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Organotantalum Bis(amidinate) Complexes: Synthesis and Characterization of Methyl, Methylidene, Benzyl, and Imido Derivatives

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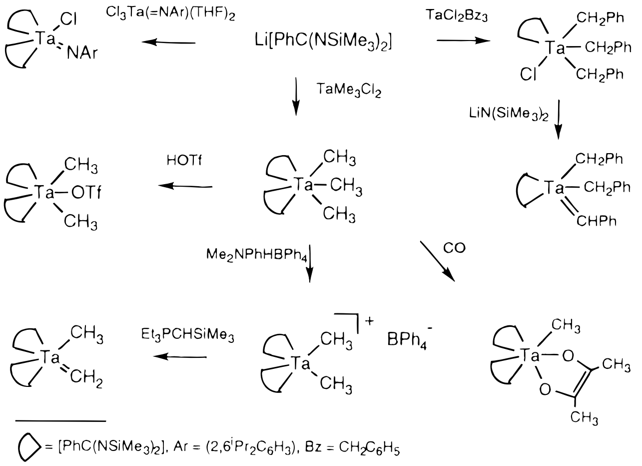
Summary: A new series of tantalum complexes incorporating bis(trimethylsilyl)benzamidinate ligands has been prepared and fully characterized; examples include species with alkyl, alkylidene, and imido functionalities.

Amidinates are a versatile group of ligands containing two nitrogen donor atoms, related in structure to (and isoelectronic with) carboxylates. They are known to coordinate to an exceedingly wide range of metals and non-metals,[1−3] usually binding through both nitrogens in a bidentate fashion to one or two metal centers. We are interested in comparing the chemistry of metal bis(amidinate) systems with the more commonly studied bis(cyclopentadienyl) ligand fragment, with the expectation that the lower electron count at the metal in the former will lead to enhanced electrophilic behavior relative to Cp_2M systems.[4]

Considering the usefulness of amidinate ligands in early transition metal chemistry,[5−10] it is somewhat surprising that there are relatively few reports of tantalum amidinates,[11−16] particularly in light of the wealth of interesting organotantalum chemistry reported to-date.[17,18] (Trimethylsilyl)benzamidinate derivatives are particularly attractive for our purposes: they are simple to prepare and handle, they display excellent solubility in nonreactive solvents, their steric bulk dissuades dimerization, and electronic factors may be probed by substitution on the phenyl group.[19] Following our recent studies of (porphyrin)TaR_3 complexes,[20] we now describe an entry into related amidinate chemistry with the synthesis and characterization of a new series of tantalum bis(benzamidinate) complexes involving alkyl, alkylidene, and imido functionalities.

Scheme 1



As shown in Scheme 1, reaction of 2 equiv of the lithium benzamidinate $[PhC(NSiMe_3)_2]Li$ with trimethyltantalum dichloride gave $[PhC(NSiMe_3)_2]TaMe_3$, which was isolated as beige crystals in reasonable yields from concentrated hexanes.[21]

The trimethyl derivative dissolves in hydrocarbons and ethers to form air-sensitive solutions that are stable for several days at room temperature. Somewhat surprisingly for an early transition metal organometallic, the solid may be handled in air briefly without detectable decomposition. Room-temperature ^1H NMR spectroscopy shows broad resonances for the metal-bound methyls; upon cooling of the sample to −60 °C this signal splits into two peaks of relative ratio 2:1 indicating two different methyl environments that interconvert with a $\Delta G^‡$ at the coalescence temperature (0 °C) of 12.7 kcal/mol. X-ray crystallography, carried out on the closely related *p*-tolylbenzamidinate derivative, confirmed the inequivalence of the methyl groups, as shown in Figure 1.[22] The metal-bound methyls are

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[19] For crystallographic reasons, the related *p*-tolylbenzamidinate derivates were prepared in some cases. Their reactivity appears to be identical to the phenyl derivatives. Spectroscopic data are given as Supporting Information.

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[21] Full characterization data are provided as Supporting Information.

[22] Crystallographic data for $C_{31}H_{59}N_4Si_4Ta$: monoclinic, $P2_1/c$, a = 13.045(4) Å, b = 18.454(5) Å, c = 16.922(4) Å, β = 108.39(2)°, V = 3866(2) Å^3, Z = 4, ρ_{calcd} = 1.34 g/cm^3, μ = 29.88 cm^{-1}, T = −119 °C. Data were collected using an Enraf-Nonius CAD4 diffractometer and the structure refined on F using standard least-squares and Fourier techniques. The final residuals for 362 variables refined against 3067 data for which $I > 3\sigma(I)$ were R = 0.033 and R_w = 0.031.

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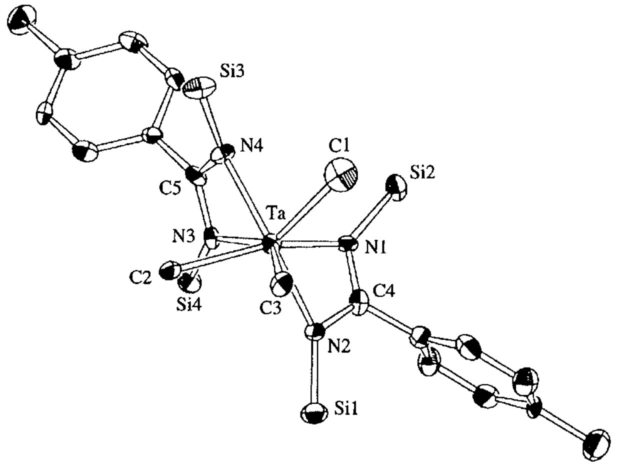

Figure 1. ORTEP drawing of $[TolC(NSiMe_3)_2]_2TaMe_3$ with 50% probability thermal ellipsoids (methyl groups on silicons removed for clarity).

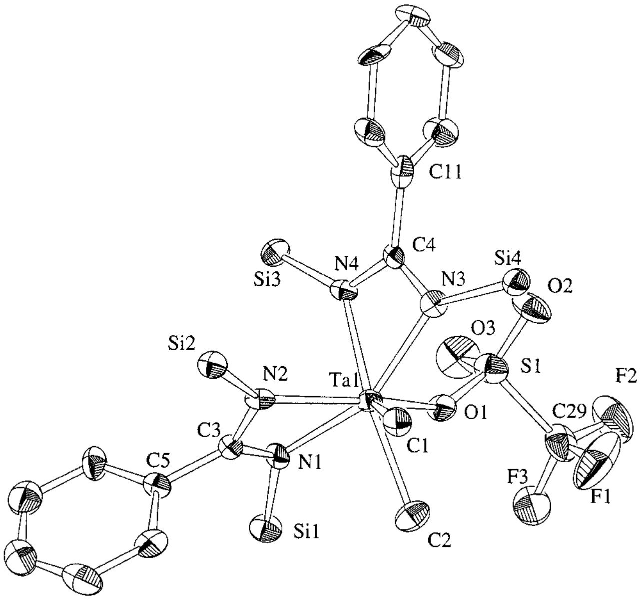

Figure 2. ORTEP drawing of $[PhC(NSiMe_3)_2]_2TaMe_2(O_3SCF_3)$ with 50% probability thermal ellipsoids (methyl groups on silicons removed for clarity).

arranged in an arc with the two outer carbons, C(10) and C(11), 130° apart, and the inner carbon, C(12), 75–80° from the outer two. While the Ta–C bonds appear to be inequivalent (2.22(1), 2.26(1), and 2.29(1) Å), the relatively high esd's suggest that at least the latter two values are effectively equivalent. The Ta–N distances range from 2.15(1) to 2.29(1) Å with the amidinates being bound asymmetrically, such that there is one short and one long Ta–N bond in each amidinate, which in turn leads to the observation of inequivalent C–N bonds. As is common in bis(amidinate) complexes, the two longest M–N bonds are seen when ligands with a strong trans influence are present. In this instance these appear to be the two methyl groups C(2) and C(3). For comparison, the Ta–C and Ta–N bond lengths are effectively identical to those seen in $[CyN(SiMe_3)_2]_2TaMeCl_2$ (Ta–C 2.22(2) and Ta–N 2.04–2.12(2) Å).[12]

The trimethyl complex reacts rapidly with 2 equiv of CO (1 atm) at room temperature to produce the enediolate $L_2Ta(OMeC{=}CMeO)Me$, isolated as red needles from hexane. The structure is of low symmetry as judged by ^1H NMR spectroscopy, with the TMS protons appearing as four distinct peaks and the remaining three methyls each giving rise to a singlet. The enediolate methyls are shifted downfield to 2.5 ppm, compared to 0.6 ppm for the remaining Ta-bound methyl. Upon heating of the sample to 330 K, two of the TMS resonances coalesce, as do the two downfield methyl resonances, with a calculated $\Delta G^{\ddagger}$ of 16.5 kcal/mol (at 57 °C). In the ^{13}C derivative (from use of ^{13}CO) a strong ^{13}C singlet was observed at 110.8 ppm which splits the enediolate methyl protons into two doublets.[20,23–26] The ^{13}C resonance is upfield of that in the related cationic Ta enolate species $[(OEP)Ta(OMe^{13}C{=}^{13}CMeO)][BPh_4]$ which is seen at 142 ppm.[20] Solution IR spectroscopy revealed stretches at 1618 ($\nu_{C=C}$), 1247, and 1162 cm^{-1} (ν_{C-O}), which are similar to those seen in related actinide bis(cyclopentadienyl) enediolate complexes.[24]

Reaction of the trimethyl with HOTf gave good yields of the dimethyltriflate complex, whose solubility in relatively nonpolar solvents such as ether and benzene suggests that the triflate ligand is covalently bound in these solvents. In contrast, conducting solutions are formed in solvents with higher dielectric constants, such as acetonitrile, indicating the formation of the 1:1 electrolyte $\{L_2TaMe_2\}^+[OTf]^-$. The solid compound is virtually isomorphic with the trimethyl, displaying almost identical unit cell parameters as determined by X-ray crystallography.[27] The geometry is also quite similar, with the triflate ligand and the two methyls situated in the previously observed arclike fashion and the triflate located at an outer position. The Ta–O and Ta–C bond lengths, 2.175(7) and 2.18(1) Å, may be compared to the structurally related compound, $[N_3N]TaMe(OTf)$, which exhibits a longer Ta–O bond (2.243 Å) but a comparable Ta–C bond length of 2.159 Å.[28]

The free bis(amidinato)tantalum dimethyl cation was obtained as its tetraphenylborate salt by reaction of $[Me_2NPhH][BPh_4]$ with the trimethyl complex in CH_2Cl_2 or THF. The product is not soluble in hexanes or ether, sparingly soluble in benzene, and soluble in polar solvents such as methylene chloride and THF. As is common for complexes of this type, the compound prefers to oil out of solution; nonetheless microcrystalline solids can be obtained by careful recrystallization. The ^1H NMR spectrum taken in $CDCl_3$ shows a sharp singlet at 1.60 ppm for the Ta methyls, close to the corresponding value in the triflate derivative.

Deprotonation of the dimethyl cation with $Me_3P{=}CH_2$ or $Et_3P{=}CH(SiMe_3)$ gave $L_2Ta({=}CH_2)Me$, a rare example[29–31] of a tantalum methylidene. The ^1H NMR

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(27) Crystallographic data for $C_{29}H_{52}N_4OSSi_4Ta$: monoclinic, $P2_1/n$, $a = 13.4820(3)$ Å, $b = 17.8736(4)$ Å, $c = 16.4602(2)$ Å, $\beta = 98.790(1)°$, $V = 3919.9(1)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.34$ g/cm^3, $\mu = 30.23$ cm^{-1}, $T = -122$ °C. Data were collected using a Siemens SMART diffractometer/CCD area detector and the structure refined on F using standard least-squares and Fourier techniques. The final residuals for 402 variables refined against 3695 data for which $I > 3\sigma(I)$ were $R = 0.046$ and $R_w = 0.049$.

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resonance of the methyl group is in the same region as that seen for the complexes above. At δ 4.1 ppm, the proton signal of the methylidene is significantly upfield from that seen for $Cp_2Ta({=}CH_2)Me$ (δ 10.22 ppm), being closer to values seen for mono-Cp-containing alkylidenes such as $CpTa(CH^tBu)Cl_2$ (δ 3.63 ppm).[31,32] In the ^{13}C spectrum, the methylene appears as in the usual range[34] at δ 192.5 ppm (q, $^1J_{CH}$ 118 Hz).[35] Further evidence for the proposed structure comes from the reaction with protic acids, which regenerates the dimethyl cation, and X-ray crystallography, which clearly establishes the geometry. Unfortunately, disorder between the methyl and methylidene groups, which are related by a C_2 axis, limits its usefulness somewhat.[36] We note, however, that the apparent "Ta−C" bond (2.02(2) Å, an average of the Ta−C and Ta═C bonds) is effectively identical to that seen for the $Ta{=}CH_2$ bond in $Cp_2TaMe(CH_2)$ (2.03(1) Å).[37,38]

Reaction of Bz_3TaCl_2 with lithium benzamidinate afforded the mono(amidinate) complex $LTaBz_3Cl$ which was unreactive toward further amidinate substitution. Treatment with $LiN(SiMe_3)_2$ gave the benzylidene $LTa({=}CHPh)Bz_2$ along with $HN(SiMe_3)_2$ and LiCl. This reactivity mirrors that seen by Schrock for the Cp analogue $CpTa(CH_2Ph)_3Cl$.[39]

Finally, the terminal imido complex $L_2Ta({=}NAr)Cl$ was easily synthesized by treatment of $Ta({=}NAr)Cl_3(THF)_2$ with 2 equiv of lithium benzamidinate. The compound is quite soluble in nonpolar solvents and was isolated from hexanes as a bright yellow crystalline solid. ^1H NMR spectroscopy shows two inequivalent isopropyls at room temperature, no doubt due to hindered rotation as a result of the bulk of the aryl group.[40]

Further work aimed at probing reactivity of these compounds is in progress.

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Note Added in Proof: Diphenylformamidinate derivatives of tantalum were recently reported: Cotton, F. A.; Matonic, J. H.; Murillo, C. A.; Wang, X. *Bull. Soc. Chim. Fr.* **1996**, *133*, 711.

Supporting Information Available: Text providing characterization data for all new compounds and details of the X-ray structure determinations and tables of crystal and data collection parameters, temperature factor expressions, positional parameters, intramolecular distances and angles, and least-squares planes (17 pages). Ordering information is given on any current masthead page.

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