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Preparation and Structure of Tris-[(tri-t-butylphosphine)(nitrosobenzene)palladium]

M. CALLIGARIS

Istituto di Chimica, Università di Trieste, 34127 Trieste, Italy

T. YOSHIDA AND S. OTSUKA

Department of Chemistry, Faculty of Engineering Science, Toyonaka, Osaka, Japan

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During study on the reactions of coordinated organo-nitroso compounds, it was felt necessary to investigate the X-ray structure of the metal complexes to elucidate the bonding scheme between a low-valent metal and the nitroso group isoelectronic to dioxygen molecule. Although X-ray structures of various dioxygen[1] and organo azo complexes[2] of low-valent metals have been reported, only one paper deals with a low-valent metal nitrosobenzene complex, *i.e.*, $Fe_2(CO)_6(3\text{-Cl}, 2\text{-}CH_3C_6H_3NO)_2$.[3] Here we report the preparation and the molecular structure of tris-[(tri-t-butylphosphine)(nitrosobenzene)palladium].

The compound was obtained by stirring at room temperature an equimolar amount of $Pd(PBu^t_3)_2$[4] and PhNO in n-hexane. Brownish amorphous precipitates being filtered, the red filtrate was concentrated *in vacuo* to give a red powder, which was recrystallized from hot n-hexane to give $[Pd(PhNO)(PBu^t_3)]_3$ (*1*) as air-stable diamagnetic red crystals in 15% yield, m.p. 195 ~ 9 °C (dec.). This is soluble even in paraffinic hydrocarbons. Calc. for $C_{54}H_{96}N_3O_3P_3Pd_3$: C, 52.0; H, 7.76; N, 3.36; mol wt., 1248. Found: C, 52.0; H. 7.83; N. 3.36; mol wt., 1295 (vpo in benzene). Similarly obtained was $[Pd(PhNO)(PPhBu^t_2)]_3$ (*2*), m.p. 189 - 90 °C (dec.).

$$3PdL_2 + 3PhNO \xrightarrow{-3L} [Pd(PhNO)L]_3$$

Crystals are monoclinic, space group $P2_1/c$, with cell dimensions: a = 15.33, b = 14.64, c = 26.75 Å, $\beta = 97.8°$. The calculated density, assuming 4 formula units $[Pd(PhNO)(PBu^t_3)]_3$ per unit cell, is 1.394 g. cm^{-3}, in agreement with the experimental value of 1.39 g. cm^{-3}. Three-dimensional X-ray intensity data were collected on a Siemens diffractometer by the θ-2θ scan technique and Mo-Kα radiation for a maximum 2θ angle of 60°. A total of 4645 independent reflections with $I_0 > 3\sigma(I_0)$ was used in the structure determination after correction for Lorentz and polarization factors. Correction was also made taking into account the linear intensity decrease of the reference reflections observed during data collection. No correction for absorption ($\mu\cdot\rho \simeq 0.14$) or extinction was made. The structure was solved by conventional Patterson and Fourier methods and refined by the block-diagonal matrix least-squares technique. Anisotropic temperature factors were assigned to Pd atoms only. The final R value was 0.079.

The molecule of *1* consists of three Pd atoms linked by NO bridges forming an "inner" Pd–N six- and "outer" Pd–O–N nine-membered rings (Figure 1). The three phosphines and the oxygen atom lie above the Pd_3 plane while the three phenyl groups below the plane form a novel crown structure. The absence of Pd–Pd bonds is evident from the long inter-palladium distances (3.458(2) - 3.481(3) Å). The "inner" Pd–N ring has a chair-type conformation and the entire molecule possesses an approximately C_3 symmetry.

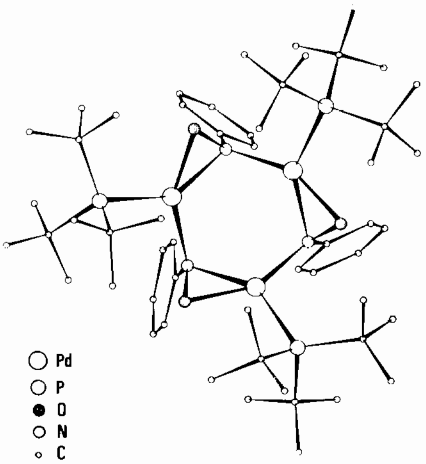

Fig. 1. The molecule as viewed along the approximate C_3 axis.

The geometry around the palladium atom is essentially planar, the mean dihedral angle between the planes defined by P–Pd–N′ and N–Pd–O being 8.3°. The nitrogen atoms show a significant distortion from the trigonal sp^2 angle, the sum of the Pd′–N–O, Pd′–N–C, and O–N–C angles being 353.3° (Figure 2).

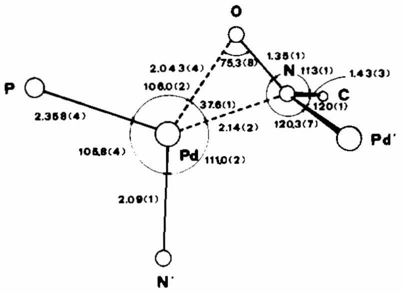

Fig. 2. The coordination geometry around the palladium atoms. Weighted average values are reported with their standard deviations in parentheses.

The N-bonded phenyl carbon and Pd′ atom bend away from the Pd atom as is the case for substituents of an olefin[5] or an azo linkage[2] coordinated to a metal. The phenyl rings are very slightly twisted around the N–C bonds, torsion angles ranging from 1.9 to 9.7°.

The N–O bond length of 1.35(1) Å may be compared with that (1.40(1) Å) in the dimeric iron complex[3] where PhNO acts as a bridging ligand. It is far longer than that (1.209(3) Å) found in *trans*-$PdCl_2(PhNO)_2$[6] where nitrosobenzene is coordinated through the nitrogen atom to Pd(II). Furthermore such a value is greater than those (1.26 - 1.27 Å)[7,8] found in some alkylnitroso dimers.

The ^1H nmr spectrum of t-butyl protons of *1* measured in benzene-d_6 shows only one sharp doublet at δ (ppm from TMS) 1.55 ($^3J_{H-P}$ = 12.0 Hz), suggesting that *1* assumes in solution a rigid structure similar to that in crystals.

The NO to metal linkage may be interpreted in terms of the DCD scheme,[9] namely the forward donation from the filled π-orbital to metal and the simultaneous back donation from the metal to the vacant π^*-orbital. This bonding scheme provides an account for the observed N–O bond lengthening and the large decrease in NO stretching frequency (1039 cm^{-1}) *vs.* 1506 cm^{-1} of the monomeric PhNO. The geometry around the N atom, suggesting a significant rehybridization at the atom, is also consistent with this interpretation. Thus the NO group in nitroso compounds may be viewed as a two center π-acid as the dioxygen molecule and the N=N group in azobenzene.[2] The π-acidity of PhNO, assessed from the NC stretching frequencies (2172.4 and 2137.8 cm^{-1}) of $Ni(PhNO)(t\text{-}BuNC)_2$,[10] was found to be comparable to PhN=NPh[11] of which electron affinity is 0.83 eV.[12]

The present study provides a rationale for the reactivity of the coordinated PhNO. The ease of the NO bond cleavage followed by the O atom and the phenyl transfer reactions[10] is ascribed to the increase in electron density in the π^*-orbital of the nitroso group.

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