tolyl)-thiourea) with dppm affords [Pd(tol$_2$TU^{-2}-*N,S*)(tol$_2$TU-*S*)(dppm-*P*)] (**1**). Complex **1** is gradually converted into [Pd$_2$(μ-S)(μ-dppm)$_2$(tol$_2$TU^{-1}-*S*)$_2$] (**2**), with a sulfide bridge *via* CS bond activation in tol$_2$TU. X-ray diffraction study shows that complex **2** has an A-frame dinuclear Pd(II) structure without a Pd-Pd.

We have been interested in the reactivity of thiourea derivatives coordinated to d^8 metals. Recently we reported the preparation of a new *P,S*-chelate with Pt(II) by the reaction of bis{bis(diphenylphosphino)methanido}platinum(II), [Pt(dppm^{-1})$_2$], and 1,3-disubstituted thioureas, R$_2$TU (R=Et, *o*-tolyl), *via* the P-CH$_2$ bond activation in dppm.[1] The same *P,S*-chelated species was also detected in the reaction system of bis(1,3-diethylthioureido)platinum(II), [Pt(Et$_2$TU^{-1}-*N,S*)$_2$] and dppm in CDCl$_3$ by ^{31}P NMR. Here we describe the results of a reaction of [Pd(tol$_2$TU^{-1}-*N,S*)$_2$] and dppm, which causes the C=S bond activation.

Dppm was added to a solution of [Pd(tol$_2$TU^{-1}-*N,S*)$_2$] in CH$_2$Cl$_2$. The mixture with *n*-pentane was kept in a refrigerator overnight, depositing orange cubes of [Pd(tol$_2$TU^{-2}-*N,S*)(tol$_2$TU-*S*)(dppm-*P*)] (**1**) in an 85% yield.[2] The *P*-unidentate coordination of dppm was confirmed by ^{31}P NMR, which shows a large difference in the chemical shifts of the two P nuclei (Δδ 52).[3] Complex **1** is unstable in organic solvents. The solution of **1** in CH$_2$Cl$_2$ was stood for five hours at room



Scheme 1.

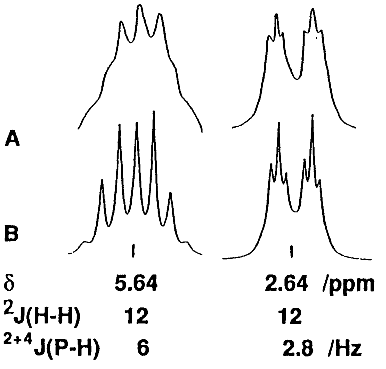
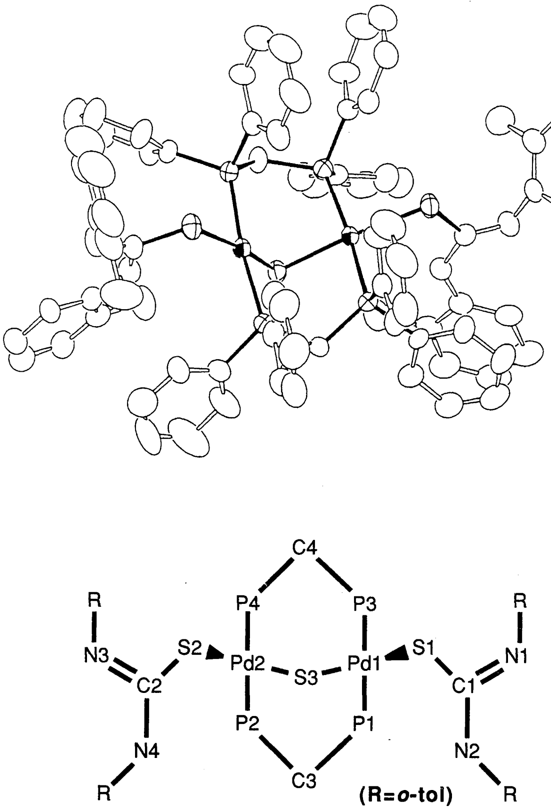


Figure 1. ^{1}H NMR of **2** for the two methylene protons (400 MHz, CDCl3). Each signal was analyzed as a doublet of virtual quintets. [(A) observed and (B) simulated].



Selected bond distances(Å) and angles(°)

Pd1-P1	2.314(2)	P1-Pd1-P3	173.20(8)
Pd1-P3	2.315(2)	S1-Pd1-S3	171.30(6)
Pd1-S1	2.386(2)	S1-Pd1-P1	90.04(8)
Pd1-S3	2.320(2)	S3-Pd1-P1	90.11(8)
Pd2-P2	2.340(2)	S1-Pd1-P3	95.17(8)
Pd2-P4	2.324(2)	S3-Pd1-P3	85.40(7)
Pd2-S2	2.381(2)	P2-Pd2-P4	172.80(9)
Pd2-S3	2.315(2)	S2-Pd2-S3	169.64(8)
S1-C2	1.779(7)	S2-Pd2-P2	96.92(7)
S2-C2	1.775(9)	S3-Pd2-P2	85.75(7)
N1-C1	1.27(1)	S2-Pd2-P4	88.88(7)
N2-C1	1.395(9)	S3-Pd2-P4	89.29(7)
N3-C2	1.28(1)	Pd1-S1-C1	105.8(3)
N4-C2	1.388(8)	Pd2-S2-C2	105.5(2)
		Pd1-S3-Pd2	92.4(6)

Figure 2. ORTEP drawing with 50% probability ellipsoids and selected bond distances and angles of complex **2**.

temperature. *n*-Pentane was added to the resulting dark red solution, which was kept in a refrigerator overnight, depositing dark red cubes of $[Pd_2(\mu\text{-}S)(\mu\text{–}dppm)_2(tol_2TU^{-1}\text{-}S)_2]\cdot CH_2Cl_2\cdot 3/4C_5H_{12}$ (**2**) in an 83% yield (Scheme 1). Since the ^{31}P NMR spectrum of **2** shows only one singlet at δ 1.3 in $CDCl_3$ (0 °C), the two dppm ligands are magnetically equivalent. On the other hand, each of the CH_2 protons in dppm is inequivalent and coupled to the other because the stereochemistry of the μ–S ligand makes different chemical enviroment for them. Figure 1 shows the experimental and simulated CH_2 proton signals of **2**. The ^{13}C NMR spectrum also reveals the existence of two types of Ph groups in dppm. These findings indicate that the chemical enviroment on each side of the P-C-P plane of dppm is different. The detailed structure of **2** has been determined by X-ray diffraction.[4] Figure 2 shows the perspective view and selected bond distances and angles. It has an A-frame structure in which two Pd atoms are bridged by one sulfide and two dppm ligands. The coordination geometry around the Pd atoms is almost planar(the deviations of the Pd1 and Pd2 atoms from least-square planes are 0.040(1) and 0.061(1) Å, respectively). There is no Pd-Pd interaction, since the distance between the two Pd atoms is 3.3469(9) Å. The N1-C1 and N3-C2 bond distances in tol_2TU are significantly shorter than N2-C1 and N4-C2, indicating N1-C1 and N3-C2 double bond character. Similar A-frame, bridged-sulfide Pd(II)[5] and Pt(II)[6] complexes, prepared by reaction of dppm complexes with propylene sulfide or RSH (R=H, alkyl) *via* C-S or H-S bond fission, have been reported. Our complex is rare example[7] which is prepared by the C=S bond activation in thioureas.

The reaction between $[Pd(tol_2TU^{-1})_2]$ and bidentate tertiary phosphine ligands other than dppm did not give complexes **1** and **2**. This implies that the bridging ability of dppm promotes this novel reaction.

It is striking that the reactivity of the Pd(II) and Pt(II) complexes containing thioureas and dppm is quite different: the former system activates the C=S bond in thioureas and the latter the $P\text{-}CH_2$ bond in dppm.

References and Notes

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2 **1**: ^1H NMR($CDCl_3$, -30 °C) δ 1.81, 2.12, 2.32, 2.43(each 3H, s, tol-CH_3), 3.33(2H, m, dppm-CH_2), 6.1-8.4(36H, Ph); ^{13}C NMR($CDCl_3$, -30°C) δ 17.9, 18.2, 18.4, 18.7(tol-*C*H3), 26.6(t, ^1J(C-P)≈35 Hz, dppm-CH_2), 120.2-140.4(Ph), 154.5(tol_2TU^{-2}-*C*S), 174.7(tol_2TU-*C*S); ^{31}P NMR($CDCl_3$, -55 °C) δ -26.5, 25.6(d, ^2J(P-P)=76 Hz). Anal. calcd for $C_{55}H_{52}N_4P_2PdS_2$: C, 65.96; H, 5.23; N, 5.59%. Found: C, 65.87; H, 5.27; N, 5.42%.

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4 Crystallographic data for **2**: $C_{84.75}H_{85}Cl_2N_4P_4Pd_2S_3$, *Mw* =1663.47, monoclinic, space group $P2_1/n$(No.14), *a*=20.035(3), *b*=19.326(4), *c*=22.247(2) Å, *V*=8041(2) Å^3, *Z*=4, μ(Mo*Kα*)=0.72 mm^{-1}, *Dm*=1.39 Mg m^{-3}, *Dx*=1.374 Mg m^{-3}. Intensity data ($I\geq 3\sigma(I)$) were collected on a Rigaku AFC-5R diffractometer with graphite monochromated Mo*Kα* radiation λ=0.71703 in the 2θ≤60°range at 296 K. The structure was solved and refined by using the Xtal 3.2 program. The current *R* value is 0.060(*Rw*=0.082) for 12358 independent absorption-corrected reflections by Gaussian method (W. R. Busing and H. A. Levy, *Acta Crystallogr.*, **10**, 180 (1957)). Anal. calcd: C, 61.19; H, 5.15; N, 3.37%. Found: C, 61.84; H, 5.15; N, 3.41%.

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