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Communications

Evidence for the Formation of a Tantalum(IV) Arene Species from Arene–Alkyl Complexes of Tantalum(III)

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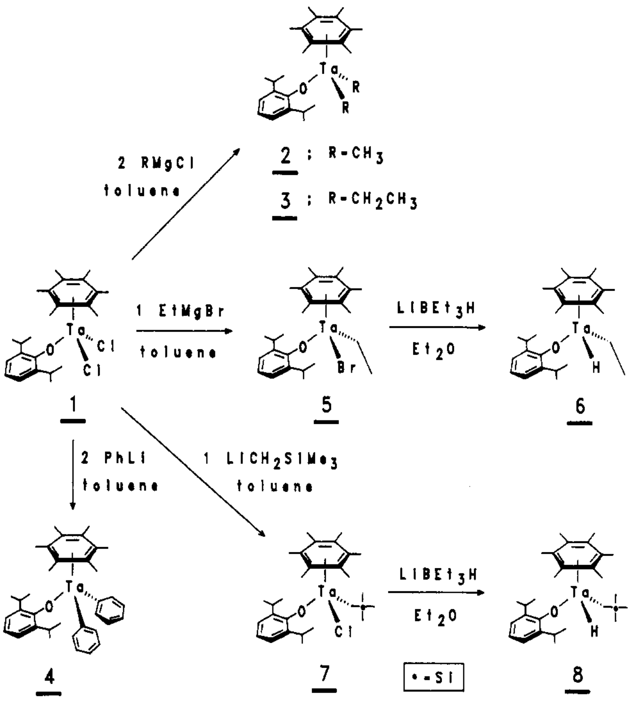
Summary: Alkylation of tantalum(III) arene complexes affords stable dialkyl and monoalkyl halide species (η^6-C_6Me_6)Ta(DIPP)R_2 (DIPP = 2,6-diisopropylphenoxide) and (η^6-C_6Me_6)Ta(DIPP)RX. The alkyl hydride complexes (η^6-C_6Me_6)Ta(DIPP)R(H) are also prepared from (η^6-C_6Me_6)Ta(DIPP)RX and $LiBEt_3H$. The arene ring in (η^6-C_6Me_6)Ta(DIPP)Et_2 exhibits a structure consistent with a diene–diyl distortion. The first evidence for the formation of a d^1 arene species is presented in cyclic voltammetry experiments on these compounds.

Intramolecular metalation of a C–H bond[1] in pentamethylcyclopentadienyl ligands (η^5-C_5Me_5) can provide isolable complexes containing the "tucked-in" η^5,η^1-$C_5Me_4CH_2$ moiety. Various mechanistic pathways may lead to these compounds, including C–H addition to an alkyl,[2] hydride,[3] or benzyne[4] ligand, C–H addition across a metal–carbon double bond,[5] or C–H oxidative addition to a d^2 metal.[6] The hexamethylbenzene ligand (η^6-C_6Me_6) has also been observed to tuck in,[7] but only by oxidative addition to a d^2 metal. This process renders labile the η^6

Scheme I



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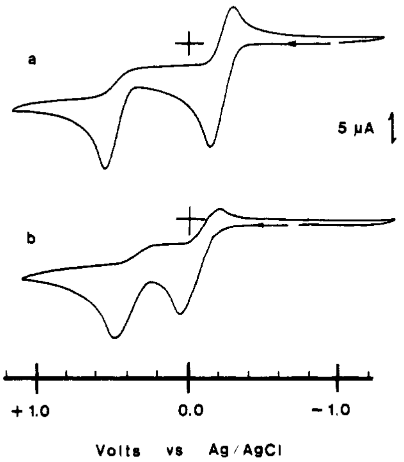

Figure 1. Cyclic voltammograms of (a) (η^6-C_6Me_6)Ta(DIPP)Ph_2 in CH_2Cl_2 and (b) (η^6-C_6Me_6)Ta(DIPP)Me_2 in THF. Both solutions were 0.1 M in $^nBu_4NPF_6$, and voltammograms were taken at a Pt-disk electrode (vs Ag/AgCl) at a scan rate of 150 mV/s.

portion of a nascent η^6,η^1-$C_6Me_5CH_2$ ligand and results in the isolation of a d^0 η^1-$C_6Me_5CH_2$ complex.[7,8] Trapping a *neutral*[9] η^6,η^1-$C_6Me_5CH_2$ complex will most likely require a $d^{n>0}$ metal, a possibility which prompted us to prepare η^6-C_6Me_6 complexes of Ta(III) containing alkyl, phenyl, and hydride ligands. We report here the preparation and properties of these compounds, including their one-electron oxidations to provide the first evidence for a d^1 arene species.

(η^6-C_6Me_6)Ta(DIPP)Cl_2[8] (1; DIPP = 2,6-diisopropylphenoxide) reacts rapidly with 2 equiv of CH_3MgBr (toluene, −60 °C) to provide, after appropriate workup, blue-violet crystals of (η^6-C_6Me_6)Ta(DIPP)Me_2 (2) in ca. 75% yield (Scheme I).[10] The analogous reactions using 2 equiv of CH_3CH_2MgBr or PhLi afford blue-violet (η^6-C_6Me_6)Ta(DIPP)Et_2 (3) and purple (η^6-C_6Me_6)Ta(DIPP)Ph_2 (4) in high yield. In contrast to the precursor dichloride 1 and the related compound (η^6-C_6Me_6)Ta(DIPP)$_2$Cl,[11] complexes 2–4 are quite stable thermally (qualitatively, 2 ≈ 4 > 3). Thus, while (η^6-C_6Me_6)Ta(DIPP)$_n$$Cl_{3-n}$ (n = 1, 2) are completely decomposed in <1 min in refluxing toluene-d_8,[8] (η^6-C_6Me_6)Ta(DIPP)Me_2 (2) and (η^6-C_6Me_6)Ta(DIPP)Ph_2 (4) are only ca. 40% decomposed after 5 days under these conditions. The only identifiable thermolysis product is C_6Me_6, while the metal-containing species reduces to an intractable, insoluble material. Even the β-H-containing complex (η^6-C_6Me_6)Ta(DIPP)Et_2 (3) decomposes more slowly than the chloride complexes.[12]

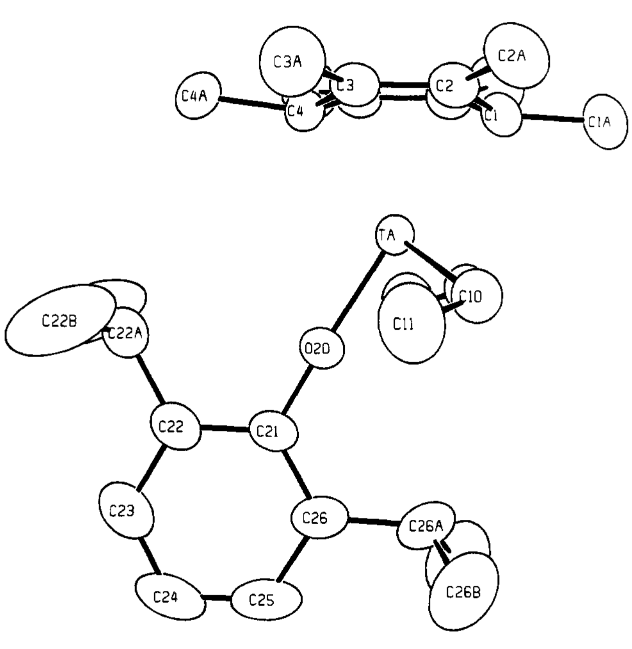

Figure 2. ORTEP drawing of (η^6-C_6Me_6)Ta(DIPP)Et_2 (3), with atoms shown as 50% probability ellipsoids.

The thermal robustness of 2–4 has permitted their full characterization. Thus, molecular ion peaks were obtained for (η^6-C_6Me_6)Ta(DIPP)Me_2 (m/z = 550) and (η^6-C_6Me_6)Ta(DIPP)Et_2 (m/z = 578) in low-resolution CI mass spectrometry studies. Cyclic voltammetry experiments on (η^6-C_6Me_6)Ta(DIPP)Ph_2 (4; CH_2Cl_2, 0.1 M in $^nBu_4NPF_6$) reveals two one-electron-oxidation processes (Figure 1). A quasi-reversible oxidation (the Ta(III) $\rightleftarrows$ Ta(IV) couple) occurs at $E_{1/2}$ = −0.22 V vs Ag/AgCl ($E_{pa} - E_{pc}$ = 120 mV), while a second, irreversible oxidation (Ta(IV) → Ta(V)) comes at E_{pa} = +0.53 V vs Ag/AgCl. A plot of i_{pa} vs the square root of the sweep rate ($v^{1/2}$) is linear (R = 0.993) for the −0.22 V oxidation, and i_{pa}/i_{pc} becomes 1.0 at scan rates >300 mV/s, so this process is best described as quasi-reversible on the CV time scale. Bulk electrolysis of a solution of 4 reveals that 1.0 ± 0.1 electron is transferred in the −0.22 V oxidation, although the resulting solution is devoid of electrochemically active species. Dilute samples of 4 may be chemically oxidized in toluene ([Cp_2Fe][BPh_4], −78 °C) to afford highly reactive solutions which exhibit an ESR signal (X-band, $\langle g \rangle$ = 1.933, peak-to-peak separation 145 G). However, ^{181}Ta hyperfine is not observed nor necessarily expected in these spectra (at room temperature or at −196 °C).[8,15] Compounds 2 and 3 also exhibit two electrochemical oxidations in THF[13] (2 and 3 are unstable in CH_2Cl_2 and N≡CMe), but both are irreversible (Figure 1). Consistent with the ease of oxidation of (η^6-C_6Me_6)Ta(DIPP)Me_2 (2) is the very low energy ionization band (at 5.91 eV) observed in its He I photoelectron spectrum.[14] Although (η^6-C_6Me_6)Ta(DIPP)$_2$Cl can be reduced by one electron,[15] 2–4 are not observed to undergo an electrochemical reduction to ca. −2 V vs Ag/AgCl in THF. All of these data support the metal center in 2–4 being more "electron rich" than in their chloride precursor and suggest that their improved thermal stability may arise through enhanced back-bonding to the arene (vide infra).

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[7] Ballard, K. R.; Gardiner, I. M.; Wigley, D. E. *J. Am. Chem. Soc.* **1989**, *111*, 2159.

[8] Arney, D. J.; Wexler, P. A.; Wigley, D. E. *Organometallics* **1990**, *9*, 1282.

[9] (a) Apparently, when δ symmetry back-bonding between a metal orbital and arene LUMO levels is lost, i.e. upon oxidizing the metal to a neutral d^0 complex, simple L → M donation is not sufficient to maintain arene coordination in a neutral complex. This does not appear to be the case when the metal center is cationic, as [(η^6-C_6Me_6)$TiCl_3$]$^+$ is a stable species. See: Solari, E.; Floriani, C.; Chiesi-Villa, A.; Guastini, C. *J. Chem. Soc., Chem. Commun.* **1989**, 1747. (b) See also: Bochmann, M.; Karger, G.; Jaggar, A. J. *J. Chem. Soc., Chem. Commun.* **1990**, 1038.

[10] Analytical and spectroscopic data for compounds 2–8 are available as supplementary material.

[11] Bruck, M. A.; Copenhaver, A. S.; Wigley, D. E. *J. Am. Chem. Soc.* **1987**, *109*, 6525.

[12] No elimination products (e.g. C_2H_6 or C_2H_4) were observed spectroscopically in the thermolysis of 3. The photolysis of 3 and 4 achieved the same decomposition results over a period of 2–3 h.

[13] Redox potentials (V vs Ag/AgCl) in THF: (η^6-C_6Me_6)Ta(DIPP)Me_2 (2), E^1_{pa} = +0.07, E^2_{pa} = +0.50; (η^6-C_6Me_6)Ta(DIPP)Et_2 (3), E^1_{pa} = +0.21, E^2_{pa} = +0.70.

[14] Jatcko, M.; Lichtenberger, D. L. Unpublished results.

[15] Wexler, P. A.; Wigley, D. E.; Koerner, J. B.; Albright, T. A. *Organometallics* **1991**, *10*, 2319.

The molecular structure of (η^6-C_6Me_6)Ta(DIPP)Et_2[16,17] (**3**; Figure 2) reveals an interesting comparison to the parent chloride. Both structures feature a coordinated C_6Me_6 ligand which shows (i) substantial folding[18] (the dihedral angle between the C(1)–C(2)–C(3)–C(4) and C(1)–C(2′)–C(3′)–C(4) planes in **3** is 27.3 (0.2)°, which compares with 26.8 (0.3)° for (η^6-C_6Me_6)Ta(DIPP)Cl_2[8]), (ii) an interruption of aromaticity within the C_6Me_6 ring (viz. a 1,4-diene type π localization), and (iii) the close approach of C(1) and C(4) to the metal (2.302 (5) and 2.187 (5) Å, respectively, compared to an average 2.481 (4) Å for the other arene carbons). These features may be attributed to a back-bonding interaction between filled metal δ functions and the arene LUMO.[8,15] In addition, the metal–carbon distances (C(1) vs C(4)) may reflect a structural trans effect since C(1) is "trans" to the strong π-donor alkoxide ligand. The rotational conformation of the arene ring in **3** is such that the ethyl Ta–C_α and alkoxide Ta–O–C_{ipso} linkages perfectly eclipse the arene carbon atoms, rather than stagger them as in (η^6-C_6Me_6)Ta(DIPP)Cl_2 (**1**).[8] Finally, the plane of the DIPP ligand is oriented perpendicular to the arene, 90° from the DIPP plane in **1**.[8]

Because α- or β-H elimination/abstraction reactions did not lead to tuck-in complexes in the dialkyls,[5a] alkyl hydrides were prepared. (η^6-C_6Me_6)Ta(DIPP)Cl_2 reacts with *1 equiv* of CH_3CH_2MgBr (toluene, −60 °C) to provide the "double exchange" product (η^6-C_6Me_6)Ta(DIPP)EtBr (**5**; m/z = 628 (^{79}Br), 630 (^{81}Br)) in >95% yield (by ^1H NMR). This reaction is no doubt driven by the lattice energy of $MgCl_2$, as the expected product (η^6-C_6Me_6)Ta(DIPP)EtCl is present in <5% yield. (η^6-C_6Me_6)Ta(DIPP)EtBr (**5**) reacts with $LiBEt_3H$ (Et_2O, −65 °C) to provide (η^6-C_6Me_6)Ta(DIPP)Et(H) (**6**) as an extremely soluble magenta solid in high yield (Scheme I). Similarly, (η^6-C_6Me_6)Ta(DIPP)(CH_2SiMe_3)Cl (**7**; prepared from **1** and 1 equiv of $LiCH_2SiMe_3$) reacts smoothly with $LiBEt_3H$ under identical conditions to afford (η^6-C_6Me_6)Ta(DIPP)(CH_2SiMe_3)(H) (**8**) as a purple solid. Both **6** and **8** exhibit a Ta*H* hydride resonance at ca. δ 5.87 (C_6D_6) and a ν(Ta–H) stretch between 1760 and 1780 cm^{-1}. While **8** is stable for months at room temperature in Et_2O, **6** decomposes slowly (to C_6Me_6 and unidentified products) over a period of hours.

The improved thermal stability of these alkyl complexes vs that of chloride complexes will allow a thorough PES characterization of their electronic structures, which has thus far not been possible for tantalum(III) arenes. Perhaps most significant is the electrochemical evidence for the formation and limited stability of a d^1 arene complex, an observation which supports their participation in the deoxygenative coupling of an acyl and a cyclopentadienyl ligand.[19] The isolation of such a complex with an appropriate counterion is an area of our continued research.

Acknowledgment. We gratefully acknowledge the support of the National Science Foundation (Grant No. CHE-8919367).

Registry No. 1, 126255-41-2; 2, 137007-18-2; 3, 137007-19-3; 4, 137007-20-6; 5, 137007-21-7; 6, 137007-22-8; 7, 137007-23-9; 8, 137007-24-0; PhLi, 591-51-5.

Supplementary Material Available: Analytical and spectroscopic data for compounds 2–8 and complete crystallographic details, including tables of atomic positional and thermal parameters, bond distances and angles, least-squares planes, and dihedral angles and ORTEP figures, for (η^6-C_6Me_6)Ta(DIPP)Et_2 (18 pages); tables of observed and calculated structure factor amplitudes (14 pages). Ordering information is given on any current masthead page.

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(16) Crystal data for $C_{28}H_{45}OTa$ (**3**): orthorhombic, *Pnma* (No. 62) (crystallographic mirror plane), a = 18.717 (4) Å, b = 12.487 (4) Å, c = 11.431 (3) Å, V = 2671.8 (11) Å^3, Z = 4, D(calc) = 1.44 g cm^{-3}, μ(Mo Kα) = 40.8 cm^{-1} (T = 23 ± 1 °C); 2811 total reflections (2456 unique), of which 2005 with $F_o^2 > 3.0\sigma(F_o^2)$ were included in the refinement. Hydrogen atoms were located (rotating anode source, 45 kV, 100 mA) and refined with B_{iso} = 5.0 Å^2; Lorentz and polarization corrections and an empirical absorption correction were applied to the data. Relative transmission coefficients ranged from 0.585 to 0.999 (average 0.789). Final R = 0.020, R_w = 0.027. The highest peak in the final difference Fourier was 0.42 e Å^{-3}.

(17) Selected bond lengths (Å) and angles (deg) for (η^6-C_6Me_6)Ta(DIPP)Et_2 (**3**) (Bz* = C_6Me_6 centroid): Ta–C(1) = 2.302 (5), Ta–C(2) = 2.513 (3), Ta–C(3) = 2.448 (4), Ta–C(4) = 2.187 (5), Ta–C(10) = 2.207 (4), Ta–O(20) = 1.912 (3); Bz*–Ta–C(10) = 109.38 (9), Bz*–Ta–O(20) = 151.0 (1), C(10)–Ta–C(10′) = 103.1 (1), O(20)–Ta–C(10) = 88.0 (1), Ta–O(20)–C(21) = 177.4 (3), Ta–C(10)–C(11) = 113.1 (3), C(1)–Ta–O(20) = 170.9 (2).

(18) A summary of structurally characterized "bent arenes" appears in ref 8.

(19) A transient Ta(IV) arene complex, (arene)Ta(O)Cl_2, is a possible intermediate in this reaction. See: Meyer, T. Y.; Messerle, L. *J. Am. Chem. Soc.* **1990**, *112*, 4564.

Synthetic Routes to the First P-Metalated Phosphiranes: Synthesis and Structure of (η^5-Cyclopentadienyl)dicarbonyl[2,2,3-tris(trimethylsilyl)-1λ^3-phosphacyclopropyl]iron

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Summary: Metallophosphiranes **2a–c** have been obtained by heterogeneous metalation of $ClPCH(SiMe_3)C(SiMe_3)_2$ (**1**) or by reaction of the corresponding *P*-Me_5C_5-substituted phosphirane **4** with $(CO)_3Mo(MeCN)_3$ via a C_5Me_5 shift from phosphorus to the transition metal. One of the final products **2a** has been characterized by X-ray structure analysis.

The coordination chemistry of phosphorus-containing small ring systems is well established, and a vast number of such species, including saturated as well as unsaturated three-membered P/C-ring systems, are known.[1] Only recently this chemistry has been further expanded by in-

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(1) Mathey, F. *Chem. Rev.* **1990**, *90*, 997 and references cited therein.

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