(13) S. R. Langhoff, E. R. Davidson, and C. W. Kern, *J. Chem. Phys.*, **63**, 4800 (1975).

(14) K. Lonsdale, H. J. Milledge, and K. V. K. Rao, *Proc. R. Soc. London, Ser. A*, **255**, 82 (1960).

(15) The x-ray observations are, of course, for the ground state but we expect a similar arrangement of axes in T_{2211} as the structure is still comparatively rigid. The 6° deviation mentioned in ref 4 will only have a 1–2% effect. See also H. Hope, J. Bernstein, and K. N. Trueblood, *Acta Crystallogr., Sect B*, **28,** 1733 (1972).

(16) Address correspondence to this author at the Chemical Research Center, Allied Chemical, Morristown, N.J. 07964.

E. Wasserman,*[16] R. S. Hutton
Bell Laboratories
Murray Hill, New Jersey 07974

F. B. Bramwell
Brooklyn College
Brooklyn, New York 11210

Received November 24, 1975

The Preparation and Structure of the Linear Tripalladium Cations $(CH_3NC)_8Pd_3^{2+}$ and $(CH_3NC)_6\{(C_5H_5)_3P\}_2Pd_3^{2+}$

Sir:

Reactions between metal ions in different formal oxidation states can be used to form metal–metal bonds. Two examples using reaction partners with d^8 and d^6 electronic configurations are shown in reactions 1[1] and 2.[2]

$$Rh(CNC_6H_{11})_4^+ + RhI_2(CNC_6H_{11})_4^+ \rightleftarrows Rh_2I_2(CNC_6H_{11})_8^{2+} \quad (1)$$

$$17Pt(CN)_4^{2-} + 3PtCl_2(CN)_4^{2-} + 40K^+ + 60H_2O \rightarrow 2K_{20}Pt_{10}(CN)_{40}Cl_3 \cdot 30H_2O \quad (2)$$

In the first case a dimeric, formally Rh(II) species, is formed while in the latter case the solid, known as Krogmann's salt, has a more complex but still well-defined stoichiometry and contains parallel, linear columns of platinum atoms which ideally extend for the full length of a crystal. Equations 3–5

$$(t\text{-}C_4H_9NC)_2PdI_2 + (t\text{-}C_4H_9NC)_2Pd \rightarrow (t\text{-}C_4H_9NC)_4Pd_2I_2 \quad (3)$$

$$(CH_3NC)_4Pd^{2+} + (CH_3NC)_xPd \rightarrow (CH_3NC)_6Pd_2^{2+} \quad (4)$$

$$(CH_3NC)_4Pt^{2+} + (CH_3NC)_xPd \rightarrow (CH_3NC)_6PdPt^{2+} \quad (5)$$

give examples of reactions between complexes with d^8 and d^{10} electronic configurations that also produce metal–metal bonds.[3-5] We now report a new aspect of this chemistry which has led to the preparation and structure of a linear tripalladium complex.

In contrast to reactions 1 and 2 where a single, unique product forms regardless of the reactant stoichiometry, variation of the reaction stoichiometry in the case of reaction 4 alters the product. Addition of 2 mol of $(CH_3NC)_xPd$[6] to $(CH_3NC)_4Pd^{2+}$ or addition of 1 mol of $(CH_3NC)_xPd$ to $(CH_3NC)_6Pd_2^{2+}$ in acetone solution produces $(CH_3NC)_8Pd_3^{2+}$, **1** which has been isolated as the crystalline hexafluorophosphate salt. The infrared spectrum of this solid indicates that only terminal isocyanide ligands are present (ν_{CN} 2221, 2213, 2202 cm^{-1}). The ^1H NMR spectrum of this ion in acetonitrile-d_3 consists of a single resonance at τ 6.59.[7] Addition of triphenylphosphine to **1** produces the disubstitution product $[(CH_3NC)_6\{(C_6H_5)_3P\}_2Pd_3](PF_6)_2$, **2.** Like **1, 2** contains only terminal isocyanide ligands (ν_{CN} 2216, 2186 cm^{-1}). Its ^1H NMR spectrum consists of a single methyl resonance at τ 6.77 and a phenyl resonance at 2.45, with a 3:5 intensity ratio.[7]

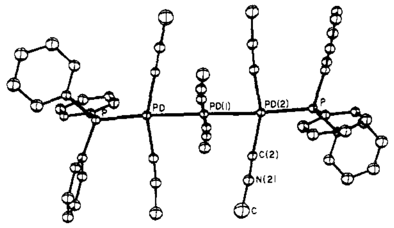

Figure 1. An ORTEP drawing of $(CH_3NC)_6\{(C_6H_5)_3P\}_2Pd_3^{2+}$ showing the 50% thermal ellipsoids.

In order to obtain an accurate and detailed description of the structure of this unprecedented species, an x-ray structural investigation was undertaken. We choose to work with **2** because of its greater stability. Air-stable, red-yellow dichroic crystals of **2** were obtained by slow diffusion in a nitrogen atmosphere of diethyl ether into an acetone solution of the complex containing excess methyl isocyanide and triphenylphosphine. Crystal data (85 K): space group $P\bar{1}$; reduced cell $a = 12.094$ (2), $b = 12.127$ (2), $c = 10.660$ (2) Å; $\alpha = 102.70$ (2), $\beta = 112.92$ (2), $\gamma = 75.49$ (2)°; $V = 1380.9$ Å^3; $\rho_{\text{exptl}}{}^{298} = 1.60$, $\rho_{\text{calcd}}{}^{85\text{ K}} = 1.66$ g/cm^3 for $Z = 1$; $\mu_{\text{Mo}K\alpha} = 11.7$ cm^{-1}. Intensity data were collected at 85 K on a Picker automated four-circle diffractometer. Using Mo Kα radiation, a total of 3568 reflections were collected by a 20-s ω scan of the most intense part of the peak at a scan speed of 0.25° min^{-1} in the range $3.5° < 2\theta < 45°$. A background curve was measured as a function of 2θ. The structure was solved and refined by Patterson, Fourier, and least-squares methods to a final R index[8] of 0.063 using 3339 reflections having $I_{\text{net}} > 2\sigma(I_{\text{net}})$. The positions of the phenyl hydrogens were easily located from a final difference Fourier while the methyl hydrogens were less well-resolved.

The structure of the cation is illustrated in Figure 1. The three palladium atoms are collinear with the two phosphorus atoms of triphenylphosphine groups, forming a five atom chain (since the point group for the molecule is $\bar{1}$, the Pd–Pd–Pd angle is constrained to 180°, the Pd(1)–Pd(2)–P angle is 173.7 (0.1)°). Each palladium atom is coordinated to two methyl isocyanides and exhibits approximate square planar geometry. The square planes are twisted away from each other such that the angle between the two five-atom least-squares planes is 74.5°. The most striking aspects of the structure are the short Pd–Pd bond at 2.5921 (5) Å and the displacement of the equatorial isocyanide towards the center of the molecule. The palladium–palladium bond in $(CH_3NC)_6Pd_2^{2+}$, which is the shortest reported palladium–palladium bond, is just slightly shorter at 2.5310 (9) Å.[9]

The displacement of the equatorial isocyanides towards the center was also observed in $(CH_3NC)_6Pd_2^{2+}$ (av Pd–Pd–C angle = 85.0 (9)°) but occurs to a greater extent in **2** (av Pd–Pd–C = 80.0 (2)°). Although the steric bulk of the axial triphenylphosphine groups could contribute to this large displacement in **2,** it is probably not the sole cause, since normal nonbonded distances between the isocyanides and the phenyl groups are found. The acute Pd–Pd–C angle brings the triply bonded carbon atom of the equatorial isocyanide to within van der Waals distance of the adjacent palladium atom.[10] For example, the Pd(1)- -C(2) distance is 2.921 Å. By contrast, the bonded Pd(2)–C(2) distance is 1.989 (8) Å. We therefore feel it likely that the inward bend of the equatorial isocyanides is in part an electronic effect arising from interaction between filled d orbitals on palladium with empty π^* orbitals on the isocyanide ligands of the adjacent metal. An analogous effect for carbonyl ligands has been termed "semibridging".[11] In the electron-precise metal carbonyl dimers the M–M–C angles range from 86.2 to 88.8°,[12] and the possibility of such an effect has been noted[13] previously. Considerably smaller angles are found in the 16-electron $(CH_3NC)_6Pd_2^{2+}$ and in **2** as well as $K_4[Ni_2(CN)_6]$[14] and $[i\text{-}Pr_4N]_2[Pt_2Cl_4(CO)_2]$[15] which have angles of 76° and 82.7°, respectively. From these values we conclude that semibridging is more important in unsaturated metal–metal bonded species than in their electron-precise counterparts.

Further investigations of these compounds are in progress. Attempts to make longer metal center chains by reactions related to eq 3-5 are in progress. Complexes **1** and **2** are coordinatively unsaturated and preliminary investigations indicate that they are more reactive than the surprisingly robust[4,16] $(CH_3NC)_6Pd_2^{2+}$. For example, recrystallization of **1** and **2** can only be accomplished in the presence of excess ligands.

Acknowledgment. This work has been supported by the National Science Foundation.

References and Notes

(1) A. L. Balch and M. M. Olmstead, *J. Am. Chem. Soc.*, **98,** 2354 (1976).

(2) For reviews dealing with Krogmann's salt see H. Krogmann, *Angew. Chem., Int. Ed. Engl.*, **8,** 35 (1969), and J. S. Miller and A. J. Epstein, *Prog. Inorg. Chem.*, **20,** 1 (1976).

(3) S. Otsuka, Y. Tatsuno, and K. Ataka, *J. Am. Chem. Soc.*, **93,** 6705 (1971).

(4) J. R. Boehm, D. J. Doonan, and A. L. Balch, *J. Am. Chem. Soc.*, **98,** 4845 (1976).

(5) M. F. Rettig, E. A. Kirk, and P. M. Maitlis, *J. Organomet. Chem.*, **111,** 113 (1976).

(6) Pd(0) isocyanide complexes frequently occur as polymers of low solubility: L. Malatesta, *J. Chem. Soc.*, 3924 (1955); E. O. Fischer and H. Werner, *Chem. Ber.*, **95,** 703 (1962). Treatment of tris(dibenzylideneacetone) dipalladium (T. Ukai, H. Kawazura, Y. Ishii, J. J. Bonnet, and J. A. Ibers, *J. Organomet. Chem.*, **65,** 253 (1974)) with methyl isocyanide in acetone and other solvents produces stable yellow solutions which from their chemical reactivity appear to contain a Pd(0) complex here referred to as $Pd(CNCH_3)_x$.

(7) The lack of resolution of the ^1H NMR methyl resonance between different methyl isocyanide environments is not surprising. The dimer $(CH_3NC)_6Pd_2^{2+}$ undergoes both rapid exchange with free methyl isocyanide and an intraionic fluxional process which exchanges axial and equatorial isocyanide ligands. With **1** and **2** the lack of resolution may be due to either insufficient chemical shift differences, a fluxional process, or exchange with adventitious traces of free isocyanide. Attempts to rule out the latter through the addition of solid palladium chloride to scavenge free isocyanide have led only to sample decomposition.

(8) $R = \Sigma \| F_o| - |F_c\| / \Sigma |F_o|$.

(9) S. Z. Goldberg and R. Eisenberg, *Inorg. Chem.*, **15,** 535 (1976).

(10) Van der Waals radii are estimated from values of L. Pauling, "The Nature of the Chemical Bond", Cornell University Press, Ithaca, N.Y., 1960: –C≡, 1.4 Å; –N≡, 1.35 Å; the covalent radius for Pd is 1.38 Å, and the van der Waals radius is perhaps 0.5 Å longer.

(11) F. A. Cotton, *Prog. Inorg. Chem.*, **21,** 1 (1976).

(12) M. F. Bailey and L. F. Dahl, *Inorg. Chem.*, **4,** 1140 (1965); L. B. Handy, J. K. Ruff, and L. F. Dahl, *J. Am. Chem. Soc.*, **92,** 7312 (1970); G. L. Simon, A. W. Adamson, and L. F. Dahl, *J. Am. Chem. Soc.*, **94,** 7654 (1972); F. A. Cotton, T. G. Dunne, and J. S. Wood, *Inorg. Chem.*, **3,** 1495 (1964).

(13) R. A. Levenson and H. B. Gray, *J. Am. Chem. Soc.*, **97,** 6042 (1975).

(14) O. Jarchow, *Z. Kristallogr., Kristallgeom., Kristallphys., Kristallchem.*, **136,** 122 (1973).

(15) A. Modinos and P. Woodward, *J. Chem. Soc., Dalton Trans.*, 1516 (1975).

(16) J. R. Boehm and A. L. Balch, *J. Organomet. Chem.*, **112** C20 (1976).

Alan L. Balch,* John R. Boehm
Håkon Hope, Marilyn M. Olmstead
Department of Chemistry, University of California
Davis, California 95616
Received July 12, 1976

Bimolecular Electron Transfer Processes of Electronically Excited Tris(2,2′-bipyridine)chromium(III)

Sir:

Recent reports on the facile electron transfer reactions of the lowest excited state of tris(2,2′-bipyridine)ruthenium(II), $(^3CT)Ru(bpy)_3^{2+}$,[1-10] have focused attention on the general problem of the redox properties of excited states of transition metal complexes.

Tris(2,2′-bipyridine)chromium(III), $Cr(bpy)_3^{3+}$, appears to be an ideal candidate for investigations on bimolecular excited-state processes. The lowest excited state of this complex, i.e., the metal-centered doublet state, $(^2MC)Cr(bpy)_3^{3+}$, is remarkably long lived in fluid solutions (τ = 53 μs in aqueous deaerated solution at 25 °C) and can be conveniently monitored by means of the moderately efficient emission centered at 727 nm.[11] The complex is appreciably photostable in acidic solutions.[12] A recent communication by Bolletta et al.[13] has shown that the doublet state of $Cr(pby)_3^{3+}$ can be efficiently quenched by $Ru(bpy)_3^{2+}$. Since the energies of $(^2MC)Cr(bpy)_3^{3+}$ and $(^3CT)Ru(bpy)_3^{2+}$ are 13 800 and 17 100 cm^{-1}, respectively, energy transfer is forbidden in this system. Thus, the assumption was made that the quenching takes place via the thermodynamically allowed electron transfer from the quencher to the excited state of $Cr(bpy)_3^{3+}$.[13] Here we present the results of some flash photolysis experiments which provide direct evidence for the occurrence of electron transfer in the quenching of the $Cr(bpy)_3^{3+}$ doublet state.

Flash photolysis[14] of aqueous pH 3 solutions of $Cr(bpy)_3^{3+}$ gives rise to a transient absorption with maxima at 390 and 445 nm. The absorption decays by first-order kinetics with a lifetime of 47 μs, a value which compares well with the lifetime of the phosphorescent emission. The transient absorption can be assigned to a transition from the $(^2MC)Cr(bpy)_3^{3+}$ state to upper doublet states.[12]

The $Fe(H_2O)_6^{2+}$ ion is an efficient quencher of the $Cr(bpy)_3^{3+}$ phosphorescence ($k_q = 4.1 \times 10^7\ M^{-1}\ s^{-1}$ at μ = 1). When pH 3 solutions containing 5×10^{-5} M $Cr(bpy)_3^{3+}$ and 2×10^{-3} M $FeSO_4$ are flashed, the expected quenching of the doublet absorption is observed and a new transient absorption is formed with maxima at 470 and 560 nm. The spectrum of the new transient absorption matches closely the reported spectrum of $Cr(bpy)_3^{2+}$.[15] The formation of the reduced complex upon quenching of the doublet state is a clear proof of the occurrence of a mechanism involving electron transfer from the quencher to the excited complex (reaction 1).

$$(^2MC)Cr(bpy)_3^{3+} + Fe(H_2O)_6^{2+} \rightarrow Cr(bpy)_3^{2+} + Fe(H_2O)_6^{3+} \qquad (1)$$

The $Cr(bpy)_3^{2+}$ absorption disappears after the flash by fast second-order[16] kinetics ($k_2 = 7.3 \times 10^8\ M^{-1}\ s^{-1}$ at μ = 0.2) due to the thermal back-electron-transfer reaction (reaction 2), which involves a free energy change of −23.5 kcal/mol.

$$Cr(bpy)_3^{2+} + Fe(H_2O)_6^{3+} \rightarrow Cr(bpy)_3^{3+} + Fe(H_2O)_6^{2+} \qquad (2)$$

A similar approach has been used with $Ru(bpy)_3^{2+}$ as a quencher of the $Cr(bpy)_3^{3+}$ doublet state. When solutions containing 1×10^{-4} M $Cr(bpy)_3^{3+}$ and 3.3×10^{-5} M $Ru(bpy)_3^{2+}$ (pH 3, μ = 0.2) are flashed, the characteristic transient absorption of $Cr(bpy)_3^{2+}$ is again observed. In order to interpret this result, however, the peculiar quenching behavior of the system is to be taken into account. Bolletta et al. have shown[13] that $Ru(bpy)_3^{2+}$ is a good quencher of the $Cr(bpy)_3^{3+}$ ^2MC excited state ($k_q = 4.0 \times 10^8\ M^{-1}\ s^{-1}$ at μ = 0.2), but that at the same time $Cr(bpy)_3^{3+}$ is an efficient quencher of the ^3CT excited state of $Ru(bpy)_3^{2+}$ ($k_q = 3.3 \times 10^9\ M^{-1}\ s^{-1}$ at μ = 0.2). The solutions used in the flash experiment are such that both components absorb a significant fraction of the exciting light and each of the complexes significantly quenches the excited state of the other one. Thus, the observed $Cr(bpy)_3^{2+}$ formation could arise by several pathways, namely, reaction 3 followed by reaction 5, reaction 4 followed by reaction 6, or reaction 4 followed by reaction 7 and reaction 5.