$(t\text{-Bu})](NMe_2)_3$ ($Ta{=}N = 1.77\ (2)$ Å) are marginally shorter than the $Ta{=}N$ distances observed in the $Ta{=}NN{=}Ta$ systems of $[Ta({=}CHCMe_3)(CH_2CMe_3)(PMe_3)_2]_2(\mu\text{-}N_2)$[1] ($Ta{=}N = 1.842\ (8)$ and $1.837\ (8)$ Å) and $[TaCl_3(P(bz)_3)(THF)]_2(\mu\text{-}N_2)$[2] ($Ta{=}N = 1.796\ (5)$ Å (twice)). These values also help to confirm our previous assignment of $Ta(\mu\text{-}N_2)Ta$ 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.

Acknowledgment. This work was supported by the National Science Foundation through Grant CHE80-23448 (to M.R.C.).

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.

Contribution from the Department of Chemistry,
State University of New York at Buffalo, Buffalo, New York 14214

Crystal Structure and Molecular Geometry of a Dinuclear Formyl Complex of Tantalum, $[(\eta^5\text{-}C_5Me_4Et)TaCl_2]_2(\mu\text{-}H)(\mu\text{-}CHO)$. A Unique "Side-On" Bridging Mode for the Formyl Ligand

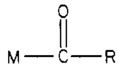
MELVYN ROWEN CHURCHILL* and HARVEY J. WASSERMAN

Received April 8, 1981

The complex $[(\eta^5\text{-}C_5Me_4Et)TaCl_2]_2(\mu\text{-}H)(\mu\text{-}CHO)$, 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, $\alpha = 82.98\ (2)°$, $\beta = 103.91\ (2)°$, $\gamma = 105.56\ (2)°$, $V = 1364.9\ (6)$ 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 $2\theta = 3.8\text{-}45.0°$ (Mo Kα radiation). The molecule contains two $[(\eta^5\text{-}C_5Me_4Et)TaCl_2]$ 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.

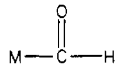
Introduction

Transition-metal σ-acyls (**1**) have been known for more than 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 $[(PPh_2)_2N^+][Fe(CO)_4(CHO)^-]$, reported in 1973;[3] the first structural characterization of a σ-formyl complex, $(\eta^5\text{-}C_5H_5)Re(PPh_3)(NO)(\eta^1\text{-}CHO)$, appeared in 1979.[4] A structural study of the heterobimetallic complex, $(\eta^5\text{-}C_5H_5)_2W({=}CHO)Zr(H)(\eta^5\text{-}C_5Me_5)_2$ has also been reported;[5] here, the μ-CHO ligand behaves as a bifunctional oxycarbene ligand.



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

1

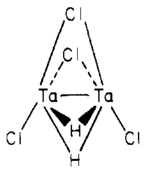


$$M{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}H$$

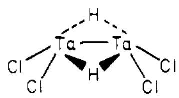
2

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 $Cp' = \eta^5\text{-}C_5Me_4Et$).[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 $[(PMe_3)_2TaCl_2]_2(\mu\text{-}Cl)_2(\mu\text{-}H)_2$ 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

---

(1) Churchill, M. R. *Perspect. Struct. Chem.* **1970**, *3*, 91.
(2) Churchill, M. R.; Chen, K.-N. *Inorg. Chem.* **1976**, *15*, 788 and references therein.
(3) Collman, J. P.; Winter, S. R. *J. Am. Chem. Soc.* **1973**, *95*, 4089.
(4) Wong, W. K.; Tam, W.; Strouse, C. E.; Gladysz, J. A. *J. Chem. Soc., Chem. Commun.* **1979**, 530.
(5) Wolczanski, P. T.; Threlkel, R. S.; Bercaw, J. E. *J. Am. Chem. Soc.* **1979**, *101*, 218.
(6) Belmonte, P.; Schrock, R. R.; Churchill, M. R.; Youngs, W. J. *J. Am. Chem. Soc.* **1980**, *102*, 2858.
(7) Churchill, M. R.; Youngs, W. J. *Inorg. Chem.* **1981**, *20*, 382.
(8) (a) Sattelberger, A. P.; Wilson, R. B., Jr.; Huffman, J. C. *J. Am. Chem. Soc.* **1980**, *102*, 7111. (b) A recent structural study of the related species $Cp'_2Ta_2Cl_3Me(H)_2$ shows only *terminal* Cl and Me ligands—compatible with structure **7**: Belmonte, P. A.; Schrock, R. R.; Day, C. S. *J. Am. Chem. Soc.*, in press.
(9) See ref 7, p 382, right-hand column.
(10) Churchill, M. R.; Wasserman, H. J. *J. Chem. Soc., Chem. Commun.* **1981**, 274.

0020-1669/82/1321-0226$01.25/0 © 1982 American Chemical Society

Scheme I

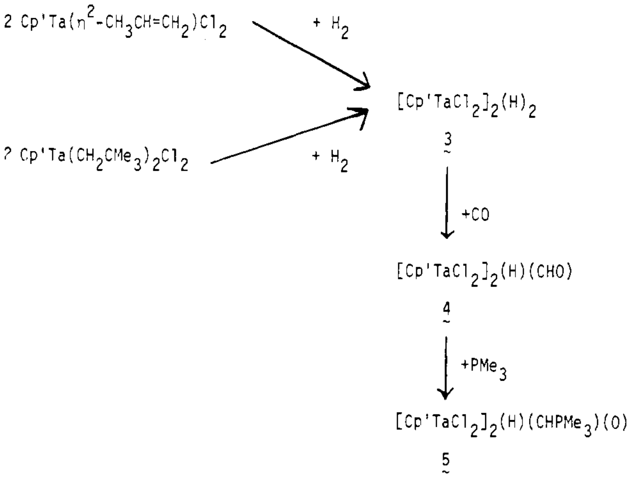


Table I. Data for the X-ray Diffraction Study of $[(\eta^5\text{-}C_5Me_4Et)TaCl_2]_2(\mu\text{-}H)(\mu\text{-}CHO)$

(A) Crystal Parameters

$a = 11.1137\ (33)$ Å
$b = 14.8563\ (42)$ Å
$c = 8.8578\ (24)$ Å
$\alpha = 82.977\ (22)°$
$\beta = 103.908\ (21)°$
$\gamma = 105.562\ (22)°$
$V = 1365.0\ (6)$ Å^3
cryst system: triclinic
space group: $P\bar{1}$
$Z = 2$
mol wt = 832.3
ρ(calcd) = 2.02 g cm^{-3}
$T = 23$ °C

(B) Data Collection and Processing

radiation: graphite-monochromatized Mo Kα ($\bar{\lambda} = 0.710\,730$ Å)
reflctns measd: $\pm h, \pm k, +l$
scan type: coupled θ(cryst)–2θ(counter)
2θ range: 3.8–45.0°
scan speed: 2.55° min^{-1}
scan width: symmetrical, $[1.8 + \Delta(\alpha_2 - \alpha_1)]°$
reflctns collected: 3587 independent
std reflctns: 700, 105, and 1,10,0 measured after every 97 reflctns; no significant changes observed
$w = [\sigma(|F_o|)^2 + (0.035|F_o|)^2]^{-1}$
$\mu = 88.4$ cm^{-1}
reflctns used for empirical abs cor: $\bar{1}\bar{1}3$ ($2\theta = 14.58°$), $\bar{1}\bar{1}4$ (19.12°), $\bar{2}\bar{1}5$ (23.18°), $\bar{2}06$ (28.06°), $\bar{3}17$ (32.80°), $\bar{4}18$ (38.03°), $\bar{1}\bar{1}9$ (43.31°)
rel abs factors: 2.12 → 2.63

Technology. The complex is difficult to handle in solution. Since we initially believed the complex to be air sensitive, crystals were sealed into thin glass capillaries inside a specially modified KSE inert-atmosphere (Ar) drybox. We later discovered, however, that crystals exposed to the air remained unchanged indefinitely.

A crystal of dimensions 0.10 × 0.17 × 0.43 mm was selected for the diffraction study. It was mounted along its extended [001] direction on a Syntex P2$_1$ automated diffractometer. Initial experimental techniques, as well as those used for collection of intensity data, have been described earlier.[11] Details pertinent to the current analysis are presented in Table I.

The raw diffraction data were corrected for the effects of absorption utilizing an empirical method based on seven sets of ψ scans of close-to-axial reflections. A description of this method has appeared;[12] the reflections used are listed in Table I.

(B) Solution and Refinement. The positions of the two tantalum atoms were determined from an unsharpened Patterson function. All remaining nonhydrogen atoms were located from a subsequent difference-Fourier calculation. Full-matrix least-squares refinement, minimizing the function $\sum w(|F_o| - |F_c|)^2$, was then carried out incorporating positional and anisotropic thermal parameters for all nonhydrogen atoms; this led to $R_F = 5.9\%$.[13]

Table II. Final Positional Parameters, with Esd's, for $[(\eta^5\text{-}C_5Me_4Et)TaCl_2]_2(\mu\text{-}H)(\mu\text{-}CHO)$

atom	*x*	*y*	*z*
Ta(1)	0.21405 (4)	0.26982 (3)	0.27140 (5)
Ta(2)	−0.08477 (5)	0.21259 (3)	0.12177 (5)
Cl(1)	0.27578 (36)	0.28051 (28)	0.03158 (39)
Cl(2)	0.32218 (34)	0.15086 (23)	0.38452 (39)
Cl(3)	−0.04994 (44)	0.23503 (38)	−0.13460 (42)
Cl(4)	−0.14044 (42)	0.35006 (25)	0.14821 (57)
O	0.06816 (80)	0.15026 (55)	0.20456 (91)
C(1)	0.0447 (10)	0.19387 (78)	0.3349 (13)
C(11)	0.3204 (11)	0.34056 (79)	0.5166 (12)
C(12)	0.4106 (12)	0.37075 (90)	0.4201 (15)
C(13)	0.3604 (15)	0.42721 (86)	0.2949 (15)
C(14)	0.2380 (14)	0.43142 (83)	0.3130 (15)
C(15)	0.2147 (11)	0.37799 (76)	0.4522 (13)
C(16)	0.3392 (16)	0.2841 (10)	0.6666 (15)
C(17)	0.5408 (15)	0.3511 (13)	0.4535 (20)
C(18)	0.4302 (19)	0.4799 (12)	0.1745 (20)
C(19)	0.1577 (19)	0.49657 (94)	0.2168 (20)
C(20)	0.1046 (13)	0.3744 (10)	0.5274 (18)
C(21)	0.1418 (16)	0.4483 (12)	0.6443 (21)
C(31)	−0.3120 (15)	0.1574 (10)	0.1271 (21)
C(32)	−0.2460 (13)	0.1151 (10)	0.2559 (15)
C(33)	−0.1882 (12)	0.05350 (84)	0.2036 (13)
C(34)	−0.2191 (11)	0.06092 (83)	0.0418 (15)
C(35)	−0.2940 (11)	0.12322 (86)	−0.0111 (14)
C(36)	−0.4015 (22)	0.2127 (14)	0.1297 (31)
C(37)	−0.2453 (21)	0.1247 (15)	0.4245 (20)
C(38)	−0.1231 (16)	−0.0147 (11)	0.3049 (21)
C(39)	−0.1855 (16)	0.0030 (11)	−0.0611 (20)
C(40)	−0.3572 (13)	0.1438 (11)	−0.1724 (18)
C(41)	−0.4838 (20)	0.0719 (15)	−0.2252 (21)
H16A[a]	0.2944	0.2206	0.6509
H16B	0.3072	0.3074	0.7400
H16C	0.4278	0.2879	0.7049
H17A	0.5407	0.3067	0.3848
H17B	0.5608	0.3266	0.5581
H17C	0.6029	0.4074	0.4386
H18A	0.4017	0.4470	0.0818
H18B	0.5194	0.4859	0.2119
H18C	0.4140	0.5403	0.1528
H19A	0.0957	0.4635	0.1351
H19B	0.2119	0.5489	0.1735
H19C	0.1156	0.5175	0.2820
H20A	0.0336	0.3847	0.4489
H20B	0.0813	0.3144	0.5789
H21A	0.0715	0.4449	0.6900
H21B	0.1647	0.5084	0.5932
H21C	0.2124	0.4381	0.7232
H36A	−0.3569	0.2767	0.1384
H36B	−0.4403	0.1914	0.2164
H36C	−0.4655	0.2060	0.0361
H37A	−0.1778	0.1763	0.4638
H37B	−0.2329	0.0690	0.4844
H37C	−0.3247	0.1348	0.4310
H38A	−0.0333	0.0067	0.3131
H38B	−0.1530	−0.0738	0.2605
H38C	−0.1413	−0.0205	0.4055
H39A	−0.1030	0.0324	−0.0804
H39B	−0.2468	−0.0029	−0.1570
H39C	−0.1852	−0.0573	−0.0111
H40A	−0.3736	0.2039	−0.1798
H40B	−0.3017	0.1438	−0.2389
H41A	−0.5213	0.0878	−0.3298
H41B	−0.5402	0.0716	−0.1597
H41C	−0.4683	0.0115	−0.2188

[a] B_{iso} for H atoms in 6.0 Å^2.

Attempts to locate the hydrogen atoms of the molecule (especially the formyl hydrogen atom or the bridging hydride ligand) were unsuccessful. Our attempts included the method of using only lower order reflections [$((\sin\theta)/\lambda)_{max} < 0.35$ Å^{-1}].

Hydrogen atoms of the η^5-C$_5$Me$_4$Et ligands were now placed in

---

(11) Churchill, M. R.; Lashewycz, R. A.; Rotella, F. J. *Inorg. Chem.* **1977**, *16*, 265.

(12) Churchill, M. R.; Hollander, F. J.; Hutchinson, J. P. *Inorg. Chem.* **1977**, *16*, 2655.

(13) The discrepancy indices are defined as follows: $R_F\ (\%) = (\sum||F_o| - |F_c||/|F_o|) \times 100$; $R_{wF}\ (\%) = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2} \times 100$; GOF $= [\sum w(|F_o| - |F_c|)^2/(NO - NV)]^{1/2}$.

Table III. Anisotropic Thermal Parameters[a] (Å^2) for $[(\eta^5\text{-C}_5\text{Me}_4\text{Et})\text{TaCl}_2](\mu\text{-H})(\mu\text{-CHO})$

atom	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Ta(1)	2.974 (27)	3.070 (26)	2.763 (25)	0.006 (18)	1.275 (18)	−0.972 (16)
Ta(2)	2.998 (28)	3.070 (26)	2.848 (26)	0.217 (18)	0.820 (18)	−0.602 (17)
Cl(1)	4.93 (18)	7.45 (21)	3.91 (15)	0.09 (15)	2.44 (13)	−1.68 (14)
Cl(2)	4.60 (17)	4.22 (15)	5.26 (16)	1.32 (13)	0.74 (13)	−1.24 (12)
Cl(3)	6.11 (24)	11.45 (32)	3.17 (15)	−2.61 (22)	1.34 (15)	−0.71 (17)
Cl(4)	5.80 (22)	3.61 (16)	10.64 (30)	1.75 (15)	−0.24 (20)	−1.31 (17)
O	3.63 (41)	3.79 (38)	4.01 (38)	0.73 (31)	1.30 (31)	−1.03 (29)
C(1)	2.01 (49)	3.74 (53)	3.21 (49)	0.14 (40)	0.81 (39)	−1.01 (39)
C(11)	2.86 (54)	3.71 (53)	2.94 (49)	0.00 (43)	1.08 (42)	−1.40 (40)
C(12)	3.12 (60)	4.62 (62)	4.66 (63)	−0.46 (48)	2.22 (50)	−2.78 (52)
C(13)	5.99 (84)	3.28 (57)	4.21 (63)	−0.96 (54)	2.83 (59)	−0.82 (48)
C(14)	4.64 (74)	3.02 (55)	4.69 (64)	−0.17 (49)	0.67 (54)	−0.80 (46)
C(15)	3.01 (57)	2.91 (50)	3.80 (55)	−0.09 (42)	0.79 (44)	−1.64 (42)
C(16)	7.23 (94)	5.39 (71)	3.53 (60)	1.58 (65)	0.97 (58)	−1.73 (51)
C(17)	3.35 (74)	7.9 (10)	8.1 (10)	−1.52 (67)	0.73 (67)	−3.76 (79)
C(18)	8.2 (12)	7.2 (10)	7.0 (10)	−4.10 (87)	3.89 (87)	−1.82 (74)
C(19)	8.4 (11)	2.47 (59)	8.9 (11)	0.74 (63)	−0.19 (86)	0.08 (61)
C(20)	3.22 (64)	4.61 (67)	8.18 (89)	−0.04 (51)	2.87 (61)	−2.10 (61)
C(21)	5.65 (87)	6.61 (86)	9.2 (10)	1.53 (68)	3.90 (79)	−3.98 (77)
C(31)	4.77 (80)	4.13 (68)	9.3 (11)	0.53 (59)	3.88 (79)	−0.98 (68)
C(32)	3.44 (64)	5.30 (70)	3.88 (60)	−1.26 (55)	1.56 (51)	−1.27 (52)
C(33)	3.19 (58)	3.60 (55)	3.64 (59)	−0.26 (45)	0.61 (46)	0.42 (44)
C(34)	1.84 (49)	3.42 (53)	5.04 (66)	−0.11 (42)	0.75 (44)	−1.39 (45)
C(35)	2.21 (52)	4.02 (57)	4.41 (60)	0.73 (44)	1.19 (45)	−0.30 (45)
C(36)	10.0 (15)	6.8 (11)	17.3 (20)	1.9 (10)	8.5 (15)	−2.7 (12)
C(37)	9.8 (14)	10.9 (14)	6.16 (92)	−2.7 (11)	5.0 (10)	−3.88 (89)
C(38)	4.32 (79)	5.00 (76)	8.7 (10)	−0.42 (61)	−0.70 (71)	2.03 (71)
C(39)	6.04 (93)	4.98 (75)	8.9 (10)	1.12 (67)	1.90 (76)	−3.16 (70)
C(40)	2.88 (64)	5.99 (79)	7.05 (86)	1.39 (57)	0.26 (58)	0.58 (64)
C(41)	7.8 (12)	9.0 (12)	6.21 (94)	0.0 (10)	−1.17 (84)	1.06 (83)

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

Table IV. Intramolecular Distances (Å) with Esd's for $[(\eta^5\text{-C}_5\text{Me}_4\text{Et})\text{TaCl}_2]_2(\mu\text{-H})(\mu\text{-CHO})$

(A) Distances from the Tantalum Atoms			
Ta(1)-Ta(2)	3.186 (1)		
Ta(1)-Cl(1)	2.360 (4)	Ta(2)-Cl(3)	2.364 (4)
Ta(1)-Cl(2)	2.387 (4)	Ta(2)-Cl(4)	2.339 (4)
Ta(1)-C(1)	2.085 (12)	Ta(2)-C(1)	2.119 (11)
Ta(1)-O	2.094 (8)	Ta(2)-O	2.089 (9)
Ta(1)-C(11)	2.424 (11)	Ta(2)-C(31)	2.447 (18)
Ta(1)-C(12)	2.469 (13)	Ta(2)-C(32)	2.435 (14)
Ta(1)-C(13)	2.464 (13)	Ta(2)-C(33)	2.441 (12)
Ta(1)-C(14)	2.408 (12)	Ta(2)-C(34)	2.426 (12)
Ta(1)-C(15)	2.401 (11)	Ta(2)-C(35)	2.442 (13)
Ta(1)···Cp(1)	2.115 (-)	Ta(2)···Cp(2)	2.112 (-)
(B) Carbon-Oxygen Distance			
C(1)-O	1.496 (14)		
(C) Internal C-C Distances for the η^5-C_5Me_4Et Ligands			
C(11)-C(12)	1.418 (18)	C(31)-C(32)	1.380 (22)
C(12)-C(13)	1.404 (19)	C(32)-C(33)	1.424 (20)
C(13)-C(14)	1.426 (23)	C(33)-C(34)	1.389 (17)
C(14)-C(15)	1.422 (17)	C(34)-C(35)	1.374 (18)
C(15)-C(11)	1.402 (18)	C(35)-C(31)	1.456 (22)
(D) External C(sp^2)-C(sp^3) Distances for the η^5-C_5Me_4Et Ligands			
C(11)-C(16)	1.484 (17)	C(31)-C(36)	1.457 (30)
C(12)-C(17)	1.505 (23)	C(32)-C(37)	1.516 (22)
C(13)-C(18)	1.491 (24)	C(33)-C(38)	1.488 (21)
C(14)-C(19)	1.535 (23)	C(34)-C(39)	1.496 (21)
C(15)-C(20)	1.514 (20)	C(35)-C(40)	1.468 (20)
(E) External C(sp^3)-C(sp^3) Distances for the η^5-C_5Me_4Et Ligands			
C(20)-C(21)	1.510 (23)	C(40)-C(41)	1.530 (27)

idealized (staggered) positions with d(C−H) = 0.95 Å,[14] and refinement continued. At final convergence the discrepancy indices were $R_F = 5.7\%$, $R_{wF} = 6.7\%$, and GOF = 1.49 electrons for all 3587 reflections (with none rejected). The corresponding indices for those 3172 data with $|F_o| > 3\sigma(|F_o|)$ were $R_F = 5.0\%$, $R_{wF} = 6.5\%$, and GOF = 1.54 electrons.

Table V. Interatomic Angles (Deg) for $[(\eta^5\text{-C}_5\text{Me}_4\text{Et})\text{TaCl}_2]_2(\mu\text{-H})(\mu\text{-CHO})$

(A) Angles around the Tantalum Atoms			
Cl(1)-Ta(1)-Cl(2)	93.9 (1)	Cl(3)-Ta(2)-Cl(4)	102.1 (2)
Cl(1)-Ta(1)-C(1)	129.5 (3)	Cl(3)-Ta(2)-C(1)	129.1 (3)
Cl(1)-Ta(1)-O	90.3 (3)	Cl(3)-Ta(2)-O	92.6 (3)
Cl(2)-Ta(1)-C(1)	92.3 (3)	Cl(4)-Ta(2)-C(1)	103.8 (3)
Cl(2)-Ta(1)-O	79.9 (2)	Cl(4)-Ta(2)-O	139.0 (3)
C(1)-Ta(1)-O	42.0 (4)	C(1)-Ta(2)-O	41.6 (4)
(B) Angles from Cp(1) and Cp(2)			
Cp(1)-Ta(1)-Cl(1)	111.9	Cp(2)-Ta(2)-Cl(3)	107.8
Cp(1)-Ta(1)-Cl(2)	106.4	Cp(2)-Ta(2)-Cl(4)	105.7
Cp(1)-Ta(1)-C(1)	114.1	Cp(2)-Ta(2)-O	105.7
Cp(1)-Ta(1)-O	156.0	Cp(2)-Ta(2)-C(1)	106.1
Cp(1)-Ta(1)-Ta(2)	124	Cp(2)-Ta(2)-Ta(1)	142.5
(C) Angles within the μ-CHO Ligand			
Ta(1)-C(1)-Ta(2)	98.6 (5)	Ta(1)-O-Ta(2)	99.2 (4)
Ta(1)-C(1)-O	69.3 (5)	Ta(2)-C(1)-O	68.1 (5)
Ta(1)-O-C(1)	68.7 (5)	Ta(2)-O-C(1)	70.3 (6)
(D) Interior Angles of the C_5Me_4Et Ligands			
C(15)-C(11)-C(12)	108.9 (11)	C(35)-C(31)-C(32)	107.8 (14)
C(11)-C(12)-C(13)	107.8 (12)	C(31)-C(32)-C(33)	108.3 (13)
C(12)-C(13)-C(14)	107.9 (12)	C(32)-C(33)-C(34)	106.9 (11)
C(13)-C(14)-C(15)	107.9 (12)	C(33)-C(34)-C(35)	110.7 (11)
C(14)-C(15)-C(11)	107.5 (11)	C(34)-C(35)-C(31)	106.2 (12)
(E) Exterior Angles of the C_5Me_4Et Ligands			
C(16)-C(11)-C(15)	125.6 (11)	C(36)-C(31)-C(35)	125.9 (16)
C(16)-C(11)-C(12)	125.4 (12)	C(36)-C(31)-C(32)	125.5 (17)
C(17)-C(12)-C(11)	125.6 (12)	C(37)-C(32)-C(31)	126.2 (15)
C(17)-C(12)-C(13)	126.4 (13)	C(37)-C(32)-C(33)	125.2 (14)
C(18)-C(13)-C(12)	124.9 (14)	C(38)-C(33)-C(32)	125.4 (12)
C(18)-C(13)-C(14)	127.0 (14)	C(38)-C(33)-C(34)	127.1 (12)
C(19)-C(14)-C(13)	125.6 (13)	C(39)-C(34)-C(33)	124.8 (12)
C(19)-C(14)-C(15)	125.7 (13)	C(39)-C(34)-C(35)	124.3 (12)
C(20)-C(15)-C(14)	125.4 (11)	C(40)-C(35)-C(34)	127.8 (12)
C(20)-C(15)-C(11)	126.6 (11)	C(40)-C(35)-C(31)	125.6 (13)
C(15)-C(20)-C(21)	110.8 (12)	C(35)-C(40)-C(41)	112.3 (14)

We used our in-house Syntex XTL system (based on a Data General NOVA 1200 computer) for all calculations. The analytical form of

---

[14] Churchill, M. R. *Inorg. Chem.* **1973**, *12*, 1213.

Table VI. Least Squares Planes[a] and Atomic Deviations (Å) Therefrom for $[(\eta^5\text{-}C_5Me_4Et)TaCl_2]_2(\mu\text{-}H)(\mu\text{-}CHO)$

(A) Cyclopentadienyl Plane 1

$-0.1060X - 0.8436Y - 0.5263Z = -6.7958$

C(11)*	0.002 (11)	C(16)	−0.073 (14)
C(12)*	0.001 (13)	C(17)	−0.081 (18)
C(13)*	−0.004 (13)	C(18)	−0.130 (18)
C(14)*	0.005 (12)	C(19)	−0.203 (15)
C(15)*	−0.004 (11)	C(20)	−0.189 (14)
Ta(1)	2.1136 (4)	C(21)	−1.648 (17)
Cl(1)	3.053 (4)	Cl(2)	2.836 (3)

(B) Cyclopentadienyl Plane 2

$0.6662X + 0.7457Y - 0.006Z = -1.1796$

C(31)*	−0.005 (16)	C(36)	−0.227 (23)
C(32)*	0.006 (15)	C(37)	−0.093 (23)
C(33)*	−0.004 (13)	C(38)	−0.177 (17)
C(34)*	0.000 (12)	C(39)	−0.104 (17)
C(35)*	0.003 (13)	C(40)	−0.127 (16)
Ta(2)	2.1254 (5)	C(41)	−1.585 (22)
Cl(3)	2.839 (5)	Cl(4)	2.787 (4)

(C) Ta(1)–C(1)–O System

$-0.5329X + 0.5241Y - 0.6644Z = 0.1652$

(D) Ta(2)–C(1)–O System

$0.4898X + 0.8456Y - 0.2122Z = 1.4022$

(E) Cl(3)–Ta(2)–Cl(4) Plane

$-0.8143X - 0.4623Y - 0.3511Z = -0.1352$

(F) Cl(1)–Ta(1)–Cl(2) Plane

$-0.5970X - 0.7248Y - 0.3438Z = -4.1374$

Dihedral Angles of Note (Deg)

A/F	31.16	C/F	80.40
B/E	152.27	D/E	35.67
C/D	71.15	E/F	19.62

[a] Atoms used in calculating the plane are marked with an asterisk. Planes are in Cartesian (Å) coordinates.

scattering factors for neutral atoms was used;[15a] the contribution of all nonhydrogen atoms were corrected for both the real and imaginary components of anomalous dispersion.[15b]

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

Results and Discussions

Intramolecular distances are shown in Table IV, while interatomic angles are collected in Table V and least-squares planes are presented in Table VI. The atomic labeling scheme is indicated by Figure 1.

The molecule contains two tantalum atoms [Ta(1)–Ta(2) = 3.186 (1) Å], each of which is linked to an $\eta^5\text{-}C_5Me_4Et$ ligand [Ta(1)···Cp(1)[16] = 2.115 Å, Ta(2)···Cp(2) = 2.112 Å] and to two terminal chloride ligands [Ta(1)–Cl(1) = 2.360 (4) Å, Ta(1)–Cl(2) = 2.387 (4) Å; Ta(2)–Cl(3) = 2.364 (4) Å, Ta(2)–Cl(4) = 2.339 (4) Å]. In addition, the two tantalum atoms are bridged by a μ-, η^2-, $\eta^{2'}$-formyl ligand and, we believe, by a μ-hydride ligand[17] (which was *not* located directly in the course of the structural analysis).

The two tantalum atoms are *not* equivalent, and the molecule has only C_1 symmetry. The overall structure has many similarities to that of $[(\eta^5\text{-}C_5Me_4Et)TaCl_2]_2(\mu\text{-}H)(\mu\text{-}CHPMe_3)(\mu\text{-}O)$,[7] particularly if we regard the formyl ligand as occupying *two* coordination positions on each tantalum atom. Within the framework of this description, each tantalum atom has a "3,4,1" coordination geometry. (Here the "3" represents the three formal coordination sites occupied by the cyclopentadienyl ligand; there are 4 "radial" ligands and 1 unique "axial" ligand trans to the Cp centroid.)

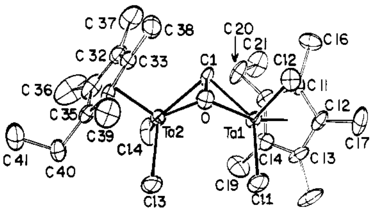


Figure 1. Labeling of atoms in the $[(\eta^5\text{-}C_5Me_4Et)TaCl_2]_2(\mu\text{-}H)(\mu\text{-}CHO)$ molecule (ORTEP-II diagram; 30% ellipsoids).

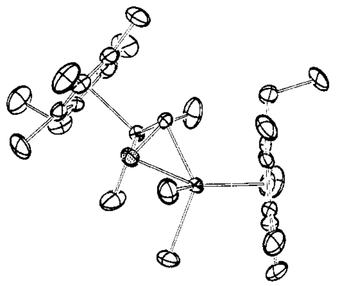


Figure 2. $[(\eta^5\text{-}C_5Me_4Et)TaCl_2]_2(\mu\text{-}H)(\mu\text{-}CHO)$ molecule viewed edge-on to the cyclopentadienyl systems. Note the four radial ligands on Ta(2) (left of diagram) and the three radial and one axial ligand on Ta(1). The oxygen atom is stippled. (ORTEP-II diagram.)

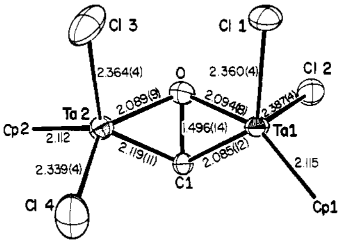


Figure 3. Distances within the molecular core.

Around Ta(2), the Cp(2)–Ta(2)–L angles are equivalent [Cp(2)–Ta(2)–Cl(3) = 107.8°, Cp(2)–Ta(2)–Cl(4) = 105.7°, Cp(2)–Ta(2)–O = 105.7°, Cp(2)–Ta(2)–C(1) = 106.1°], and the bridging hydride ligand presumably is associated with an *axial* site on Ta(2) such that Cp(2)–Ta(2)–H ~ 180°. Angles between the radial ligands are close to symmetrical: the restricted angle C(1)–Ta(2)–O is only 41.6 (4)°, but other cis angles are Cl(3)–Ta(2)–Cl(4) = 102.1 (2)°, Cl(3)–Ta(2)–O = 92.6 (3), and Cl(4)–Ta(2)–C(1) = 103.8 (3); the trans diradial angles are Cl(3)–Ta(2)–C(1) = 129.1 (3)° and Cl(4)–Ta(2)–O = 139.0 (3)°.

The observable interligand angles around Ta(1) fall into a far less symmetrical pattern. Thus, three of the observed Cp(1)–Ta(1)–L angles are close to equivalent, but the fourth is not [Cp(1)–Ta(1)–Cl(1) = 111.9°, Cp(1)–Ta(1)–Cl(2) = 106.4°, Cp(1)–Ta(1)–C(1) = 114.1°, as compared to Cp(1)–Ta(1)–O = 156.0°]. In this case it appears that the formyl system is attempting to span a radial and an axial site and that the μ-hydride ligand is associated with a *radial* site on Ta(1). A perusal of the diradial angles around Ta(1) confirms this assumption. While the angles Cl(1)–Ta(1)–Cl(2) and Cl(2)–Ta(1)–C(1) are close to 90° [93.9 (1) and 92.3 (3)°, respectively], and angle Cl(1)–Ta(1)–C(1) is increased to 129.5 (3)°; the μ-hydride ligand presumably occupies this "hole" in the coordination surface of Ta(1) in such a manner that the trans diradial Cl(2)–Ta(1)–H angle is comparable

---

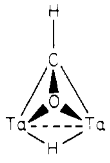
(15) "International Tables for X-Ray Crystallography"; Kynoch Press: Birmingham, England, 1974; Vol. IV: (a) pp 99–101; (b) pp 149–150.

(16) Cp(1) is the centroid of the cyclopentadienyl system defined by atoms C(11)–C(15); Cp(2) is the centroid of the C(31)–C(35) system.

(17) Both μ-hydride and the hydrogen atom of the μ-formyl group were detected by ^1H and ^{13}C NMR studies (see ref 6).

to the trans diradial Cl(1)-Ta(1)-C(1) angle of 129.5 (3)°.

The distribution of observable ligands about the two tantalum atoms is clearly shown in Figure 2; the μ-hydride ligand bridges an axial site on Ta(2) and a radial site on Ta(1). The Ta(μ-H)(μ-CHO)Ta core may be drawn as in **8**.



8

We now come to a consideration of the bridging formyl ligand. As shown in Figure 3, this ligand (although not occupying equivalent sites on the two tantalum atoms; vide supra) appears to bonded to the two tantalum atoms with essentially equivalent metal-ligand distances (Å): Ta(1)-C(1) = 2.085 (12) and Ta(2)-C(1) = 2.119 (11); Ta(1)-O = 2.094 (8) and Ta(2)-O = 2.089 (9). The Ta(1)-C(1)-Ta(2) and Ta(1)-O-Ta(2) angles are (respectively) 98.6 (5) and 99.2 (4)°; the Ta(1)-[C(1)-O]-Ta(2) system has a "butterfly" geometry in which the Ta(1)-C(1)-O plane is displaced by 71.15° from coplanarity with the Ta(2)-C(1)-O system.

The C(1)-O distance of 1.496 (14) Å is unusually long for a carbon-oxygen single bond. (The average C-O bond length in alcohols, ethers, or epoxides is 1.43 Å;[18] Pauling[19] suggests r(C) = 0.772 Å and r(O) = 0.66 Å, also predicting d(C-O) = 1.43 Å.) This activation of the C(1)-O bond is consistent with the observation that it is cleaved by attack of PMe_3 on C(1) [see last step of Scheme I].

All other distances and angles in the molecule are normal.

Acknowledgment. This work has been supported by the National Science Foundation (Grant CHE80-23448, to M.R.C.). We are most grateful to Patricia Belmonte for her persistent efforts in obtaining crystals of this complex and to Professor R. R. Schrock for his continuing interest in these studies.

Registry No. 4, 74167-06-9.

Supplementary Material Available: A listing of observed and calculated structure factor amplitudes (21 pages). Ordering information is given on any current masthead page.

---

(18) "Interatomic Distances", *Spec. Publ.-Chem. Soc.* **1965**, *No. 18*, S20s.

(19) Pauling, L. "The Nature of the Chemical Bond", 3rd ed.; Cornell University Press: Ithaca, NY, 1960; Table 7-2, p 224.

Contribution from the Department of Chemistry, University of Arizona, Tucson, Arizona 85721,
and Laboratoire de Chimie de Coordination du CNRS, Associé à l'Université Paul Sabatier, 31400 Toulouse, France

Oxygen Atom Transfer Reactions. 2. Reaction of Carbon Monoxide with $Ni(NO_2)_2(PMe_3)_2$: Structure of Nitronitrosylbis(trimethylphosphine)nickel, $Ni(NO_2)(NO)(PMe_3)_2$

J. KRIEGE-SIMONDSEN,[1a] G. ELBAZE,[1b] M. DARTIGUENAVE,[1b] R. D. FELTHAM,*[1a]
and Y. DARTIGUENAVE[1b]

Received May 19, 1981

The reaction between CO and $Ni(NO_2)_2(PMe_3)_2$, which forms CO_2 and $Ni(NO_2)(NO)(PMe_3)_2$ as final products, is associative and indicates the presence of $Ni(NO_2)_2(CO)(PMe_3)_2$ as an intermediate or transition state. The crystal and molecular structure of $Ni(NO_2)(NO)(PMe_3)_2$ has been determined by single-crystal X-ray diffraction at 293 and 135 K. This compound crystallizes in the monoclinic space group $C_{2h}^5 - P2_1/c$ with four molecules in a unit cell of dimensions a = 7.751 (2) Å, b = 12.611 (3) Å, c = 14.328 (4) Å, and β = 96.93 (3)° at 293 K and a = 7.648 (5) Å, b = 12.468 (11) Å, c = 13.956 (11) Å, and β = 95.88 (6)° at 135 K. Full-matrix least-squares refinement of the 293 K data set based on 1811 unique reflections having $F_o^2 > 3\sigma(F_o^2)$ converged with R_1 = 0.0456 and R_2 = 0.0713. The room-temperature structure consists of discrete $Ni(NO_2)(NO)(PMe_3)_2$ molecules with distorted tetrahedral geometry about the nickel atom. The P-Ni-P angle is 106.06 (7)°, and the N-Ni-N angle is 126.2 (3)°. Important interatomic distances are Ni-P(1) = 2.243 (2), Ni-P(2) = 2.243 (2), Ni-N(O_2) = 1.997 (6), and Ni-N(O) = 1.652 (7) Å. Except for the significantly shortened distance of 2.228 (3) Å found for Ni-P(1), the bond distances at 135 K do not differ from those at 293 K. Only minor differences in the bond angles were noted. The thermal parameters of the nitrosyl oxygen atom, O(3), are decreased significantly, with no indication of disorder of the nitrosyl ligand. The nonequivalent Ni-P distances observed at 135 K may be evidence of vibronic coupling with low-lying excited states of the complex.

Introduction

The recent isolation of pentacoordinate monocarbonyl complexes of divalent nickel, $NiX_2(CO)(PR_3)_2$ (X = halide; PR_3 = PMe_3, PMe_2Ph, $PMePh_2$, PPh_3), and the structural characterization of one of them,[2a] $Ni(CO)I_2(PMe_3)_2$, have prompted us to examine the reaction of $Ni(NO_2)_2(PMe_3)_2$ with CO.

The reaction of CO with the closely related complexes $Ni(NO_2)_2(PEt_3)_2$[2b,3] and $Ni(NO_2)_2(DPPE)$[4] (DPPE = $Ph_2PCH_2CH_2PPh_2$) has been studied in some detail and has been shown to proceed via reaction 1. Kinetic evidence

$$Ni(NO_2)_2L_2 + CO \rightarrow Ni(NO_2)(NO)L_2 + CO_2 \quad (1)$$

---

(1) (a) University of Arizona. (b) l'Université Paul Sabatier.

(2) (a) Saint-Joly, C.; Mari, A.; Gleizes, A.; Dartiguenave, M.; Dartiguenave, Y.; Galy, J. *Inorg. Chem.* **1980**, *19*, 2403. Saint-Joly, C.; Dartiguenave, M.; Dartiguenave, Y. *Adv. Chem. Ser.* **1979**, *No. 173*, 152. (b) Booth, G.; Chatt, J. *J. Chem. Soc.* **1962**, 2099.

(3) Doughty, D. T.; Gordon, G.; Stewart, R. P. *J. Am. Chem. Soc.* **1979**, *101*, 2645.

(4) Feltham, R. D.; Kriege, J. *J. Am. Chem. Soc.* **1979**, *101*, 5064.