was taken as the infinite delay time and a 4K transform was used. The probe temperature was approximately 34°.

(4) On sabbatical leave from Georgia State University.

(5) To whom correspondence should be addressed. Recipient of a U.S. Public Health Career Development Award, 1970.

P. Adawadkar, W. D. Wilson,[4] W. Brey, E. J. Gabbay*[5]
Department of Chemistry, University of Florida
Gainesville, Florida 32611

Received December 13, 1974

Hexakis(methyl isocyanide)dipalladium(I). Preparation, Structure, and Fluxional Behavior

Sir:

Although palladium(I) complexes have been proposed as intermediates in a number of palladium-catalyzed organic reactions,[1] only a few compounds of this type have been isolated.[2-6] With the possible exception of the ill-defined solid $[Pd(C_6H_6)(H_2O)(ClO_4)]_n$,[3] all of these complexes are diamagnetic, ligand-bridged dimers. The presence of direct Pd–Pd bonding in these systems has been inferred from the absence of paramagnetism and, in the two cases where X-ray structures are available,[2,5] from the proximity of the Pd atoms. We now report the first example of a cationic Pd(I) dimer containing only terminal isocyanide ligands.

The colorless solution formed by adding excess methyl isocyanide to an aqueous solution of $Na_2(PdCl_4)$ becomes pale yellow during 18 hr at room temperature. Following precipitation with ammonium hexafluorophosphate complex **1** having the empirical formula $[Pd(CNCH_3)_3(PF_6)]$ is obtained in 80% yield. Complex **1** is an electrolyte in nitromethane solution and the dimeric formulation $[Pd_2(CNCH_3)_6][PF_6]_2$ follows unambiguously from measurements of the equivalent conductance over a range of concentrations for **1** and for a series of related PF_6^- salts of known composition. The infrared spectrum of **1** (fluorocarbon mull) shows only absorptions typical of terminal isocyanide ligands: ν(C—H) 3040, 2975, 2928; ν(C≡N) 2260, 2252, 2240, 2234; δ(C—H) 1452, 1410. The low-temperature ^{1}H NMR spectrum (acetone-d_6, −30 to −90°) consists of resonances at τ 6.22 (singlet, relative intensity 2) and 6.31 (s, 1).

Complex **1** crystallizes from acetone-2-propanol as its acetone solvate in the triclinic space group $P\bar{1}$. Crystal data: a = 12.281 (2), b = 12.544 (3), c = 10.388 (2) Å; α = 111.03 (1), β = 111.12 (1), γ = 75.95 (1)°; V = 1381.6 Å^3; ρ_{exptl} = 1.87 (1), ρ_{calcd} = 1.87 g/cm^3 for Z = 2; μ_{mo} = 14.96 cm^{-1}. Intensity data were collected on a Picker FACS-1 diffractometer, and the structure was solved by the usual heavy atom methods using 3249 independent, absorption-corrected reflections with $F_o^2 > 3\sigma(F_o^2)$. In the final refinements all nonhydrogen atoms except those of the solvent were allowed to vibrate according to an anisotropic thermal model and the conventional discrepancy indices R and R' converged to values of 0.045 and 0.057, respectively.

The structure of the cationic dimer is illustrated in Figure 1. A metal-metal bond of length 2.5310 (9) Å joins the two Pd atoms, each of which possesses an essentially square-planar coordination geometry with the Pd-Pd bond occupying one of the coordination sites. The dihedral angle between the two coordination planes is 86.2° and the overall complex symmetry is nearly D_{2d}. The four "equatorial" Pd-C bonds are structurally equivalent, and their average length is significantly shorter than that of the two "axial" Pd-C bonds, 1.963 (5) vs. 2.049 (6) Å. An additional structural feature, which may bear on mechanisms formulated to account for the fluxional behavior of the complex in solution (vide infra), is the average Pd-Pd-cis C bond angle of 85.0 (9)° indicating displacement of the equatorial isocyanide ligands toward the neighboring Pd atom. A complete table of distances and angles may be found in the microfilm edition of this journal.

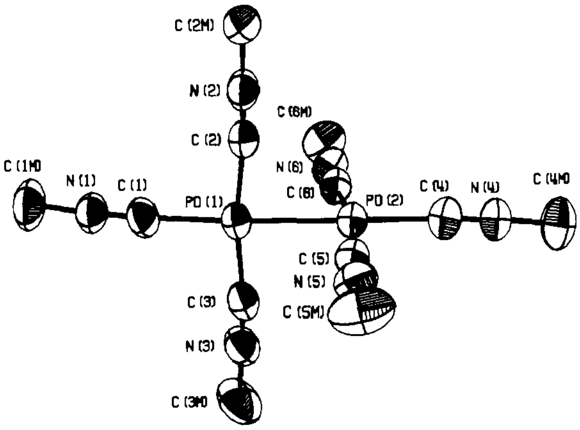


Figure 1. A perspective drawing of $[Pd_2(CNCH_3)_6]^{2+}$ showing the numbering scheme used. Bond distances and angles follow this article in the microfilm edition.

Complex **1** is the first Pd(I) dimer which does not contain bridging ligands in the solid state. A similar geometry has been reported for the Ni(I) complex $[Ni_2(CN)_6]^{4-}$,[7] and the vibrational spectra described for the dimeric Pt(I) complex $[Pt_2(CO)_2(Cl)_4]^{2-}$ [8] can be interpreted in terms of the present structural arrangement. The Pd–Pd distance in **1** is the shortest recorded for this bond. For comparison, values of 2.58 (1) and 2.686 (7) Å are reported respectively for the ligand-bridged dimers $[Pd(Al_2Cl_7)(C_6H_6)]_2$[2] and $[Pd_2(C_3H_5)(PPh_3)_2(I)]$.[5]

While the ^{1}H NMR spectrum of **1** is acetone-d_6 solution at or below −30° is consistent with the solid state geometry, warming the solution causes the two methyl resonances to broaden and eventually coalesce. At 35° the spectrum of **1** consists of a single resonance at τ 6.35. The dynamic process (or processes) responsible for the temperature dependence of the ^{1}H NMR spectrum appear to be intraionic in nature. The temperature dependence of the ^{1}H NMR spectrum was not altered by changing the dimer concentration or by adding palladium chloride which should scavenge free methyl isocyanide[9] that might catalyze exchange through an associative process. Several intraionic pathways seem plausible. Since $[Pd_2(CNCH_3)_6]^{2+}$ may be viewed as the result of the bonding of two d^9 $Pd(CNCH_3)_3^+$ fragments, the only vacant molecular orbital composed mainly of metal d functions is the σ^* orbital of the metal-metal bond. This means that deformations at the metal center may be facile because of limited ligand field stabilization effects. One pathway which appears to follow the normal modes of vibration involves the formation of a symmetric D_{3d} "staggered ethane" type structure. A second equilibration mechanism invokes a mixed Pd(II)-Pd(0) intermediate or transition state with square-planar and tetrahedral geometry about the respective metal centers. A third pathway involves exchange through bridging isocyanide ligands. The operation of this last process has been demonstrated in the case of $(\eta^5\text{-}C_5H_5)_2Fe_2(CO)_3(CNC(CH_3)_3)$.[10]

The complex reaction sequence which leads to the formation of **1** from $[PdCl_4]^{2-}$ and methyl isocyanide has not been fully elucidated. The initial steps are known to involve formation of $[Pd(CNCH_3)_4]^{2+}$ [11] and this is probably followed by nucleophilic attack by water or hydroxide ion at a metal-bound isocyanide carbon. Further investigations concerning the formation and reactions of **1** are currently in progress.

Acknowledgment. This research was supported by Grant GM 18357 from the National Institutes of Health. R.E. and S.Z.G. gratefully acknowledge the donors of the Petroleum Research Fund, administered by the American Chemical Society, in partial support of this research.

Supplementary Material Available. A table of distances and angles will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D.C. 20036. Remit check or money order for $4.00 for photocopy or $2.50 for microfiche, referring to code number JACS-75-1961.

References and Notes

(1) P. M. Maitlis, "The Organic Chemistry of Palladium", Vol. I and II, Academic Press, New York, N.Y., 1971, pp 28–29.

(2) G. Allegra, A. Immirzi, and L. Porri, *J. Am. Chem. Soc.*, **87**, 1394 (1965).

(3) J. M. Davidson and C. Triggs, *J. Chem. Soc. A*, 1324 (1968).

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

(5) Y. Kobayashi, Y. Iitaka, and H. Yamazaki, *Acta Crystallogr., Sect. B*, **28**, 899 (1972).

(6) P. L. Goggin and J. Mink, *J. Chem. Soc., Dalton Trans.*, 534 (1974).

(7) O. Jarchow, H. Schulz, and R. Nast, *Angew. Chem., Int. Ed. Engl.*, **9**, 71 (1970).

(8) P. L. Goggin and R. J. Goodfellow, *J. Chem. Soc., Dalton Trans.*, 2355 (1973).

(9) E. L. Muetterties, *Inorg. Chem.*, **13**, 495 (1974).

(10) R. D. Adams, F. A. Cotton, and J. M. Troup, *Inorg. Chem.*, **13**, 257 (1974).

(11) J. S. Miller and A. L. Balch, *Inorg. Chem.*, **11**, 2069 (1972).

Daniel J. Doonan, Alan L. Balch*
Department of Chemistry, University of California
Davis, California 95616

Stephen Z. Goldberg, Richard Eisenberg*
Department of Chemistry, University of Rochester
Rochester, New York 14627

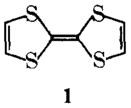
Joel S. Miller
Webster Research Center, Xerox Corporation
Webster, New York 14580

Received October 21, 1974

A New Approach to the Preparation of Tetrathiafulvalenium Salts

Sir:

Salts of 1,4,5,8-tetrathiafulvalene (TTF) exhibit unusual temperature dependent electric[1-3] and magnetic[4-6] properties. These salts were prepared by direct oxidation of TTF (**1**) by an acceptor (e.g., Cl_2,[1] I_2,[1] TCNQ,[3] TCM,[7] TNAP[8]). Such an approach precludes the preparation of TTF salts containing anions which are not derived from strong oxidizing agents (e.g., SCN^-). A logical approach to a more general preparation of TTF salts can be based on the metathetical reaction



1

$$TTFX + MZ \longrightarrow TTFZ + MX \qquad (1)$$

provided, of course, TTFX, MZ, and MX are soluble in a particular solvent and TTFZ is not.

Table I[a]

Compound	% Yield	$R(\Omega)$[b]	$\sigma_{\parallel}$[i] $(\Omega^{-1}\ cm^{-1})$
$(TTF)_3(BF_4)_2$	60	$>10^6$	
$(TTF)_{15}(NCS)_8$[c]	70	2–6	250 (310)[j]
$(TTF)_{15}(NCSe)_8$[c]	45	7	15
$(TTF)_{11}I_8$[c,d]	28	0.5	365
$(TTF)_{24}I_{63}$[c,e]	37	4.5	
$(TTF)_8I_{15}$[c,f]	75	55	
$(TTF)_2Pt(CN)_4$	92	$>10^6$	
$(TTF)_2Cu(Mnt)_2$[g]	60	$>10^6$	
$(TTF)_2Co(Mnt)_2$[g]	69	$>10^6$	
$(TTF)_2Ni(Mnt)_2$[g]	70	$>10^6$	
$(TTF)_2Pt(Mnt)_2$[g]	70	$>10^6$	
TTF $Pt(Mnt)_2$[g,h]	94	$>10^6$	

[a] All elemental analyses based on C, H, and N.[10] [b] Determined at room temperature on ca. 0.1 mg compressed in a glass capillary between two steel pistons of 2 mm diameter. [c] Corresponds to "$(TTF)_2(NCS)$". This and other compounds below exhibit "nonstoichiometric" elemental analyses which are best described (within 0.1–0.05% of experimental) by the formulas given in the table. [d] This compound is also known as "TTF_3I_2" it was prepared from $(TTF)_3(BF_4)_2$ and $Bu_4N^+I_3-$ and forms hollow needles. [e] Corresponds to $TTF_2-{}^2/_3I_7$. Prepared from $(TTF)_3(BF_4)_2$ and $Bu_4N^+I_3-$. It has the appearance of silver wool. [f] Corresponds exactly to TTF_8I_{15}. Also prepared from $Bu_4N^+I_3-$ and $(TTF)_3(BF_4)_2$. [g] Prepared from $(TTF)_3(BF_4)_2$ and $(Bu_4N)_2M(mnt)_2$, where mnt = maleonitriledithiolato ($N{\equiv}CC(S^-){=}C(S^-)C{\equiv}N$) and M = Cu, Co, Ni, Pt, etc. [h] Prepared from $Bu_4NPt(mnt)_2$ and $(TTF)_3(BF_4)_2$. [i] $\sigma_{\parallel}$ = conductivity determined on the long axis of the crystal via a four-probe technique.[3] [j] $\sigma_{\parallel}$ at 220°K.

We expected TTF salts of BF_4^-, PF_6^-, SbF_6^-, and Ph_4B^- to be soluble in solvents such as tetrahydrofuran or acetonitrile. Here we describe an efficient preparation of a fluoroborate salt and its use in metathetical syntheses.

At first we tried to prepare the fluoroborate salt from silver fluoroborate and TTF but could not separate the product efficiently from colloidal silver. We discovered reaction 2 to be a convenient method for the preparation of a soluble TTF salt.[9]

$$3TTF + 2HBF_4 + H_2O_2 \xrightarrow{CH_3CN} \underset{\text{I}}{TTF_3(BF_4)_2} + 2H_2O \qquad (2)$$

The fluoroborate I is a purple, crystalline solid,[10] soluble in warm acetonitrile, but sparingly soluble in cold acetonitrile, acetone, methyl acetate. As shown in Table I, it is quite useful in the synthesis of new TTF salts.[11] These preparations were surprisingly simple. High dilutions were necessary to obtain large single crystals. When more concentrated solutions were employed, higher yields of microcrystalline powders were obtained.

Previously, a number of "onium" salts of TCNQ were prepared via metathesis.[12] We found $Et_3NH(TCNQ)_2$ to be best suited for metathesis in acetonitrile. The TTF(TCNQ) thus obtained consisted of small, poorly defined crystals. It appears that in this case the direct, redox synthesis affords the largest crystals.

When an excess of tetrabutylammonium selenocyanate was used in the above metathesis, the reaction mixture was bleached to light orange color. When this solution was allowed to stand at room temperature overnight, black needles of "$(TTF)_2(SeCN)$" formed. One may infer from this that reversible redox of TTF^+ and $SeCN^-$ may be occurring.

Fluoride and tetraphenylboride (as the Et_4N^+ and Na^+ salts, respectively) react irreversibly (bleaching) with