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The Ta(μ-N_2)Ta System. 3.[1,2] Crystal Structure of an Octahedral Tantalum(V) Imide Complex, *mer*-Ta(=NPh)(THF)(PEt_3)Cl_3, and Comparisons with Related Ta(μ-N_2)Ta Systems

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The complex *mer*-Ta(=NPh)(THF)(PEt_3)Cl_3 has been subjected to a single-crystal X-ray diffraction study. It crystallizes in the centrosymmetric monoclinic space group $P2_1/c$ with a = 10.0157 (23) Å, b = 15.9764 (38) Å, c = 14.2234 (36) Å, β = 107.303 (17)°, and Z = 4. Diffraction data (Mo Kα, 2θ = 3.8–46.0°) were collected with a Syntex P2$_1$ diffractometer, and the structure was refined to R_F = 3.5% and R_{wF} = 3.5% for all 3037 data (R_F = 2.7%, R_{wF} = 3.3% for those 2627 data with $|F_o| > 3\sigma(|F_o|)$). The central Ta(V) ion is octahedrally coordinated by three meridional chloride ligands (Ta—Cl = 2.366 (2)–2.389 (2) Å), a triethylphosphine ligand (Ta—P = 2.667 (2) Å), a tetrahydrofuran ligand (Ta—O = 2.379 (4) Å), and a phenylimido ligand (Ta=N = 1.765 (5) Å).

Introduction

We have recently reported details of two structural studies of complexes containing a Ta(μ-N_2)Ta system, viz., [Ta(=CHCMe$_3$)(CH_2CMe_3)(PMe_3)$_2$]$_2$(μ-N_2)[1,3] and [TaCl$_3$(P(bz)$_3$)(THF)]$_2$(μ-N_2).[2] Dimensions within the Ta(μ-N_2)Ta cores of these molecules led to our referring to them as diimido complexes, with formal Ta=N double bonds and a Ta=N-N=Ta skeleton. In order to clarify this situation, we decided to carry out a structural analysis of a related tantalum imido complex. While such species are not common,[4] a route to the species *mer*-Ta(=NPh)(THF)(PEt_3)Cl_3 has been developed.[5] (See Scheme I.)

Scheme I

$$\mathrm{Ta(CH_2CMe_3)_2Cl_3} \xrightarrow[-\mathrm{CMe_4}]{+\mathrm{THF}}$$
$$cis,mer\text{-}\mathrm{Ta({=}CHCMe_3)(THF)_2Cl_3} \xrightarrow[-\mathrm{Me_3CCH{=}CHPh}]{+\mathrm{PhN{=}CHPh}}$$
$$cis,mer\text{-}\mathrm{Ta({=}NPh)(THF)_2Cl_3} \xrightarrow[-\mathrm{THF}]{+\mathrm{PEt_3}}$$
$$mer\text{-}\mathrm{Ta({=}NPh)(THF)(PEt_3)Cl_3}$$

We now report the results of a single-crystal X-ray structural analysis of *mer*-Ta(=NPh)(THF)(PEt_3)Cl_3 and comparisons of its molecular parameters with those of [TaCl$_3$(P(bz)$_3$)(THF)]$_2$(μ-N_2).

Experimental Section

X-ray Data Collection. A sample consisting of large lemon yellow crystalline plates was kindly provided by Professor R. R. Schrock of MIT. Data collection was carried out on a Syntex P2$_1$ automated diffractometer operated under ambient conditions of temperature and pressure. The crystal used had been cleaved to give an irregular fragment measuring approximately 0.16 × 0.30 × 0.46 mm and was sealed into a capillary under an inert atmosphere (Ar). Unit cell constants, based on a least-squares refinement of the setting angles of the unresolved Mo K$\bar{\alpha}$ peaks of 25 reflections (27° < 2θ < 32°), are listed in Table I together with other crystal data. The details of our diffractometer operations have been published previously.[6]

Table I. Experimental Data for the X-ray Diffraction Study of *mer*-Ta(=NPh)(THF)(PEt_3)Cl_3

(A) Crystal Parameters at 23 (1) °C

a, Å: 10.0157 (23)
b, Å: 15.9764 (38)
c, Å: 14.2234 (36)
β, deg: 107.303 (17)
V, Å^3: 2173.0 (9)

crystal system: monoclinic
space group: $P2_1/c$
Z = 4
mol wt: 568.68
ρ(calcd), g cm^{-3}: 1.74

(B) Data Collection

radiation: Mo Kα (λ = 0.710 730 Å)
2θ limits, deg: 3.8–46.0
scan type: θ(crystal)–2θ(counter)
scan width, deg: symmetrical [2.0 + $\Delta(\alpha_2-\alpha_1)$]
scan speed, deg min^{-1}: 2.55
reflctns collected: 3234 total yielding 3077 unique data
reflctns measd: $+h,+k,\pm l$
abs coeff, cm^{-1}: 57.7
stds: 700, 008, and 0,12,0 measured every 97 reflections showed no significant changes
abs cor: empirical, based on ψ scans of four close to axial reflections with I(max)/I(min) = 1.47–1.61

Solution and Refinement of the Structure. The Syntex XTL crystallographic program package[7] (including some local modifications) was used for all calculations. The analytical scattering factors for neutral atoms were used along with real and imaginary anomalous dispersion corrections.[8] An empirical ψ scan method was used to correct the raw intensity data for absorption.

The structure was then solved by conventional Patterson and difference-Fourier techniques and was refined (minimizing $\sum w(\Delta F)^2$) by full-matrix least squares using an "ignorance factor" of 0.02. The final model, in which all atoms were refined anisotropically and all hydrogen atoms were fixed in idealized positions [d(C–H) = 0.95 Å],[9] consisted of 208 variables refined against all 3037 unique data (none rejected), giving an "overdetermination" ratio of 14.6:1. The residuals[10] were R_F = 3.5%, R_{wF} = 3.5%, and GOF = 1.17. The residuals based on those 2627 reflections with $|F_o| > 3\sigma(|F_o|)$ were R_F = 2.7%, R_{wF} = 3.3%, and GOF = 1.20. A correction for the effects of secondary extinction was applied in the form of eq 1 where k was determined

$$|F_{o,\mathrm{cor}}| = |F_{o,\mathrm{uncor}}|(1.0 + kI_o) \qquad (1)$$

by a least-squares fit of $|F_o|$ vs. $|F_c|$ for those 42 reflections with $I > 2 \times 10^5$. The value determined for k was 1.19×10^{-7}.

Final positional and thermal parameters are listed in Tables II and III.

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(1) Churchill, M. R.; Wasserman, H. J. *Inorg. Chem.* **1981**, *20*, 2899.
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(3) Turner, H. W.; Fellman, J. D.; Rocklage, S. M.; Schrock, R. R.; Churchill, M. R.; Wasserman, H. J. *J. Am. Chem. Soc.* **1980**, *102*, 7809–7811.
(4) See footnotes 1–4 of ref 5.
(5) Rocklage, S. M.; Schrock, R. R. *J. Am. Chem. Soc.* **1980**, *102*, 7808–7809.
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(7) "Syntex XTL Operations Manual", 2nd ed.; Syntex Analytical Instruments (now Nicolet XRD Division): Cupertino, CA, 1976.
(8) "International Tables for X-Ray Crystallography"; Kynoch Press: Birmingham, England, 1974; Vol. 4, pp 99–101 and 149–150.
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(10) $R_F = [\sum||F_o| - |F_c||/\sum|F_o|] \times 100$. $R_{wF} = [\sum w(|F_o| - |F_c|)^2/\sum|F_o|^2]^{1/2} \times 100$. GOF = $[\sum w(|F_o| - |F_c|)^2/(\mathrm{NO} - \mathrm{NV})]^{1/2}$; NO = number of observations and NV = number of variables.

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Table II. Fractional Coordinates for *mer*-Ta(=NPh)(THF)(PEt$_3$)Cl$_3$[a]

	x	*y*	*z*
Ta	0.22201 (2)	0.12318 (1)	0.28976 (2)
P	0.17818 (17)	0.28792 (9)	0.28808 (11)
Cl(1)	0.18416 (20)	0.12418 (11)	0.44619 (12)
Cl(2)	0.31452 (17)	0.15726 (12)	0.15788 (11)
Cl(3)	0.30211 (19)	−0.01809 (10)	0.30061 (13)
O	0.45650 (41)	0.15104 (29)	0.38515 (31)
N	0.04723 (46)	0.10959 (26)	0.21631 (33)
C(1)	−0.08557 (58)	0.09513 (33)	0.14917 (41)
C(2)	−0.20534 (67)	0.10043 (41)	0.17633 (54)
C(3)	−0.33288 (68)	0.08469 (46)	0.10738 (64)
C(4)	−0.34009 (71)	0.06358 (43)	0.01299 (58)
C(5)	−0.22278 (79)	0.05886 (43)	−0.01500 (51)
C(6)	−0.09376 (68)	0.07500 (40)	0.05422 (49)
C(7)	0.08166 (68)	0.32195 (39)	0.16436 (48)
C(8)	0.04774 (79)	0.41418 (45)	0.15197 (56)
C(9)	0.07377 (82)	0.32261 (39)	0.36595 (52)
C(10)	−0.07108 (86)	0.28478 (48)	0.34300 (66)
C(11)	0.32999 (77)	0.35675 (41)	0.32664 (55)
C(12)	0.42300 (90)	0.35794 (53)	0.26070 (76)
C(13)	0.57684 (79)	0.12509 (55)	0.35443 (62)
C(14)	0.69807 (84)	0.12222 (55)	0.44641 (75)
C(15)	0.65833 (88)	0.18506 (52)	0.51073 (62)
C(16)	0.5045 (76)	0.1735 (51)	0.49023 (50)
H(2)	−0.2009	0.1147	0.2420
H(3)	−0.4163	0.0886	0.1258
H(4)	−0.4283	0.0521	−0.0333
H(5)	−0.2279	0.0447	−0.0808
H(6)	−0.0107	0.0719	0.0351
H(7A)	0.1357	0.3080	0.1218
H(7B)	−0.0041	0.2919	0.1448
H(8A)	−0.0023	0.4253	0.0851
H(8B)	0.1320	0.4456	0.1699
H(8C)	−0.0077	0.4295	0.1929
H(9A)	0.1233	0.3089	0.4321
H(9B)	0.0636	0.3816	0.3594
H(10A)	−0.1171	0.3065	0.3872
H(10B)	−0.0635	0.2256	0.3500
H(10C)	−0.1233	0.2983	0.2773
H(11A)	0.2971	0.4121	0.3299
H(11B)	0.3849	0.3394	0.3903
H(12A)	0.4986	0.3953	0.2867
H(12B)	0.3706	0.3759	0.1966
H(12C)	0.4584	0.3032	0.2570
H(13A)	0.5941	0.1643	0.3092
H(13B)	0.5609	0.0713	0.3245
H(14A)	0.7825	0.1376	0.4334
H(14B)	0.7081	0.0681	0.4753
H(15A)	0.6789	0.2401	0.4941
H(15B)	0.7059	0.1645	0.5781
H(16A)	0.4615	0.2238	0.5019
H(16B)	0.4850	0.1299	0.5296

[a] B_{iso} value for the H atoms is 6.0 Å^2.

Discussion

Interatomic distances and angles are collected in Tables IV and V. The scheme used for labeling atoms is shown in Figure 1, while Figure 2 provides a stereoscopic view of the molecule.

The tantalum atom is in a slightly distorted octahedral environment in which the three chloride ligands occupy meridional sites, with Ta–Cl distances ranging from 2.366 (2) to 2.389 (2) Å and Cl(1)–Ta–Cl(3) = 95.19 (6)°, Cl(3)–Ta–Cl(2) = 93.73 (6)°, and Cl(1)–Ta–Cl(2) = 160.91 (6)°. The central chloride ligand, Cl(3), is trans to a triethylphosphine ligand, and the octahedral coordination geometry about tantalum is completed by a tetrahydrofuran ligand and a =NPh ligand.

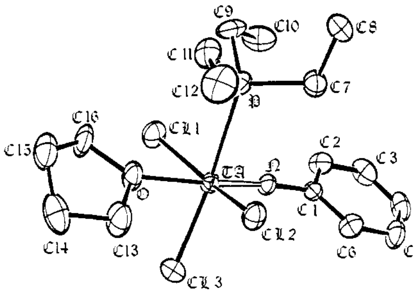

Figure 1. Labeling of atoms in the *mer*-Ta(=NPh)(THF)(PEt$_3$)Cl$_3$ molecule [ORTEP-II diagram; 30% ellipsoids; hydrogen atoms omitted].

The coordination sphere about the tantalum atom is thus very similar to that of each tantalum atom in the dimeric species [TaCl$_3$(P(bz)$_3$)(THF)]$_2$(μ-N$_2$).[2] An interesting feature of both molecules is the systematic distortion of the chloride ligands away from the nitrogen-containing ligand. Thus, the N–Ta–Cl angles are all obtuse; in the present molecule, they range from 96.39 (15) to 100.21 (15)° and average 98.4 [19]°.[11] Consequently, the O–Ta–Cl angles are all acute, ranging from 81.81 (11) to 87.27 (11)° and averaging 83.9 (30)°. A similar trend was also observed in the structure of [TaCl$_3$(THF)$_2$]$_2$(=NCMe=CMeN=).[12] However, in the present molecule the P–Ta–N angle is only slightly acute, with ∠P–Ta–N = 89.11 (15)° and the O–Ta–P angle is 87.27 (11)°. Thus the phosphine ligand does not symmetrically bisect the O–Ta–N angle of 176.14 (18)°. In the [TaCl$_3$(P(bz)$_3$)(THF)]$_2$(μ-N$_2$) molecule, the P–Ta–N angle was significantly more acute [85.61 (15)°], the P–Ta–O angle significantly more obtuse [92.83 (15)°], and the O–Ta–N system slightly closer to linearity [∠O–Ta–N = 178.00 (17)°].

The tantalum–triethylphosphine bond length in the Ta(=NPh)(THF)(PEt$_3$)Cl$_3$ molecule is 2.667 (2) Å. Although no Ta–PEt$_3$ distances are available for comparison, we note that the tantalum–tribenzylphosphine bond length is slightly larger [2.689 (1) Å] and tantalum–trimethylphosphine distances are generally shorter, ranging from about 2.51 to 2.60 Å in complexes of various coordination geometry (cf. ref 2). These results agree with both the expected order of phosphine basicity [PMe$_3$ > PEt$_3$ > P(bz)$_3$] and steric interference due to ligand "cone-angle" [PMe$_3$ < PEt$_3$ < P(bz)$_3$].

The phenylimido ligand bonds to the complex through a Ta=N bond of length 1.765 (5) Å. The Ta=NR system is close to linearity with ∠Ta–N–C(1) = 173.3 (4)°. Linear M–N–R arrangements have been observed in all but a few terminal imido complexes;[13] the exceptions are usually cases with *high* electron counts.

We are aware of only one previous structural characterization of a monomeric alkylimido complex of tantalum.[14] In the ten-electron complex Ta[=N(*t*-Bu)](NMe$_2$)$_3$, the tantalum–imide bond length is Ta=N = 1.77 (2) Å, while the three equivalent Ta–N single-bond lengths are 1.99 (2) Å. The Ta=N—R angle in this species is restricted by symmetry to 180°, and NMR and theoretical calculations suggest that the imido nitrogen in this complex is intermediate between that in electrophilic alkylimido species (such as (O=)$_3$Os=N(*t*-Bu)[15]) and nucleophilic derivatives such as Ph$_3$P=NR[16] (which has a bent P=N—R system with a sterically active lone pair of electrons on nitrogen).

The present complex has 14 valence electrons associated with the tantalum atom and has a close to linear Ta=N—R linkage. Information in its chemical reactivity is limited, but

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(11) Esd's on average distances and angles are calculated by the "scatter" formula given and are enclosed in square brackets: $[\sigma] = [\sum_{i=1}^{N}(d_i - \bar{d})^2/(N-1)]^{1/2}$.

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(13) Nugent, W. A.; Haymore, B. L. *Coord. Chem. Rev.* **1980**, *31*, 123–175; see especially Table 1, p 132.

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(15) Chong, A. D.; Oshima, K.; Sharpless, K. B. *J. Am. Chem. Soc.* **1977**, *99*, 3420.

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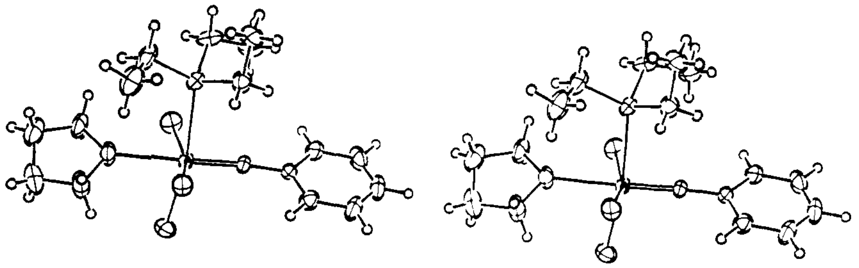


Figure 2. Stereoscopic view of the *mer*-Ta(=NPh)(THF)(PEt_3)Cl_3 molecule. [Hydrogen atoms are artificially reduced for clarity.]

Table III. Anisotropic Thermal Parameters (Å^2) for *mer*-Ta(=NPh)(THF)(PEt_3)Cl_3 [a]

	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Ta	2.55 (1)	3.31 (1)	2.58 (1)	−0.09 (1)	0.50 (1)	−0.33 (1)
P	3.64 (7)	3.28 (7)	3.10 (7)	−0.63 (6)	0.71 (6)	−0.35 (5)
Cl(1)	5.72 (9)	6.02 (9)	3.38 (7)	0.02 (7)	2.04 (7)	0.19 (6)
Cl(2)	3.89 (7)	5.99 (8)	3.32 (7)	0.08 (6)	1.44 (6)	−0.12 (6)
Cl(3)	4.92 (9)	4.16 (7)	5.28 (9)	1.17 (6)	1.26 (7)	0.10 (6)
O	2.84 (19)	6.43 (24)	3.70 (20)	0.13 (17)	0.03 (16)	−0.34 (18)
N	2.41 (21)	3.53 (22)	2.89 (21)	−0.20 (16)	0.34 (17)	−0.56 (16)
C(1)	2.79 (26)	2.61 (22)	3.07 (26)	−0.14 (19)	0.44 (20)	−0.25 (19)
C(2)	3.31 (31)	4.31 (32)	5.36 (36)	−0.50 (23)	1.17 (27)	−0.96 (27)
C(3)	2.66 (31)	5.36 (35)	7.45 (49)	−0.18 (26)	1.29 (31)	0.50 (35)
C(4)	3.34 (34)	5.03 (36)	5.49 (40)	−0.82 (27)	−0.94 (29)	0.94 (30)
C(5)	5.30 (41)	5.11 (36)	3.89 (32)	−1.05 (31)	−0.87 (29)	−0.18 (27)
C(6)	4.12 (33)	4.41 (32)	4.58 (33)	−0.83 (26)	1.50 (27)	−0.55 (26)
C(7)	4.30 (33)	4.09 (31)	4.25 (32)	−0.12 (25)	0.60 (25)	0.17 (25)
C(8)	5.51 (40)	4.60 (32)	5.50 (39)	1.40 (30)	0.75 (31)	0.56 (30)
C(9)	7.50 (45)	3.30 (30)	4.97 (36)	−0.13 (29)	2.86 (32)	−1.37 (26)
C(10)	6.34 (45)	5.47 (40)	8.77 (55)	−0.48 (34)	3.97 (41)	−0.84 (37)
C(11)	5.17 (38)	4.19 (32)	5.29 (37)	−1.95 (27)	0.27 (30)	−0.12 (27)
C(12)	5.60 (45)	7.06 (48)	9.35 (61)	−3.81 (37)	1.94 (42)	−0.71 (41)
C(13)	3.38 (34)	10.78 (63)	5.30 (41)	0.67 (36)	0.44 (30)	−0.95 (38)
C(14)	3.75 (37)	8.43 (55)	7.75 (54)	−0.04 (35)	0.28 (35)	2.27 (43)
C(15)	6.29 (47)	6.40 (43)	5.53 (43)	−1.37 (36)	−1.16 (35)	0.51 (35)
C(16)	4.47 (36)	7.71 (45)	3.33 (31)	−0.39 (33)	−0.99 (26)	−1.08 (31)

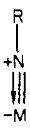
[a] The anisotropic thermal parameters enter the expression for the calculated structure factor in the form $\exp[-{}^1/_4(h^2a^{*2}B_{11} + k^2b^{*2}B_{22} + l^2c^{*2}B_{33} + 2hka^*b^*B_{12} + 2hla^*c^*B_{13} + 2klb^*c^*B_{23})]$.

Table IV. Interatomic Distances (Å) with Esd's

(A) Distances from the Tantalum Atom			
Ta-Cl(1)	2.366 (2)	Ta-P	2.667 (2)
Ta-Cl(2)	2.389 (2)	Ta-O	2.379 (4)
Ta-Cl(3)	2.385 (2)	Ta-N	1.765 (5)
(B) Distances within the Phenylimido Ligand			
N-C(1)	1.407 (8)	C(4)-C(5)	1.350 (11)
C(1)-C(2)	1.368 (9)	C(5)-C(6)	1.396 (10)
C(2)-C(3)	1.383 (11)	C(6)-C(1)	1.367 (9)
C(3)-C(4)	1.365 (12)		
(C) Distances within the THF Ligand			
O-C(13)	1.459 (9)	C(15)-C(16)	1.491 (12)
C(13)-C(14)	1.498 (13)	C(16)-O	1.472 (8)
C(14)-C(15)	1.490 (13)		
(D) Distances within the PEt_3 Ligand			
P-C(7)	1.821 (7)	C(7)-C(8)	1.511 (10)
P-C(9)	1.821 (8)	C(9)-C(10)	1.515 (12)
P-C(11)	1.824 (8)	C(11)-C(12)	1.506 (13)

one would anticipate its recognition as an electrophilic species (with an electron-deficient nitrogen atom).

The chemistry of imido complexes has been reviewed.[13] The metal–nitrogen bond in monomeric complexes with terminal (linear) M=N—R systems is generally regarded as having a bond order between 2 and 3, with a significant contribution from the structure



$R-{}^{+}N\equiv{}^{-}M$

Table V. Interatomic Angles (Deg) with Esd's

(A) Angles about the Tantalum Atom			
N-Ta-O	176.14 (18)	O-Ta-Cl(3)	83.35 (11)
N-Ta-P	89.11 (15)	P-Ta-Cl(1)	85.97 (6)
N-Ta-Cl(1)	98.59 (15)	P-Ta-Cl(2)	82.49 (5)
N-Ta-Cl(2)	96.39 (15)	P-Ta-Cl(3)	170.30 (6)
N-Ta-Cl(3)	100.21 (15)	Cl(1)-Ta-Cl(2)	160.91 (6)
O-Ta-P	87.27 (11)	Cl(1)-Ta-Cl(3)	95.19 (6)
O-Ta-Cl(1)	82.50 (11)	Cl(2)-Ta-Cl(3)	93.73 (6)
O-Ta-Cl(2)	81.81 (11)		
(B) Angle about Nitrogen			
Ta-N-C(1)	173.27 (40)		
(C) Angles Involving the Phenylimido Ligand			
N-C(1)-C(2)	122.0 (5)	N-C(1)-C(6)	118.4 (5)
C(1)-C(2)-C(3)	119.4 (7)	C(4)-C(5)-C(6)	119.1 (7)
C(2)-C(3)-C(4)	120.7 (7)	C(5)-C(6)-C(1)	120.7 (6)
C(3)-C(4)-C(5)	120.5 (7)	C(6)-C(1)-C(2)	119.6 (6)
(D) Angles Involving the THF Ligand			
Ta-O-C(13)	122.6 (4)	Ta-O-C(16)	126.4 (4)
C(13)-O-C(16)	108.9 (5)		
O-C(13)-C(14)	105.9 (7)	C(14)-C(15)-C(16)	104.2 (7)
C(13)-C(14)-C(15)	102.7 (7)	C(15)-C(16)-O	103.6 (6)
(E) Tantalum-Phosphorus-Carbon Angles			
Ta-P-C(7)	110.00 (22)	Ta-P-C(11)	118.17 (24)
Ta-P-C(9)	114.68 (24)		
(F) Phosphorus-Carbon-Carbon Angles			
P-C(7)-C(8)	116.1 (5)	P-C(11)-C(12)	115.8 (6)
P-C(9)-C(10)	115.7 (5)		
(G) Carbon-Phosphorus-Carbon Angles			
C(7)-P-C(9)	105.1 (3)	C(9)-P-C(11)	102.2 (3)
C(7)-P-C(11)	105.4 (3)		

In keeping with this, we find that the Ta=NR linkages in the present complex [Ta=N = 1.765 (5) Å] and in Ta[=N-

(t-Bu)](NMe$_2$)$_3$ (Ta=N = 1.77 (2) Å) are marginally shorter than the Ta=N distances observed in the Ta=NN=Ta systems of [Ta(=CHCMe$_3$)(CH$_2$CMe$_3$)(PMe$_3$)$_2$]$_2$(μ-N$_2$)[1] (Ta=N = 1.842 (8) and 1.837 (8) Å) and [TaCl$_3$(P(bz)$_3$)(THF)]$_2$(μ-N$_2$)[2] (Ta=N = 1.796 (5) Å (twice)). These values also help to confirm our previous assignment of Ta(μ-N$_2$)Ta systems as formally Ta=NN=Ta (rather than, e.g., Ta$\leftarrow$N$\equiv$N$\rightarrow$Ta).

Other geometric features of the molecule are normal and consistent with observations on related molecules.

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Registry No. *mer*-Ta(=NPh)(THF)(PEt$_3$)Cl$_3$, 79482-72-7.

Supplementary Material Available: Table of observed and calculated structure factor amplitudes (17 pages). Ordering information is given on any current masthead page.

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Crystal Structure and Molecular Geometry of a Dinuclear Formyl Complex of Tantalum, [(η^5-C$_5$Me$_4$Et)TaCl$_2$]$_2$(μ-H)(μ-CHO). A Unique "Side-On" Bridging Mode for the Formyl Ligand

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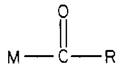
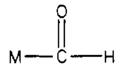
The complex [(η^5-C$_5$Me$_4$Et)TaCl$_2$]$_2$(μ-H)(μ-CHO), prepared by Belmonte and Schrock, has been studied via a single-crystal X-ray structural analysis. The complex crystallizes in the centrosymmetric triclinic space group $P\bar{1}$ with a = 11.114 (3) Å, b = 14.856 (4) Å, c = 8.858 (2) Å, α = 82.98 (2)°, β = 103.91 (2)°, γ = 105.56 (2)°, V = 1364.9 (6) Å^3, and Z = 2. Data were collected on a Syntex P2$_1$ automated four-circle diffractometer, and the structure was refined to R_F = 5.7% for all 3587 reflections (none rejected) with 2θ = 3.8-45.0° (Mo Kα radiation). The molecule contains two [(η^5-C$_5$Me$_4$Et)TaCl$_2$] fragments bridged by a "side-on" formyl group [Ta(1)-C(1) = 2.085 (12) Å, Ta(2)-C(1) = 2.119 (11) Å; Ta(1)-O = 2.094 (8) Å, Ta(2)-O = 2.089 (9) Å] and by a hydride ligand. The Ta(1)-[C(1)-O]-Ta(2) system has a "butterfly" configuration with a bend of 71.15° about the C(1)-O axis. The C(1)-O linkage is significantly activated, being lengthened to 1.496 (14) Å.

Introduction

Transition-metal σ-acyls (**1**) have been known for more than

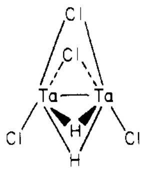

$$\mathrm{M{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}R}$$
1


$$\mathrm{M{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}H}$$
2

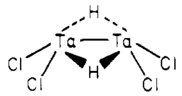
20 years and have been fully characterized via X-ray diffraction studies.[1,2] In contrast to this, the synthesis of σ-formyl complexes (**2**) has proved to be significantly more difficult. The first successful synthesis was that of [(PPh$_2$)$_2$N$^+$][Fe(CO)$_4$(CHO)$^-$], reported in 1973;[3] the first structural characterization of a σ-formyl complex, (η^5-C$_5$H$_5$)Re(PPh$_3$)(NO)(η^1-CHO), appeared in 1979.[4] A structural study of the heterobimetallic complex, (η^5-C$_5$H$_5$)$_2$W(=CHO)Zr(H)(η^5-C$_5$Me$_5$)$_2$ has also been reported;[5] here, the μ-CHO ligand behaves as a bifunctional oxycarbene ligand.

Schrock and his co-workers[6] have recently discovered the reaction sequence below (Scheme I), wherein H$_2$ and CO are assembled on a ditantalum complex to yield a hydrido-formyl derivative, which further reacts with PMe$_3$ to form a hydrido-oxo-(phosphonium ylide) complex.

We have previously determined the structure of the hydrido-oxo-(phosphonium ylide) species **5** (with Cp′ = η^5-C$_5$Me$_4$Et).[7] The species [Cp′TaCl$_2$]$_2$(H)$_2$ (**3**) has not been characterized structurally, although possible core structures include **6** (by analogy with the complex [(PMe$_3$)$_2$TaCl$_2$]$_2$(μ-Cl)$_2$(μ-H)$_2$ characterized by Sattelberger et al.[8a]) and **7**.[8b]



6



7

The remaining product, the hydrido-formyl complex **4**, has proved very difficult to crystallize.[9] Recently crystals were obtained and a structural study initiated. A preliminary account of this work has appeared previously.[10] Full details appear below.

Experimental Section

(A) Data Collection. A crystalline sample of the material was isolated *with great difficulty* by Patricia Belmonte working with Professor Richard R. Schrock at the Massachusetts Institute of

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(9) See ref 7, p 382, right-hand column.

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