# Formation of Tantalum “Tuck-in” Complexes by Activation of Methyl C−H Bonds in Pentamethylcyclopentadiene Groups by Carbazole Ligation

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The reaction of [Cp*TaCl$_4$] with the potassium salt of carbazole (cbK, >3 equiv) in hydrocarbon solvents leads to the species [(C$_5$Me$_4$CH$_2$)Ta(cb)$_2$Cl] (**1**), in which one of the ring methyl C−H bonds of the Cp* ligand has been cleaved along with free cbH. Spectroscopic and structural studies of **1** show a lack of a plane of symmetry through the molecule with nonequivalent cb ligands. A minor component of the reaction mixture is believed to be the substitutional isomer **2**, in which both carbazole ligands are equivalent. Alkylation of **1** with LiCH$_2$SiMe$_3$ or PhCH$_2$MgCl generates the corresponding monoalkyl derivatives [(C$_5$Me$_4$CH$_2$)Ta(cb)$_2$(R)] (**7** or **8**, respectively). Structural studies of **1**, **7**, and **8** support an $\eta^1$:$\eta^5$-CH$_2$C$_5$Me$_4$ ($\sigma$:$\eta^5$-CH$_2$C$_5$Me$_4$) description for the metalated ligands, with significant slippage toward an $\eta^1$:$\eta^3$-CH$_2$C$_5$Me$_4$ resonance form. To compare the extent of $\pi$-bonding between cb and dialkylamido ligands, the complex [(cb)$_2$Ta(NMe$_2$)$_3$] (**9**) was synthesized and structurally characterized. The molecular structure of **9** consists of a tbp arrangement of nitrogen atoms with trans, axial cb ligands. The Ta−cb distances are 0.2 Å longer than the Ta−NMe$_2$ distances. An improved (safer) procedure for the synthesis of [Ta(NMe$_2$)$_5$] is presented.

## Introduction

There is a growing body of research which demonstrates that the ring methyl groups in the important pentamethylcyclopentadienyl (Cp*) ligand can be activated at early d-block metal centers. This work has stimulated considerable discussion as to the relative merits of describing the resulting ligand as either a (1,2,3,4-tetramethylcyclopentadienyl)methyl or a tetramethylfulvene group. Bercaw and co-workers observed an early example in the system [TiH(CH$_2$C$_5$Me$_4$)($\eta^5$-C$_5$Me$_5$)], in which a hydrogen atom was transferred to the titanium from a methyl group.[1] Upon examining the reactivity of [Cp*$_2$Ti] with N$_2$O, Bottomley discovered a related complex where the ligand bridges two titanium atoms.[2] Thermolysis reactions of [Cp*$_2$ZrPh$_2$] were found to produce [Cp*ZrPh(C$_5$Me$_4$CH$_2$)] by a pathway which involves an intramolecular arene elimination and subsequent methyl C−H scission.[3] The thermolysis of [Cp*$_2$Hf(CH$_2$C$_6$H$_5$)$_2$] occurs by an α-H abstraction process to generate the alkylidene, which rearranges to form [Cp*(C$_5$Me$_4$CH$_2$)HfCH$_2$C$_6$H$_5$] prior to formation.[4] There have been fewer examples of group 5 Cp* complexes involving ring methyl group C−H bond cleavage. Gibson and co-workers observed a double intramolecular ring metalation in the formation of [{C$_5$Me$_3$(CH$_2$)$_2$}Ta(H)$_2$(PMe$_3$)$_2$].[5] More recently niobium and tantalum complexes with a “tetramethylfulvene” ligand[6] were reacted with sulfur to produce novel niobium and tantalum disulfides.[7]

We have recently been investigating the inorganic and organometallic chemistry of ligands derived from the carbazole nucleus.[8] During our investigation of the group 5 metal chemistry of the carbazole ligand, we have isolated a series of tantalum ring metalated compounds. This paper reports the synthesis and characterization of these compounds.

## Results and Discussion

**Synthesis of Compounds and Spectroscopic Characterization.** The reaction of [Cp*TaCl$_4$] with the potassium salt of carbazole (cbK)[9] in hydrocarbon solvents led to the formation of complex mixtures.

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[1] (a) Bercaw, J. E. *J. Am. Chem. Soc.* **1974**, *96*, 5084. (b) Bercaw, J. E.; Marvich, R. H.; Bell, L. G.; Brintzinger, H. H. *J. Am. Chem. Soc.* **1972**, *94*, 1219. (c) McDade, C.; Green, J. C.; Bercaw, J. E. *Organometallics* **1982**, *1*, 1629.

[2] Bottomley, F.; Lin, I. J. B.; White, P. S. *J. Am. Chem. Soc.* **1981**, *103*, 703.

[3] (a) Schock, L. E.; Brock, C. P.; Marks, T. J. *Organometallics* **1987**, *6*, 232. (b) Schock, L. E.; Marks, T. J. *J. Am. Chem. Soc.* **1988**, *110*, 7701.

[4] Bulls, A. R.; Schaefer, W. P.; Serfas, M.; Bercaw, J. E. *Organometallics* **1987**, *6*, 1219.

[5] Carter. S. T.; Clegg, W.; Gibson, V. C.; Kee, T. P.; Sanner, R. D. *Organometallics* **1989**, *8*, 253.

[6] Antonelli, D. M.; Schaefer, W. P.; Parkin, G.; Bercaw, J. E. *J. Organomet. Chem.* **1993**, *462*, 213.

[7] (a) Brunner, H.; Gehart, G.; Meier, W.; Wachter, J.; Burgemeister, T. *J. Organomet. Chem.* **1995**, *493*, 163. (b) Brunner, H.; Wachter, J.; Gehart, G.; Leblanc, J.; Moise, C. *Organometallics* **1996**, *15*, 1327.

[8] (a) Riley, P. N.; Profilet, R. D.; Salberg, M. M.; Fanwick, P. E.; Rothwell, I. P. *Polyhedron* **1998**, *17*, 773. (b) Riley, P. N.; Fanwick, P. E.; Rothwell, I. P. *J. Chem. Soc., Chem. Commun.* **1997**, 1109. (c) Riley, P. N.; Profilet, R. D.; Fanwick, P. E.; Rothwell, I. P. *Organometallics* **1996**, *15*, 5502. (d) Profilet, R. D.; Fanwick, P. E.; Rothwell, I. P. *Polyhedron* **1992**, *12*, 1559.

[9] Appler, H. *J. Organomet. Chem.* **1988**, *350*, 217.

10.1021/om990388a CCC: $18.00

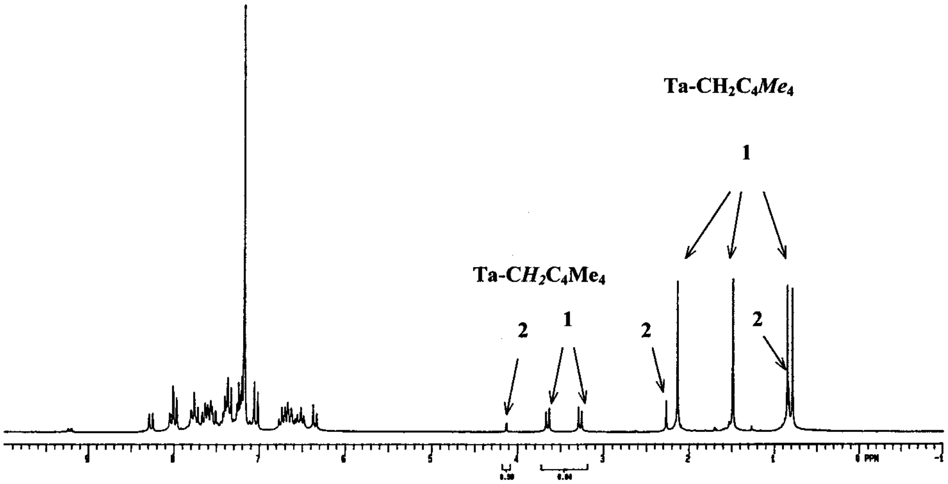
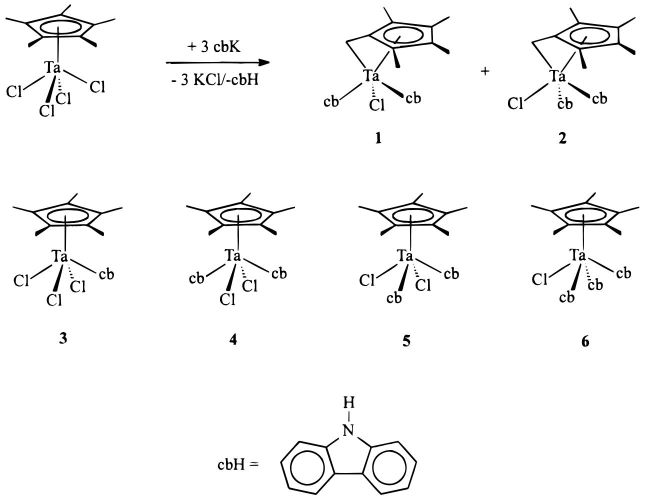


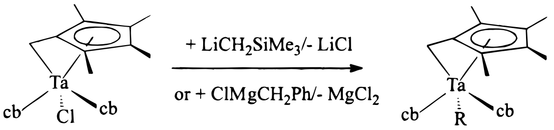
**Figure 1.** $^1H$ NMR spectrum ($C_6D_6$, 200 MHz) of the reaction mixture of **1** and **2**.

**Scheme 1**



Following the reaction by $^1H$ NMR showed the presence of a series of (unisolated) intermediates prior to formation (5 equiv of cbK, excess) of a reaction mixture containing free carbazole and two major organometallic components. The major component was identified as the species [($C_5Me_4CH_2$)Ta(cb)$_2$Cl] (**1**), in which one of the ring methyl C−H bonds of the Cp* ligand has been cleaved (Scheme 1). Compound **1** was isolated pure as an orange crystalline solid in moderate yield. The diastereotopic methylene protons of **1** exhibit an AB pattern in the $^1H$ NMR spectrum ($^2J_{H-H} = 7.32$ Hz) (Figure 1). The observed coupling constant for the diastereotopic protons has an intermediate value between those found for geminal hydrogens attached to sp$^2$-hybridized carbons (0−3 Hz) and sp$^3$-hybridized carbons (12−15 Hz),[10] and this is discussed in more detail below. Four singlets were observed for the methyl groups on the metalated Cp* ligand that remain unbound to the tantalum metal center. The minor component of the initial reaction mixture is believed to be the substitutional isomer **2**. This compound contains a plane of symmetry through the methylene group, resulting in a singlet for the C*H*$_2$ protons and pairs of nonequivalent methyl signals.

**Scheme 2**



**7**; R = $CH_2SiMe_3$
**8**; R = $CH_2Ph$

The formation of **1** and **2** presumably proceeds via the mono-, *cis*-bis- and/or *trans*-bis-, and tris(carbazole) intermediates **3**−**6** (Scheme 1). Although none of these intermediates were isolated, it seems reasonable that the final products result via CH bond activation and elimination of 1 equiv of carbazole from compound **6**. We have shown that isolated **1** does not produce any **2** upon thermolysis in $C_6D_6$ solution at 100 °C for weeks. This indicates that the ratio **1**/**2** observed reflects the rates of methyl CH bond activation by the two types of cb ligands in **6**.

Reaction of **1** with 1 equiv of the alkylating agents $LiCH_2SiMe_3$ and $PhCH_2MgCl$ led to the corresponding monoalkyl derivatives **7** and **8**, respectively (Scheme 2). The $^1H$ NMR spectrum of **7** (Figure 2) shows signals consistent with the structure shown, in which there is no plane of symmetry through the molecule. Specifically, two diastereotopic methylene groups are present along with four nonequivalent ring methyl signals. A similar pattern is observed for the benzyl compound **8**. In both compounds the $^2J_{H-H}$ coupling constants for the alkyl methylene exceeds that measured for the ring-metalated methylene group.

**Structural Studies.** To confirm the molecular geometry and to gain further insight into the bonding of the [$C_5Me_4CH_2$] ligand, compounds **1**, **7**, and **8** were subjected to single-crystal X-ray diffraction studies (Figures 3−5 and Tables 1−3). The first parameters of note are the Ta−N(cb) distances. The major reason for studying this ligand is the expectation that it will undergo much more reduced nitrogen p to metal d $\pi$-bonding than traditional dialkylamido ligation. The molecular structures of all three compounds can be approximately described as three-legged piano stools with the metalated methyl group oriented over (“cis to”) a carbazole ligand. In all three structures the Ta−N distance to this cb ligand is slightly longer than the

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[10] Emsley, J. W.; Feeney, J.; Sutclife, L. H. *High-Resolution Nuclear Magnetic Resonance Spectroscopy*; Pergamon Press: New York, 1966; p 710.

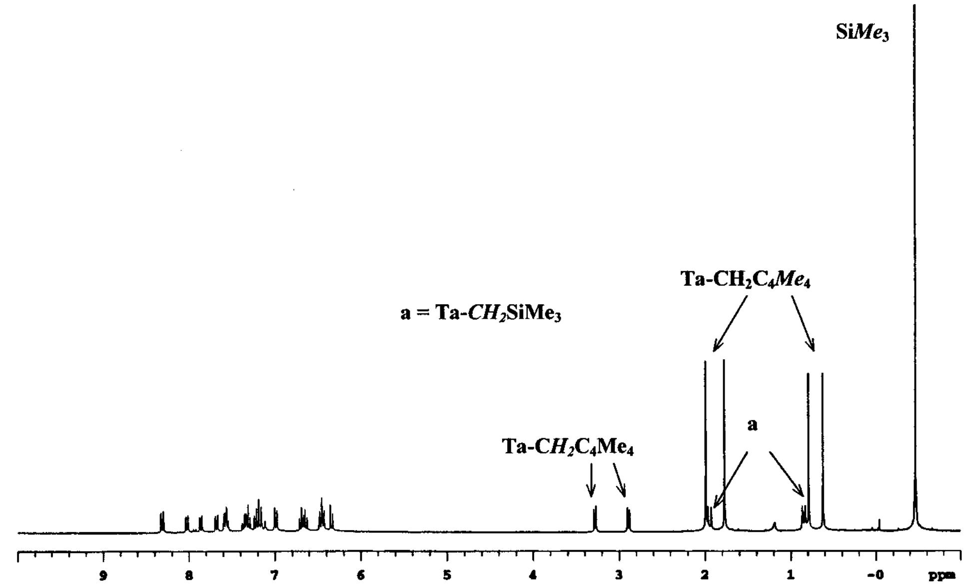

**Figure 2.** $^1$H NMR spectrum ($C_6D_6$, 300 MHz) of **7**.

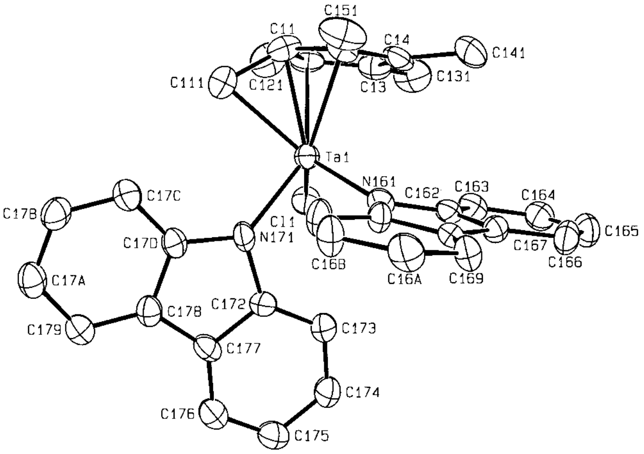

**Figure 3.** ORTEP view of [($C_5Me_4CH_2$)Ta(cb)$_2$Cl] (**1**).

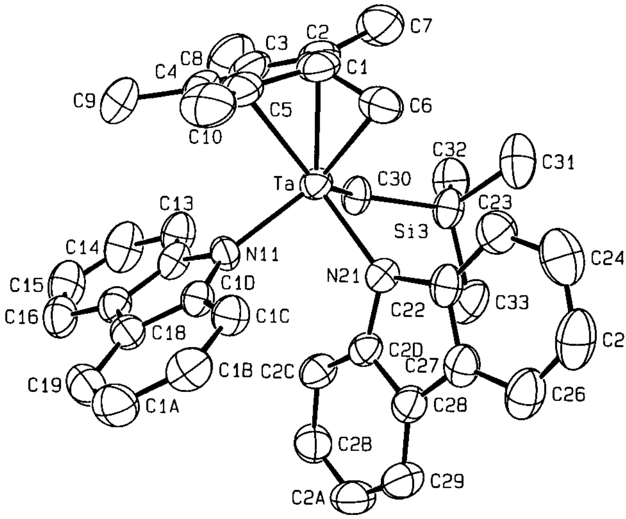

**Figure 4.** ORTEP view of [($C_5Me_4CH_2$)Ta(cb)$_2$($CH_2SiMe_3$)] (**7**).

distance to the other cb ligand (Tables 1−3). This difference in Ta−N(cb) distances is 0.04(1), 0.037(8), and 0.059(8) Å for **1**, **7**, and **8** respectively. However, all Ta−N(cb) distances are themselves longer than typical Ta−N(dialkylamido) distances for such groups bound to

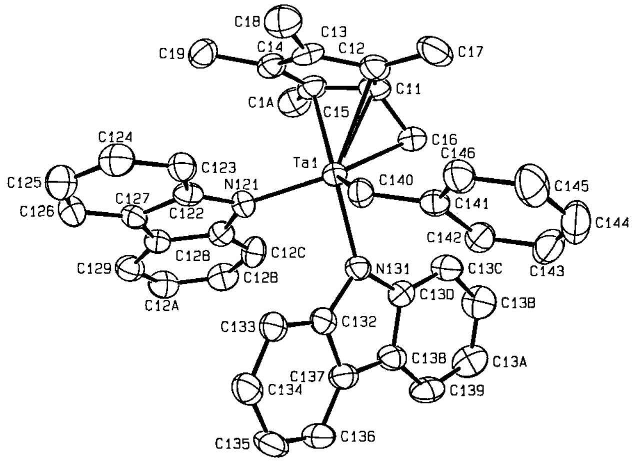

**Figure 5.** ORTEP view of [($C_5Me_4CH_2$)Ta(cb)$_2$($CH_2Ph$)] (**8**).

**Table 1. Selected Bond Distances (Å) and Bond Angles (deg) for [($C_5Me_4CH_2$)Ta(cb)$_2$Cl] (1)**

| | | | |
|---|---|---|---|
| Ta-Cl(1) | 2.331(2) | Ta−C(12) | 2.405(7) |
| Ta−N(161) | 2.054(6) | Ta−C(15) | 2.369(7) |
| Ta−N(171) | 2.098(7) | Ta−C(14) | 2.683(8) |
| Ta−C(111) | 2.258(8) | Ta−C(13) | 2.692(8) |
| Ta−C(11) | 2.207(8) | C(12)−C(13) | 1.42(1) |
| C(11)−C(12) | 1.43(1) | C(13)−C(14) | 1.41(1) |
| C(11)−C(15) | 1.44(1) | C(14)−C(15) | 1.41(1) |
| C(11)−C(111) | 1.46(1) | | |

| | | | |
|---|---|---|---|
| Cl(1)−Ta−C(111) | 116.8(2) | Cl(1)−Ta−N(161) | 110.8(2) |
| Cl(1)−Ta−N(171) | 87.7(2) | C(111)−Ta−N(161) | 131.8(3) |
| C(11)−C(111)−Ta | 69.0(5) | N(161)−Ta−N(171) | 85.1(2) |
| C(111)−Ta−N(171) | 89.7(3) | | |

formally d$^0$ Ta(V) metal centers. Early work by Chisholm et al. established that significant nitrogen p to tantalum d $\pi$-bonding resulted in Ta−N(amido) distances that were considerably shorter than Ta−C(sp$^3$ alkyl) distances within the same molecule.[11] On the basis of covalent radii the Ta−N(sp$^2$) distances are expected to be 0.1 Å shorter than Ta−C(sp$^3$ alkyl) distances when no $\pi$-bonding is present. However,

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[11] Chisholm, M. H.; Tan, L.-S.; Huffman, J. C. *J. Am. Chem. Soc.* **1982**, *104*, 4879.

**Table 2. Selected Bond Distances (Å) and Bond Angles (deg) for [$(C_5Me_4CH_2)Ta(cb)_2(CH_2SiMe_3)$] (7)**

| | | | |
|---|---|---|---|
| Ta−C(30) | 2.143(5) | Ta−N(11) | 2.079(4) |
| Ta−C(6) | 2.246(6) | Ta−N(21) | 2.116(4) |
| Ta−C(1) | 2.206(5) | Ta−C(2) | 2.415(6) |
| Ta−C(5) | 2.369(5) | Ta−C(4) | 2.708(2) |
| Ta−C(3) | 2.714(2) | C(2)−C(3) | 1.41(1) |
| C(1)−C(6) | 1.423(9) | C(3)−C(4) | 1.41(1) |
| C(1)−C(2) | 1.431(9) | C(4)−C(5) | 1.41(1) |
| C(1)−C(5) | 1.437(9) | | |

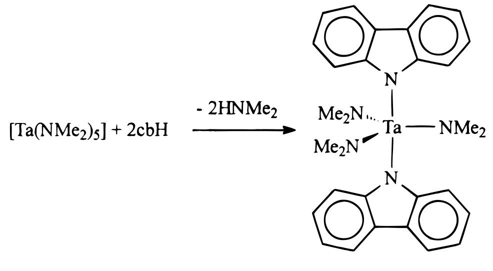
| | | | |
|---|---|---|---|
| C(6)−Ta−C(30) | 117.4(2) | C(30)−Ta−N(11) | 107.9(2) |
| C(1)−C(6)−Ta | 69.8(3) | C(1)−Ta−N(21) | 127.3(2) |
| C(1)−Ta−N(11) | 123.1(2) | N(11)−Ta−N(12) | 86.8(2) |
| C(30)−Ta−N(21) | 89.4(2) | | |

**Table 3. Selected Bond Distances (Å) and Bond Angles (deg) for [$(C_5Me_4CH_2)Ta(cb)_2(CH_2Ph)$] (8)**

| | | | |
|---|---|---|---|
| Ta−C(140) | 2.194(5) | Ta−N(121) | 2.063(4) |
| Ta−C(16) | 2.254(6) | Ta−N(131) | 2.122(4) |
| Ta−C(11) | 2.203(5) | Ta−C(12) | 2.418(5) |
| Ta−C(15) | 2.345(5) | Ta−C(14) | 2.663(5) |
| Ta−C(13) | 2.674(5) | C(12)−C(13) | 1.434(8) |
| C(11)−C(16) | 1.448(7) | C(13)−C(14) | 1.392(8) |
| C(11)−C(12) | 1.425(8) | C(14)−C(15) | 1.405(8) |
| C(11)−C(15) | 1.430(7) | | |

| | | | |
|---|---|---|---|
| C(16)−Ta−C(140) | 115.2(2) | C(140)−Ta−N(121) | 108.4(2) |
| C(11)−C(16)−Ta | 69.1(3) | C(16)−Ta−N(131) | 92.0(2) |
| C(16)−Ta−N(121) | 136.1(2) | N(121)−Ta−N(131) | 84.1(2) |
| C(140)−Ta−N(131) | 89.0(2) | | |

**Scheme 3**



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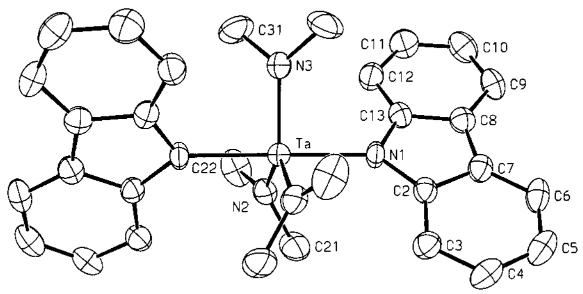


**Figure 6.** ORTEP view of [$(cb)_2Ta(NMe_2)_3$] (**9**).

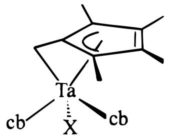
**Table 4. Selected Bond Distances (Å) and Bond Angles (deg) for [$(cb)_2Ta(NMe_2)_3$] (9)**

| | | | |
|---|---|---|---|
| Ta−N(3) | 1.928(7) | Ta−N(1) | 2.171(5) |
| Ta−N(2) | 1.964(6) | Ta−N(1) | 2.172(5) |
| Ta−N(2) | 1.964(6) | | |

| | | | |
|---|---|---|---|
| N(3)−Ta−N(2) | 116.7(2) | N(2)−Ta−N(1) | 90.8(2) |
| N(3)−Ta−N(2) | 116.7(2) | N(2)−Ta−N(1) | 88.9(2) |
| N(2)−Ta−N(2) | 126.8(3) | N(2)−Ta−N(1) | 90.8(2) |
| N(3)−Ta−N(1) | 90.4(1) | N(2)−Ta−N(1) | 88.9(2) |
| N(3)−Ta−N(1) | 90.4(1) | N(1)−Ta−N(1) | 179.3(3) |

dialkylamido ligands bound to Ta(V) metal centers are >0.2 Å shorter than corresponding Ta−C distances. Using this Chisholm criterion, it can be seen that we predict negligible $\pi$-bonding for the carbazole ligands in **7** and **8**, as the Ta−N distances are <0.1 Å shorter than the Ta−$CH_2SiMe_3$ and Ta−$CH_2Ph$ distances (Tables 2 and 3). This indicates that the two aryl rings which are coplanar with the nitrogen p orbital in carbazole effectively compete with the metal center for this electron density. A similar situation was observed for $\eta^1$(N)-bound indolyl ligands.[12] To confirm these assumptions, the compound [$(cb)_2Ta(NMe_2)_3$] (**9**) was isolated by treating [$Ta(NMe_2)_5$] (*Caution*! please see Experimental Section)[13] with cbH (Scheme 3). The molecular structure of **9** (Figure 6 and Table 4) consists of a tbp arrangement of nitrogen atoms around the Ta metal center with *trans*, axial cb ligands. The Ta−cb distances of 2.171(5) and 2.172(5) Å are over 0.2 Å longer than the Ta−$NMe_2$ distances of 1.928(7)−1.964(6) Å. Hence, there is clearly strong evidence that carbazole ligation is undergoing little $\pi$-bonding to the metal center in these derivatives.

The most important feature of the molecular structures of **1**, **7**, and **8** concerns the bonding of the [$C_5Me_4$-$CH_2$] ligand. It can be seen (Tables 2 and 3) that the Ta−$CH_2C_5Me_4$ distances in **7** and **8**, 2.246(6) and 2.254(6) Å, are only slightly longer than the discrete Ta−$CH_2$-$SiMe_3$ and Ta−$CH_2Ph$ distances of 2.143(5) and 2.194(5) Å in these molecules. This bond length, taken with other parameters within the molecules strongly supports an $\eta^1$:$\eta^5$-$CH_2C_5Me_4$ ($\sigma$:$\eta^5$-$CH_2C_5Me_4$) description for these ligands. However, as with previously reported "tuck-in" derivatives of high-valent early d-block metals, the distances between the metal center and the two carbon atoms *meta* to the metalated carbon are very long, ranging from 2.663(5) to 2.714(2) Å for the three structurally characterized compounds (Tables 1−3).



These distances are much longer than typically found for Cp* derivatives of Ta(V): e.g., a distance of 2.445(1) Å in [Cp*Ta(=$CHBu^t$)($\eta^2$-$C_2H_4$)($PMe_3$)].[14] In this latter compound the corresponding distances to the ethylene are 2.228(3) and 2.285(3) Å. Given the long distances to the two distal carbon atoms within the metalated Cp* ring, it is also reasonable to describe the bonding as $\eta^1$:$\eta^3$-$CH_2C_5Me_4$ for compounds **1**, **7**, and **8** as shown.[15]

## Experimental Section

All operations were carried out under a dry nitrogen atmosphere or in vacuo either in a Vacuum Atmosphere Dri-

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[12] Parker, K. G.; Noll, B.; Pierpont, C. G.; Rakowski DuBois, M. *Inorg. Chem.* **1996**, *35*, 3228.

[13] Serious safety concerns have been raised dealing with the original procedure: Bradley, D. C.; Thomas, M. *Can. J. Chem.* **1962**, *40*, 1355. For the synthesis of [$Ta(NMe_2)_5$], see: Chesnut, R. W.; Rothwell, I. P.; Banasak Holl, M.; Wolczanski, P. T. *Chem. Eng. News* **1990**, *68*(31), 2.

[14] Schultz, A. J.; Brown, R. K.; Williams, J. M.; Schrock, R. R. *J. Am. Chem. Soc.* **1981**, *103*, 169.

[15] Since the submission of this paper, similar conclusions have been described for "tuck-in" derivatives of *ansa*-bridged titanocenes; see: Lee, H.; Bonanno, J. B.; Hascall, T.; Cordaro, J. C.; Parkin, G. *J. Chem. Soc., Dalton Trans.* **1999**, 1365.

Lab or by standard Schlenk techniques. Hydrocarbon solvents were dried by distillation from sodium/benzophenone and stored under dry nitrogen. [Cp*$TaCl_4$] and [$TaCl_5$] were purchased from Strem Chemicals Inc. and used as received. The compound [$LiNMe_2$] was purchased from Aldrich Chemicals and used as received. The $^1$H and $^{13}$C NMR spectra were recorded on Varian Associates Gemini 200 and INOVA 300 MHz spectrometers and were referenced to protio impurities of commercial benzene-*d*$_6$. Microanalyses were obtained in house at Purdue University.

**Synthesis of [($C_5Me_4CH_2$)Ta(cb)$_2$Cl] (1).** To a benzene (50 mL) solution of [Cp*$TaCl_4$] (1.00 g, 2.18 mmol) was added 5.0 equiv (excess) of 9-potassiocarbazole (2.24 g, 10.91 mmol) over a 10 min period, during which time the solution slowly changed from brown to red. The solution was stirred for 20 h, filtered, concentrated in vacuo, and carefully layered with *n*-hexane. The orange crystals of pure **1** that precipitated out of solution were washed with hexane and dried in vacuo. Yield: 0.75 g (45%). The supernatant was found to contain **1**, **2**, and carbazole when analyzed by NMR. Anal. Calcd for $C_{34}H_{30}N_2ClTa\cdot C_6H_6$ (**1**): C, 63.12; H, 4.77; N, 3.68; Cl, 4.66. Found: C, 63.10; H, 4.65; N, 3.75; Cl, 4.76. $^1$H NMR ($C_6D_6$, 30 °C): for **1**, $\delta$ 0.80 (s, 3H), 0.86 (s, 3H), 1.50 (s, 3H), 2.15 (s, 3H, $C_5Me_4$), 3.22, 3.60 [AB pattern, $^2J_{H-H} = 7.32$ Hz, 2 H, Ta$-$C$H_2C_5(CH_3)_4$], 6.29$-$8.23 (m, aromatics); for **2**, $\delta$ 0.83 (s, 6H), 2.27 (s, 6H, $C_5Me_4$), 4.14 [s, 2 H, Ta$-$C$H_2C_5(CH_3)_4$], 6.27$-$9.24 (m, aromatics). Selected $^{13}$C NMR ($C_6D_6$, 30 °C): $\delta$_9.85, 10.40, 11.72, 11.81 ($CH_3$); 90.70 (Ta$-CH_2$).

**Synthesis of [($C_5Me_4CH_2$)Ta(cb)$_2$($CH_2SiMe_3$)] (7).** To a benzene (15 mL) solution of [($C_5Me_4CH_2$)Ta(cb)$_2$Cl] (**1**; 0.25 g, 0.33 mmol) was added 2.5 equiv of $LiCH_2SiMe_3$ (77 mg, 0.82 mmol) over a 5 min period, during which time the solution slowly changed from orange to yellow. The solution was stirred for 12 h and filtered, and the solvent was removed in vacuo, affording a yellow oil. Addition of pentane (2 mL) led to the precipitation of a yellow solid, which was washed with pentane and dried in vacuo. Crystals suitable for X-ray diffraction were obtained from benzene/hexane solutions. Yield: 0.05 g (20%). Anal. Calcd for $C_{38}H_{41}N_2SiTa\cdot{}^1/_2C_6H_6$: C, 63.64; H, 5.73; N, 3.62. Found: C, 63.35; H, 5.61; N, 3.62. $^1$H NMR ($C_6D_6$, 30 °C): $\delta$ $-$0.46 (s, Si$Me_3$); 0.62 (s, 3H), 0.79 (s, 3H), 1.77 (s, 3H), 1.99 (s, $C_5Me_4$); 0.85, 1.95 (AB pattern, $^2J_{H-H} = 10.74$ Hz, 2 H, Ta$-$C$H_2SiMe_3$); 3.22, 3.60 [AB pattern, $^2J_{H-H} = 7.32$ Hz, 2 H, Ta$-$C$H_2C_5(CH_3)_4$]; 6.36$-$8.24 (m, aromatics). Selected $^{13}$C NMR ($C_6D_6$, 30 °C): $\delta$ 3.21 [(Si$CH_3)_3$)]; 10.59, 11.43, 12.87 ($CH_3$); 81.31 (Ta$-CH_2SiMe_3$); 88.39 (Ta$-CH_2$).

**Synthesis of [($C_5Me_4CH_2$)Ta(cb)$_2$($CH_2Ph$)] (8).** To a benzene (15 mL) solution of [($C_5Me_4CH_2$)Ta(cb)$_2$Cl] (0.30 g, 0.39 mmol) was added an $Et_2O$ solution of $PhCH_2MgCl$ (0.59 mL, 0.59 mmol) over a 5 min period, during which time the solution slowly changed from orange to red. The solution was stirred for 12 h, filtered, concentrated in vacuo, and carefully layered with *n*-hexane. The resulting orange-red solid was discarded, and the supernatant was concentrated in vacuo and layered with hexane, affording an orange solid. Yield: 0.04 g (14%). $^1$H NMR ($C_6D_6$, 30 °C): $\delta$ 0.62 (s, 3H), 0.79 (s, 3H), 1.77 (s, 3H), 1.99 (s, $C_5Me_4$); 2.58, 3.00 (AB pattern, $^2J_{H-H} = 10.74$ Hz, 2 H, Ta$-$C$H_2$Ph); 3.00, 3.24 [AB pattern, $^2J_{H-H} = 7.45$ Hz, 2 H, Ta$-$C$H_2C_5(CH_3)_4$]; 6.38$-$8.10 (m, aromatics). Selected $^{13}$C NMR ($C_6D_6$, 30 °C): $\delta$ 10.53, 11.28, 11.63 ($CH_3$); 86.91 (Ta$-CH_2$Ph); 89.62 (Ta$-CH_2$).

**Synthesis of [Ta($NMe_2$)$_5$].** The original method reported for the synthesis of [Ta($NMe_2$)$_5$]$^{13}$ in pentane can lead to an unreacted $LiNMe_2/TaCl_5$ mixture, which can detonate or undergo a highly exothermic solid-state metathesis reaction upon isolation. We find that the following procedure can be used for the synthesis of [Ta($NMe_2$)$_5$], but again care must be taken to make sure the reaction has initiated before a large amount of $TaCl_5$ is added to the $LiNMe_2$.

To a light yellow solution of $LiNMe_2$ (50.00 g, 0.98 mol) in diethyl ether (400 mL) and hexane (400 mL) at 0 °C was added an initial sample of [$TaCl_5$] (ca. 5 g). The temperature of the reaction mixture was slowly increased to 25 °C, and the addition of $TaCl_5$ (total amount 63.30 g, 0.18 mol) was continued slowly over a 2 h period (note: if the addition of $TaCl_5$ is too rapid, the solution will reflux). The reaction suspension became dark yellow during the addition and was yellow-brown upon completion. After the mixture was stirred for 24 h, the solvent was removed in vacuo and the crude brown material was extracted with 600 mL of benzene and filtered, yielding a brown filtrate. The benzene was removed in vacuo, and the brown solid was sublimed at 90 °C ($10^{-2}$ mm), affording the pure product as an orange powder. Yield: 23.07 g (33%). $^1$H NMR ($C_6D_6$, 30 °C): $\delta$ 3.27 (s, N$Me_2$).

**Synthesis of [(cb)$_2$Ta($NMe_2$)$_3$] (9).** To a toluene solution (20 mL) of [Ta($NMe_2$)$_5$] (0.50 g, 1.25 mmol) was added carbazole (0.48 g, 2.87 mmol). The yellow solution was heated at 110 °C for 36 h, during which time the solution became clear orange. The solvent was removed in vacuo, and the resulting yellow-orange solid was washed with hexane and dried in vacuo. Yield: 0.33 g (41%). Anal. Calcd for $C_{30}H_{34}N_5Ta$: C, 55.81; H, 5.31; N, 10.85. Found: C, 55.51; H, 5.08; N, 10.20. $^1$H NMR ($C_6D_6$, 30 °C): $\delta$ 3.02 (s, 18 H, N$Me_2$), 7.26$-$8.20 (m, 16 H, aromatics).

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**Supporting Information Available:** Description of the experimental procedures for X-ray diffraction studies, including tables of thermal parameters, bond distances and angles, intensity data, torsion angles, and mutiplicities for **1**, **7**, **8**, and **9**. This material is available free of charge via the Internet at http://pubs.acs.org.

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