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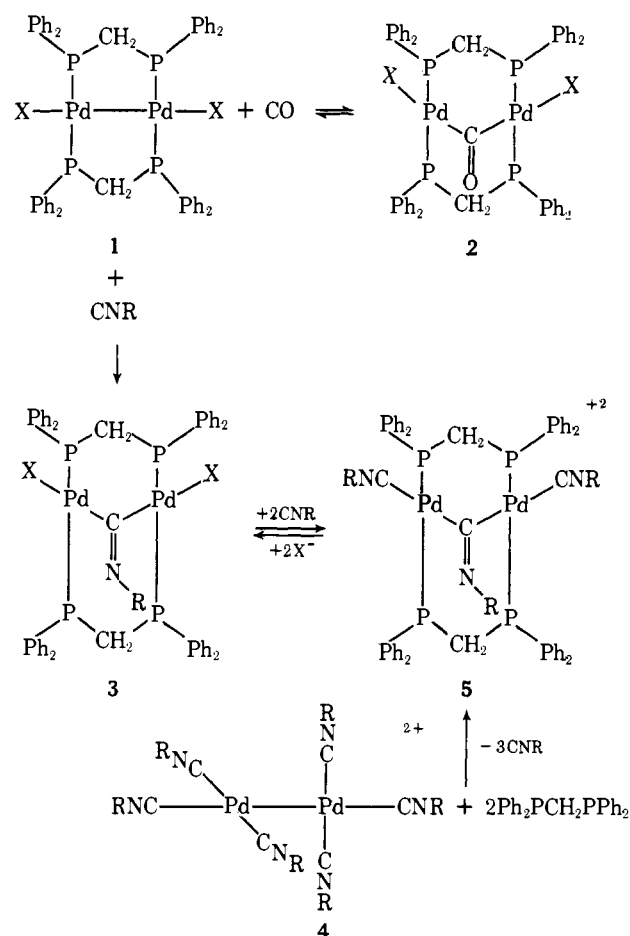
Insertion of Isocyanides and Carbon Monoxide into Metal-Metal Bonds. Preparation and Structure of $[\text{Pd}_2(\text{CNCH}_3)_3(\text{C}_6\text{H}_5)_2\text{PCH}_2\text{P}(\text{C}_6\text{H}_5)_2]_2[\text{PF}_6]_2$

Sir:

Recent suggestions¹ that polynuclear metal complexes may exhibit heretofore unobserved modes of catalytic activity have stimulated interest in the behavior of such complexes and particularly those complexes (e.g., $\text{Os}_3\text{H}_2(\text{CO})_{10}$ ² and $(\eta^5\text{-C}_5\text{H}_5)_2\text{Mo}_2(\text{CO})_4$ ³) containing unsaturated metal-metal bonds. Here we report some addition reactions of two coordinatively unsaturated palladium(I) dimers. The most conspicuous feature of these reactions is the expansion of the palladium-palladium distance which occurs upon formation of an isocyanide or carbon monoxide bridge. In contrast, with most other complexes containing monohapto, doubly bridging carbon monoxide or isocyanide ligands, these ligands span two metal centers which are generally thought to be connected by a direct metal-metal bond.⁴

When a dichloromethane solution of the phosphine bridged palladium(I) dimer $\text{Pd}_2(\text{dpm})_2\text{X}_2$ ⁵ (**1**, X = Cl, Br) (dpm, $\text{Ph}_2\text{PCH}_2\text{PPh}_2$) is exposed to 1 atm of carbon monoxide, 1 equiv of carbon monoxide is absorbed and the dark red crystalline complex $\text{Pd}_2(\text{dpm})_2(\text{CO})\text{X}_2$ (**2**) may be isolated. This product contains only a bridging carbonyl (ν_{CO} 1704 cm^{-1} , X

Scheme I



= Cl). Carbon monoxide addition to **1** is readily reversed. Refluxing a dichloromethane solution of **2** or heating solid **2** at 56 °C under vacuum causes it to revert to **1**. Although numerous examples of reversible carbon monoxide bonding to terminal sites in metal complexes are known, to our knowledge this is the first case in which reversible carbon monoxide bonding to a bridging position occurs.

Addition of isocyanides to **1** proceeds similarly to produce $\text{Pd}_2(\text{dpm})_2(\text{CNR})\text{X}_2$ (**3**, R = CH₃, C₆H₁₁, C₆H₅, *p*-CH₃C₆H₄; X = Cl, Br) (Scheme I). However, the addition of isocyanide has not yet been reversed. The infrared spectra of the crystalline yellow orange products indicate that only bridging isocyanide ligands are present in the products (ν_{CN} 1624-1677 cm^{-1}). Related isocyanide complexes are obtained when $\text{Pd}_2(\text{CNR})_6(\text{PF}_6)_2$ (**4**, R = CH₃ or *p*-CH₃C₆H₄)⁶ is treated with dpm. Crystalline 1:2 electrolytes of the stoichiometry $[\text{Pd}_2(\text{dpm})_2(\text{CNR})_3][\text{PF}_6]_2$ (**5**) are obtained. Solution infrared spectra of these cations reveal the presence of both terminal (ν_{CN} 2183-2231 cm^{-1}) and bridging (ν_{CN} 1640-1680 cm^{-1}) isocyanide ligands. Complexes of the types **3** and **5** are interconverted by exchange of terminal ligands. Addition of halide ion to solutions of **5** causes **3** to precipitate. Although **3** has extremely limited solubility, it readily dissolves in acetone or acetonitrile in the presence of an excess of isocyanide to form **5**.

Because of the low CN or CO stretching frequencies observed in the infrared spectra of these bridged complexes **2**, **3**, and **5**, an x-ray structural determination of **5** was undertaken to obtain precise structural data on one member of this group. Crystals of $[\text{Pd}_2(\text{dpm})_2(\text{CNCH}_3)_3](\text{PF}_6)_2$ were obtained as an acetone solvate by slow diffusion of diethyl ether into an

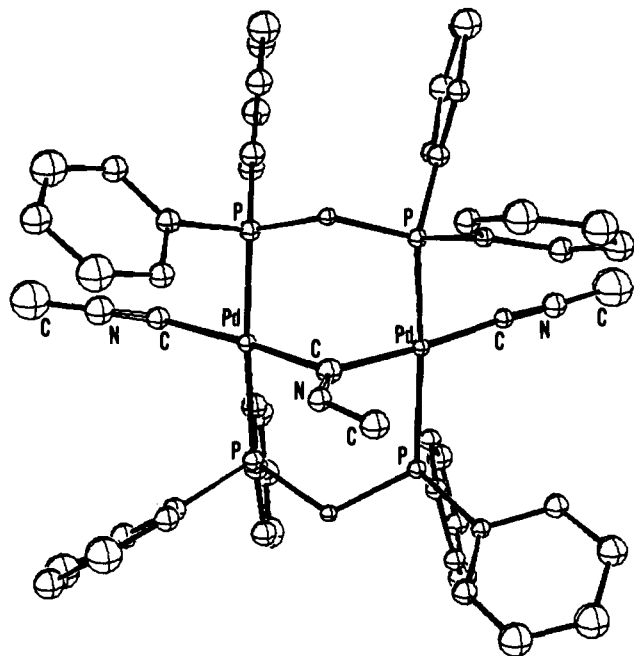


Figure 1. An ORTEP drawing of $\text{Pd}_2(\text{CNCH}_3)_3(\text{dpm})_2^{2+}$ showing the 50% thermal ellipsoids.

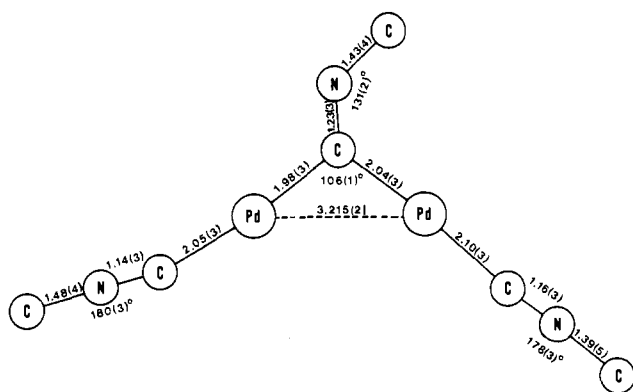


Figure 2. Bond distances and angles with the $\text{Pd}_2(\text{CNCH}_3)_3$ planar unit.

acetone solution of **5**. Crystal data (85 K): orthorhombic, space group $C2mb$ (no. 39); cell dimensions $a = 18.933$ (2), $b = 27.498$ (2), $c = 11.713$ (2) Å; $V = 6098.4$ Å³; $\rho_{\text{exptl}} 298$ K = 1.48 g/cm³ for $Z = 4$; $\mu_{\text{Mo K}\alpha} = 8.15$ cm⁻¹. Intensity data were collected at 85 K on a Picker automated four-circle diffractometer using Mo K α radiation. A 40-s ω scan of the most intense part of the peak at a scan speed of 0.5° min⁻¹ was used. A background curve was measured as a function of 2θ . A total of 2092 reflections were collected in the range $2\theta \leq 45^\circ$. The structure was solved and refined isotropically for all atoms except hydrogen atoms by Patterson, Fourier, and least-squares methods to a final R index of 0.080 using 1990 reflections having $I_{\text{net}} > 2\sigma(I_{\text{net}})$.

An ORTEP drawing of the cation is shown in Figure 1. A crystallographic mirror plane passes through the two palladium atoms and three isocyanide ligands. Above and below each palladium atom, and essentially normal to the plane at this point, are the four phosphorus atoms of the two dpm ligands. The palladium to phosphorus distances averages 2.31 (1) Å. A third coordination site for each palladium atom is occupied by a nearly linear, terminal methyl isocyanide, while the fourth

is a shared, bent, methyl isocyanide bridge. The coordination about each palladium is nearly planar with the two squares connected at one corner by the bridging isocyanide. The palladium-palladium distance is 3.215 (2) Å. This distance should be compared to the Pd-Pd distances in complexes lacking bridging carbonyl or isocyanide ligands: **1** (2.699 Å),⁵ $\text{Pd}_2(\text{CNCH}_3)_6^{2+}$ (2.531 Å),⁷ and $\text{Pd}_3(\text{CNCH}_3)_6(\text{PPh}_3)_2^{2+}$ (2.5921 Å).⁸ Similarly the Pt-Pt distances in the carbonyl or isocyanide bridged complexes are shorter than the Pd-Pd distance in **5**: $(\mu_2\text{-}t\text{-BuNC})_3(t\text{-BuNC})_3\text{Pt}_3$ (2.632 Å),⁹ $\text{Pt}_4(\text{PPhMe}_2)_4(\mu_2\text{-CO})_5$ (2.790 and 2.752),¹⁰ and $\text{Pt}_3(\text{PPh}_2\text{Bz})_3(\mu_2\text{-CO})_3$ (2.65 Å).¹¹ A conventional 16-electron count for each square planar palladium center can be achieved for **5** without invoking the presence of a metal-metal bond.

Other interesting aspects of the cation geometry can be appreciated from a drawing of the atoms in the plane of symmetry (Figure 2). The bent isocyanide ligand bridges the two palladium atoms symmetrically. Its C-N distance is significantly longer than those of the terminal isocyanides.

On the basis of the observed structure of **5**, we expect that **2** and **3** also contain related structural units with long Pd-Pd distances. The interrelationships of complexes **1** to **5** are shown in the accompanying scheme.

Although most η^1 -carbonyl and η^1 -isocyanide bridging ligands span metal centers which are generally acknowledged to be directly bonded, current theories on the bonding in such bridging units do not demand the presence of a direct metal-metal bond. In the present case the flexibility of the bridging dpm ligand contributes to the product stability by allowing for the expansion of Pd-Pd distance while minimizing steric interaction between ligands in the coordination spheres of the two palladium centers.

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Supplementary Material Available: A table of atomic positions and isotopic thermal parameters (1 page). Ordering information is given on any current masthead page.

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