Intramolecular Activation of Aliphatic and Aromatic Carbon–Hydrogen Bonds by Tantalum(III) Metal Centers: Synthesis and Structure of the Bis-Metalated Compounds Ta(OC₆H₃Bu^tCMe₂CH₂)₂Cl and Ta(OC₆H₃PhC₆H₄)₂(OAr-2,6-Ph₂) (OAr-2,6-Ph₂ = 2,6-Diphenylphenoxide)

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The reduction of the mixed chloro aryloxides $Ta(OAr-2,6-Bu^t_2)_2Cl_3$ (1) and $Ta(OAr-2,6-Ph_2)_3Cl_2$ (2) (OAr-2,6-Bu^t_2 = 2,6-di-*tert*-butylphenoxide; OAr-2,6-Ph₂ = 2,6-diphenylphenoxide) with sodium amalgam in hydrocarbon solvents has been investigated. Treatment of toluene solutions of either 1 or 2 with sodium amalgam (2Na/Ta) leads to the bis-cyclometalated Ta(V) compounds $Ta(OC_6H_3Bu^tCMe_2CH_2)_2Cl$ (3) and $Ta(OC_6H_3PhC_6H_4)_2(OAr-2,6-Ph_2)$ (4), respectively, in high yield. Solid-state X-ray diffraction studies of 3 and 4 show both compounds to contain related structures involving a trigonal-bipyramidal coordination environment about the tantalum atom. The two six-membered metallacycle rings chelate the metal between the two trans axial positions (occupied by oxygen atoms) and two of the equatorial positions that are occupied by the new metal–carbon bonds. The remaining equatorial position is occupied by a Cl atom or OAr-2,6-Ph₂ ligand for 3 and 4, respectively. Spectroscopic data on 3 and 4 are entirely consistent with the maintenance of these structures in solution. The formation of these bis-cyclometalated compounds is argued to proceed via Ta(III) intermediates which undergo facile oxidative addition of aliphatic or aromatic CH bonds to produce a monometalated, monohydride intermediate. A second ring closure involving loss of H₂ then leads to the observed products. Some support for this is provided by the formation of the mono-cyclometalated compound $Ta(OC_6H_3Bu^tCMe_2CH_2)(OAr-2,6-Bu^t_2)(BH_4)Cl$ (6) on treatment of 1 with LiBH₄. Mild thermolysis of 6 yields 3, H₂, and B₂H₆. Attempts to trap out a Ta(III) intermediate by treating 2 with Na/Hg in the presence of PMe₂Ph only yielded the bis-metalated adduct $Ta(OC_6H_3PhC_6H_4)_2$-$(OAr-2,6-Ph_2)(PMe_2Ph)$ (5). Crystal data for $TaClO_2C_{28}H_{40}$ (3) at 19 °C: $a = 10.589$ (3) Å, $b = 11.726$ (7) Å, $c = 11.892$ (8) Å, $\alpha = 107.12$ (5)°, $\beta = 97.69$ (5)°, $\gamma = 89.53$ (4)°, $Z = 2$, $d_{calcd} = 1.485$ g cm⁻³ in space group $P\bar{1}$. For $TaO_3C_{61}H_{45}$ (4) in C_7H_8 at 22 °C: $a = 11.983$ (1) Å, $b = 20.948$ (2) Å, $c = 9.7609$ (9) Å, $\alpha = 97.588$ (9)°, $\beta = 101.979$ (9)°, $\gamma = 77.92$ (1)°, $Z = 2$, $d_{calcd} = 1.433$ g cm⁻³ in space group $P\bar{1}$.

Introduction

A particularly interesting facet of the area of transition-metal-mediated activation of carbon–hydrogen bonds involves the various mechanistic pathways for the reaction which have been elucidated.[2-8] A number of general regimes exist, the two most prominent being the oxidative addition pathway involving reaction with electron-rich, low-valent metal systems[3-5] and more electrophilic (hete-rolytic) pathways associated with high-valent d-block lanthanide and actinide metal systems.[6-8] In the area of early d-block metal chemistry we have shown that the ligands 2,6-di-*tert*-butylphenoxide (OAr-2,6-Bu^t₂) and 2,6-diphenylphenoxide (OAr-2,6-Ph₂) can undergo the intramolecular activation of their aliphatic and aromatic CH bonds at d⁰ metal centers.[9] Activation by alkyl,[10] alkylidene,[11] and benzyne[12] functional groups has been shown to be possible. In this paper we wish to report the facile cyclometalation of both of these ligands at Ta(III) metal centers. These reactions are of some mechanistic interest as they represent sequential activation of identical CH bonds by oxidative addition and then heterolytic pathways at the same metal center.

Results and Discussion

The two mixed chloro aryloxides $Ta(OAr-2,6-Bu^t_2)_2Cl_3$ (1)[13] and $Ta(OAr-2,6-Ph_2)_3Cl_2$ (2)[14] have been shown to be useful substrates for the synthesis of alkyl and alkylidene compounds containing these bulky aryloxide ligands.

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Table I. Fractional Coordinates and Isotropic Thermal Parameters for $Ta(OC_6H_3Bu^tCMe_2CH_2)_2Cl$ (3)^a

atom	x	y	z	B, A^2
Ta	0.18749 (8)	0.29502 (9)	0.04284 (9)	2.77 (2)
Cl	0.1914 (5)	0.4909 (5)	0.0441 (5)	5.0 (2)
O(10)	0.265 (1)	0.237 (1)	−0.09 (1)	3.4 (3)
O(20)	0.109 (1)	0.320 (1)	0.180 (1)	3.5 (3)
C(11)	0.255 (2)	0.151 (2)	−0.207 (1)	3.3 (4)
C(12)	0.139 (2)	0.091 (2)	−0.250 (1)	2.7 (5)
C(13)	0.133 (2)	0.003 (2)	−0.356 (2)	3.6 (5)
C(14)	0.236 (2)	−0.025 (2)	−0.416 (2)	4.7 (6)
C(15)	0.350 (2)	0.043 (2)	−0.376 (2)	3.8 (5)
C(16)	0.362 (1)	0.132 (1)	−0.268 (1)	2.3 (4)
C(21)	0.117 (2)	0.301 (2)	0.291 (2)	3.9 (5)
C(22)	0.236 (1)	0.270 (2)	0.337 (2)	2.7 (5)
C(23)	0.244 (2)	0.246 (2)	0.444 (2)	3.6 (5)
C(24)	0.143 (2)	0.251 (2)	0.502 (2)	4.1 (6)
C(25)	0.028 (2)	0.288 (2)	0.457 (2)	3.7 (5)
C(26)	0.010 (2)	0.316 (2)	0.352 (2)	3.1 (5)
C(121)	0.019 (2)	0.127 (2)	−0.191 (1)	2.7 (5)
C(122)	0.045 (2)	0.162 (2)	−0.053 (2)	5.1 (6)
C(123)	−0.030 (2)	0.236 (2)	−0.227 (2)	4.1 (5)
C(124)	−0.084 (2)	0.029 (2)	−0.229 (2)	5.2 (6)
C(161)	0.481 (2)	0.212 (2)	−0.222 (2)	4.2 (5)
C(162)	0.581 (2)	0.180 (2)	−0.312 (2)	5.7 (7)
C(163)	0.454 (2)	0.344 (2)	−0.201 (2)	5.7 (7)
C(164)	0.552 (2)	0.192 (3)	−0.106 (2)	7.7 (8)
C(221)	0.358 (1)	0.278 (2)	0.277 (2)	3.1 (5)
C(222)	0.329 (2)	0.217 (2)	0.140 (2)	3.4 (5)
C(223)	0.399 (2)	0.409 (2)	0.309 (2)	5.6 (6)
C(224)	0.466 (2)	0.207 (2)	0.324 (2)	6.3 (7)
C(261)	−0.120 (2)	0.354 (2)	0.298 (2)	3.5 (5)
C(262)	−0.102 (2)	0.463 (2)	0.258 (2)	5.5 (6)
C(263)	−0.210 (2)	0.388 (2)	0.395 (2)	5.6 (7)
C(264)	−0.183 (2)	0.252 (2)	0.196 (2)	5.2 (6)

^{a} Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as $(^4/_3)[a^2\beta(1,1) + b^2\beta(2,2) + c^2\beta(3,3) + ab(\cos \gamma)\beta(1,2) + ac(\cos \beta)*(1,3) + bc(\cos \alpha)-*B(2,3)]$.

Table II. Selected Bond Distances (Å) and Angles (deg) for $Ta(OC_6H_3Bu^tCMe_2CH_2)_2Cl$ (3)

|			
Ta–Cl	2.293 (5)	Ta–O(10)	1.87 (1)
Ta–O(20)	1.87 (1)	Ta–C(122)	2.13 (2)
Ta–C(222)	2.13 (2)		
Cl–Ta–O(10)	95.6 (4)	O(10)–Ta–O(20)	168.1 (5)
Cl–Ta–O(20)	96.3 (4)	O(10)–Ta–C(122)	82.7 (9)
Cl–Ta–C(122)	126.5 (6)	O(10)–Ta–C(222)	91.0 (6)
Cl–Ta–C(222)	124.6 (5)	C(122)–Ta–C(222)	108.9 (8)
O(20)–Ta–C(122)	90.0 (7)		

Thermolysis is then typically found to lead to the elimination of alkane and the formation of new six-membered metallacycle rings.[9] Work by ourselves and others has also shown that reduction of either homoleptic aryloxides or mixed chloro aryloxides of Nb and Ta can lead to lower valent metal compounds containing aryloxide ligation.[15,16] The work of Wolczanski has shown that siloxide derivatives of Ta(III) can be obtained by reduction of Ta(V) substrates and furthermore can be reagents for carrying out small molecule activation and reduction.[17,18] In con-

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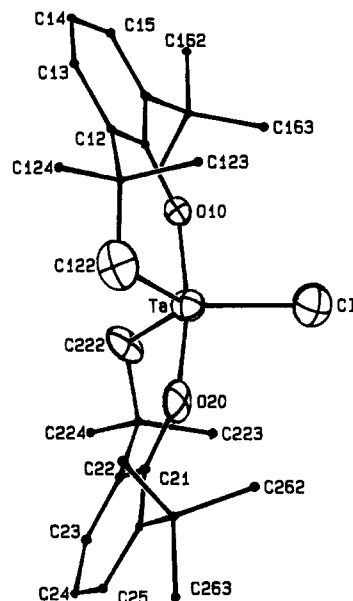
Figure 1. ORTEP view of $Ta(OC_6H_3Bu^tCMe_2CH_2)_2Cl$ (3) emphasizing the central coordination sphere.

trast to this behavior we find that the reduction of toluene solutions of 1 or 2 with sodium amalgam (2Na/Ta) results in formation of the cyclometalated Ta(V) compounds $Ta(OC_6H_3Bu^tCMe_2CH_2)_2Cl$ (3) and $Ta(OC_6H_3PhC_6H_4)_2$-$(OAr-2,6-Ph_2)$ (4) in high yield (eq 1 and 2). As the re-

(1)

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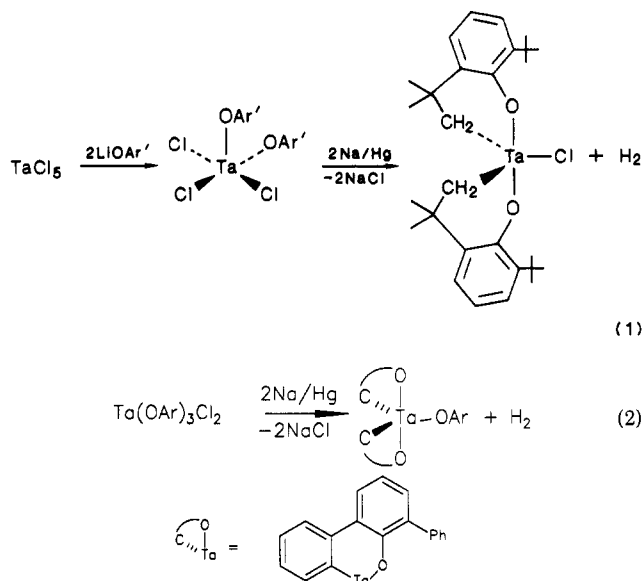
duction proceeds, the initially red (1) or yellow (2) reaction mixtures turn dark green before finally forming yellowish brown suspensions containing the products. The biscyclometalated compound 3 has previously been isolated from the thermolysis of the phenyl compound Ta-$(OC_6H_3Bu^tCMe_2CH_2)(OAr-2,6-Bu^t_2)(Cl)(Ph)$.[12] The spectroscopic data on 3 obtained by reduction of 1 is identical with that previously reported. A single-crystal X-ray diffraction analysis of 3 was carried out and confirmed not only the stoichiometry but also the coordination geometry about the metal as previously assumed on the basis of spectroscopic data. An ORTEP view of 3 is shown in Figure 1 while Table I contains fractional coordinates and isotropic thermal parameters. Some selected bond distances and angles for 3 are given in Table II. The molecule can be seen to adopt a trigonal-bipyramidal structure for the TaO_2C_2Cl core with trans, axial oxygen

Table III. Fractional Coordinates and Isotropic Thermal Parameters for Ta(OC₆H₃PhC₆H₄)₂(OAr-2,6-Ph₂) (4)[a]

atom	x	y	z	B, Å²
Ta	0.16679 (1)	0.29434 (1)	0.07987 (2)	3.177 (4)
O(10)	0.2657 (2)	0.3363 (1)	0.2268 (3)	3.56 (6)
O(20)	0.9540 (3)	0.7308 (1)	0.0628 (3)	3.79 (7)
O(30)	0.2646 (3)	0.2102 (1)	0.0764 (3)	4.21 (7)
C(11)	0.2526 (4)	0.3865 (2)	0.3287 (4)	3.6 (1)
C(12)	0.1565 (4)	0.3952 (2)	0.3932 (4)	3.8 (1)
C(13)	0.8563 (4)	0.5504 (2)	0.5037 (5)	4.7 (1)
C(14)	0.7772 (5)	0.5092 (2)	0.4701 (5)	5.2 (1)
C(15)	0.6821 (4)	0.5203 (2)	0.5344 (5)	4.9 (1)
C(16)	0.3366 (4)	0.4270 (2)	0.3647 (5)	4.0 (1)
C(21)	0.0560 (4)	0.7035 (2)	0.1414 (4)	3.8 (1)
C(22)	0.0734 (4)	0.6374 (2)	0.1653 (4)	3.8 (1)
C(23)	0.1B46 (4)	0.6110 (2)	0.2362 (6)	5.1 (1)
C(24)	0.2694 (5)	0.6468 (3)	0.2806 (6)	5.9 (1)
C(25)	0.2474 (4)	0.7130 (3)	0.2622 (6)	5.6 (1)
C(26)	0.1394 (4)	0.7427 (2)	0.1914 (5)	4.5 (1)
C(31)	0.3011 (4)	0.1535 (2)	-0.0022 (5)	3.9 (1)
C(32)	0.3009 (4)	0.0935 (2)	0.0460 (5)	4.2 (1)
C(33)	0.6646 (5)	0.9637 (2)	0.0383 (6)	5.3 (1)
C(34)	0.6319 (5)	0.9612 (3)	0.1648 (6)	5.9 (1)
C(35)	0.6288 (5)	0.9018 (3)	0.2064 (6)	5.5 (1)
C(36)	0.6615 (4)	0.8432 (2)	0.1257 (5)	4.4 (1)
C(121)	0.0728 (4)	0.3504 (2)	0.3611 (5)	3.8 (1)
C(122)	0.0560 (3)	0.3094 (2)	0.2320 (4)	3.55 (9)
C(123)	0.9696 (4)	0.2703 (2)	0.2107 (5)	4.3 (1)
C(124)	0.9073 (4)	0.2680 (3)	0.3146 (6)	5.2 (1)
C(125)	0.9277 (5)	0.3059 (3)	0.4405 (6)	6.1 (1)
C(126)	-0.0076 (4)	0.6535 (3)	0.5374 (5)	5.2 (1)
C(161)	0.4400 (4)	0.4143 (2)	0.2975 (5)	4.5 (1)
C(162)	0.5123 (5)	0.3530 (3)	0.2925 (7)	6.6 (2)
C(163)	0.6092 (5)	0.3424 (3)	0.2317 (9)	8.6 (2)
C(164)	0.6366 (5)	0.3918 (4)	0.1745 (8)	8.2 (2)
C(165)	0.5663 (5)	0.4519 (3)	0.1756 (7)	6.7 (2)
C(166)	0.4678 (4)	0.4640 (3)	0.2379 (6)	5.2 (1)
C(221)	0.9781 (4)	0.5985 (2)	0.1245 (4)	3.43 (9)
C(222)	0.1298 (4)	0.3802 (2)	0.9647 (4)	3.47 (9)
C(223)	0.2120 (4)	0.4212 (2)	-0.0088 (5)	4.1 (1)
C(224)	0.8085 (4)	0.5186 (2)	0.0634 (5)	4.5 (1)
C(225)	0.9135 (4)	0.4993 (2)	0.1491 (5)	4.4 (1)
C(226)	-0.0031 (4)	0.5378 (2)	0.1802 (4)	4.1 (1)
C(261)	0.1144 (5)	0.8140 (2)	0.1738 (5)	5.4 (1)
C(262)	0.0128 (6)	0.8544 (3)	0.2031 (7)	7.0 (2)
C(263)	-0.0073 (7)	0.9207 (3)	0.1926 (9)	9.7 (2)
C(264)	0.0731 (9)	0.9476 (3)	0.1538 (9)	11.8 (3)
C(265)	0.1720 (8)	0.9096 (3)	0.1207 (8)	11.5 (2)
C(266)	0.1965 (6)	0.8419 (3)	0.1317 (6)	7.9 (2)
C(321)	0.2664 (4)	0.0883 (2)	0.1810 (5)	4.5 (1)
C(322)	0.1619 (5)	0.1225 (3)	0.2160 (6)	5.6 (1)
C(323)	0.1313 (6)	0.1152 (3)	0.3409 (6)	7.1 (2)
C(324)	0.2035 (6)	0.0733 (3)	0.4327 (6)	7.4 (2)
C(325)	0.3055 (6)	0.0388 (3)	0.4010 (6)	6.9 (2)
C(326)	0.3379 (5)	0.0457 (3)	0.2763 (6)	5.7 (1)
C(361)	0.6524 (4)	0.7802 (2)	0.1718 (5)	4.8 (1)
C(362)	0.5829 (5)	0.7392 (3)	0.0900 (6)	6.1 (1)
C(363)	0.5678 (6)	0.6835 (3)	0.1425 (8)	7.4 (2)
C(364)	0.6204 (6)	0.6671 (3)	0.2719 (7)	8.2 (2)
C(365)	0.8669 (7)	0.7065 (4)	0.3523 (8)	9.6 (2)
C(366)	0.7069 (6)	0.7640 (3)	0.3055 (7)	7.5 (2)
C(401)	0.6103 (8)	0.1466 (4)	0.4174 (9)	10.1 (2)*
C(402)	0.2786 (7)	0.8820 (4)	0.5314 (9)	9.1 (2)*
C(403)	0.8065 (8)	0.1010 (5)	0.386 (1)	10.5 (2)*
C(404)	0.7697 (7)	0.1137 (4)	0.2411 (9)	9.8 (2)*
C(405)	0.6565 (7)	0.1410 (4)	0.1965 (9)	9.5 (2)*
C(406)	0.5717 (7)	0.1588 (4)	0.2708 (8)	8.7 (2)*
C(407)	0.474 (1)	0.8372 (6)	0.495 (1)	14.9 (4)*

[a] Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as $(⁴/₃)[a²β(1,1) + b²β(2,2) + c²β(3.3) + ab(\cos γ)β(1,2) + ac(\cos β)B(1,3) + bc(\cos α)β(2,3)]$.

Table IV. Selected Bond Distances (Å) and Angles (deg) for Ta(OC₆H₃PhC₆H₄)₂(OAr-2,6-Ph₂) (4)

Ta-O(10)	1.905 (2)	Ta-O(20)	1.897 (2)
Ta-O(30)	1.903 (3)	Ta-C(122)	2.142 (4)
Ta-C(222)	2.165 (4)		
O(10)-Ta-O(20)	168.1 (1)	O(20)-Ta-O(30)	95.0 (1)
O(10)-Ta-O(30)	96.9 (1)	O(20)-Ta-C(122)	90.5 (1)
O(10)-Ta-C(122)	83.5 (1)	O(20)-Ta-C(222)	82.3 (1)
O(30)-Ta-C(122)	113.4 (1)	Ta-O(10)-C(11)	136.8 (2)
O(30)-Ta-C(222)	137.4 (1)	Ta-O(30)-C(31)	147.1 (3)

torial positions so that a chelate bite of 82.5° (average) is maintained. As with previously characterized chelate rings of this type,[9,10,12] the large M–O–C angle ensures little puckering of the six-membered rings. The remaining equatorial position about the metal is occupied by the chlorine atom.
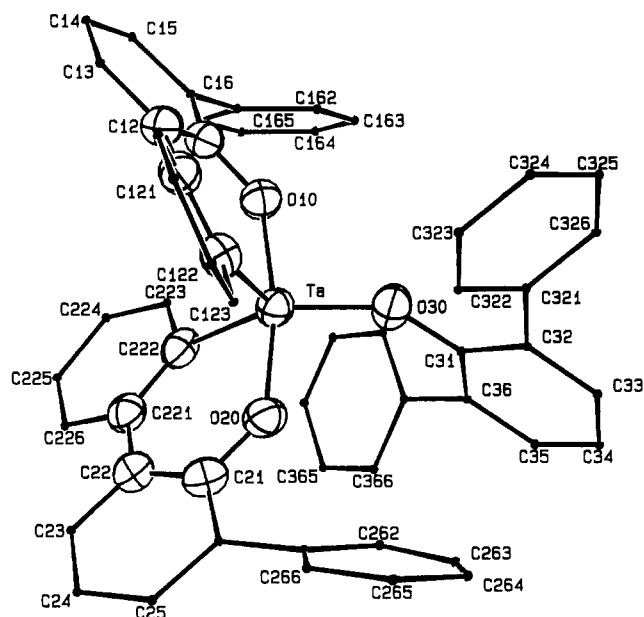
The ¹H and ¹³C NMR spectra of compound 4 are consistent with the presence of cyclometalated 2,6-diphenylphenoxide rings. Particularly characteristic in the ¹³C NMR spectrum is the resonance for the new Ta–C-(aryl) carbon at δ 202.2 ppm. This is the region where the ipso carbon atoms of simple tantalum(V) aryl ligands typically resonate.[12] The ¹H NMR spectrum of 4 is contained entirely in the δ 6.5–8.0 ppm region and is complex. However, high-field spectra do allow structure to be resolved. Analysis of this pattern confirms the presence of cyclometalated rings, and certainly the spectrum is inconsistent with the simple patterns typical of unmetalated OAr-2,6-Ph ligands.[19] A single-crystal X-ray diffraction analysis of 4 was performed for direct comparison with the alkyl counterpart 3. An ORTEP view of 4 is shown in Figure 2 while fractional coordinates and isotropic thermal parameters are contained in Table III. Selected bond distances and angles are collected in Table IV. A strong similarity between the coordination environments of both 3 and 4 can be seen (Figures 1 and 2). In 4 the equatorial positions about the metal atom are now occupied by two aryl carbon atoms along with the oxygen atom of an unmetalated OAr-2,6-Ph₂ group. The arrangement of atoms about the metal center in 4 is also essentially identical with that found in the mixed aryl aryloxide Ta(OAr-2,6-Prⁱ₂)₃(C₆H₅)₂ showing[21] that the formation of the six-membered chelate ring has little structural impact. The formation of the chelate ring in 4 does have the effect of twisting the metalated aryl ring so that it is now closer to coplanar with the central phenoxy ring (angles of 12.2° and 23.1°). In unmetalated 2,6-diphenylphenoxide ligands the angle between the central, phenoxy ring and the 2,6-phenyl groups is typically larger. For example angles in 4 for the non-metalated rings are 45.6°, 51.6°, 51.9°, and 56.0°.

The possible pathways for the formation of bis-cyclometalated 3 and 4 by reduction of the halide precursors is of interest. The work of Wolczanski et al. has shown that reduction of the compound Ta(silox)₃Cl₂ (silox = Buᵗ₃SiO) with 2Na/Hg leads to the intensely colored Ta-(silox)₃ which is a powerful reducing agent.[17] On standing for long periods of time, the formation of a monohydride compound by intramolecular oxidative addition of a CH bond of a silox ligand is observed. Hence, it seems reasonable that the reduction of 1 or 2 initially will produce the Ta(III) compounds [Ta(OAr-2,6-Buᵗ₂)₂Cl]ₙ and [Ta-(OAr-2,6-Ph₂)₃]ₙ, respectively. An intramolecular oxidative

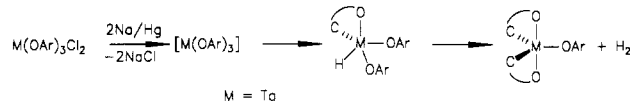(19) Smith, G. D.; Fanwick, P. E.; Rothwell, I. P. *J. Am. Chem. Soc.* **1989**, *111*, 750.

(20) (a) Kerschner, J. L.; Fanwick, P. E.; Rothwell, I. P. *J. Am. Chem. Soc.* **1987**, *109*, 5840. (b) Kerschner, J.L.; Fanwick, P. E.; Rothwell, I. P. *Organometallics* **1988**, *7*, 1871.

(21) Steffey, B. D.; Fanwick, P. E.; Rothwell, I. P., results to be published.

atoms. These oxygen atoms are also contained in two six-membered metallacycle rings which chelate the metal through the new metal–carbon bonds formed by the activation and metalation of one of the CH bonds of a *tert*-butyl group. These two carbon atoms occupy equa-

Figure 2. ORTEP view of $Ta(OC_6H_3PhC_6H_4)_2(OAr-2,6-Ph_2)$ (4) emphasizing the central coordination sphere and chelate ring.

Scheme I

$$M(OAr)_3Cl_2 \xrightarrow[-2NaCl]{2Na/Hg} [M(OAr)_3] \longrightarrow \underset{H}{\overset{O}{\underset{OAr}{C}}} M - OAr \longrightarrow \overset{O}{\underset{C}{\overset{C}{\underset{O}{}}}} M - OAr + H_2$$

$$M = Ta$$

addition pathway would then lead to monohydride intermediates (Scheme I). However, in this study only the bis-cyclometalated compounds are isolated. It is known that early d-block lanthanide and actinide metal hydride ligands are potent groups for carrying out CH bond activation via a heterolytic pathway[6-8] (vide infra). Hence it seems reasonable that facile elimination of H_2 will occur from the aryloxy, hydride intermediate to generate the observed products. A similar scenario has been proposed for the bis-cyclometalation of $OAr-2,6-Ph_2$ ligands at W(II) metal centers.[20]

Attempts to trap out intermediates in the reduction of **2** by addition of the phosphine ligand PMe_2Ph led only to the isolation of the simple adduct $Ta(OC_6H_3PhC_6H_5)_2(OAr-2,6-Ph_2)(PMe_2Ph)$ (5) as a white crystalline material. The signal due to the PMe_2Ph methyl groups in the ^1H NMR resonates to high field and appears broad in the spectrum. The upfield shifting of these methyl groups is an effect typically seen for the protons of groups bound to metal centers that contain 2,6-diphenylphenoxide ancillary ligation. This is a consequence of the diamagnetic anisotopy of the phenyl substituents of $OAr-2,6-Ph_2$ ligands coupled with their tendency to pack so as to present their faces to other groups in the metal coordination sphere.[14,20]

The treatment of the tri-chloride substrate 1 and with lithium borohydride in hydrocarbon solvents is also found to lead to facile cyclometalation. Stirring a mixture of $Ta(OAr-2,6-Bu^t_2)_2Cl_3$ (1) and $LiBH_4$ (excess) in toluene solution results in the slow loss of the red color of 1 with formation of a pale yellow suspension. suitable workup is found to lead to the isolation of a borohydride compound of tantalum, $Ta(OC_6H_3Bu^tCMe_2CH_2)(OAr-2,6-Bu^t_2)$-$(BH_4)Cl$ (6) in moderate yield. Although the synthesis of 6 is reproducible and its analytical data are correct, its ^1H and ^{13}C NMR spectra indicate the presence of a mixture of isomers. At low temperatures the ^1H NMR of 6 shows a series of resonances both due to Bu^t and CMe_2 groups

as well as a number of AB patterns of differing intensities due to diastereotropic $Ta-CH_2CMe_2$ alkyl linkages. We interpret the complexity of the ^1H NMR of 6 as indicative of the presence of a number of isomeric forms in solution. A simple analysis of 6 based on the idealized trigonal-bipyramidal geometry, in which BH_4^- occupies a single coordination site, indicates the possibility of at least three isomers. This assumes that the cyclometalated chelate ring is arranged with its oxygen atom in an axial position. The adoption of a square-pyramidal structure would also make available many other possible isomers. At room temperature the ^1H NMR of 6 is broad, presumably due to exchange of the isomeric forms present on the NMR time scale. Also at room temperature, two broad, equal intensity resonances at δ 4.4 and 4.7 ppm can be seen. These we believe to be due to the BH_4^- ligand bound to the tantalum metal center.[22,23] The equal intensity of these two "humps" implies that binding to the metal is occurring in a $Ta(\mu-H)_2BH_2$ fashion with the exchange of terminal and bridging hydride groups being slightly below the coalescence point at 30 °C. The infrared spectrum of 6 as a Nujol mull shows $\nu(B-H)$ bands at 2453, 2517, 2576 and 1880 cm^{-1}.

Warming solutions of 6 in toluene-d_8 above 40 °C results in the formation of H_2 (GC analysis) along with the bis-cyclometalated compound 3 and B_2H_6. This thermal conversion is essentially quantitative as estimated by ^1H NMR spectra. This result is particularly significant as the borohydride 6 can be thought of as the monohydride intermediate proposed for the formation of 3 from 1, only it is now stabilized by coordination to a BH_3 unit. The fact that the second ring closure in 6 takes place under mild conditions is supportive of the idea that the monohydride intermediate may itself be too reactive to allow its detection.

Experimental Section

$Ta(OC_6H_3CMe_2CH_2)_2Cl$ (3). To a solution of $Ta(OAr-2,6-Bu^t_2)_2Cl_3$ (1) (1.0 g, 1.43 mmol) in toluene (50 mL) was added a sodium amalgam containing Na metal (0.07 g, 3.1 mmol). The reaction mixture was stirred rigorously for 24 h at room temperature. The initially deep red solution soon became dark green, finally turning orange. The mixture was decanted off of the mercury pod and filtered and the solvent removed in vacuo to give the crude product. Recrystallization by slow cooling of a toluene/hexane solution gave orange crystals of product. Yield: 61%. The spectroscopic properties of 3 obtained in this manner were identical with those previously reported.[12a]

$Ta(OC_6H_3PhC_6H_4)_2(OAr-2,6-Ph_2)$ (4). An essentially identical procedure to that above, only using $Ta(OAr-2,6-Ph_2)_3Cl_2$ (2) (1.0 g, 1.29 mmol) and Na (0.07 g, 3.1 mmol), yielded 4 as a bright yellow solid in 70% yield. Anal. Calcd for $TaC_{54}H_{37}O_3$: C, 70.70; H, 4.08. Found: C, 70.88; H, 4.19. Large blocks of 4 suitable for crystallographic study were obtained by slow cooling of a hot (100

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Table V. Crystal Data and Data Collection Parameters

	3	4
formula	$TaClO_2C_{28}H_{40}$	$TaO_3C_{61}H_{45}$
fw	625.03	1006.99
space group	$P\bar{1}$	$P\bar{1}$
a, Å	10.589 (3)	11.983 (1)
b, Å	11.726 (7)	20.948 (2)
c, Å	11.892 (8)	9.7609 (9)
α, deg	107.12 (5)	97.588 (9)
β, deg	97.69 (5)	101.979 (9)
γ, deg	89.53 (4)	77.92 (1)
V, Å^3	1397 (3)	2333.8 (7)
Z	2	2
d_{calcd}, g cm^{-3}	1.485	1.433
cryst dimens, mm	0.28 × 0.15 × 0.04	0.57 × 0.40 × 0.35
temp, °C	19.	22.
radiatn (wavelength)	Mo Kα (0.710 73 Å)	Mo K$_\alpha$ (0.710 73 Å)
monochromater	graphite	graphite
linear abs coef, cm^{-1}	40.02	23.71
abs correctn applied	empirical^a	empirical^a
diffractometer	Enraf-Nonius CAD4	Enraf-Nonius CAD4
scan method	ω–2θ	ω–2θ
h,k,l limits:	−11 to +11, −12 to +12, 0 to 12	0 to 12, −21 to +22, −10 to +10
2θ range, deg	4.00–45.00	4.00–45.00
scan width, deg	0.83 + 0.35 tan θ	0.57 + 0.35 tan θ
takeoff angle, deg	2.80	2.80
programs used	Enraf-Nonius SDP	Enraf-Nonius SDP
F_{000}	628.0	1016.0
p factor used in weighting	0.040	0.040
data collected	3632	6065
unique data	3632	6065
data with $I > 3.0\sigma(I)$	1939	5399
no. of variables	288	551
largest shift/esd in final cycle	0.01	0.01
R	0.055	0.026
R_W	0.059	0.036
goodness of fit	1.173	1.404

^{a} Walker, N.; Stuart, D. *Acta Crystallogr., Sect. A* **1983**, *A39*, 158. ^{b} Flack, H. D. *Acta Crystallogr., Sect. A* **1977**, *A33*, 890.

°C) saturated toluene solution. ^{1}H NMR (C_6D_6, 30 °C): δ 6.7–8.2 (multiplets). ^{13}C NMR (C_6D_6, 30 °C): δ 202.2 [Ta–C(ipso)].

Ta(OC$_6$H$_3$PhC$_6$H$_4$)$_2$(OAr-2,6-Ph$_2$)(PMe$_2$Ph) (5). An identical procedure used above, only this time using 2 (2.0 g, 2.02 mmol), Na (0.1 g, 4.35 mmol), and added PMe$_2$Ph (0.56 g, 4.05 mmol) led to the isolation of the white phosphine adduct 5 in 78% yield. Anal. Calcd for TaC$_{62}$H$_{48}$PO$_3$: C, 70.59; H, 4.77; P, 2.94. Found: C, 71.04; H, 4.93; P, 2.99. ^{1}H NMR (C_6D_6, 30 °C): δ 0.70 (d, P*Me$_2$*Ph), 6.5–8.3 (complex overlapping multiplets due to aromatic signals). ^{13}C NMR (C_6D_6, 30 °C): δ 190.1 (Ta–C$_{ipso}$), 13.44 (d, P*Me$_2$*Ph). ^{31}P NMR (C_6D_6, 30 °C): δ −38.60.

Ta(OC$_6$H$_3$Bu^{t}CMe$_2$CH$_2$)(OAr-2,6-Bu^t)(BH$_4$)(Cl) (6). To 0.5 g of Ta(OC$_6$H$_3$Bu$^t_2$-2,6)$_2$Cl$_3$ dissolved in benzene (30 mL) was added 0.63 g of LiBH$_4$ (4 equiv). The reaction was stirred for 24 h, during which time the dark orange solution turned dark

green. The solution was filtered, and the solvent was removed from the yellow filtrate. The resulting crude product is a light yellow solid, which can be recrystallized from hexane. Yield: 0.37 g, 81%). Anal. Calcd for TaC$_{28}$H$_{45}$O$_2$BCl: C, 52.48; H, 7.07; Cl, 5.53; B, 1.68. Found: C, 52.77; H, 7.11; Cl, 5.68; B, 1.69. ^{1}H NMR (470 MHz, C$_7$D$_8$, 30 °C): δ 1.24 (s, OC$_6$H$_3$*Bu^t*-CMe$_2$CH$_2$), 1.30 (s, OC$_6$H$_3$Bu^t-C*Me$_2$*CH$_2$), 1.38 (s, OC$_6$H$_3$*Bu$^t_2$*), (OC$_6$H$_3$Bu^t-CMe$_2$C*H$_2$* signals are obscured by Bu^t peaks), 4.3, 4.7 (br, Ta*H$_2$*-B*H$_2$*), 6.65–7.10 (m, O*C$_6$H$_3$*Bu^t and O*C$_6$H$_3$*Bu^t-CMe$_2$CH$_2$). ^{13}C NMR (C$_6$D$_6$, 30 °C): δ 30.7 (OC$_6$H$_3$C*Me$_3$*-CMe$_2$CH$_2$), 32.3 (OC$_6$H$_3$C*Me$_3$*), 35.2 (OC$_6$H$_3$*C*Me$_3$-CMe$_2$CH$_2$), 35.3 (OC$_6$H$_3$*C*Me$_3$), 36.4 (C$_6$H$_3$CMe$_3$-C*Me$_2$*CH$_2$), 39.2 (OC$_6$H$_3$CMe$_3$-*C*Me$_2$CH$_2$), 90.9 (OC$_6$H$_3$CMe$_3$-CMe$_2$*C*H$_2$); IR (Nujol mull, KBr plates): 2440, 2500, 1445, 1180 cm^{-1}.

Crystallographic Studies

Ta(OC$_6$H$_3$Bu^{t}CMe$_2$CH$_2$)$_2$Cl (3) and Ta(OC$_6$H$_3$PhC$_6$H$_4$)$_2$- (OAr-2,6-Ph$_2$) (4). Crystal data and data collection parameters are given in Table V. A suitable crystal of each of the two compounds was mounted in a glass capillary in a random orientation. Cell constants and an orientation matrix for data collection were obtained from least-squares refinement using the scattering angles of 25 reflections in the range 4° < θ < 12° for 3 and 19° < θ < 21° for 4 as measured by the computer-controlled diagonal slit method of centering. As a check on crystal quality, ω scans of several intense reflections were measured and the width at half-height was found to be 0.83° for 3 and 0.57 for 4 with a takeoff angle of 2.8°. Systematic absences and subsequent least-squares refinement indicated the space group $P\bar{1}$ for both compounds. The data were collected at room temperature in both cases by using the ω–θ scan technique. The scan rate varied from 2° to 20°/min in ω, and data were collected to a maximum 2θ of 45°. Moving crystal, moving counter background counts were made by scanning an additional 25% above and below the scan width. The counter aperture was adjusted as a function of θ. For intense reflections an attenuator (factor 12.9) was automatically inserted in front o f the detector. As a check on crystal and electronic stability three standard reflections were remeasured every 2000 s of beam time. A total loss of intensity of 51% for 3 and only 6% for 4 was observed, and a linear decay correction was applied in the former case.

The structures were solved by using the Patterson heavy-atom method to reveal the position of the tantalum atoms. The remaining heavy atoms were located in succeeding difference Fourier syntheses. Hydrogen atoms were located and added to the structures, but their positions were not refined. All calculation including the full-matrix least-squares refinement were performed by using Enraf-Nonius SDP on a VAX computer.

Supplementary Material Available: Listings of anisotropic thermal parameters and full bond distances and angles for 3 and 4 (19 pages); listings of observed and calculated structure factor amplitudes for 3 and 4 (52 pages). Ordering information is given on any current masthead page.