CHEMISTRY LETTERS, pp. 1057-1058, 1992.

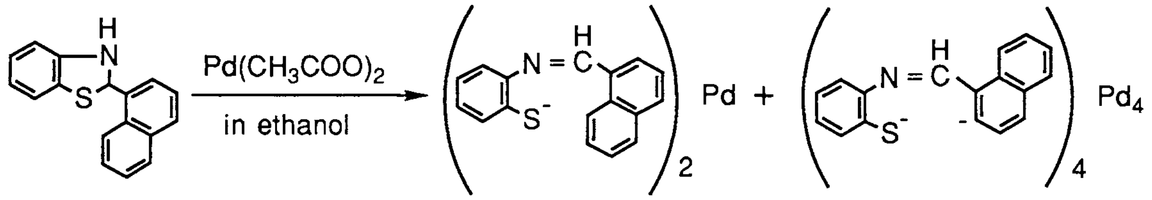
Crystal and Molecular Structure of Tetra-palladium Cluster with a *C,N,S*-Tridentate Ligand

Tatsuya KAWAMOTO and Yoshihiko KUSHI*
Coordination Chemistry Laboratories, Institute for Molecular Science,
Myodaiji, Okazaki 444

2-(1-Naphthyl)benzothiazoline, 1-nabz, reacts with palladium(II) acetate to yield, in addition to the expected bis[2-*N*-(1-naphthylmethylideneamine)benzenethiolato]palladium(II), a minor by-product tetrakis[2-*N*-(1-naphtylmethylideneamine)benzenethiolato-C^{o},*N*,*S*]-tetrapalladium(II) (**2**) of composition $C_{68}H_{44}N_4Pd_4S_4$; the novel structure of **2** is established by X-ray diffraction.

Recently we have described the preparation and characterization of monohelical palladium complex with two ferrocenyl groups.1) In the course of our investigation of molecular helicity, we have now found that the reaction of 1-nabz with palladium(II) acetate produces bis[2-*N*-(1-naphthylmethylideneamine)benzenethiolato]palladium(II) (**1**) and the unusual cluster **2** featuring a rare *C,N,S*-tridentate ligand derived from orthometallation of the pendant side chain.

The **1** and **2** were prepared by heating at 70 °C for 30 min 1-nabz of 0.52 g (1.97 mmol) with palladium(II) acetate of 0.22 g (0.98 mmol) in ethanol of 20 cm^3 (Scheme 1) and could be distinguished by inspection of the crystal shapes under a microscope (red needle-like **1** and deep red square bipyramidal **2**).2)



1-nabz **1** **2**

Scheme 1.

The structure of **2** was determined by X-ray diffraction (Fig. 1).3) This cluster **2** has a crystallographically imposed symmetry $\bar{4}$. The core of **2** consists of an eight-membered ring of alternating Pd and S atoms similar to the skeletal structure of palladous sulfide, PdS.4) The remaining two sites of each square planar Pd coordination sphere are occupied by the 2-benzenethiolato nitrogen and the *ortho* carbon of the 1-naphthyl unit. Thus each of the four monomeric PdL units consists of five-membered *N,S*-bonded chelate and five-membered *N,C*-bonded chelate rings. The Pd1-Pd2 bond length is 3.180(1) Å. This distance is too long to be considered the result of a Pd-Pd direct bond, but close enough for a Pd···Pd interaction.[5)]

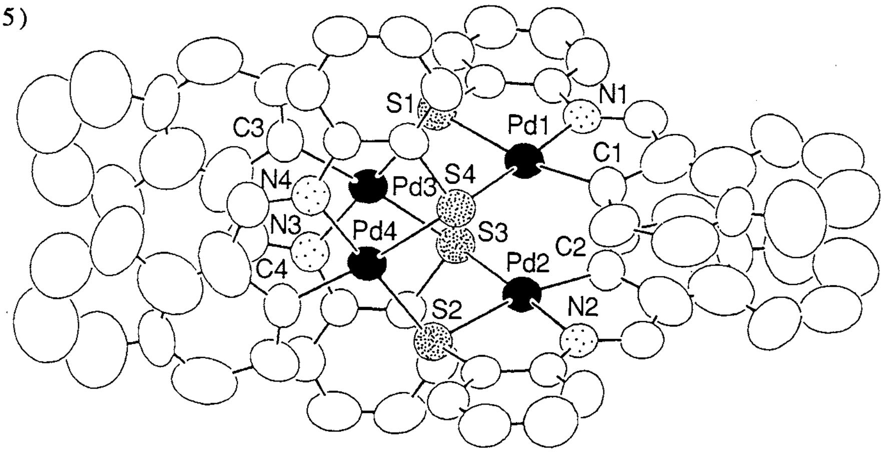


Fig. 1. X-Ray structure of **2**. Selected interatomic distances (Å) and angles (°); Pd1-Pd2 3.180(1), Pd1-S1 2.365(2), Pd1-N1 2.032(6), Pd1-C1 2.014(8), Pd1-S4 2.317(2), S1-Pd1-S4 94.2(2), S1-Pd1-N1 84.9(2), N1-Pd1-C1 85.9(3), S4-Pd1-C1 94.9(3), Pd1-S1-Pd3 111.9(2).

Nicholas and co-workers have quite recently reported an analogous tetranuclear cluster with a *C,N,O*-tridentate ligand (**3**).[6)] The cluster **3** has approximate C_2 symmetry. Each of the four monomeric PdL units consists of six-membered *N,O*-bonded chelate and five-membered *N,C*-bonded chelate rings. Consequently Pd-Pd distances in **2** are shorter than those in **3** (Pd-Pd $\geq$ 3.47 Å) and Pd_4S_4 ring in **2** is a rigid framework compared with Pd_4O_4 ring in **3**.

References

1) T. Kawamoto and Y. Kushi, *Chem. Lett.*, **1992**, 297.

2) The ratio **1** : **2** was ca. 10 : 1. Satisfactory ^1H NMR and analytical data have been obtained for the complex **1**. ^1H NMR ($CDCl_3$, 400 MHz): δ 9.27 (d, *J* = 7 Hz, 2H), δ 8.38 (s, 2H), δ 7.96 (d, *J* = 8 Hz, 2H), δ 7.83 (d, *J* = 7 Hz, 2H), δ 7.48 (dd, *J* = 8 and 1 Hz, 2H), δ 7.32 (t, *J* = 8 Hz, 2H), δ 7.24 (t, *J* = 8 Hz, 2H), δ 7.09 (t, *J* = 8 Hz, 2H), δ 6.88 (dt, *J* = 8 and 1 Hz, 2H), δ 6.81 (t, *J* = 8 Hz, 2H), δ 6.64 (d, *J* = 8 Hz, 2H), δ 6.43 (d, *J* = 8 Hz, 2H). Anal. Found: C, 58.10; H, 3.54; N, 3.75%. Calcd for $C_{34}H_{24}N_2PdS_2 \cdot CH_2Cl_2$: C, 58.71; H, 3.66; N, 3.91%. (It was purified by recrystallization from CH_2Cl_2).

3) Crystal data for $C_{17}H_{11}NPdS \cdot 0.5C_2H_5OH$: Tetragonal, $I4_1/a$, $a = b = 15.798(3)$, $c = 23.728(4)$ Å, $V = 5922$ Å^3, $Z = 16$, $Dc = 1.75$ g cm^{-3}, λ(Mo $K\alpha$) = 0.71069 Å, $\mu = 13.67$ cm^{-1}, $R = 0.061$, $Rw = 0.064$ for 2284 reflections ($|Fo| > 3\sigma(|Fo|)$).

4) N. E. Brese, P. J. Squattrito, and J. A. Ibers, *Acta Crystallogr., Sect. C*, **41**, 1829 (1985).

5) A. D. Burrows, D. M. P. Mingos, and H. R. Powell, *J. Chem. Soc., Dalton Trans.*, **1992**, 261 and references cited therein.

6) H. Yang, M. A. Khan, and K. M. Nicholas, *J. Chem. Soc., Chem. Commun.*, **1992**, 210.

(Received March 30, 1992)