J. Am. Chem. Soc. 1982, 104, 4879–4884

Crystal and Molecular Structures of *tert*-Butyltetrakis(dimethylamido)tantalum(V), Bromo(*p*-tolyl)tris(dimethylamido)tantalum(V), and [(Trimethylsilyl)methyl]tetrakis(*N*,*N*-dimethylcarbamato)tantalum(V). Evidence for Stabilization of σ-Alkyl Ligands by Strongly π-Donating Ligands in Early Transition Metal Chemistry

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Abstract: The preparations of the new compounds $Ta(NMe_2)_4R$ and $Ta(O_2CNMe_2)_4R$, where R = *t*-Bu, *i*-Pr, Et, and CH_2SiMe_3, and $Ta(NMe_2)_3(p\text{-tolyl})Br$ are reported from metathetic reactions involving chloro(dimethylamido)tantalum(V) compounds and organolithium reagents. The compounds are thermally stable at room temperature: the alkyl groups *t*-Bu, *i*-Pr, and Et do not show facile β-hydrogen elimination reactions. The structural characterizations of $Ta(NMe_2)_4(t\text{-Bu})$, $Ta(O_2CNMe_2)_4CH_2SiMe_3$, and $Ta(NMe_2)_3(p\text{-tolyl})Br$ are reported. The central TaN_4C skeleton of the $Ta(NMe_2)_4(t\text{-Bu})$ molecule is a square-based pyramid: the four nitrogen atoms lie in a plane 0.50 (2) Å below the tantalum atom. The C–Ta bond distance is 2.24 (2) Å, and the average N–Ta distance is 2.02 Å. The Ta atom is contained in the NC_2 planes of the dimethylamido ligands: the four dihedral angles between the C–Ta–N planes and their respective C–N–C planes fall within 42–52°. The $Ta(O_2CNMe_2)_4(CH_2SiMe_3)$ moleule has a pentagonal-bipyramidal central unit. Two bidentate carbamato ligands, the methylene carbon of the Me_3SiCH_2 ligand, and the Ta atom lie in the pentagonal plane, and monodentate carbamato ligands occupy axial positions with a trans O–Ta–O angle = 171.5 (2)°. The Ta–C distance is 2.171 (7) Å; the Ta–O equatorial distances are 2.132 (5), 2.131 (5), 2.146 (5), and 2.108 (5) Å; and the Ta–O axial distances are 1.932 (5) and 1.944 (5) Å. The central TaN_3CBr moiety of the $Ta(NMe_2)_3(p\text{-tolyl})Br$ molecule corresponds closely to a trigonal bipyramid with one dimethylamido ligand and the bromide in the axial positions: the Br–Ta–N angle is 173.1 (5)°. Pertinent bond distances are Ta–Br = 2.606 (3) Å, Ta–N (axial) = 1.97 (2) Å, Ta–N (equatorial) = 1.94 (2) and 1.95 (2) Å, and Ta–C = 2.18 (2) Å. The structural parameters associated with these three compounds indicate that ligand-to-metal π bonding is an important common feature. This effectively ties up metal d orbitals that would otherwise be available for C–H···M interactions, leading to β-hydrogen elimination reactions. This proposal, that strongly π-donating ligands, such as Me_2N^-, can stabilize σ-alkyl groups in early transition metal complexes, is discussed in light of previous published work. Crystal data for $Ta(NMe_2)_4(t\text{-Bu})$: space group $P2_1cn$, $a = 14.284$ (3) Å, $b = 8.261$ (2) Å, $c = 14.214$ (4) Å, $Z = 4$, and $d_c = 1.641$ g cm^{-3}; for $Ta(O_2CNMe_2)_4(CH_2SiMe_3)$: space group $P\bar{1}$, $a = 15.321$ (8) Å, $b = 9.801$ (6) Å, $c = 9.187$ (5) Å, $\alpha = 92.70$ (2)°, $\beta = 117.95$ (2)°, $\gamma = 88.57$ (2) Å, $d_c = 1.693$ g cm^{-3}; for $Ta(NMe_2)_3(p\text{-tolyl})Br$: space group $P2_1/n$, $a = 11.387$ (3) Å, $b = 19.440$ (8) Å, $c = 7.796$ (2) Å, $\beta = 102.84$ (1)°, $d_c = 1.912$ g cm^{-3}.

The ability of transition elements to abstract β-hydrogen atoms from coordinated σ-alkyl ligands is now well recognized,[1] and many early attempts to synthesize alkyl metal complexes failed because of kinetically facile decomposition pathways involving this reaction as the first step.[2] Even alkyl ligands lacking β-hydrogen atoms, so-called "β-elimination-stabilized alkyls", can undergo hydrogen abstraction at either the α- or γ-carbons, and the early transition elements have yielded a variety of interesting products derived from the former process.[3] We wish, on the basis of the chemistry described in this paper and that already to be found in the literature, to draw attention to the stabilizing influence that strong π-donor ligands can impart to alkyl complexes of the early transition elements. Strong π-donor ligands, such as Me_2N, π bond to metal atomic orbitals which otherwise would be available for mischievous M···H–C interactions.

Results and Discussion

Syntheses. $Ta(NMe_2)_4R$ Compounds. The simple metathetic reaction involving $TaCl(NMe_2)_4$ and organolithium reagents (1:1) carried out in hexane at ca. −40 °C has allowed the isolation of $Ta(NMe_2)_4R$ compounds, where R = CH_2SiMe_3, *t*-Bu, *i*-Pr, and Et, as pale yellow or off-white waxy solids or viscous liquids. All the new compounds are extremely air sensitive but thermally quite stable at room temperature and may be stored in vacuo or under a nitrogen atmosphere indefinitely. All the compounds are extremely soluble in aliphatic and aromatic hydrocarbon solvents. Elemental analyses and NMR characterization data are given in the Experimental Section.

$Ta(O_2CNMe_2)_4R$ Compounds. The addition of bone-dry CO_2 to $Ta(NMe_2)_4R$ compounds in hydrocarbon solvents leads to insertion into the Ta–NMe_2 bonds and the formation of $Ta(O_2CNMe_2)_4R$, where R = CH_2SiMe_3, *t*-Bu, *i*-Pr, and Et. This type of CO_2 insertion appears general for transition-metal dimethylamides.[4] The $Ta(O_2CNMe_2)_4R$ compounds are notably less soluble in hexane and pentane than their dimethylamido precursors, though they are soluble in benzene and toluene, which has allowed their characterization by NMR spectroscopy in these solvents. Characterization data are given in the Experimental Section.

$Ta(NMe_2)_3(p\text{-tolyl})Br$. This compound was obtained fortuitously from the reaction between $TaCl_2(NMe_2)_3$ and *p*-tolyllithium (2 equiv) in hexane. The ^1H NMR spectrum of crude-hexane-soluble products obtained from this reaction suggested the possibility of two species, one being $Ta(NMe_2)_3(p\text{-tolyl})_2$. Fractional crystallization yielded $Ta(NMe_2)_3(p\text{-tolyl})Br$ as the lesser soluble compound. The presence of a bromide ligand (deduced from X-ray work) instead of chloride was surprising, though not without precedent.[5] The source of bromide must be traced to impurities

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[3] Schrock, R. R. *Acc. Chem. Res.* **1979**, *12*, 98.

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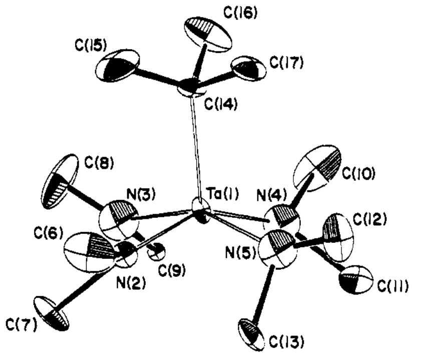

Figure 1. ORTEP view of the Ta(NMe$_2$)$_4$(*t*-Bu) molecule viewed perpendicular to the Ta–C axis, emphasizing the square-based pyramidal geometry of the central TaN$_4$C moiety and giving the atom numbering scheme used in the tables. Atoms are represented by thermal ellipsoids drawn at the 50% probability level.

Table I. Fractional Coordinates and Isotropic Thermal Parameters for the Ta(NMe$_2$)$_4$(*t*-Bu) Molecule[a]

atom	*x*	*y*	*z*	B_{iso}, Å^2
Ta(1)	−2500*	−1406 (1)	−886.6 (5)	12
N(2)	−1612 (19)	−3379 (28)	−745 (16)	23 (5)
N(3)	−3533 (17)	−2962 (30)	−807 (16)	19 (5)
N(4)	6711 (17)	63 (30)	8342 (16)	23 (5)
N(5)	−1382 (16)	−382 (25)	−1622 (15)	16 (4)
C(6)	−636 (19)	−3237 (32)	−391 (18)	27 (5)
C(7)	−1748 (21)	−5083 (35)	−1061 (19)	33 (6)
C(8)	−3667 (23)	−4102 (37)	−1 (22)	40 (6)
C(9)	5742 (19)	6655 (31)	8509 (18)	26 (5)
C(10)	−4241 (18)	454 (31)	−1411 (18)	24 (5)
C(11)	−3147 (19)	521 (33)	−2653 (20)	31 (5)
C(12)	−1183 (20)	1318 (34)	−1694 (19)	32 (5)
C(13)	−693 (21)	−1218 (33)	−2226 (20)	35 (6)
C(14)	−2391 (29)	−291 (21)	549 (12)	18 (4)
C(15)	−2081 (21)	−1487 (36)	1300 (22)	42 (6)
C(16)	−3390 (22)	225 (40)	849 (23)	41 (6)
C(17)	−1748 (21)	1198 (37)	551 (21)	37 (6)

[a] Fractional coordinates are ×10^4 for non-hydrogen atoms and ×10^3 for hydrogen atoms. B_{iso} values are ×10. Isotropic values for those atoms refined anisotropically are calculated by using the formula given by Hamilton (Hamilton, W. C. *Acta Crystallogr.* 1959, *12*, 609). Parameters marked by an asterisk were not varied.

Table II. Bond Distances (Å) for the Ta(NMe$_2$)$_4$(*t*-Bu) Molecule

Ta(1)–N(2)	2.07 (2)	N(3)–C(9)	1.46 (4)
Ta(1)–N(3)	1.96 (2)	N(4)–C(10)	1.44 (3)
Ta(1)–N(4)	1.99 (2)	N(4)–C(11)	1.48 (3)
Ta(1)–N(5)	2.09 (2)	N(5)–C(12)	1.44 (3)
Ta(1)–C(14)	2.24 (2)	N(5)–C(13)	1.48 (3)
N(2)–C(6)	1.49 (4)	C(14)–C(15)	1.52 (4)
N(2)–C(7)	1.49 (4)	C(14)–C(16)	1.55 (5)
N(3)–C(8)	1.49 (4)	C(14)–C(17)	1.54 (4)

Table III. Bond Angles (Deg) for the Ta(NMe$_2$)$_4$(*t*-Bu) Molecule

N(2)–Ta(1)–N(3)	86 (1)	Ta(1)–N(3)–C(9)	130 (2)
N(2)–Ta(1)–N(4)	152 (1)	C(8)–N(3)–C(9)	106 (2)
N(2)–Ta(1)–N(5)	84 (1)	Ta(1)–N(4)–C(10)	123 (2)
N(2)–Ta(1)–C(14)	101 (1)	Ta(1)–N(4)–C(11)	127 (2)
N(3)–Ta(1)–N(4)	90 (1)	C(10)–N(4)–C(11)	108 (2)
N(3)–Ta(1)–N(5)	150 (1)	Ta(1)–N(5)–C(12)	126 (2)
N(3)–Ta(1)–C(14)	106 (1)	Ta(1)–N(5)–C(13)	128 (2)
N(4)–Ta(1)–N(5)	85 (1)	C(12)–N(5)–C(13)	106 (2)
N(4)–Ta(1)–C(14)	107 (1)	Ta(1)–C(14)–C(15)	113 (2)
N(5)–Ta(1)–C(14)	104 (1)	Ta(1)–C(14)–C(16)	107 (2)
Ta(1)–N(2)–C(6)	123 (2)	Ta(1)–C(14)–C(17)	112 (2)
Ta(1)–N(2)–C(7)	129 (2)	C(15)–C(14)–C(16)	105 (2)
C(6)–N(2)–C(7)	107 (2)	C(15)–C(14)–C(17)	110 (3)
Ta(1)–N(3)–C(8)	124 (2)	C(16)–C(14)–C(17)	109 (2)

Table IV. Fractional Coordinates and Isotropic Thermal Parameters for the Ta(NMe$_2$)$_3$(*p*-tolyl)Br Molecule[a]

atom	*x*	*y*	*z*	B_{iso}, Å^2
Ta(1)	5425.3 (4)	1771.7 (2)	1284 (1)	11
Br(2)	6303 (1)	1780 (1)	4667 (2)	29
N(3)	5321 (9)	2761 (5)	1136 (13)	18 (2)
C(4)	5777 (13)	3278 (7)	123 (20)	29 (2)
C(5)	4529 (13)	3057 (7)	2189 (19)	26 (2)
N(6)	6819 (8)	1267 (5)	892 (12)	17 (2)
C(7)	7313 (12)	645 (7)	1878 (19)	26 (2)
C(8)	7506 (11)	1452 (7)	9553 (16)	21 (2)
N(9)	4625 (8)	1685 (5)	−1250 (13)	16 (1)
C(10)	3793 (13)	2186 (8)	−2330 (19)	29 (2)
C(11)	4517 (12)	1023 (7)	−2140 (18)	25 (2)
C(12)	3927 (9)	1191 (6)	1920 (14)	14 (2)
C(13)	4096 (10)	597 (6)	2959 (15)	16 (2)
C(14)	3112 (10)	200 (6)	3254 (14)	16 (2)
C(15)	1940 (10)	425 (6)	2546 (14)	16 (2)
C(16)	1761 (11)	1027 (6)	1537 (16)	21 (2)
C(17)	2714 (10)	1396 (6)	1236 (15)	18 (2)
C(18)	883 (11)	8 (7)	2857 (17)	25 (2)

[a] Fractional coordinates are ×10^4 for non-hydrogen atoms and ×10^3 for hydrogen atoms. B_{iso} values are ×10. Isotropic values for those atoms refined anisotropically are calculated by using the formula given by Hamilton (Hamilton, W. C. *Acta Crystallogr.* 1959, *12*, 609). Parameters marked by an asterisk were not varied.

in the *p*-tolyllithium, which was prepared from the reaction between *p*-tolyl bromide and *n*-butyllithium. A logical synthesis of this compound has not been attempted, but because of the solubility differences between Ta(NMe$_2$)$_3$(*p*-tolyl)$_2$ and Ta(NMe$_2$)$_3$(*p*-tolyl)Br, reactions employing TaCl$_2$(NMe$_2$)$_3$ and 1 equiv of *p*-tolyllithium in the presence of LiBr should prove successful. Analytical data and ^{1}H NMR data are given in the Experimental Section.

Solid-State Structures. Ta(NMe$_2$)$_4$(*t*-Bu). An ORTEP view of the Ta(NMe$_2$)$_4$(*t*-Bu) molecule found in the crystalline state is shown in Figure 1. Final atomic positional parameters are given in Table I. Anisotropic thermal parameters are available in the supplementary data. Bond distances and angles are given in Tables II and III, respectively.

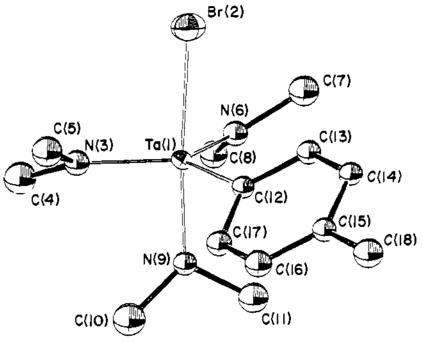

Figure 2. ORTEP view of the Ta(NMe$_2$)$_3$(*p*-tolyl)(Br) molecule, emphasizing the trigonal-bipyramidal geometry of the central TaN$_3$CBr moiety and giving the atom numbering scheme used in the tables. Atoms are represented by thermal ellipsoids drawn at the 50% probability level.

The central TaN$_4$C skeleton corresponds closely to an idealized square-based pyramid. Within the limits of experimental error, the four nitrogen atoms lie in a plane 0.50 (2) Å below the tantalum atom. The tantalum atom is contained in each of the four NC$_2$ planes associated with the planar Me$_2$N ligands. The four dihedral angles between the C–Ta–N planes and the respective C–N–C planes fall within the range 42–52°. The Ta–N–C angles may be classified as proximal for those directed toward the *t*-Bu ligand and distal for those directed away from it. The former are slightly larger than the latter, an observation that can readily be explained by steric repulsive interactions. Finally, it should be noted that the molecule has no overall elements of symmetry

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Table V. Bond Distances (A) for the $Ta(NMe_2)_3(p\text{-tolyl})Br$ Molecule

Ta(1)-Br(2)	2.606 (3)	N(9)-C(10)	1.48 (3)
Ta(1)-N(3)	1.94 (2)	N(9)-C(11)	1.43 (3)
Ta(1)-N(6)	1.95 (2)	C(12)-C(13)	1.44 (3)
Ta(1)-N(9)	1.97 (2)	C(12)-C(17)	1.44 (3)
Ta(1)-C(12)	2.18 (2)	C(13)-C(14)	1.44 (3)
N(3)-C(4)	1.43 (3)	C(14)-C(15)	1.38 (3)
N(3)-C(5)	1.50 (3)	C(15)-C(16)	1.43 (3)
N(6)-C(7)	1.48 (3)	C(15)-C(18)	1.55 (3)
N(6)-C(8)	1.47 (3)	C(16)-C(17)	1.39 (3)

Table VI. Bond Angles (Deg) for the $Ta(NMe_2)_3(p\text{-tolyl})Br$ Molecule

Br(2)-Ta(1)-N(3)	94.2 (5)	C(7)-N(6)-C(8)	112 (2)
Br(2)-Ta(1)-N(6)	91.6 (5)	Ta(1)-N(9)-C(10)	125 (1)
Br(2)-Ta(1)-N(9)	173.1 (5)	Ta(1)-N(9)-C(11)	123 (1)
Br(2)-Ta(1)-C(12)	85.6 (5)	C(10)-N(9)-C(11)	110 (2)
N(3)-Ta(1)-N(6)	121.6 (6)	Ta(1)-C(12)-C(13)	122 (1)
N(3)-Ta(1)-N(9)	90.1 (7)	Ta(1)-C(12)-C(17)	120 (1)
N(3)-Ta(1)-C(12)	119.0 (7)	C(13)-C(12)-C(17)	118 (2)
N(6)-Ta(1)-N(9)	90.7 (6)	C(12)-C(13)-C(14)	120 (2)
N(6)-Ta(1)-C(12)	119.4 (7)	C(13)-C(14)-C(15)	120 (2)
N(9)-Ta(1)-C(12)	87.6 (7)	C(14)-C(15)-C(16)	120 (2)
Ta(1)-N(3)-C(4)	135 (1)	C(14)-C(15)-C(18)	120 (2)
Ta(1)-N(3)-C(5)	112 (1)	C(16)-C(15)-C(18)	120 (2)
C(4)-N(3)-C(5)	112 (1)	C(15)-C(16)-C(17)	121 (2)
Ta(1)-N(6)-C(7)	123 (1)	C(12)-C(17)-C(16)	120 (2)
Ta(1)-N(6)-C(8)	125 (1)		

Table VII. Fractional Coordinates and Isotropic Thermal Parameters for the $Ta(CH_2SiMe_3)(O_2CNMe_2)_4$ Molecule[a]

atom	x	y	z	B_{iso}, A^2
Ta(1)	2632.2 (2)	3164.7 (3)	122.9 (3)	13
C(2)	1206 (5)	2969 (7)	54 (9)	18
Si(3)	71 (1)	2459 (2)	−1883 (3)	19
C(4)	222 (6)	741 (9)	−2756 (12)	36
C(5)	−990 (6)	2309 (8)	−1408 (11)	27
C(6)	−265 (6)	3791 (9)	−3456 (11)	32
O(7)	2698 (3)	1169 (5)	935 (6)	16
O(8)	3966 (3)	2025 (5)	849 (6)	17
C(9)	3615 (5)	1007 (7)	1263 (8)	15
N(10)	4129 (4)	−72 (6)	1936 (7)	17
C(11)	3722 (6)	−1121 (7)	2512 (9)	21
C(12)	5174 (6)	−172 (8)	2381 (10)	25
O(13)	1943 (4)	5069 (5)	−812 (6)	18
O(14)	3466 (4)	4696 (5)	−290 (6)	19
C(15)	2729 (5)	5543 (7)	−802 (8)	16
N(16)	2762 (5)	6770 (6)	−1305 (8)	22
C(17)	1888 (6)	7679 (7)	−1909 (10)	27
C(18)	3667 (7)	7291 (8)	−1222 (10)	27
O(19)	2249 (3)	2458 (5)	−2092 (5)	15
O(20)	2809 (4)	392 (5)	−2397 (7)	23
C(21)	2435 (5)	1477 (7)	−2973 (9)	16
N(22)	2162 (5)	1813 (6)	−4537 (7)	19
C(23)	1678 (6)	3090 (8)	−5225 (10)	25
C(24)	2300 (6)	824 (8)	−5658 (9)	23
O(25)	3219 (4)	3869 (5)	2395 (6)	18
O(26)	4289 (4)	2549 (5)	4384 (6)	22
C(27)	3830 (5)	3621 (7)	3961 (9)	18
N(28)	3896 (4)	4660 (6)	5019 (7)	19
C(29)	4503 (6)	4506 (9)	6796 (10)	30
C(30)	3334 (6)	5919 (8)	4512 (10)	25

[a] Fractional coordinates are $\times 10^4$. B_{iso} values are $\times 10$. Isotropic values for those atoms refined anisotropically are calculated by using the formula given by Hamilton (Hamilton, W. C. *Acta Crystallogr.* **1959**, *12*, 609).

Table VIII. Bond Distances (A) for the $Ta(CH_2SiMe_3)(O_2CNMe_2)_4$ Molecule

Ta(1)-O(7)	2.108 (5)	O(19)-C(21)	1.332 (9)
Ta(1)-O(8)	2.132 (5)	O(20)-C(21)	1.222 (9)
Ta(1)-O(13)	2.131 (5)	O(25)-C(27)	1.327 (10)
Ta(1)-O(14)	2.146 (5)	O(26)-C(27)	1.233 (10)
Ta(1)-O(19)	1.932 (5)	N(10)-C(9)	1.298 (10)
Ta(1)-O(25)	1.944 (5)	N(10)-C(11)	1.477 (10)
Ta(1)-C(2)	2.171 (7)	N(10)-C(12)	1.464 (11)
Ta(1)-C(9)	2.529 (8)	N(16)-C(15)	1.321 (10)
Ta(1)-C(15)	2.549 (8)	N(16)-C(17)	1.473 (11)
Si(3)-C(2)	1.880 (8)	N(16)-C(18)	1.460 (11)
Si(3)-C(4)	1.893 (9)	N(22)-C(21)	1.352 (10)
Si(3)-C(5)	1.896 (9)	N(22)-C(23)	1.475 (10)
Si(3)-C(6)	1.880 (10)	N(22)-C(24)	1.470 (10)
O(7)-C(9)	1.302 (9)	N(28)-C(27)	1.342 (10)
O(8)-C(9)	1.288 (10)	N(28)-C(29)	1.474 (11)
O(13)-C(15)	1.296 (10)	N(28)-C(30)	1.462 (11)
O(14)-C(15)	1.290 (10)		

Table IX. Bond Angles (Deg) for the $Ta(CH_2SiMe_3)(O_2CNMe_2)_4$ Molecule

O(7)-Ta(1)-O(8)	61.5 (2)	C(4)-Si(3)-C(6)	111.3 (5)
O(7)-Ta(1)-O(13)	155.1 (2)	C(5)-Si(3)-C(6)	108.0 (5)
O(7)-Ta(1)-O(14)	144.0 (2)	Ta(1)-O(7)-C(9)	92.7 (4)
O(7)-Ta(1)-O(19)	90.7 (2)	Ta(1)-O(8)-C(9)	92.0 (4)
O(7)-Ta(1)-O(25)	90.0 (2)	Ta(1)-O(13)-C(15)	92.9 (4)
O(7)-Ta(1)-C(2)	77.6 (3)	Ta(1)-O(14)-C(15)	92.4 (5)
O(7)-Ta(1)-C(9)	30.9 (2)	Ta(1)-O(19)-C(21)	143.6 (5)
O(7)-Ta(1)-C(15)	174.4 (2)	Ta(1)-O(25)-C(27)	146.2 (5)
O(8)-Ta(1)-O(13)	143.4 (2)	C(9)-N(10)-C(11)	120.7 (7)
O(8)-Ta(1)-O(14)	82.5 (2)	C(9)-N(10)-C(12)	121.3 (7)
O(8)-Ta(1)-O(19)	86.7 (2)	C(11)-N(10)-C(12)	117.3 (7)
O(8)-Ta(1)-O(25)	86.2 (2)	C(15)-N(16)-C(17)	120.6 (8)
O(8)-Ta(1)-C(2)	138.9 (3)	C(15)-N(16)-C(18)	121.5 (7)
O(8)-Ta(1)-C(9)	30.6 (2)	C(17)-N(16)-C(18)	118.0 (7)
O(8)-Ta(1)-C(15)	112.9 (2)	C(21)-N(22)-C(23)	122.7 (7)
O(13)-Ta(1)-O(14)	60.9 (2)	C(21)-N(22)-C(24)	120.6 (7)
O(13)-Ta(1)-O(19)	90.2 (2)	C(23)-N(22)-C(24)	116.6 (7)
O(13)-Ta(1)-O(25)	92.7 (2)	C(27)-N(28)-C(29)	120.1 (7)
O(13)-Ta(1)-C(2)	77.6 (3)	C(27)-N(28)-C(30)	123.8 (7)
O(13)-Ta(1)-C(9)	173.9 (2)	C(29)-N(28)-C(30)	116.0 (7)
O(13)-Ta(1)-C(15)	30.5 (2)	Ta(1)-C(2)-Si(3)	121.4 (4)
O(14)-Ta(1)-O(19)	87.5 (2)	Ta(1)-C(9)-O(7)	56.4 (4)
O(14)-Ta(1)-O(25)	87.0 (2)	Ta(1)-C(9)-O(8)	57.4 (4)
O(14)-Ta(1)-C(2)	138.2 (3)	Ta(1)-C(9)-N(10)	176.2 (6)
O(14)-Ta(1)-C(9)	113.1 (2)	O(7)-C(9)-O(8)	113.6 (6)
O(14)-Ta(1)-C(15)	30.4 (2)	O(7)-C(9)-N(10)	123.1 (7)
O(19)-Ta(1)-O(25)	171.5 (2)	O(8)-C(9)-N(10)	123.3 (7)
O(19)-Ta(1)-C(2)	97.6 (3)	Ta(1)-C(15)-O(13)	56.6 (4)
O(19)-Ta(1)-C(9)	89.8 (2)	Ta(1)-C(15)-O(14)	57.2 (4)
O(19)-Ta(1)-C(15)	88.9 (2)	Ta(1)-C(15)-N(16)	179.0 (6)
O(25)-Ta(1)-C(2)	90.8 (3)	O(13)-C(15)-O(14)	113.9 (7)
O(25)-Ta(1)-C(9)	86.4 (2)	O(13)-C(15)-N(16)	122.5 (7)
O(25)-Ta(1)-C(15)	89.6 (2)	O(14)-C(15)-N(16)	123.6 (7)
C(2)-Ta(1)-C(9)	108.4 (3)	O(19)-C(21)-O(20)	122.4 (7)
C(2)-Ta(1)-C(15)	108.0 (3)	O(19)-C(21)-N(22)	113.9 (6)
C(9)-Ta(1)-C(15)	143.4 (3)	O(20)-C(21)-N(22)	123.7 (7)
C(2)-Si(3)-C(4)	111.7 (4)	O(25)-C(27)-O(26)	122.3 (7)
C(2)-Si(3)-C(5)	108.4 (4)	O(25)-C(27)-N(28)	113.7 (7)
C(2)-Si(3)-C(6)	110.3 (4)	O(26)-C(27)-N(28)	124.0 (8)
C(4)-Si(3)-C(5)	107.0 (4)		

despite the fact that the local TaN_4C unit is close to C_{4v}. This too is expected since the imposition of a *tert*-butyl group, which is a threefold rotor, C_3, upon a four-bladed propeller $Ta(NC_2)_4$ destroys all possibilities for symmetry other than the trivial, E.

$Ta(NMe_2)_3(p\text{-tolyl})Br$. An ORTEP view of the $Ta(NMe_2)_3(p\text{-tolyl})Br$ molecule is shown in Figure 2. Final atomic positional parameters are given in Table IV. Bond distances and angles are given in Tables V and VI, respectively. The central TaN_3CBr unit corresponds closely to an idealized trigonal bipyramid, as evidenced by the fact that the sum of the angles N(3)–Ta(1)–N(6), N(6)–Ta(1)–C(12), and N(3)–Ta(1)–C(12) = 360°, within the limits of experimental error, and the trans angle N(9)–Ta(1)–Br(2) = 173.1 (5)°.

$Ta(O_2CNMe_2)_4(CH_2SiMe_3)$. An ORTEP view of the $Ta(O_2CNMe_2)_4(CH_2SiMe_3)$ molecule is shown in Figure 3. Final atomic positional parameters are given in Table VII. Anisotropic thermal parameters are available in the supplementary data. Bond distances and bond angles are given in Tables VIII and IX, respectively. The central TaO_6C skeleton corresponds closely to an idealized pentagonal bipyramid. The tantalum atom, the

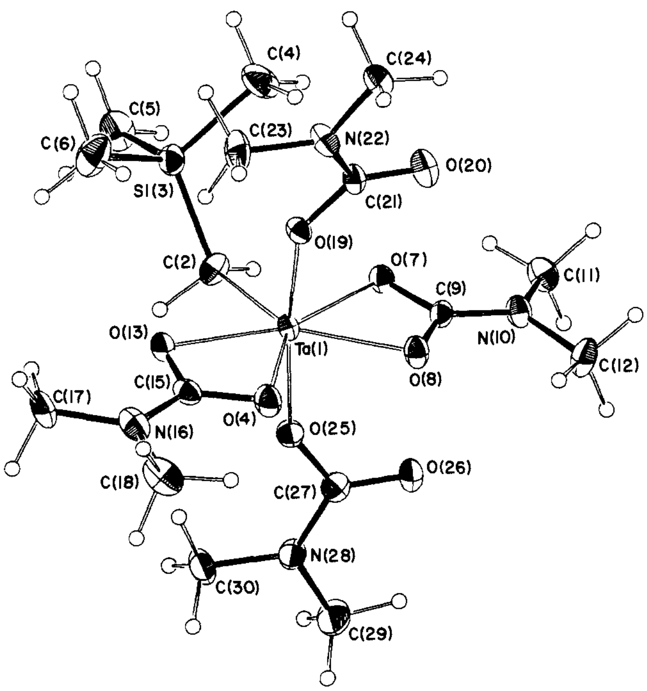

Figure 3. ORTEP view of the $Ta(O_2CNMe_2)_4(CH_2SiMe_3)$ molecule, viewed almost perpendicular to the pentagonal plane which contains the Ta–C bond and the two bidentate O_2CNMe_2 ligands, showing the atom numbering scheme used in the tables. Atoms are represented by thermal ellipsoids drawn at the 50% probability level.

methylene carbon atom of the $(CH_3)_3SiCH_2$ ligand, C(2), and the four oxygen atoms of the bidentate O_2CNMe_2 ligands, O(7), O(8), O(13), and O(14), are coplanar to within 0.05 (2) Å. The trans O(19)–Ta(1)–O(25) angle is 171.5 (2)°, and the six nonhydrogen atoms of each O_2CNMe_2 ligand are essentially coplanar.

Comparisons with Related Structures. The structure of $Ta(NMe_2)_4(t\text{-}Bu)$ is closely related to that found[6] for $Nb(NMe_2)_5$ and $Nb(NC_5H_{10})_5$, where NC_5H_{10} is piperidide. The latter two molecules have NbN_5 skeletons that come close to an idealized square-based pyramid. In $Ta(NMe_2)_4(t\text{-}Bu)$, the *tert*-butyl group replaces the axial NR_2 ligand. The average angles subtended at tantalum and the average Ta–N distances are the same, within the limits of experimental error, as the related parameters for $Nb(NMe_2)_5$. The energy difference between the square-based pyramid and trigonal-bipyramid geometries in these d^0 complexes is evidently small, since the related $Ta(NEt_2)_5$ molecule has a close to idealized trigonal-bipyramidal TaN_5 moiety.[7] Furthermore, the structure of $Ta(NSi_2Me_6)_2Cl_3$ has a trigonal-bipyramidal TaN_2Cl_3 unit in which the two silylamido ligands occupy equatorial positions[8] (N–Ta–N = 115°). There is little difference between equatorial and axial Ta–Cl bond distances. The structures of $Ta(NSi_2Me_6)_2Cl_3$ and $Ta(NMe_2)_3(p\text{-tolyl})(Br)$ are thus closely related.

The structure of $Ta(O_2CNMe_2)_4(CH_2SiMe_3)$ is closely related to that found[9] for $Ta(NMe_2)_2(O_2CNMe_3)_3$. Both adopt pentagonal-bipyramidal structures by the use of two bidentate O_2CNMe_2 ligands that coordinate in the pentagonal plane. The key feature to these and the other structures described here is ligand-to-metal π bonding.

Structural Evidence for Ligand-to-Tantalum π Bonding. Direct structurual evidence for ligand(Me_2N or Me_2NCO_2)-to-tantalum π bonding can be obtained from the metal–ligand distances reported here and a comparison of these with those found in related compounds. We use here an argument that has previously[10] been applied to $M_2R_2(NMe_2)_4$ compounds (M = Mo and W). The electronegativities of carbon and nitrogen are sufficiently similar that their bond lengths to a common third atom, Ta, should not be differently affected to any significant extent by ionic character. Hence, one should safely predict that a Ta–NMe_2 pure σ bond will be shorter than a Ta–R (alkyl) bond by the difference between the covalent radii for sp^3-hybridized carbon (0.77 Å) and sp^2-hybridized nitrogen (0.67 Å). The Ta–N and Ta–C bond distances in $Ta(NMe_2)_4(t\text{-}Bu)$ differ by 0.2 Å, which suggests that a roughly 0.1 Å shortening may be due to π bonding, Me_2N-p to Ta-d. In a square-based pyramid, the basal and axial ligands use different metal d orbitals to form σ bonds, and this factor may be expected to lead to small differences in bond length even for an idealized ML_5 molecule. In $Nb(NMe_2)_5$ and $Nb(NC_5H_{10})_5$, the axial M–N distance is shorter by 0.05 Å (averaged) relative to the M–N basal distances. It could then be that the shortening of the Ta–N bonds due to π bonding is greater than the 0.1 Å, which is based solely on considerations of the covalent radii of sp^2 nitrogen and sp^3 carbon. In the $Ta(NMe_2)_3(p\text{-tolyl})(Br)$ molecule, the equatorial Ta–N_{sp^2} and Ta–C_{sp^2} distances differ by 0.2 Å. Here it is safe to say that there is relatively little, if any, Ta–tolyl π bonding and that the markedly shorter Ta–N bond distances reflect a high degree of Ta–N double character. It may also be noted that the average Ta–N bond distance in $Ta(NMe_2)_3(p\text{-tolyl})(Br)$ is shorter than the average Ta–N bond distance in $Ta(NMe_2)_4(t\text{-}Bu)$ by ca. 0.05 Å. This can be understood in terms of (i) the introduction of a more electron-withdrawing group, Br, for NMe_2 (assuming the substitution of *p*-tolyl for *t*-Bu has a minimal effect) and (ii) the fact that counting the Me_2N^- ligand as a four-electron donor, $\sigma^2\pi^2$, allows tantalum to achieve 18 valence shell electrons in $Ta(NMe_2)_4(t\text{-}Bu)$, whereas in $Ta(NMe_2)_3(p\text{-tolyl})(Br)$ only a 16 valence shell of electrons is achieved. In the latter molecule, Me_2N-to-Ta π donation is expected to be enhanced on both accounts. Finally, it should be recognized that the Ta–N distance is less than the Ta=C_{sp^2} distance, 2.03 (1) Å, found in $Cp_2Ta(=CH_2)(CH_3)$.[3]

The structural evidence for O-to-Ta π bonding in $Ta(O_2CNMe_2)_4(CH_2SiMe_3)$ is particularly fascinating. The Ta–O distances to the monodentate O_2CNMe_2 ligands are short, 1.94 Å (averaged), comparable to those in the linear μ-oxo bridged dimer $[(Me_2NH)Cl_2(Me_2N)_2Ta]_2O$.[16] The Ta–O distance of 1.94 Å may be compared with Ta–O = 2.052 (6) Å for the monodentate O_2CNMe_2 ligand in $Ta(O_2CNMe_2)_3(NMe_2)_2$. In the latter molecule, the monodentate O_2CNMe_2 ligand again occupies an axial position of a pentagonal bipyramid. If the Me_2N^- ligands are counted as four-electron donors, then the monodentate O_2CNMe_2 ligand need only contribute a σ pair of electrons since the formation of seven σ bonds and two π bonds satisfies the 18-electron rule. This line of reasoning assumes that the Me_2N^- ligand is a much better π donor than the O_2CNMe_2 ligand. There is good structural evidence to support this in a number of mixed dimethylamido–carbamato metal complexes. The best example is probably seen in the structure of $W(NMe_2)_3(O_2CNMe_2)_3$, which has a *fac*-WN_3O_3 octahedral unit with very short W–N distances, 1.922 (7) Å, and long W–O distances, 2.041 (6) Å, indicative of double and single bonds, respectively.[4]

Symmetry Considerations. It is, of course, necessary to be sure that symmetry requirements are met in accounting for the formation of ligand-to-metal π bonds and the presence of planar $M–NC_2$ units and short M–N bonds is not sufficient evidence to allow the assignment of a M–N double bond. For example, the presence of short M–N distances, 1.96 Å (average), and planar $M–NC_2$ units in $M_2(NMe_2)_6$ (M≡M) compounds (M = Mo[11] and W[12]) might lead an uncritical observer to believe that the metal atoms attain an 18 valence shell of electrons as a result of

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forming a M≡M bond ($\sigma^2\pi^4$) and three Mo–N double bonds ($\sigma^2\pi^2$). However, a consideration of the symmetry of the $M_2(NC_2)_6$ unit reveals that the metal atoms can only receive a total of eight π electrons from the six Me_2N ligands. The average M–N bond order is thus 1.67, not 2, and the metal atoms only attain a 16 valence shell of electrons. For both $Ta(NMe_2)_4(t\text{-}Bu)$ and $Ta(O_2CNMe_2)_4(CH_2SiMe_3)$, however, symmetry considerations do permit the formation of metal–ligand double bonds and the attainment of an 18 valence shell of electrons by the metal atoms.

The $Ta(NC_2)_4C$ unit in $Ta(NMe_2)_4(t\text{-}Bu)$ has virtual C_4 symmetry with the C_4 axis being coincident with the Ta–C bond, which we will define as the z axis. The dimethylamido π-type orbitals, the p orbitals, transform as A + B + E in the symmetry group C_4. If we assume that metal–ligand σ bonds are formed by using tantalum s, p_x, p_y, $d_{x^2-y^2}$, and d_{z^2}, then we find that remaining metal atomic orbitals, namely the d_{xz}, d_{yz} (E), d_{xy} (B), and p_z (A), have the appropriate symmetry to interact with the dimethylamido lone pairs. It is therefore possible to count each Me_2N^- ligand as a four-electron donor $\sigma^2\pi^4$ and for tantalum to attain an 18 valence shell of electrons.

For $Ta(O_2CNMe_2)_4(CH_2SiMe_3)$, we may define the axial O–Ta–O bonds to be coincident with the z axis. For formation of seven metal–ligand σ bonds, tantalum may use s, p_x, p_y, $d_{x^2-y^2}$, and d_{xy} atomic orbitals for the five σ bonds in the pentagonal plane and p_z and d_{z^2} atomic orbitals to form bonds to the two axial monodentate O_2CNMe_2 ligands. The only metal atomic orbitals not used in forming σ bonds are the d_{xz} and d_{yz} orbitals, which have the appropriate symmetry to form π bonds to the axial monodentate O_2CNMe_2 ligands. Thus, with seven σ bonds and two π bonds, tantalum attains an 18 valence shell of electrons.

Stabilizing Influence of π-Donor Ligands on σ-Alkyl Ligands. In general, π-donor ligands such as Me_2N^- may stabilize early transition metal complexes in high oxidation states in a thermodynamic sense by their ability to form strong bonds. However, this stabilization is not what we believe to be the principal factor that allows the isolation of the β-hydrogen-containing alkyl complexes described herein. Rather, it is that metal atomic orbitals which would otherwise be available for mischevious M···H—C interactions are involved in metal–ligand π bonding. We believe that this behavior is not well recognized and has not been explicitly stated before. We do note, however, that there are other examples in the literature that support this view. (1) Burger and Neese[13] prepared a thermally stable (<100 °C) series of compounds of formula $(R_2N)_3TiR'$, where R = Me and Et and R′ = Me, Et, *n*-Pr, *i*-Pr, *n*-Bu, and *t*-Bu. (2) Andersen[14] has reported thermally stable compounds of the form $RM(NSi_2Me_6)_3$, where M = Zr and Hf, and $Et_2Zr(NSi_2Me_6)_2$. (3) An extensive series of dinuclear compounds of formula $1,2\text{-}M_2R_2(NMe_2)_4$ (M≡M), where M = Mo and W and R = Et, *i*-Pr, *n*-Bu, *i*-Bu, and *t*-Bu, have been prepared[15] in this laboratory. The stabilizing influence of π-donor ligands by suppressing the β-hydrogen abstraction reaction of σ-alkyl ligands is expected to be most effective in the chemistry of the early transition elements where the formation of σ bonds would not alone satisfy the EAN rule. This has been used to advantage by Schrock and co-workers[16] in the reactions of metallacycles formed by the addition of terminal and internal olefins to early transition metal–carbene complexes. Specifically complexes of the type $M(CHR)L_2X_3$ (M = Nb or Ta, R = CMe_3 or Ph, L = a tertiary phosphine, and X = Cl or Br) react with terminal olefins to give the organic products of β-hydride rearrangement of the four possible intermediate metallacyclobutane complexes (no metathesis products or cyclopropanes were observed), whereas with $M(CHCMe_3)(OCMe_3)_2Cl(PMe_3)$ only metathesis products were obtained.

Experimental Section

General Procedures and Materials. General procedures and the preparation of $[Ta(NMe_2)_3Cl_2]_2$ have been described.[17] $TaCl_5$ (99% purity) was purchased from Apache Chemical Co. and used without purification. $Ta(NMe_2)_5$ was prepared according to the method of Bradley and Thomas.[18] *n*-Butyllithium (ca. 2.4 M in hexane) from Ventron Corp. was used without purification. *tert*-Butyllithium and isopropyllithium were purchased from Organomet Co. and freshly sublimed (ca. 70 °C (10^{-4} torr)) prior to use. Ethyllithium was prepared from ethyl bromide and lithium wire in hexane and sublimed at ca. 80 °C (10^{-4} torr).

Physical and Analytical Measurements. Elemental analyses were obtained from Alfred Bernhardt Mikroanalytisches Laboratorium, Elbach, West Germany, and Canadian Microanalytical Services, Vancouver, Canada, using dry-box sampling techniques.

Infrared spectra were obtained from Nujol mulls between CsI or KBr plates on a Perkin-Elmer 283 spectrophotometer.

^1H NMR spectra were recorded on a Varian HR-220 instrument equipped with variable-temperature accessories. ^{13}C NMR spectra were recorded on a Varian XL-100 spectrometer. NMR solvents were toluene-d_8 or benzene-d_6.

Mass spectra were obtained on an AEI MS-902 spectrometer courtesy of Peter Cook, Department of Chemistry, Queen Mary College, London.

Preparation of $TaCl(NMe_2)_4$. $Ta(NMe_2)_5$ (1.05 g, 2.62 mmol) and $[Ta(NMe_2)_3Cl_2]_2$ (1.00 g, 2.62 mmol) were placed in a 100-mL round-bottomed flask together with a magnetic stir bar. Hexane (50 mL) was added and the resultant yellow suspension was refluxed for ca. 24 h. A yellow solution was formed along with a very small quantity of white solid, which was removed by filtration. The solvent was stripped in vacuo to yield a yellow microcrystalline solid, $TaCl(NMe_2)_4$: 1.95 g (95% yield based on Ta); IR (cm^{-1}) 2785 vs, 1442 s, 1421 ms, 1250 vs (br), 1139 vs, 1055 m, 1048 m, 972 s (sh), 952 vs (br), 802 ms (br), 722 m, 674 m, 603 w, 559 vs, 548 s (sh), 329 s, 289 w, 282 w, 250 ms, 242 m. ^1H NMR (toluene-d_8, 220 MHz, 16 °C) δ 3.25 (s).

In the mass spectrometer, the parent ion $TaCl(NMe_2)_4^+$ was observed, but the most abundant ion corresponded to $TaCl(NMe_2)_3^+$. Anal. Calcd for $TaClN_4C_8H_{24}$: C, 24.5; H, 6.16; N, 14.3; Cl, 9.03. Found: C, 24.3; H, 6.04; N, 14.2; Cl, 9.08.

Preparation of $Ta(CH_2SiMe_3)(NMe_2)_4$. $TaCl(NMe_2)_4$ (1.80 g, 4.59 mmol) was dissolved in hexane (ca. 40 mL) in a 100-mL round-bottomed flask, and the solution was cooled to −40 °C. $LiCH_2SiMe_3$ (0.43 g, 4.57 mmol), dissolved in hexane (20 mL), was slowly added via an addition funnel. The resultant yellow solution was stirred at −40 °C for 1 h and then warmed slowly to room temperature (2 h). The solvent was stripped and the light yellow residue extracted with hexane (3 × 10 mL) until the filtrate was clear. Again the solvent was stripped, yielding a yellow viscous liquid, $Ta(CH_2SiMe_3)(NMe_2)_4$: 1.66 g (81% yield based on Ta); ^1H NMR (benzene-d_6, 16 °C) δ 0.23 (s, $SiMe_3$), 0.44 (s, CH_2), 3.18 (s, NMe_2); ^{13}C NMR (benzene-d_6, 24 °C) δ 4.0 (q, $SiMe_3$, $J_{CH} = 116.5$ Hz), 45.8 (q, NMe_2, $J_{CH} = 138.7$ Hz), 54.4 (t, CH_2, $J_{CH} = 101.2$ Hz). Anal. Calcd for $TaSiN_4C_{12}H_{35}$: C, 32.4; H, 7.88; N, 12.6. Found: C, 33.0; H, 8.12; N, 12.9.

Preparation of $Ta(NMe_2)_4(i\text{-}Pr)$. $TaCl(NMe_2)_4$ (0.61 g, 1.55 mmol) was dissolved in hexane (20 mL) and cooled to −40 °C. *i*-PrLi (0.08 g, 1.60 mmol) in hexane (40 mL) was added slowly from an addition funnel. A white precipitate formed. After the addition of *i*-PrLi was complete (ca. 30 min), the reaction mixture was stirred at −40 °C for 1 h and then allowed to warm slowly to room temperature and stirred for an additional 1 h. The solvent was stripped and the yellow residue was extracted with hexane (3 × 10 mL portions). The yellow filtrate was evaporated to dryness under vacuum, yielding a fine microcrystalline product, $Ta(NMe_2)_4(i\text{-}Pr)$: 0.5 g (80% yield based on Ta); ^{13}C NMR (benzene-d_6, 24 °C) δ 21.8 ($CH\mathit{Me}_2$), 45.2 (NMe_2), 64.3 ($\mathit{C}HMe_2$); ^1H NMR (benzene-d_6, 16 °C) δ 1.69 (m, $CHMe_2$, 7 H), 3.17 (s, NMe_2, 24 H). Anal. Calcd for $TaN_4C_{11}H_{31}$: C, 33.0; H, 7.75; N, 14.0. Found: C, 32.6; H, 7.56; N, 13.7%.

Preparation of $Ta(NMe_2)_4(Et)$. $TaCl(NMe_2)_4$ (0.61 g, 1.52 mmol) was dissolved in hexane (20 mL), and the solution was cooled to −40 °C. To this stirred solution was added dropwise via an addition funnel EtLi (0.06 g, 1.66 mmol) in hexane (40 mL). The solution became opaque as a finely divided precipitate formed. The solution was stirred for 1 h at −40 °C, allowed to warm to room temperature, and then stirred for a further 2 h. The solvent was stripped and the dried residue extracted with hexane (3 × 10 mL). Evaporation of the hexane from the hexane soluble extract gave a yellow waxy solid. Sublimation (40 °C (10^{-4} torr)) yielded yellow needles: 0.32 g (55% yield based on Ta); ^{13}C NMR

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(benzene-d_6, 24 °C) δ 11.2 (CH_2CH_3), 44.8 (CH_2CH_3), 45.0 (NMe_2); ^{1}H NMR (toluene-d_8, 16 °C) δ 1.06 (q, CH_2), 1.55 (t, CH_3), 3.07 (s, NMe_2). Anal. Calcd for $TaN_4C_{10}H_{29}$: C, 31.1; H, 7.51; N, 14.5. Found: C, 30.9; H, 7.32; N, 14.3.

Preparation of $Ta(NMe_2)_4$(*t*-Bu). $TaCl(NMe_2)_4$ (1.10 g, 2.86 mmol) was dissolved in hexane (40 mL) in a 100-mL round-bottomed flask, fitted with a magnetic stirrer. The resultant yellow solution was cooled to −78 °C, and *t*-BuLi (0.18 g, 2.86 mmol), dissolved in hexane (20 mL), was added slowly. The solution was stirred magnetically; a fine precipitate of LiCl formed. After the addition of *t*-BuLi was complete (ca. 30 min), the solution was stirred at −78 °C for 2 h, allowed to warm to room temperature, and stirred for another 2 h. The solvent was stripped and the resulting light brown residue extracted with hexane (3 × 10 mL). The yellow hexane extraction was concentrated to ca. 3 mL and cooled to −10 °C overnight to yield pale yellow crystals, $Ta(NMe_2)_4$(*t*-Bu), 0.84 g (70% yield based on Ta), which were used in the subsequent X-ray study and in further spectroscopic characterization: ^{1}H NMR (benzene-d_6, 16 °C) δ 1.38 (s, CMe_3), 3.2 (s, NMe_2); ^{13}C NMR (benzene-d_6, 24 °C) δ 33.9 (CMe_3) 46.6 (NMe_2), 69.3 (CMe_3). $Ta(NMe_2)_4$(*t*-Bu) could be sublimed at 50 °C (10^{-4} torr) with some decomposition.

Preparation of $Ta(NMe_2)_3$(*p*-tolyl)Br. $[Ta(NMe_2)_3Cl_2]_2$ (0.51 g, 0.66 mmol) was suspended in hexane (ca. 20 mL), and *p*-tolyllithium (0.25 g, 2.63 mmol) in Et_2O (30 mL) was added slowly from an addition funnel at −40 °C. The resultant yellow reaction mixture was stirred for 0.5 h at −40 °C and then allowed to warm to room temperature over a period of 2 h. The solvent was stripped, and the sticky residue was extracted with hexane. Stripping the hexane yielded a yellow viscous liquid. Hexane (1.5 mL) was added to yield a yellow solution, which was chilled at −10 °C. After 20 min, yellow crystals formed, $Ta(NMe_2)_3$(*p*-tolyl)Br, which were used in the subsequent X-ray study. ^{1}H NMR for $Ta(NMe_2)_3$(*p*-tolyl)Br (benzene-d_6, 16 °C) δ 2.16 (s, C_6H_4Me), 3.08 (s, NMe_2), 7.26 and 7.95 (AA′BB′, aromatic protons). Anal. Calcd for $Ta(NMe_2)_3$(*p*-tolyl)Br: C, 32.2; H, 5.16; N, 8.68. Found: C, 33.5; H, 5.51; N, 8.81. Calcd for $Ta(NMe_2)_3$(*p*-tolyl)$_2$: C, 51.4; H, 6.85; N, 8.99.

Preparation of $Ta(CH_2SiMe_3)(O_2CNMe_2)_4$. $Ta(CH_2SiMe_3)(NMe_2)_4$ (1.80 g, 4.05 mmol) was dissolved in hexane (40 mL) in a 100-mL round-bottomed flask. The resultant solution was subjected to three cycles of freeze–pump–thaw, and then CO_2 (14.5 mmol) was added by use of a calibrated vacuum manifold. A white precipitate was formed. The pale yellow reaction mixture was stirred for 0.5 h at room temperature. The solvent was stripped, and the off-white solids were washed with copious quantities of hexane (ca. 150 mL) until the filtrate was colorless. The white insoluble solids were collected and dried, $Ta(CH_2SiMe_3)(O_2CNMe_2)_4$: 1.81 g (72% yield based on Ta); ^{1}H NMR (benzene-d_6, 16 °C), δ 0.47 (s, $SiMe_3$), 2.13 (s, CH_2SiMe_3), 2.59 (s, O_2CNMe_2); ^{13}C NMR (benzene-d_6, 24 °C) δ 2.40 ($SiMe_3$), 34.7 (O_2CNMe_2), 77.6 (CH_2SiMe_3), 163.5 (O_2CNMe_2), IR (cm^{-1}, Fluorolube, KBr plates) 3012 vw, 2944 s, 2920 m, sh, 2890 m, sh, 2862 w, 2700 vw, 1680 vs, 1668 vs, 1453 vs, 1408 vs, 1375 vs cm^{-1}; IR (Nujol, Br plates) 1258 vs, 1133 vs, 1032 vs, 962 m, 940 m, 848 sh, 837 vs, 825 s, 759 s, 747 vs, 722 m, 685 w, 677 vs, 662 vs, 595 s, 489 s, 433 vs, 408 sh. In the mass spectrometer, the ion of highest mass corresponded to $Ta(O_2CNMe_2)_4^+$ (m/e = 533) followed by ions at m/e = 489, 445, and 401, suggesting the stepwise loss of either CO_2 or NMe_2 or O_2CNMe_2 (88) from $Ta(O_2CNMe_2)_4^+$. Anal. Calcd for $Ta(CH_2SiMe_3)(O_2CNMe_2)_4$: C, 31.0; H, 5.64; N, 9.03. Found: C, 31.6; H, 5.64; N, 8.8.

$Ta(NMe_2)_4R + CO_2$. Related reactions involving $Ta(NMe_2)_4R$, where R = *t*-Bu and *i*-Pr, gave $TaR(O_2CNMe_2)_4$ as white microcrystalline compounds from hexane solution. The compounds $TaR(O_2CNMe_2)_4$ were sufficiently soluble in toluene-d_8 to allow characterization by ^{1}H NMR spectroscopy (toluene-d_8, 16 °C): for Ta(*t*-Bu)$(O_2CNMe_2)_4$ δ 2.39 (s, CMe_3, 9 H), 2.59 (s, O_2CNMe_2, 24 H); Ta(*i*-Pr)$(O_2CNMe_2)_4$ δ = 2.46 (d, $CHMe_2$, 6 H, J_{HH} = 7.5 Hz), 2.60 (s, O_2CNMe_2, 24 H). Because of the sparing solubility of Ta(*i*-Pr)$(O_2CNMe_2)_4$, the methine proton resonance could not be unambiguously characterized.

X-ray Structure Determinations. General operating procedures were as described previously.[19]

$Ta(NMe_2)_4$(*t*-Bu). A yellow crystal of dimensions 0.12 × 0.20 × 0.15 mm was selected. The cell dimensions obtained from 42 reflections at −163 °C with Mo Kα (λ 0.71069 Å) were as follows: a = 14.284 (3) Å, b = 8.261 (2) Å, c = 14.214 (4) Å, V = 1677.3 (5) Å^3, Z = 4, d_{calcd} = 1.641 g cm^{-3}, with space group $P2_1cn$.

A total of 1372 reflections were collected by the standard moving-crystal moving-detector techniques with the following values: scan speed 4.0 min^{-1}, scan width 2.0 + dispersion, single background time at extremes of scan 3 s, aperture size 3.0 × 4.0 mm. The limits of data collection were 5° < 2θ < 50°. Of the 1154 unique reflections, the number with $F > 2.33\sigma(F)$ was 994. The linear absorption coefficient was 64.67 cm^{-1}.

The structure was solved by direct methods and refined by full-matrix techniques. Attempts to vary all atoms anisotropically were unsuccessful, with several of the atoms refining to nonpositive definite thermal parameters. For this reason, the final refinement allowed only the Ta atom to vary anisotropically.

The final residues are $R(F)$ = 0.041 and $R_w(F)$ = 0.041. The goodness of fit for the last cycle was 1.121, and the maximum Δ/σ was 0.05.

$Ta(CH_2SiMe_3)(O_2CNMe_2)_4$. A transparent, nearly colorless crystal of dimensions 0.12 × 0.12 × 0.17 mm was chosen. The cell dimensions obtained from 24 reflections at −162 °C with Mo Kα (λ 0.71069 Å) were as follows: a = 15.321 (8) Å, b = 9.801 (6) Å, c = 9.187 (5) Å, α = 92.70 (2)°, β = 117.95 (2)°, γ = 88.57 (2)°, V = 1217 (4) Å^3, Z = 2, d_{calcd} = 1.693 g cm^{-3}, with space group $P\bar{1}$.

A total number of 4485 reflections were collected by standard moving-crystal moving-detector techniques with the following values: scan speed 4.0 min^{-1}, scan width 2.0 + dispersion, single background time at extremes of scan 5 s, aperture size 3.0 × 4.0 mm. The limits of data collection were 5° < 2θ < 50°. Of the 4305 unique reflections, the number with $F > 2.33\sigma(F)$ was 3950.

The structure was solved by using Patterson techniques and Fourier syntheses. All non-hydrogen atoms were easily located and refined. A difference Fourier synthesis based on the heavy atom refinement located approximately half of the hydrogen atom positions, and on the basis of their positions, idealized coordinates were calculated for all hydrogen atoms. The latter were included as fixed-atom contributors in the final cycles of refinement. The final residuals are $R(F)$ = 0.040 and $R_w(F)$ = 0.040. The goodness of the fit for the last cycle was 1.324, and the maximum Δ/σ was 0.05.

$Ta(NMe_2)_3$(*p*-tolyl)Br. From a much larger crystal, a yellow crystal of dimensions 0.24 × 0.12 × 0.32 mm was cleaved and used for the study. The cell dimensions obtained from 36 reflections at −162 °C with Mo Kα (λ 0.71069 Å) were as follows: a = 11.387 (3) Å, b = 19.440 (8) Å, c = 7.796 (2) Å, β = 102.84 (1)°, V = 1682.5 (9) Å^3, Z = 4, d_{calcd} = 1.912 g cm^{-3}, with space group $P2_1/N$.

A total of 5321 reflections were collected by standard moving-crystal moving-detector techniques with the following values: scan speed 4.0 min^{-1}, scan width 2.0 + dispersion, single background time at extremes of scan 4 s, aperture size 3.0 × 4.0 mm. The limits of data collection were 5° ≤ 2θ ≤ 50°. Of the 2037 unique reflections, the number with $F > 2.33\sigma(F)$ was 1828.

The structure was readily solved by direct methods and Fourier techniques. Attempts to refine all atoms anisotropically were unsuccessful, with C(17) and C(18) converging to nonpositive definite thermal parameters. In addition, many of the atoms exhibited exaggerated anisotropic motion, presumably due to a lack of an absorption coefficient. Attempts to correct the data for absorption by using the approximate crystal dimensions were unsuccessful. A second sample was finally examined in an attempt to improve the model. While the second crystal was significantly smaller (maximum dimension = 0.10 mm), there was little improvement and the residuals were in fact larger. For this reason, only the refinement of crystal I is reported. Final residuals are $R(F)$ = 0.069 and $R_w(F)$ = 0.072. The goodness of fit for the last cycle was 1.714, and the maximum Δ/σ was 0.05.

Acknowledgment. We thank the National Science Foundation, the Marshall H. Wrubel Computing Center, and the taxpayers of the state of Indiana for financial support of this work. M.H.C. is the recipient of a Camille and Henry Dreyfus Teacher-Scholar Grant, 1979–84.

Registry No. $Ta(NMe_2)_4$-*t*-Bu, 82482-91-5; $Ta(NMe_2)_3$(*p*-tolyl)Br, 82482-90-4; $Ta(CH_2SiMe_3)(O_2CNMe_2)_4$, 82482-83-5; $Ta(NMe_2)_4$-*i*-Pr, 82482-89-1; Ta(*t*-Bu)$(O_2CNMe_2)_4$, 82482-82-4; Ta(*i*-Pr)$(O_2CNMe_2)_4$, 82482-81-3; $TaCl(NMe_2)_4$, 82482-88-0; $Ta(NMe_2)_5$, 19824-59-0; $[Ta(NMe_2)_3Cl_2]_2$, 77071-68-2; $LiCH_2SiMe_3$, 1822-00-0; $Ta(NMe_2)_4(Et)$, 82482-87-9; $Ta(CH_2SiMe_3)(NMe_2)_4$, 82482-86-8; CO_2, 124-38-9.

Supplementary Material Available: Tables of anisotropic thermal parameters and observed and calculated structure factors (69 pages). Ordering information is given on any current masthead page.

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[19] Huffman, J. C.; Lewis, L. N.; Caulton, K. G. *Inorg. Chem.* **1980**, *19*, 2755.