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Contribution from the Laboratorium für Chemische und Mineralogische Kristallographie, Universität, Bern, Switzerland, and the Laboratorium für Anorganische Chemie, Eidgenössische Technische Hochschule, Zürich, Switzerland

Preparation, Characterization, and Crystal, Molecular, and Electronic Structure of $(H_2EDTA)^{99}Tc^{IV}(\mu\text{-}O)_2{}^{99}Tc^{IV}(H_2EDTA)\cdot 5H_2O$. A 2.33-Å Tc–Tc Distance Which May Represent a $\sigma^2\pi^2\delta^{*2}$ Bond

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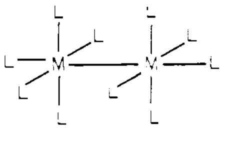
The preparation, elemental and titrimetric analysis, magnetic properties, and optical spectrum of $(H_2EDTA)^{99}Tc^{IV}(\mu\text{-}O)_2{}^{99}Tc^{IV}(H_2EDTA)\cdot 5H_2O$ are described. An X-ray structure determination ($R_w = 0.047$) shows an almost planar four-membered $Tc(\mu\text{-}O)_2Tc$ ring. Each EDTA coordinates to one Tc by two N's and two O's, and two carboxylate groups are protonated and noncoordinating (Figure 1). Interatomic distances provide strong support for a Tc(IV) oxidation state. The Tc–Tc distance is short at 2.33 Å; the molecule is diamagnetic and shows a strong optical absorption band at 20 200 cm^{-1} ($\epsilon \sim 2000$). Extended Hückel calculations suggest a partly antibonding $\sigma^2\pi^2\delta^{*2}$ configuration for the six metal d electrons rather than the fully bonding $\sigma^2\pi^2\delta^2$ configuration expected from naive application of the 18-electron rule. None of the available evidence contradicts this assignment, but more experiments are needed to prove it.

Introduction

The main structural alternatives known to be available to M_2L_{10} complexes are: (a) Cotton complexes with direct metal–metal bonding as in L_5MML_5 (**1**) or (b) double bridging



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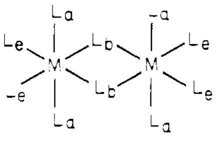

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by two ligands L as in $L_4M(\mu\text{-}L)_2ML_4$ (**2**).[1] Both possibilities have been investigated experimentally and theoretically for a wide variety of ligands L, both donors D and acceptors A, for various metals M in different d-electron configurations d^n. In class b, there are two main structural types. One of them typically shows long MM distances and paramagnetism; it will generally be $D_4M(\mu\text{-}D)_2MD_4$. The other type shows short MM distances and diamagnetism; it generally is $A_4M(\mu\text{-}D)_2MA_4$. In this paper we want to present the structure of $(H_2EDTA)Tc^{IV}(\mu\text{-}O)_2Tc^{IV}(H_2EDTA)$ (**3**) (EDTA = ethylenediamine-*N,N,N′,N′*-tetraacetate) which is formally $D_4M(\mu\text{-}D)_2MD_4$, but unlike most other examples it shows a very short MM distance (2.33 Å) and diamagnetism.

Experimental Section

Cautionary Remark. The complex was prepared in several small batches to minimize the risk of severe radioactive contamination. As a consequence, the samples for X-ray analysis, elemental analysis, and alkalimetric titration came from different batches.

Preparations. An ammonium pertechnetate solution (Oak Ridge National Laboratory) is passed through a cation-exchange column in the H^+ form. Then 0.1 mmol of $HTcO_4$ in 10 mL of water are mixed with 0.2 mmol of Na_2H_2EDTA, and an excess of $NaHSO_3$ (about 2 mmol) is added (if less EDTA is used, Tc is partly found in the reduced hydrolyzed form as TcO_2). The solution is kept between 70 and 80 °C during several days and analyzed periodically by paper chromatography (solid phase, paper Nr. 2043 a, Schleicher-Schüll; eluant: acetonitrile/water 70:30, v/v). As soon as the chromatogram shows only the desired product, the solution is cooled to room temperature and the water is allowed to evaporate very slowly until crystals appear.

The raw product was a mixture of red-brown, dark, and white crystals: $(Tc(H_2EDTA)O)_2$, Na_2SO_4, and H_4EDTA, respectively. With the help of a microscope, one of the red-brown crystals was chosen for X-ray analysis. The raw product was recrystallized from 0.01 M $HClO_4$, yielding a fine powder. This product was used for chemical analysis.

Analysis. The product was analyzed for Tc with the use of a liquid scintillation counter (Mark II, Nuklear Chicago) calibrated with a TcO_4^- solution of known concentration. The analysis for C, H, and N was done in the laboratories of H. Malissa and G. Reuter (Engelskirchen, Germany). Anal. Calcd for $(Tc(H_2EDTA)O)_2\cdot 9H_2O$: Tc, 20.0; C, 24.0; H, 4.86; N, 5.73. Anal. Calcd for $(Tc(H_2EDTA)O)_2\cdot 5H_2O$: Tc, 24.2; C, 29.4; H, 3.5; N, 6.9. Found: Tc, 20.4; C, 24.7; H, 4.72; N, 5.76.

The experimental analytical data fit best for a nonahydrate, whereas the crystal structure shows only a pentahydrate. A possible source of systematic error in the elemental analysis is coprecipitation, even after recrystallization, of small amounts of $Na_2SO_4\cdot 10H_2O$ or H_4EDTA. In view of the crystal structure determination, we tend to formulate the compound as a pentahydrate.

Chemical and Physical Properties. Alkalimetric titration shows two acid protons per Tc with a $pK \approx 3$. Optical spectra between 12 500 and 50 000 cm^{-1} have been recorded on a Beckmann DB-GT spectrometer from aqueous solutions (0.08–0.8 mmol) in a 10-mm cell. They show a strong band at 20 200 cm^{-1} (ϵ 2000 ± 300) and a poorly resolved band at 16 700 cm^{-1} (ϵ <200). Above 30 000 cm^{-1}, the spectrum rises steadily.

Magnetic measurements were performed by the Faraday method between 77 and 300 K on a powdered sample. The small, temperature-independent signal indicated diamagnetism.

X-ray Diffraction Experiment. Crystal data were as follows: $C_{20}H_{28}N_4O_{18}Tc_2\cdot 5H_2O$; $M = 816.5$; $d_{calcd} = 1.82$ g cm^{-3}; $\mu = 19.2$ cm^{-1}; dark crystal of approximately ellipsoidal shape, 0.10 × 0.15 × 0.25 mm;[3] orthorhombic; $a = 18.41$ (1), $b = 10.96$ (1), $c = 16.25$ (1) Å; determined from 14 reflections (12.5° < θ < 15°) on a CAD 4 diffractometer; $Pna2_1$; $Z = 4$. (Space group was determined from systematic absences and successful structure refinement.)

Intensity measurements were as follows: CAD 4 diffractometer; Mo Kα ($\lambda = 0.71073$ Å); graphite monochromator; ω scan; variable scan speed; required $\sigma(I)/I = 0.03$; 4430 reflections measured with $\theta \leq 28°$; 3085 unique observations with $I > \sigma(I)$ (2855 with $I > 3\sigma(I)$); no absorption correction.

Structure Analysis and Refinement. Tc positions were determined from a Patterson synthesis. All other nonhydrogen atom positions were determined from successive Fourier syntheses. Full-matrix, weighted least-squares refinement was carried out with 2 Tc and 8 O anisotropic and with methylene hydrogen atoms fixed in calculated positions. The weighting scheme $1/\sigma^2(F_o)$ was obtained from $\sigma^2(F_o^2) = [\sigma^2(I) + (0.05I)^2]/(Lp)^2$, $\sigma^2(I) = P + 4B$ and $I = P - 2B$ (P is

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* To whom correspondence should be addressed at Universität Bern.

[1] The literature on this subject is vast and connected to many names. The following papers have served the authors to gain an overview: (a) Cotton, F. A. *Acc. Chem. Res.* **1978**, *11*, 225. (b) Chisholm, M. H. *Transition Met. Chem.* **1978**, *3*, 321. (c) Vahrenkamp, H. *Angew. Chem.* **1978**, *90*, 403. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 379. (d) Trogler, W. C.; Gray, H. B. *Acc. Chem. Res.* **1978**, *11*, 232. (e) Shaik, S.; Hoffmann, R.; Fisel, C. R.; Summerville, R. H. *J. Am. Chem. Soc.* **1980**, *102*, 4555.

[2] "International Tables of X-Ray Crystallography"; Kynoch Press: Birmingham, England, 1974; Vol. IV, Tables 2.2B and 2.3.1.

[3] Structure Determination Package, SDP, User's Guide, Revision, Enraf-Nonius: Delft, April 1980.

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Table I. Positional and Isotropic Thermal Parameters and Their Esd's (in Terms of the Last Significant Digit)

atom	x	y	z	B,[a] Å^2
Tc(1)	−0.10637 (3)	0.04915 (5)	0.00000 (0)	
Tc(2)	−0.20598 (3)	−0.05231 (5)	−0.05635 (4)	
O(12)	0.0530 (4)	−0.2236 (6)	0.2152 (5)	
O(13)	0.0563 (4)	−0.0282 (6)	0.2448 (4)	
O(16)	−0.0708 (4)	0.5182 (7)	−0.0977 (8)	
O(17)	0.0336 (3)	0.4286 (6)	−0.0794 (6)	
O(22)	−0.3649 (4)	0.2231 (7)	−0.2695 (5)	
O(23)	−0.3739 (4)	0.0255 (6)	−0.2949 (5)	
O(26)	−0.2402 (4)	−0.5252 (6)	0.0254 (5)	
O(27)	−0.3413 (4)	−0.4249 (6)	0.0438 (6)	
O(41)	0.1924 (4)	0.1233 (7)	0.8273 (6)	
O(42)	0.1862 (3)	0.2160 (5)	0.0659 (5)	
O(43)	0.5021 (4)	0.1143 (7)	0.6186 (5)	
O(44)	0.0094 (4)	0.2847 (8)	0.3471 (12)	
O(45)	0.1923 (6)	0.5009 (11)	0.2792 (9)	
O(31)	−0.1516 (3)	−0.0962 (5)	0.0403 (3)	1.49 (8)
O(32)	−0.1617 (3)	0.0946 (5)	−0.0943 (3)	1.79 (9)
O(10)	−0.1616 (3)	0.1587 (5)	0.0764 (3)	1.88 (9)
O(11)	−0.1954 (4)	0.1758 (6)	0.2072 (4)	3.50 (13)
O(18)	−0.0259 (3)	−0.0380 (4)	−0.0601 (4)	1.73 (8)
O(19)	0.0777 (3)	−0.0184 (5)	−0.1266 (4)	2.66 (11)
O(20)	−0.1530 (3)	−0.1666 (5)	−0.1321 (3)	1.81 (9)
O(21)	−0.1416 (3)	−0.2298 (5)	−0.2609 (4)	2.21 (10)
O(28)	−0.2840 (3)	0.0364 (5)	0.0073 (3)	1.84 (8)
O(29)	−0.3788 (4)	0.0204 (6)	0.0914 (4)	3.42 (13)
N(11)	−0.0361 (3)	0.0355 (6)	0.1109 (4)	1.7 (1)
N(12)	−0.0346 (3)	0.2075 (6)	−0.0247 (4)	1.6 (1)
N(21)	−0.2758 (3)	−0.0399 (6)	−0.1652 (4)	1.7 (1)
N(22)	−0.2764 (4)	−0.2072 (6)	−0.0239 (4)	1.9 (1)
C(10)	−0.1528 (4)	0.1394 (8)	0.1557 (5)	2.2 (1)
C(11)	−0.0850 (5)	0.0708 (8)	0.1817 (6)	2.5 (1)
C(12)	0.0367 (5)	−0.1077 (8)	0.2005 (5)	2.5 (2)
C(13)	−0.0088 (4)	−0.0900 (7)	0.1222 (5)	1.9 (1)
C(14)	0.0237 (4)	0.1244 (7)	0.0997 (5)	2.0 (1)
C(15)	−0.0014 (4)	0.2396 (7)	0.0571 (5)	1.9 (1)
C(16)	−0.0761 (4)	0.3135 (7)	−0.0575 (6)	2.2 (1)
C(17)	−0.0300 (5)	0.4241 (9)	−0.0760 (6)	3.2 (2)
C(18)	0.0217 (4)	0.1659 (7)	−0.0852 (5)	2.0 (1)
C(19)	0.0267 (4)	0.0271 (7)	−0.0910 (5)	1.7 (1)
C(20)	−0.1716 (4)	−0.1658 (7)	−0.2107 (5)	1.9 (1)
C(21)	−0.2309 (4)	−0.0795 (7)	−0.2360 (5)	1.7 (1)
C(22)	−0.3501 (5)	0.1064 (8)	−0.2522 (6)	2.5 (2)
C(23)	−0.3029 (5)	0.0870 (8)	−0.1797 (5)	2.2 (1)
C(24)	−0.3402 (4)	−0.1247 (7)	−0.1472 (5)	1.8 (1)
C(25)	−0.3154 (4)	−0.2386 (8)	−0.1037 (5)	2.2 (1)
C(26)	−0.2336 (4)	−0.3163 (7)	0.0040 (6)	2.2 (1)
C(27)	−0.2790 (4)	−0.4269 (7)	0.0260 (5)	2.1 (1)
C(28)	−0.3265 (4)	−0.1649 (8)	0.0402 (5)	2.2 (1)
C(29)	−0.3309 (4)	−0.0258 (7)	0.0482 (5)	2.0 (1)
H111	−0.0568	0.1235	0.2203	
H112	−0.1004	−0.0056	0.2108	
H131	0.0222	−0.1116	0.0737	
H132	−0.0513	−0.1466	0.1248	
H141	0.0628	0.0857	0.0656	
H142	0.0439	0.1462	0.1549	
H151	−0.0384	0.2821	0.0922	
H152	0.0410	0.2955	0.0483	
H161	−0.1135	0.3372	−0.0156	
H162	−0.1009	0.2876	−0.1093	
H181	0.0700	0.1987	−0.0681	
H182	0.0088	0.1987	−0.1409	
H211	−0.2085	−0.0061	−0.2622	
H212	−0.2630	−0.1216	−0.2770	
H231	−0.2595	0.1412	−0.1858	
H232	−0.3310	0.1121	−0.1296	
H241	−0.3639	−0.1478	−0.2003	
H242	−0.3759	−0.0805	−0.1117	
H251	−0.3587	−0.2901	−0.0906	
H252	−0.2816	−0.2848	−0.1403	
H261	−0.2051	−0.2925	0.0538	
H262	−0.1998	−0.3402	−0.0412	
H281	−0.3100	−0.1994	0.0941	
H282	−0.3760	−0.1966	0.0269	

[a] The value of B for the H atoms is 2.5 Å^2.

Table II. Coordination Geometry at Tc(1) and Tc(2) (and Their Average Values) and Geometric Parameters for 4[a]

Distances, Å

	$i = 1, j = 2$[b]	$i = 2, j = 1$[c]	av[d]	4[d]
Tc(*i*)–O(31)	1.913 (5)	1.923 (5)	1.913 (8)	1.960
Tc(*i*)–O(32)	1.907 (5)	1.907 (5)		
Tc(*i*)–O(*i*0)	2.004 (5)	2.007 (5)	2.011 (7)	1.978
Tc(*i*)–O(*i*8)	2.014 (5)	2.020 (5)		
Tc(*i*)–N(*i*1)	2.223 (6)	2.190 (6)	2.207 (16)	2.081
Tc(*i*)–N(*i*2)	2.217 (6)	2.198 (7)		
Tc(1)···Tc(2)	2.331 (1)		2.331	2.950
O(31)···O(32)	3.03 (1)		3.03	2.582
O(*i*0)···O(*j*8)	2.85 (1)	2.97 (1)	2.91	3.297

Angles, Deg

	$i = 1, j = 2$[b]	$i = 2, j = 1$[c]	av[d]	4[d]
Tc–O(3*i*)–Tc	74.9 (*1*)	75.4 (*1*)	75.2	97.6
O(31)–Tc(*i*)–O(32)	105.1 (2)	104.7 (2)	104.9	82.4
N(*i*1)–Tc(*i*)–N(*i*2)	81.5 (2)	84.0 (2)	82.8	84.7
N(*i*1)–Tc(*i*)–O(3*i*)	85.4 (2)	86.4 (2)	86.3 (1.3)	96.6
N(*i*2)–Tc(*i*)–O(3*j*)	88.2 (2)	85.3 (2)		
N(*i*1)–Tc(*i*)–O(*i*0)	80.4 (2)	80.2 (2)	80.5 (4)	82.1
N(*i*2)–Tc(*i*)–O(*i*8)	81.1 (2)	80.2 (2)		
N(*i*1)–Tc(*i*)–O(*i*8)	86.2 (2)	88.1 (2)	87.1 (8)	90.4
N(*i*2)–Tc(*i*)–O(*i*0)	86.9 (2)	87.2 (2)		
O(31)–Tc(*i*)–O(*i*0)	93.8 (2)	95.3 (2)	95.0 (1.7)	93.9
O(32)–Tc(*i*)–O(*i*8)	97.3 (2)	93.6 (2)		
O(31)–Tc(*i*)–O(*i*8)	95.2 (2)	94.2 (2)	95.1 (1.4)	93.7
O(32)–Tc(*i*)–O(*i*0)	94.0 (2)	97.0 (2)		
O(31)–Tc(*i*)–N(*ij*)	166.7 (2)	168.6 (2)	168.1 (1.0)	175.5
O(32)–Tc(*i*)–N(*ii*)	168.5 (2)	168.7 (2)		
O(*i*0)–Tc(*i*)–O(*i*8)	163.2 (2)	163.6 (2)	163.4	169.9
Tc(*j*)–Tc(*i*)–O(*i*0)	97.5 (2)	99.0 (2)	98.3 (1.0)	95.1
Tc(*j*)–Tc(*i*)–O(*i*8)	99.3 (2)	97.4 (2)		

[a] Standard deviations are in terms of the last significant digit if not indicated otherwise. [b] Tc(1). [c] Tc(2). [d] Averaged according to approximate $2/m$ symmetry.

the count during the scan, B the count for the two background measurements). Real and imaginary scattering factors were used for neutral atoms.[2] $R = 0.040$ and $R_w = 0.047$; the esd for an observation of unit weight = 1.22. There were a total of 3085 observations with $I > \sigma(I)$ for 272 variables. The extinction coefficient obtained was $g = 0.25\ (11) \times 10^{-7}$ ($F_c = F_o(1 + gIc)$). Residual electron density within 1.2 Å from Tc was ≤ 0.3 e Å^{-3}; residual electron density within 1.2 Å from O(29) was ≤ 0.4 e Å^{-3}; 4 other maxima were located at distances $\geq$1.2 Å from any atom in the model with $0.3 \leq \Delta\rho \leq 0.5$ e Å^{-3}. All calculations were performed with the SDP program package of Enraf-Nonius.[3]

The results are compiled in Tables I–IV and Figures 1 and 2. Anisotropic mean square amplitudes of vibration and F_o/F_c tables are deposited as supplementary material.

Extended Hückel Calculations.[4] These have been performed on the model $(NH_3)_2(OH)_2Tc^{IV}(\mu\text{-}O)_2Tc^{IV}(NH_3)_2$. The geometry of the nonhydrogen atoms is that given in Table II (third column); the carbon atoms on N and O have been replaced by hydrogen atoms at 1.02 (N) and 0.96 Å (O), respectively. The $N_2Tc(\mu\text{-}O)_2TcN_2$ fragment was planar. The Coulomb integrals for the metal atoms were determined by self-consistent charge calculations using wave functions for M^+:[5] Tc:H(4d,4d) = −14.5 eV; Tc:H(5s,5s) = −11.1 eV; Tc:H(5p,5p) = −7.3 eV. Coulomb integrals for the other atoms are found in ref 6. Exchange integrals $H(i,j)$ were approximated as $1.75 \cdot (H(i,i) + H(j,j)) \cdot S(i,j)/2$. Some calculations were made at elongated and compressed M–M

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(4) Hoffmann, R.; Lipscomb, W. N. *J. Chem. Phys.* **1962**, *36*, 3179.

(5) (a) Barenovskii, V. I.; Nikol'skii, A. B. *Teor. Eksp. Khim.* **1967**, *3*, 527; *Theor. Exp. Chem. (Engl. Transl.)* **1967**, *3*, 309. (b) Basch, H.; Gray, H. B. *Theor. Chim. Acta* **1966**, *4*, 367.

(6) Summerville, R. H.; Hoffmann, R. *J. Am. Chem. Soc.* **1976**, *98*, 7240.

(7) Srdanov, G.; Herak, R.; Radanović, D. J.; Veselinović, D. S. *Inorg. Chim. Acta* **1980**, *38*, 37.

Table III. Geometry of Chelate Rings Involving Acetate Groups (Top) and Ethylenediamine Groups (Bottom) (and Their Averages) and the Geometry of 4

	N(11), C(11), etc.	N(12), C(18), etc.	N(21), C(21), etc.	N(22), C(28), etc.	av[a]	4[a]
N–C, Å	1.51 (1)	1.50 (1)	1.48 (1)	1.47 (1)	1.49 (2)	1.476
C–C, Å	1.52	1.53	1.50	1.53	1.52 (2)	1.520
C–O, Å	1.32	1.31	1.32	1.29	1.31 (2)	1.294
C=O, Å	1.21	1.21	1.21	1.24	1.22 (2)	1.224
TcNC, deg	104.7 (6)	107.0 (6)	106.3 (6)	107.3 (6)	106.3 (1.2)	107.9
NCC, deg	113.9 (7)	112.7 (7)	112.2 (7)	114.0 (7)	113.2 (9)	111.9
CC–O, deg	117.1 (8)	118.4 (7)	117.1 (8)	116.7 (8)	117.3 (8)	116.1
CC=O, deg	120.1 (8)	119.2 (7)	120.8 (8)	119.6 (8)	119.9 (7)	120.5
O–C=O, deg	122.9 (8)	122.3 (7)	122.1 (8)	123.8 (9)	122.8 (8)	123.3
C–OTc, deg						
NCCO, deg	–1	–15	20	9		
CCOTc, deg	–21	4	0	4		
COTcN, deg	25	5	–13	–11		
OTcNC, deg	–22	–12	21	14		
TcNCC, deg	18	17	–27	–16		

	N11, C14	N12, C15	N21, C24	N22, C25	av[a]	4[a]
N–C, Å	1.48 (1)	1.51 (1)	1.53 (1)	1.52 (1)	1.51 (2)	1.489
C–C, Å	1.51 (1)		1.51 (1)		1.51	1.527
TcNC, deg						107.5
NCC, deg	112.2 (7)	109.5 (7)	110.9 (6)	110.9 (7)	110.9 (1.1)	109.5
NTcNC, deg	8	20	–11	–16	14	13.7
TcNCC, deg	–36	–45	39	43	–41	–38.4
NCCN, deg	57		–58		58	52.2

[a] 2/*m* symmetry averaged parameters.

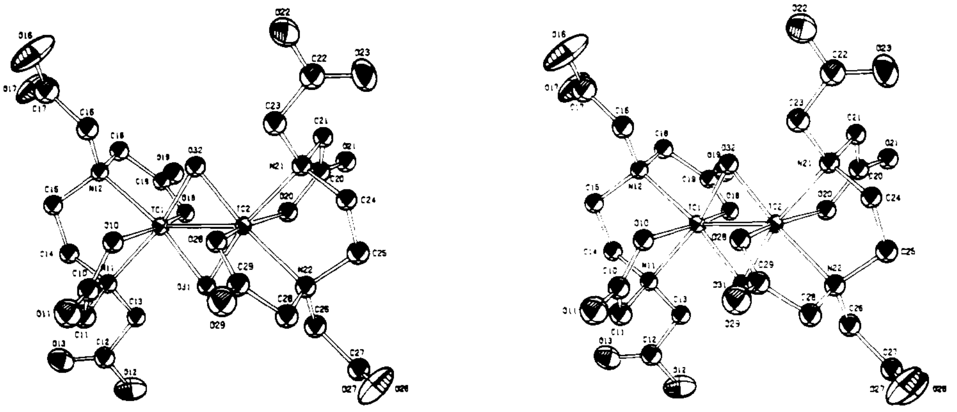


Figure 1. Stereoscopic drawing of the $(EDTA)Tc(\mu-O)_2Tc(EDTA)$ molecule.[18]

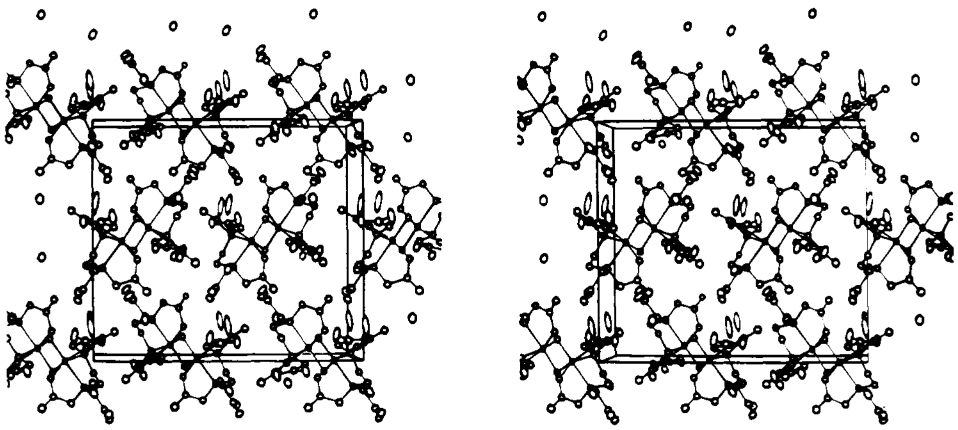


Figure 2. Stereoscopic drawing of unit cell contents.[18]

distances; for these, the M–O distances were kept at the values of Table II.

Discussion

Description of the Molecular Structure (Figure 1). The central $Tc(\mu-O)_2Tc$ unit completes its coordination by two H_2EDTA molecules, one for each Tc. The axial positions are occupied by the oxygen atoms of two carboxylate groups, the equatorial ones by amine nitrogens. Two acetate fragments of each EDTA are not involved in coordination; they point away from the metal atoms and form hydrogen bridges with the water of crystallization. The symmetry of the complex is approximately 2/*m* with the twofold axis along the Tc–Tc bond. Distances and angles averaged according to the ap-

Table IV. Geometry of Noncoordinated Acetate Groups

	N11, C13, etc.	N12, C16, etc.	N21, C23, etc.	N22, C26, etc.	av[a]
NC, Å	1.48 (1)	1.49 (1)	1.50 (1)	1.50 (1)	1.49 (1)
CC, Å	1.54 (1)	1.51 (1)	1.48 (1)	1.52 (1)	1.51 (3)
C–O, Å	1.33 (1)	1.32 (1)	1.34 (1)	1.29 (1)	1.32 (2)
C=O, Å	1.19 (1)	1.17 (1)	1.21 (1)	1.18 (1)	1.19 (2)
TcNC, deg	111.2 (6)	111.7 (6)	112.4	112.2 (6)	111.9 (6)
NCC, deg	114.0 (7)	114.2 (7)	112.1 (7)	114.8 (7)	113.8 (1.1)
CC–O, deg	113.2 (8)	111.1 (9)	115.1 (8)	111.1 (8)	112.6 (1.9)
CC=O, deg	125.2 (8)	127.1 (9)	124.4 (9)	125.3 (9)	125.5 (1.2)
O–C=O, deg	121.7 (9)	121.4 (9)	120.5 (9)	123.6 (9)	121.8 (1.3)
TcNCC, deg	177	180	180	179	179
NCC–O, deg	–172	174	171	–161	170
NCC=O, deg	8	–13	–8	21	13

[a] $2/m$ symmetry averaged values.

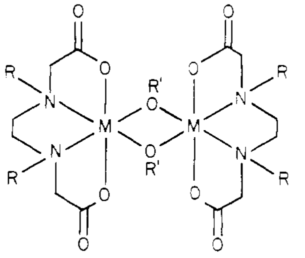
Table V. Hydrogen Bonds (Å) Shorter Than 3 Å (esd ≈ 0.01 Å)

O(41)···HO(22)	2.53	O(43)···HO(12)	2.58
O(41)H···O(19)	2.73	O(43)H···O(29)	2.75
O(41)···O(45)	2.63	O(43)H···O(23)	2.85
O(42)···HO(26)	2.58	O(44)···HO(16)	2.59
O(42)H···O(28)	2.92	O(44)H···O(20)	2.96
O(42)H···O(21)	2.94	O(45)···O(45)	2.63

proximate $2/m$ symmetry are given in Tables II–IV.

The TcO_2Tc four-membered ring is nearly planar (deviations: Tc(1) 0.01 Å, Tc(2) 0.01 Å, O(31) –0.01 Å, O(32) –0.01 Å). The deviations of the nitrogen atoms from this plane are significant (N(11) –0.14 Å, N(12) 0.11 Å, N(21) 0.16 Å, N(22) –0.16 Å) and are to the side of the carboxylate chelate ring.

Reference will be made to the analogous complex $(EDDA)Cr^{III}(\mu\text{-}OH)_2Cr^{III}(EDDA)$ (EDDA = ethylenediamine-*N*,*N'*-diacetate) (**4**) which has a very similar structure

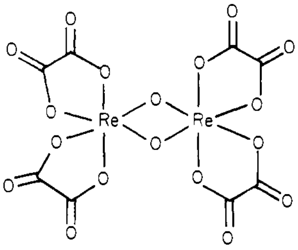


3, M = Tc(IV), R' = – (i.e., O^{2-}), R = CH_2COOH
4, M = Cr(III), R' = R = H

except that the oxo groups are replaced by hydroxy groups and the dangling acetate groups by hydrogen atoms. An averaged geometry is given in Tables II and III.

Hydrogen Bonds. Possible hydrogen bonds between carboxylate groups and water of hydration are listed in Table V. It is noteworthy that the oxygens O(12), O(16), O(22), and O(26) of the carboxylates form relatively strong hydrogen bonds to O(43), O(44), O(41), and O(42), respectively (2.53–2.59 Å). In all four cases the carboxylate oxygen atoms belong to the noncoordinating acetyl groups and carry the protons which were also found by titration. The evidence for this is the corresponding C–O distances of ~1.3 Å, about 0.1 Å longer than those to O(13), O(17), O(23), and O(27) (~1.2 Å). By analogous reasoning O(19), O(20), O(21), O(23), O(28), and O(29) are identified as acceptor atoms in the hydrogen bonds to O(41), O(42), O(43), and O(44). The water oxygen atoms O(44) and O(45) show only two and one hydrogen bonds shorter than 3 Å; at the same time they show extremely high thermal motion. Judging from the number and arrangement of water molecules, it is very unlikely that two extra protons per two Tc's are present in the lattice (see next section).

Identity of the Molecule. This point is not entirely unambiguous. There are two possibilities: $(H_2EDTA)Tc^{III}(\mu\text{-}OH)_2Tc^{III}(EDTAH_2)$ with d^4–d^4 electron configuration or $(H_2EDTA)Tc^{IV}(\mu\text{-}O)_2Tc^{IV}(EDTAH_2)$ with d^3–d^3 electron configuration. The literature provides arguments for both alternatives.[8] The main differences between the two are the protons at the μ-oxo atoms and the electron count on Tc. These differences as well as the presence of the protons at EDTA cannot be established by direct interpretation of diffraction data because of the heavy scatterer Tc. Whereas the protons on EDTA have been identified by acidimetric titration, no clearcut analytical or spectroscopic evidence is available to distinguish between (μ-O) and (μ-OH) groups. However, the Tc–O distances favor oxo over hydroxy bridges. In the two bridges, the Tc–O distances average 1.912 Å, comparable to the distances in oxo-bridged Mo,[9] W,[10] and Re compounds[11] but shorter than the distances in hydroxy-[12] and phenoxy-[13] bridged Mo compounds (~2.04 Å). Further evidence for oxo bridges comes from comparing the trans influence of bridging O vs. bridging OH groups in bioctahedral complexes (**2**) of the type $D_4M(\mu\text{-}O)_2MD_4$ and $D_4M(\mu\text{-}OH)_2MD_4$. In $(acac)_2Ti^{IV}(\mu\text{-}O)_2Ti^{IV}(acac)_2$ (acac = acetylacetonate anion), the axial Ti-O(acac) bond lengths average 1.971 Å;[14] the equatorial distances average 2.051 Å, about 0.09 Å longer. Similarly for $(ox)_2Re^{IV}(\mu\text{-}O)_2Re^{IV}(ox)_2$ (**5**) (ox = oxalate dianion), the axial and equatorial distances average 2.04 and



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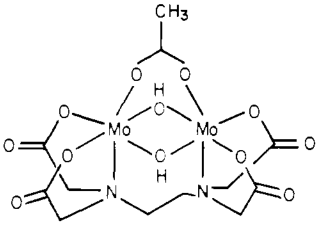

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2.09 Å, respectively,[11] a difference of 0.05 Å. The conclusion is to significant trans influence in oxo-bridged species. Corresponding numbers for the hydroxy-bridged species $(en)_2Cr^{III}(\mu\text{-}OH)_2Cr^{III}en_2$ (en = ethylenediamine), $(phen)_2Cr^{III}(\mu\text{-}OH)_2Cr^{III}(phen)_2$ (phen = phenanthroline), and $(en)_2Co^{III}(\mu\text{-}OH)_2Co^{III}(en)_2$ are 2.081 and 2.080 Å (Δ = 0.00 Å), 2.060 and 2.068 Å (Δ = 0.01 Å), and 1.965 and 1.952 Å (Δ = −0.01 Å), respectively.[15] For the dihydroxy-bridged Mo(III) dimer (**6**) Δ is ∼−0.02 Å.[12] The numbers indicate negligible trans influence. These are but a few, arbitrarily chosen examples. Since the Tc complex is of the type $O_2N_2Tc(\mu\text{-}O)_2TcN_2O_2$ with the N's equatorial and the O's axial, application of the above argument requires, as a reference, Tc–N bond distances not affected by trans influence. These are found in $(dmg)_2Tc(\mu\text{-}dmg)(\mu\text{-}OH)SnCl_3$ (dmg = dimethylglyoxime); they lie between 2.07 and 2.10 Å.[16] In $(H_2EDTA)Tc(\mu\text{-}O)_2Tc(EDTAH_2)$, the Tc–N distances are 2.20 Å, lengthened by more than 0.10 Å. In the analogous complex $(EDDA)Cr^{III}(\mu\text{-}OH)_2Cr^{III}(EDDA)$ (**4**), the Cr–N distances average 2.081 Å,[7] the same as in the $(en)_2Cr(\mu\text{-}OH)_2Cr(en)_2$ complex; thus Δ = 0.000 Å, i.e., no trans influence. We conclude that the short Tc–O distances in the oxo bridges and the strong trans influence which they exert on the Tc–N bonds represent strong evidence for oxo bridging and a Tc(IV) oxidation state.

One other alternative with Tc(III), namely, $[(H_2EDTA)Tc^{III}(\mu\text{-}O)_2Tc^{III}(H_2EDTA)]^{2-}(H_3O^+)_2\cdot 3H_2O$, can be excluded on the basis of the network of hydrogen bonds as discussed in the previous paragraph.

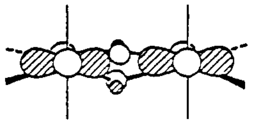
The MM Bond. The Tc–Tc distance is 2.33 Å, the shortest known to the authors in a bis(μ-O) bioctahedral complex of type **1**. It is only paralleled by $(ox)_2Re^{IV}(\mu\text{-}O)_2Re^{IV}(ox)_2$ (**5**)[11] where the Re–Re distance is 2.36 Å. Both complexes show OMO angles of 104.9° and MOM angles of 75.2°. Remotely similar is the Mo complex **6**[12] as well as the complexes $(C_6H_5)_3PCl_2Re^{IV}(\mu\text{-}O)(\mu\text{-}Cl)(\mu\text{-}C_2H_5COO)Re^{IV}Cl_2P(C_6H_5)_3$ and $(C_6H_5)_3PClRe(\mu\text{-}O)(\mu\text{-}Cl)(\mu\text{-}C_2H_5COO)_2ReClP(C_6H_5)_3$ with distances d(Mo–Mo) = 2.43 Å and d(Re–Re) = 2.52 and 2.514 Å, respectively.[17]

The short Tc–Tc and Re–Re distances of 2.33 and 2.36 Å are indicative of a strong M–M bond. They may be compared to Mo–Mo quadruple bonds ($L_5Mo\overset{4}{-}MoL_5$ (**1**); range 2.05–2.15 Å),[1] Re–Re quadruple bonds ($L_5Re\overset{4}{-}ReL_5$ (**1**); range 2.15–2.25 Å),[1] Mo–Mo triple bonds ($L_3Mo{\equiv}MoL_3$; range 2.15–2.25 Å),[1] Re–Re triple bonds ($L_3Re{\equiv}ReL_3$; range 2.20–2.30 Å),[1] etc. Mo–Mo double and single bond distances ($L_3Mo(\mu\text{-}L)_2MoL_3$) seem to be ≳2.5 Å.[9,16] The Tc, Re, and Mo complexes **3**, **5**, and **6** thus show M–M distances intermediate between those expected for M–M double and triple bonds.

Since the five compounds mentioned above formally show a d^3–d^3 electronic configuration, the 18-electron rule would lead one to expect a M≡M triple bond. But why is it long? What is the influence of the four-membered MO_2M ring on the M–M bonding? The discussion of this question owes much to a paper by Shaik et al.[1e] These authors performed extended Hückel-type (EHT) calculations on $L_4M(\mu\text{-}L)_2ML_4$-type complexes and discussed their electronic structure for a broad range of ligands (L) and M–M distances.

Electronic Structure. We have performed extended Hückel-type calculations with charge iteration for the model $(NH_3)_2(OH)_2Tc^{IV}(\mu\text{-}O)_2Tc^{IV}(OH)_2(NH_3)_2$ at a geometry analogous to the one observed in the crystal. Like Hoffmann and his co-workers,[1e] we find that the t_{2g}-type d orbitals combine into σ, π, δ*, δ, π*, and σ* MO's (**7**–**12**). Note the reversed energetic sequence: δ* is lower than δ. This may be traced to the fact that the bonding δ molecular orbital (**9**) is destabilized by p orbitals of the bridging oxygen atoms, above δ* (**12**) which does not suffer a similar effect. The destabilization is especially strong here because of the trans influence exerted by the oxo bridges: the relatively short Tc–O distance (as compared to the Tc–N distance) implies a strong overlap of oxygen p and Tc d orbitals leading to strong interaction, i.e., strong destabilization ($\Delta\epsilon(\delta \leftarrow \delta^*) \approx 0.6$ eV).

σ



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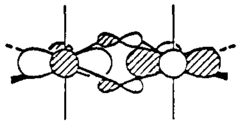
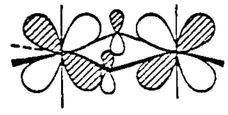


σ*

10

π



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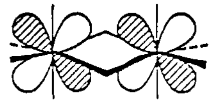
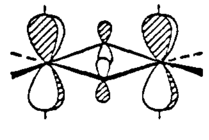


π*

11

δ



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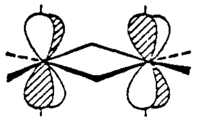

δ*

12

The computed d-electron configuration is thus $\sigma^2\pi^2\delta^{*2}$ not $\sigma^2\pi^2\delta^2$ as one would expect for a classical triple bond. Both possibilities agree with the diamagnetism observed for the Tc complex (**3**). The $\sigma^2\pi^2\delta^{*2}$ possibility does, however, provide some antibonding character to the M–M bond, an appealing feature in view of the comparatively long "M≡M triple bond" discussed in the previous paragraph. In principle, the proposed electronic structure can be tested experimentally. Oxidation and reduction of the metals by one or two electrons should *shorten* the M–M distances in **3**, **5**, and **6** rather than lengthen it.

Finally it should be noted that a strong optical absorption band is observed at 20 400 cm^{-1} (ε ∼2000). Assignment of this band has to await further experimentation.

Steric Requirements. Shaik et al.[1e] indicated that the absence of significant repulsion between axial ligands (in our case O(10), O(18), O(20), and O(28); Figure 1) is an important prerequisite for M–M bonding. This condition is met here: the O(10)···O(28) and O(18)···O(20) distances are 2.85 and 2.97 Å, respectively, approximately equal to the sum of the van der Waals radii. The O···O distances result from the combined action of the trans influence discussed earlier and the polycyclic coordination geometry adopted by EDTA: trans influence forces relatively long Tc–N distances. The geometric requirements for a-five membered carboxylate chelate ring and the tendency of the angles at C to be between 110 and 120° cause the N–Tc–O angles to be ∼10° smaller than 90°. This implies that the average Tc–Tc–O_{ax} angle is 8° larger than 90° (Figure 1) and that the O···O distances are correspondingly long. It should be noted, however, that the coordination of EDDA to Cr(III) (including the Cr–Cr–O_{ax} angles) is very similar to that of EDTA to Tc(IV) (Table II). Nevertheless, no Cr···Cr bonding is observed. It remains to be seen whether

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the absence of Cr···Cr bonding is due to subtle differences between Cr(III) and Tc(IV) coordination geometries, to the presence of hydroxy rather than oxo bridges in the Cr complex, or to an intrinsic difference in the propensity of Cr and Tc to form multiple bonds.

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Supplementary Material Available: A listing of structure factor amplitudes and anisotropic thermal parameters (13 pages). Ordering information is given on any current masthead page.

Contribution from the Istituto di Chimica Generale ed Inorganica,
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Palladium and Platinum Complexes with *cyclo*-Triphosphorus and *tetrahedro*-Tetraphosphorus as Ligands

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Simple and triple-decker sandwich complexes of palladium and platinum containing the *cyclo*-triphosphorus unit as a η^3 ligand with general formulas $[(\text{triphos})M(\eta^3\text{-}P_3)]BF_4$ (triphos = 1,1,1-tris((diphenylphosphino)methyl)ethane; M = Pd, Pt) and $[LPd(\mu\text{-}(\eta^3\text{-}P_3))PdL]Y$ (L = triphos, Y = BPh_4; L = np_3, Y = BF_4; np_3 = tris(2-(diphenylphosphino)ethyl)amine) have been synthesized and characterized. The structures of the complexes $[(\text{triphos})Pd(\eta^3\text{-}P_3)]BF_4\cdot C_2H_5OH$ (I) and $[(\text{triphos})Pd(\mu\text{-}(\eta^3\text{-}P_3))Pd(\text{triphos})]BPh_4$ (II) have been elucidated through complete X-ray analyses. The crystals of compound I are monoclinic with a = 13.084 (5) Å, b = 20.467 (7) Å, c = 17.183 (6) Å, β = 105.35 (4)°, space group $P2_1/n$, Z = 4, R = 0.065, and 1876 observed reflections. The crystals of the compound II are orthorhombic with a = 20.973 (7) Å, b = 18.464 (6) Å, c = 25.299 (8) Å, space group *Pccn*, Z = 4, R = 0.072, and 1872 observed reflections. Both in the simple and in the triple-decker sandwich complexes, the metal atom is six-coordinate. The palladium(0) compound $[(np_3)Pd(\eta\text{-}P_4)]$ contains the intact tetrahedral P_4 molecule σ bonded to the metal.

Introduction

In previous papers several complexes of 3d metals with the *cyclo*-triphosphorus (η^3-P_3) group have been described and characterized.[2] They present a simple or a triple-decker sandwich structure, the metal atom being coordinated by six phosphorus atoms. The ground state of the triple-decker complexes is a spin singlet, doublet, or triplet depending on the number of valence electrons of the complex cations.[3]

In order to extend this research, we tried to synthesize the analogous palladium and platinum derivatives.

By reacting the complexes $[MCl_2P(Bu)_3]_2$ (M = Pd, Pt) with white phosphorus and the tripodlike ligands 1,1,1-tris((diphenylphosphino)methyl)ethane (triphos) and tris(2-(diphenylphosphino)ethyl)amine (np_3) in appropriate conditions, the following complexes were synthesized: $[(\text{triphos})M(\eta^3\text{-}P_3)]BF_4$ (M = Pd, Pt) and $[LPd(\mu\text{-}(\eta^3\text{-}P_3))PdL]Y$ (L = triphos, Y = BPh_4; L = np_3, Y = BF_4). Finally, by reaction of white phosphorus with the palladium(0) complex $[Pd(np_3)]$, the compound $[(np_3)Pd(\eta\text{-}P_4)]$, containing the tetrahedral P_4 molecule bound to the metal through a phosphorus atom, was obtained.

Complete X-ray structural analyses have been carried out on the compounds $[(\text{triphos})Pd(\eta^3\text{-}P_3)]BF_4$ and $[(\text{triphos})Pd(\mu\text{-}(\eta^3\text{-}P_3))Pd(\text{triphos})]BPh_4$. $^{31}P\{^1H\}$ NMR spectra of the complexes have been recorded, and some interesting features are presented.

Experimental Section

All the solvents were reagent grade and were used without further purification. All reactions were routinely performed in an atmosphere of dry nitrogen.

The ligands triphos[4] and np_3[5] and the complexes $[MCl_2P(Bu)_3]_2$ (M = Pd, Pt)[6] were prepared according to published procedures.

Physical Measurements. Infrared and electronic spectra, conductivity measurements, and magnetic susceptibilities were measured with the use of methods already described.[7] ^{31}P NMR spectra were collected on a Varian CFT20 spectrometer operating at 31.19 MHz with proton-noise decoupling and deuterium lock. Positive chemical shifts are downfield, and they are reported relative to H_3PO_4 (0.0 ppm). The chemical shifts are reproducible to ±0.05 ppm, and the coupling constants are accurate to ±1.0 Hz. Coordination chemical shifts are reported in ppm relative to the corresponding phosphorus in the free ligand.

Analytical and conductometric data of the complexes are reported in Table I; Table II lists the $^{31}P\{^1H\}$ NMR spectra for the complexes.

Synthesis of the Complexes. $\mathbf{[(np_3)Pd(\eta\text{-}P_4)]}$. A solution of white phosphorus (1 mmol) in tetrahydrofuran (30 mL) was slowly added to a solution of $[Pd(np_3)]$ (1 mmol)[8] in benzene (30 mL), keeping the solution at 5 °C. Brown crystals which precipitated in a short time were collected and washed with benzene and light petroleum.

$\mathbf{[(triphos)M(\eta^3\text{-}P_3)]BF_4}$ **(M = Pd, Pt).** A large excess of white phosphorus (4 mmol) in tetrahydrofuran (30 mL) was added to a solution of $[PdCl_2P(Bu)_3]_2$ (1 mmol) and triphos (2 mmol) in methylene chloride (30 mL). The resulting solution was warmed for 30 min and $[N(Bu)_4]BF_4$ (2 mmol) dissolved in ethanol (10 mL) was added. Crystals of the compounds were obtained by adding ligroin (20 mL) and concentrating the solution. The crystals were collected, washed with ethanol and light petroleum, and then recrystallized from methylene chloride and ethanol; yield 45%.

$\mathbf{[LPd(\mu\text{-}(\eta^3\text{-}P_3))PdL]Y}$ **(L = np_3, Y = BF_4; L = triphos, Y = BPh_4).** These complexes were prepared by the same procedure as the above derivatives by reacting white phosphorus and the palladium dimer complex $[PdCl_2P(Bu)_3]_2$ in 1:1 ratio. The complexes crystallize by

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[8] Unpublished results of this laboratory. The $[Pd(np_3)]$ complex has been synthesized by reduction under nitrogen of a solution of K_2PdCl_4 (1 mmol) and np_3 (1 mmol) in acetone (20 mL) and ethanol (15 mL) with sodium tetrahydroborate dissolved in ethanol.

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