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Synthesis and Characterization of Tantalum(V) Dicarbollide Complexes

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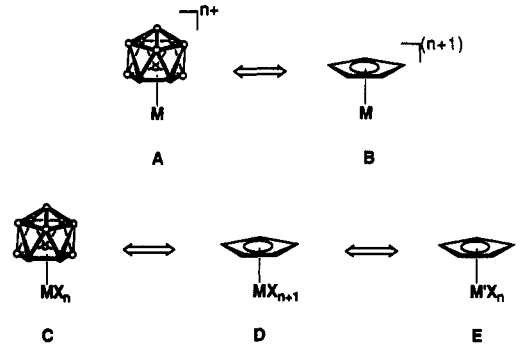
Reaction of $TaCl_5$ with $Li_2C_2B_9H_{11}$ in toluene yields $(C_2B_9H_{11})TaCl_3$ (1). Molecular weight measurements for 1 indicate a monomeric structure in benzene solution. X-ray diffraction reveals a distorted-octahedral/three-legged piano-stool structure for 1. Data for 1: a = 6.84 (1) Å, b = 9.614 (2) Å, c = 19.073 (3) Å, β = 92.37 (3)°, V = 1252 (2) Å^3, Z = 4 in space group $P2_1/c$. Reaction of 1 with TlCp′ (Cp′ = C_5H_4Me) in CH_2Cl_2 yields the bent metallocene $Cp'(C_2B_9H_{11})TaCl_2$ (2). X-ray diffraction reveals a distorted-tetrahedral structure for 2, isostructural with group 4 metallocenes. Data for 2: a = 9.519 (4) Å, b = 12.752 (6) Å, c = 7.016 (2) Å, α = 97.16 (3)°, β = 109.76 (3)°, γ = 94.15 (4)°, V = 789 (1) Å^3, Z = 2 in space group $P\bar{1}$. Reaction of $CpTaCl_4$ with $Li_2C_2B_9H_{11}$ yields $Cp(C_2B_9H_{11})TaCl_2$ (3, Cp = C_5H_5). Alkylation of 1 with MeMgBr yields $(C_2B_9H_{11})TaMe_3$ (4). Alkylation of 2 with MeMgBr yields $Cp'(C_2B_9H_{11})TaMe_2$ (5).

Introduction

The *nido*-carborane dianion $C_2B_9H_{11}^{2-}$ ("dicarbollide") binds to metals via the open B_3C_2 face in an η^5 fashion and is sterically and electronically comparable to Cp^{*-}.[1,2] An extensive main-group, d-block, and f-block element dicarbollide chemistry has been developed, primarily by Hawthorne and co-workers.[1,3,4] The use of $C_2B_9H_{11}^{2-}$ in place of Cp^- ligands provides interesting opportunities for the design of complexes with new metal/charge combinations and increased metal unsaturation. For example, the $(C_2B_9H_{11})M^{n+}$ fragment (**A**, Scheme I) is isostructural with the analogous Cp fragment $CpM^{(n+1)+}$ (**B**) but carries an overall charge which is one unit lower. Also, a $(C_2B_9H_{11})MX_n$ species (**C**) is electronically and coordinatively unsaturated relative to the analogous $CpMX_{n+1}$ species (**D**) of the same overall charge but isoelectronic with a $CpM'X_n$ (**E**) species where M′ is one group to the left of M in the periodic table.

For several years we have studied the synthesis and chemistry of cationic, d^0 metal alkyl complexes $Cp_2Zr(R)L^+$ (L = labile ligand or weakly coordinating anion), which are closely related to the $Cp_2Zr(R)^+$ active species in Cp_2ZrX_2-based Ziegler–Natta olefin polymerization catalysts.[5] To explore the effect of charge on reactivity, we recently prepared the series of neutral dicarbollide complexes $[Cp^*(C_2B_9H_{11})MCH_3]_x$ (M = Hf, Zr), which are structurally and electronically very similar to the cationic $Cp_2Zr(R)^+$ systems.[6,7] We observed high insertion and σ-bond methathesis reactivity for the neutral $[Cp^*(C_2B_9H_{11})MCH_3]_x$ species and crystallographically characterized two bent-metallocene derivatives of this type, $Cp^*(C_2B_9H_{11})Zr[C(Me){=}CMe_2]$ and $[Cp^*(C_2B_9H_{11})Zr]_2(\mu\text{-}CH_2)$. Several other early-metal and f-element bent-metallocene complexes incorporating η^5-dicarbollide ligands have been reported.[8] These results have led us to pursue the synthesis of other high-valent, early-metal alkyl systems containing the dicarbollide ligand.

Scheme I



In this paper we present the preparation and characterization of group 5 dicarbollide complexes $(C_2B_9H_{11})$-

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$TaCl_3$ (1), an analogue of $CpMCl_3$ (M = group 4 metal) derivatives, and $(C_5H_4R)(C_2B_9H_{11})TaCl_2$ (2, R = Me; 3, R = H), new d^0 metallocenes which are isoelectronic and isostructural with group 4 Cp_2MX_2 derivatives. Complexes 1–3 are intended to serve as precursors to Ta–alkyl complexes, which in turn may provide access to cationic, d^0 Ta–alkyl complexes, e.g. $Cp(C_2B_9H_{11})Ta(R)(L)^+$. Some simple alkylation chemistry of 1 and 2 is also discussed.

Experimental Section

General Procedures. All manipulations were performed on a high-vacuum line or in a glovebox under a purified N_2 atmosphere. Solvents were distilled from Na/benzophenone ketyl, except for CH_2Cl_2 and CD_2Cl_2, which were distilled from CaH_2 or P_2O_5. $TaCl_5$ was sublimed before use. *o*-Carborane (1,2-$C_2B_{10}H_{12}$, Dexsil) was used without further purification. TlCp′ was prepared by Erker's method[9] and sublimed before use. $CpTaCl_4$ was prepared by Clark's method.[10]

NMR spectra were recorded on a Bruker AC 300, WM 360, or AMX 360 spectrometer in flame-sealed or Teflon-valved tubes. ^1H and ^{13}C chemical shifts are reported versus Me_4Si and were determined by reference to the residual ^1H and ^{13}C solvent peaks. $^{11}B\{^1H\}$ NMR spectra were referenced to external $BF_3{\cdot}Et_2O$ (δ 0, C_6D_6). Elemental analyses were performed by E + R Microanalytical Laboratory, Inc.

Cryoscopic molecular weight determinations[11] were performed using a locally constructed apparatus. A benzene solution of the compound of interest was prepared in the glovebox in a tube containing a triangular magnetic stirbar and a small amount of sand (to catalyze crystallization) and sealed with an Ace Thread adaptor thru which a Yellow Springs Instrument 46004 thermistor was inserted. The tube was insulated with an airspace by means of an outer glass sleeve and then placed an ice bath, and stirring was maintained. Freezing curves (voltage vs time) were measured. Freezing-point voltages were determined by extrapolation of the voltage vs time curve to the onset of freezing and referenced to that of neat solvent. Concentrations were determined from a calibration curve (freezing-point voltage vs molality) using solutions of $Cp_2Zr(CH_2SiMe_3)_2$, $Cp'Cp^*ZrCl_2$, and Cp_2Fe as standards. The reported results are the average of at least five experiments in the concentration range 0.02–0.06 *m*.

$C_2B_9H_{13}$. The following is a modification of the literature procedure.[12] A mixture of *o*-carborane (12.0 g, 83.3 mmol), KOH (10.1 g, 180 mmol), and MeOH (200 mL, handled in air) was refluxed under N_2 for 2 days. The MeOH was removed under reduced pressure, leaving a white semisolid material. Benzene (200 mL) was added, and an azeotropic distillation was performed to remove H_2O and MeOH. The remaining white solid was dried under vacuum overnight, taken into the glovebox, pulverized, and then dried under high vacuum for 2 days at 40 °C. The solid was slurried in benzene (150 mL) under N_2, H_3PO_4 (51 mL, 85%) was added, and the two-phase mixture was stirred vigorously for 15 h. The benzene layer was quickly decanted from the lower layer to minimize exposure to air. The H_3PO_4 layer was extracted with benzene (2 × 100 mL); the benzene extracts were combined, dried over $MgSO_4$, and distilled to dryness under reduced pressure. Sublimation (40–45 °C, <0.001 mm) of the solid residue yielded $C_2B_9H_{13}$ (7.85 g, 70%) as a white solid. The ^{11}B NMR spectrum of this material was identical with the previously reported spectrum.[13] ^1H NMR (300 MHz, C_6D_6): δ 4.0–1.0 (br m, B–H), 2.56 (br s, 2 C–H), –2.1 (v br s, 2 B–H). $^{11}B\{^1H\}$ NMR (115 MHz, C_6D_6): δ 4.0 (2 B), –4.4 (2 B), –16.4 (1 B), –17.0 (1 B), –27.4 (3 B).

$Li_2C_2B_9H_{11}$. A hexane solution of ^nBuLi (9.4 mL, 2.5 M, 23.5 mmol) was added over several minutes to a stirred solution of $C_2B_9H_{13}$ (1.50 g, 11.2 mmol) in benzene (100 mL). An exothermic reaction occurred. The slurry was stirred for 8 h, briefly refluxed, and then filtered. The white solid was washed with pentane and dried under high vacuum for 2 days (yield 1.66 g, 100%). The solid is stable for months when stored under N_2 in the freezer. ^1H NMR (360 MHz, THF-d_8): δ + 2.2 to –0.5 (br m), 0.95 (s). No resonances were observed between δ –2 and –4, indicating deprotonation was complete.[14] $^{11}B\{^1H\}$ NMR (115 MHz, THF-d_8): –16.0 (br s, 3 B), –17.0 (br s, 3 B), –21.9 (s, 2 B), –39.1 (s, 1 B).[15]

$(C_2B_9H_{11})TaCl_3$ (1). Solid $Li_2C_2B_9H_{11}$ (0.71 g, 4.86 mmol) was added in portions to an orange solution of $TaCl_5$ (1.65 g, 4.61 mmol) in toluene (200 mL). The mixture was stirred for 1 day, the volatiles were removed under vacuum, and the green residue was extracted with 60 mL of a toluene/pentane mixture (1/2 by volume). The filtrate was evaporated under vacuum and the resulting solid recrystallized from pentane/toluene at –32 °C. A brown solid was isolated by filtration and sublimed at 100–110 °C (<0.001 Torr), yielding 1 as a bright yellow solid (0.72 g, 37%). Alternatively, the product may be isolated directly from the crude green residue by slow sublimation at 75 °C. ^1H NMR (360 MHz, C_6D_6): δ 3.30 (C–H), B–H resonances appear as a broad, complex multiplet from 4.7 to 2.0. ^1H NMR (CD_2Cl_2): δ 4.46 (C–H), B–H resonances appear from 4.5 to 2.2. $^{13}C\{^1H\}$ NMR (90 MHz, C_6D_6): δ 66.8 (m). $^{11}B\{^1H\}$ NMR (115 MHz, C_6D_6): δ 15.8 (1 B), 7.3 (2 B), 2.6 (2 B), –3.2 (2 B), –5.7 (br, 2 B). [^{11}B–^{11}B] COSY[16] (115 MHz, C_6D_6, numbering scheme based on X-ray structure in Figure 1): δ 15.8 (B8), 7.3 (B4, B5), 2.6 (B7, B9), –3.2 (B3, B6), –5.7 (B1 and B2). Correlations observed and relative intensities (s = strong, m = medium, w = weak): B8–(B7, B9), s; B8–(B4, B5), m; (B4, B5)–(B7, B9), s; (B4, B5)–(B3, B6), m; (B4, B5)–(B1 or B2), w; (B7, B9)–(B3, B6), w; (B3, B6)–(B1 or B2), m. Anal. Calcd for $C_2H_{11}B_9Cl_3Ta$: C, 5.72; H, 2.64; Cl, 25.34. Found: C, 5.80; H, 2.92; Cl, 25.13. Cryoscopic molecular weight determination (benzene): 407 (20). Formula weight for $C_2H_{11}B_9Cl_3Ta$: 420.

$Cp'(C_2B_9H_{11})TaCl_2$ (2). Solid TlCp′ (460 mg, 1.62 mmol) was added to a solution of 1 (682 mg, 1.62 mmol) in CH_2Cl_2 (20 mL). A white precipitate formed immediately. The mixture was stirred for 10 min and filtered through a frit covered with Celite. The Celite was washed with CH_2Cl_2 (5 mL) and toluene (2 × 5 mL). The combined filtrate and washes were concentrated to a slurry (~5 mL) under vacuum, pentane (20 mL) was added, and **2** (622 mg, 83%) was isolated as a yellow solid by filtration. ^1H NMR (360 MHz, C_6D_6): δ 6.07 (t, J = 3 Hz, 2 H, C_5H_4Me), 5.49 (t, J = 3 Hz, 2 H, C_5H_4Me), 5.02 (br s, 2 H, $C_2H_2B_9H_9$), 1.98 (s, 3 H, C_5H_4Me), the B–H resonances appear from 4.4 to 0.6. $^{13}C\{^1H\}$ NMR (90 MHz, C_6D_6): δ 135.5 (ipso C_5H_4Me), 120.9 (C_5H_4Me), 116.3 (C_5H_4Me), 74.2 (br, $C_2B_9H_{11}$), 15.5 (C_5H_4Me). $^{11}B\{^1H\}$ NMR (115 MHz, C_6D_6): δ 7.9 (1 B), –0.5 (2 B), –5.8 (2 B), –8.1 (1 B), –9.9 (2 B), –16.6 (1 B). Anal. Calcd for $C_8H_{18}B_9Cl_2Ta$: C, 20.74; H, 3.92; Cl, 15.30. Found: C, 20.63; H, 4.09; Cl, 15.54.

$(Cp)(C_2B_9H_{11})TaCl_2$ (3). Solid $Li_2C_2B_9H_{11}$ (47 mg, 0.32 mmol) was added to a slurry of $CpTaCl_4$ (124 mg, 0.32 mmol) in toluene (15 mL). The mixture was stirred overnight and filtered through a frit covered with Celite. The solution was concentrated to ~2 mL under vacuum, and pentane (10 mL) was added. A yellow solid (**3**, 70 mg) was isolated by filtration and washed with pentane. The volatiles were removed from the mother liquor, and the residue was washed with pentane to yield another 14 mg of **3** as a yellow solid (59% total yield). ^1H NMR (360 MHz, C_6D_6): δ 5.82 (s, 5 H), 5.03 (br s, 2 H), B–H resonances appear from 4.7 to 0.6. $^{13}C\{^1H\}$ NMR (90 MHz, C_6D_6): δ 119.1, 75.1 (br). $^{11}B\{^1H\}$ NMR (115 MHz, C_6D_6): δ 11.9 (1 B), 3.8 (2 B), –1.6 (2 B), –3.5 (1 B), –5.4 (2 B), –12.1 (1 B). Anal. Calcd for $C_7H_{16}B_9Cl_2Ta$: C,

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18.71; H, 3.59. Found: C, 18.79; H, 3.56.

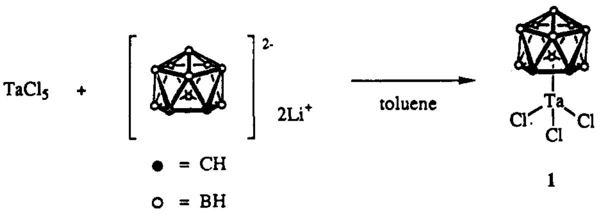
$(C_2B_9H_{11})TaMe_3$ (4). A solution of 1 (0.75 g, 1.79 mmol) in toluene (25 mL) was cooled to 0 °C, and MeMgBr (1.97 mL, 3.0 M in ether, 5.9 mmol) was added by syringe. The mixture was warmed to room temperature with stirring. After 0.5 h, the reaction mixture was filtered and the volatiles were removed under vacuum. The residue was washed with hexane several times and then dissolved in toluene (40 mL), and the solution was stirred for 4 h. The solution was filtered through a medium frit covered with Celite and evaporated under vacuum, yielding an off-white solid (4), which was dried under high vacuum for 12 h (0.57 g, 89%). ^{1}H NMR (360 MHz, C_6D_6): δ 2.41 (s, 2 H, $C_2H_2B_9H_9$), 1.14 (s, 9 H Ta*Me*), B–H resonances appear from 4.5 to 2.2. $^{13}C\{^1H\}$ NMR (90 MHz, C_6D_6): δ 86.2 (Ta*Me*), 54.7 (br m, $C_2B_9H_{11}$). ^{13}C gated decoupled NMR (90 MHz, C_6D_6): δ 86.2 (q, J = 122 Hz), 54.7 (d of m, J = 176 Hz). $^{11}B\{^1H\}$ NMR (115 MHz, C_6D_6): δ 11.6 (1 B), 2.9 (2 B), −1.9 (2 B), −8.6 (2 B), −9.4 (1 B), −10.3 (1 B). Anal. Calcd for $C_5H_{20}B_9Ta$: C, 16.75; H, 5.62. Found: C, 16.61; H, 5.42.

$Cp'(C_2B_9H_{11})TaMe_2$ (5). A solution of 2 (300 mg, 0.65 mmol) in toluene (20 mL) was cooled to 0 °C, and MeMgBr (0.56 mL, 3.0 M in ether, 1.7 mmol) was added. The reaction mixture was stirred for 1 h and filtered, and the volatiles were removed under vacuum. The residue was dissolved in benzene (20 mL), and the solution was stirred for 6 h and filtered through a fine frit covered with Celite. The solvent was removed under vacuum, yielding a yellow solid (5), which was washed with pentane and dried (241 mg, 71%). ^{1}H NMR (360 MHz, C_6D_6): δ 5.69 (s, 2 H, C_5H_4Me), 5.45 (s, 2 H, C_5H_4Me), 3.93 (br s, 2 H, $C_2H_2B_9H_9$), 1.61 (s, 3 H, C_5H_4Me), −0.05 (s, 6 H, Ta*Me*), B–H resonances appear from 4.3 to 0.2. $^{13}C\{^1H\}$ NMR (90 MHz, C_6D_6): δ 115.7 (C_5H_4Me), 113.2 (C_5H_4Me), 64.2 (br m, $C_2B_9H_{11}$), 62.7 (Ta*Me*), 14.7 (C_5H_4Me); Cp′ ipso resonance was obscured by the solvent peak. $^{13}C\{^1H\}$ NMR (90 MHz, CD_2Cl_2): δ 129.4 (Cp′ ipso), 116.6, 113.8, 64.9 (br m), 63.4, 15.6. $^{11}B\{^1H\}$ NMR (115 MHz, C_6D_6): δ 5.4 (1 B), 0.6 (2 B), −2.3 (2 B), −7.6 (1 B), −10.9 (2 B), −12.5 (1 B). Anal. Calcd for $C_{10}H_{24}B_9Ta$: C, 28.43; H, 5.72. Found: C, 28.11; H, 5.80.

X-ray Diffraction Studies of 1 and 2. Single crystals suitable for X-ray diffraction were grown by cooling a pentane/toluene solution (for 1) and by diffusing pentane into a concentrated toluene solution (for 2). Both were sealed in glass capillaries under N_2. Diffraction data were obtained with an Enraf-Nonius CAD4 diffractomer, and all calculations were made using the SDP package provided with this system.[17] Crystallographic data, data acquisition details and refinement parameters are summarized in Table I.

Results

Synthesis of $(C_2B_9H_{11})TaCl_3$ (1). Deprotonation of $C_2B_9H_{13}$ with 2 equiv of ^{n}BuLi in benzene yields $Li_2C_2B_9H_{11}$, which is a convenient, isolable, base-free dicarbollide reagent.[18] Reaction of $TaCl_5$ with $Li_2C_2B_9H_{11}$ in toluene produces $(C_2B_9H_{11})TaCl_3$ (1) as a bright yellow, air-sensitive solid in 37% isolated yield (eq 1). This reaction also produces small amounts of $(C_2B_9H_{11})_2TaCl$, which will be discussed in detail elsewhere.[19] Attempts to prepare 1 using $Na_2[C_2B_9H_{11}]\cdot2THF$ or $Tl_2C_2B_9H_{11}$ were unsuccessful. The mono(dicarbollide) complex 1 is isolated from the crude product by initial extraction with and crystallization from toluene/pentane followed by sublimation at 110 °C, or by slow sublimation of the crude product at lower temperatures (<75 °C). 1 is soluble in CH_2Cl_2 and benzene and moderately soluble in pentane but rapidly polymerizes THF.[20] Cryoscopic molecular weight determinations for 1 in benzene indicate a monomeric structure in solution.



(1)

1

Table I. Summary of Crystallographic Data for $(C_2B_9H_{11})TaCl_3$ (1) and $Cp'(C_2B_9H_{11})TaCl_2$ (2)

	1	2
empirical formula	$C_2H_{11}B_9Cl_3Ta$	$C_8H_{18}B_9Cl_2Ta$
fw	419.71	463.39
cryst size, mm	0.44 × 0.13 × 0.21	0.30 × 0.251 × 0.13
cryst color	yellow	yellow
T, K	295	295
space group	$P2_1/c$	$P\bar{1}$
a, Å	6.84 (1)	9.519 (4)
b, Å	9.614 (2)	12.752 (6)
c, Å	19.073 (3)	7.016 (2)
α, deg	90	97.16 (3)
β, deg	92.37 (3)	109.76 (3)
γ, deg	90	94.15 (4)
V, Å^3	1252 (2)	789.0 (1)
Z	4	2
d(calcd), g/cm^3	2.23	1.95
cell dimens determn	25 rflns, 13–24° (2θ)	49 rflns, 18–38° (2θ)
radiation	Mo Kα (λ = 0.7107 Å)	Mo Kα (λ = 0.7107 Å)
scan ratio θ/ω	1	1
scan limit, deg	2–25 (θ)	2–30 (θ)
scan speed, deg/min	0.7–5.5	1.5–5.0
scan range	0.8 + tan θ	0.8 + tan θ
data collected *hkl*	−8, 8; − 11, 11; −22, 22	−12, 13; ±17; −13, 7
no. of rflns collected	4675	6869
no. of unique rflns	2345	4551
decay (F^2), %	<0.9	<2
μ, cm^{-1}	92.7	77.1
structure soln	Patterson/Fourier	Patterson/Fourier
refinement[a]	all non-H anisotropic, H fixed	all non-H anisotropic, H isotropic
total no. of paramrs	136	253
R	0.051	0.020
R_w	0.059	0.029
weight[a]	P = 0.06, Q = 0.0	P = 0.04, Q = 0.0
SDOUW[b]	0.958	1.096
max param shift/esd	0.04	0.19
max resid e density, e/Å^3	1.07	1.20

[a] $w = [\sigma_F{}^2 + (PF)^2 + Q]^{-1}$. [b] Standard deviation of unit weight.

The $^{11}B\{^1H\}$ NMR spectrum of 1 consists of five signals in a 1:2:2:2:2 intensity ratio in the range δ + 15.8 to −5.7. In principle, a 1:1:1:2:2:2 pattern is consistent with C_s symmetry (as observed for 2–5). For 1, however, the resonance at δ −5.5 is significantly broader ($\nu_{1/2}$ = 114 Hz) than the rest (60–69 Hz), probably due to partial overlap of two single boron resonances. Assignment of the ^{11}B NMR resonances was determined from a [$^{11}B–^{11}B$] COSY experiment. Qualitatively, the patterns of the shift as-

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[17] Frenz, B. A. The Enraf-Nonius CAD4 SDP System. In *Computing in Crystallography*; Delft University Press: Delft, Holland, 1978; p 64.

[18] $Li_2C_2B_9H_{11}$ has also been generated in situ from $[HNMe_3][C_2B_9H_{12}]$: (a) Schubert, D. M.; Rees, W. S.; Knobler, C. B.; Hawthorne, M. F. *Organometallics* **1990**, *9*, 2938. (b) Li, J.; Logan, C. F.; Jones, M., Jr. *Inorg. Chem.* **1991**, *30*, 4866.

[19] The bis(dicarbollide) complex $(C_2B_9H_{11})_2TaCl$ was isolated as a yellow solid in 15% yield by sublimation (140–160 °C, <0.001 Torr), from the reaction of $Li_2C_2B_9H_{11}$ (435 mg, 2.98 mmol) with $TaCl_5$ (490 mg, 1.37 mmol) in refluxing toluene (30 mL, 24 h). Data for $(C_2B_9H_{11})_2TaCl$: ^{1}H NMR (300 MHz, toluene-d_8) δ 4.43 (s, $C_2H_2B_9H_9$); $^{13}C\{^1H\}$ NMR (90 MHz, toluene-d_8) δ 71.6; $^{11}B\{^1H\}$ NMR (116 MHz, toluene-d_8) δ 13.4 (1 B), 0.8 (2 B), −1.4 (2 B), −6.7 (3 B), −11.2 (1 B). Anal. Calcd for $C_4H_{22}B_{18}ClTa$: C, 9.98; H, 4.61; Cl, 7.37. Found: C, 9.80; H, 4.35; Cl, 7.70. The structure and reactivity of $(C_2B_9H_{11})_2TaCl$ are currently being investigated.

[20] A THF solution (3 mL) of 1 (30 mg) had completely solidified after 2h. For reviews and leading references to metal or other Lewis-acid-mediated THF ring-opening reactions, see: (a) Penczek, S.; Kubissa, P.; Matyjaszewski, K. *Adv. Polym. Sci.* **1980**, *37*, 1. (b) DeShong, P.; Sidler, D. R. *J. Org. Chem.* **1988**, *53*, 4892. (c) Evans, W. J.; Ulibarri, T. A.; Chamberlain, L. R.; Ziller, J. W.; Alvarez, D., Jr. *Organometallics* **1990**, *9*, 2124.

Table II. Selected Bond Distances (Å) and Angles (deg) for $(C_2B_9H_{11})TaCl_3$ (1)

Bond Distances			
Ta–Cl1	2.259 (5)	Ta–Cl2	2.233 (5)
Ta–Cl3	2.205 (5)	Ta–C1	2.42 (1)
Ta–C2	2.40 (1)	Ta–B7	2.42 (2)
Ta–B8	2.43 (2)	Ta–B9	2.37 (1)
Ta–B0[a]	1.928	C1–C2	1.60 (2)
C1–B2	1.74 (2)	C1–B3	1.69 (2)
C1–B7	1.68 (2)	C2–B2	1.75 (2)
C2–B6	1.68 (2)	C2–B9	1.68 (2)
B1–B2	1.74 (2)	B1–B3	1.78 (2)
B1–B4	1.78 (2)	B1–B5	1.78 (2)
B1–B6	1.79 (2)	B2–B3	1.76 (2)
B2–B6	1.78 (2)	B3–B4	1.77 (2)
B3–B7	1.78 (2)	B4–B5	1.78 (2)
B4–B7	1.74 (2)	B4–B8	1.78 (2)
B5–B6	1.76 (2)	B5–B8	1.79 (2)
B5–B9	1.74 (2)	B6–B9	1.74 (2)
B7–B8	1.80 (2)	B8–B9	1.76 (2)
Bond Angles			
Cl1–Ta–Cl2	97.4 (2)	Cl1–Ta–Cl3	98.0 (2)
Cl1–Ta–B0	116.2 (1)	Cl2–Ta–Cl3	100.1 (2)
Cl2–Ta–B0	116.4 (2)	Cl3–Ta–B0	124.0 (2)

[a] B0 denotes the centroid of the dicarbollide ligand.

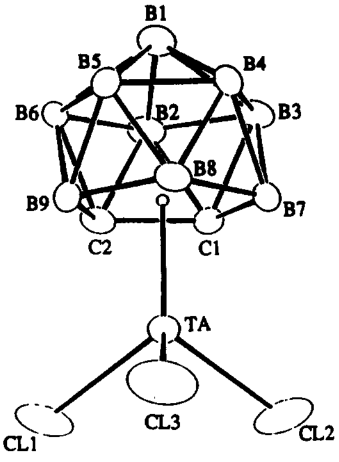

Figure 1. Structure of $(C_2B_9H_{11})TaCl_3$ (1).

Table III. Positional Parameters and *B* Values for $(C_2B_9H_{11})TaCl_3$ (1)

atom	*x*	*y*	*z*	*B*,[a] Å^2
Ta	0.19812 (8)	0.22712 (6)	0.07369 (3)	2.978 (9)
Cl1	0.347 (1)	0.0213 (5)	0.0967 (3)	9.2 (1)
Cl2	−0.1053 (7)	0.1452 (7)	0.0552 (3)	12.9 (1)
Cl3	0.286 (1)	0.2517 (6)	−0.0356 (2)	9.2 (2)
C1	0.074 (1)	0.317 (1)	0.1820 (6)	3.1 (2)
C2	0.296 (2)	0.268 (1)	0.1945 (6)	3.0 (2)
B1	0.277 (2)	0.540 (2)	0.2372 (8)	3.8 (3)
B2	0.197 (2)	0.374 (2)	0.2584 (7)	3.4 (3)
B3	0.040 (2)	0.483 (2)	0.208 (1)	3.9 (3)
B4	0.184 (2)	0.580 (2)	0.1512 (9)	3.8 (3)
B5	0.432 (2)	0.530 (2)	0.1652 (8)	3.3 (3)
B6	0.439 (2)	0.396 (2)	0.2283 (8)	3.3 (3)
B7	0.053 (2)	0.437 (2)	0.1183 (8)	3.4 (3)
B8	0.296 (2)	0.469 (2)	0.0894 (7)	3.6 (3)
B9	0.442 (2)	0.352 (2)	0.1397 (8)	3.2 (3)
H1	0.2985*	0.6170*	0.2766*	4.2**
H2	0.1677*	0.3407*	0.3100*	3.7**
H3	−0.0915*	0.5243*	0.2273*	4.4**
H4	0.1531*	0.6844*	0.1368*	4.1**
H5	0.5511*	0.5992*	0.1592*	3.5**
H6	0.5582*	0.3841*	0.2652*	3.6**
H7	−0.0712*	0.4500*	0.0838*	3.7**
H8	0.3259*	0.4980*	0.0373*	4.0**
H9	0.5724*	0.3122*	0.1189*	3.6**
H10	−0.0308*	0.2532*	0.1866*	3.5**
H11	0.3231*	0.1749*	0.2088*	3.3**

[a] Starred values denote atoms with fixed positions and double-starred values those fixed isotropically. Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as $(^4/_3)[a^2B_{11} + b^2B_{22} + c^2B_{33} + ab(\cos\gamma)B_{12} + ac(\cos\beta)B_{13} + bc(\cos\alpha)B_{23}]$.

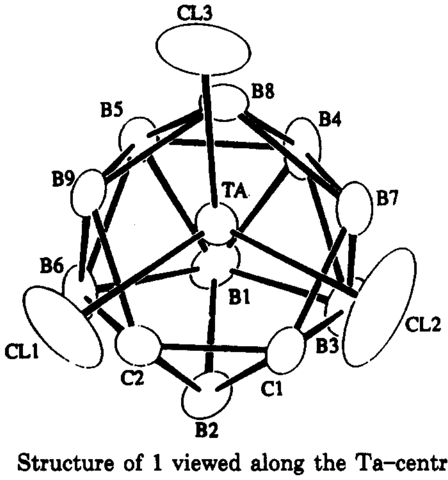

Figure 2. Structure of 1 viewed along the Ta–centroid axis.

signments for 1 are similar to those of $(C_5R_5)M(C_2B_9H_{11})$ (M = Co, Rh, Ir) and $(C_6Me_6)Ru(C_2B_9H_{11})$,[21] with the major difference being the relatively high field shift of the unique boron directly opposite Ta in the TaC_2B_9 icosahedron (B1).

The ^1H NMR spectrum for 1 consists of a broad resonance at δ 3.30 for the two C–H hydrogens and of a complex envelope of resonances between δ 4.7 and 2.0 for the nine terminal B–H hydrogens. The ^1H NMR resonances for 1 are shifted ~2 ppm downfield from those of $Li_2C_2B_9H_{11}$, consistent with formation of a neutral dicarbollide complex from the dianion in eq 1.

Structure of 1. To confirm the η^5 bonding mode for the dicarbollide ligand and to establish metrical parameters for new group 5 dicarbollide complexes, an X-ray crystal structure determination was carried out on 1. Metrical parameters and atomic coordinates are listed in Tables II and III. As Figure 1 illustrates, 1 adopts a monomeric, three-legged piano-stool structure in which the dicarbollide ligand is bound in a nearly symmetric η^5 fashion (Ta–B and Ta–C distances 2.37–2.43 Å). The two carbons in the dicarbollide ligand were identified by the bond distance trend B–B > B–C > C–C.

As shown in Figure 2, Cl3 eclipses B8 of the $C_2B_9H_{11}^{2-}$ ligand while Cl1 and Cl2 eclipse the C–B bonds. As a result of this arrangement and the longer B–H distances (vs C–H distances), steric interactions involving the $C_2B_9H_{11}^{2-}$ ligand are more severe for Cl3 than for the other Cl atoms, and Cl3 is bent further away from the $C_2B_9H_{11}^{2-}$ ligand (centroid–Ta–Cl3 angle 124.0°) than are Cl1 and Cl2 (centroid–Ta–Cl angles 116.2, 116.4°). Refinement on the H atoms was not successful. However, with the H atoms in idealized positions (see discussions of the structure of 2), all three Cl ligands lie just at the van der Waals radii of dicarbollide facial H atoms. The Ta–Cl3 distance (2.205 (5) Å) is slightly shorter than the other Ta–Cl distances (Ta–Cl1 = 2.259 (5) Å, Ta–Cl2 = 2.233 (5) Å), possibly because Cl3 is trans to the two carbons of the dicarbolide ligand, which are weaker electron donor atoms (more electronegative, lower frontier orbital coefficients)

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[21] Fontaine, X. L. R.; Greenwood, N. N.; Kennedy, J. D.; Nestor, K.; Thornton-Pett, M.; Hermanek, S.; Jelinek, T.; Stibr, B. *J. Chem. Soc., Dalton Trans.* **1990**, 681.

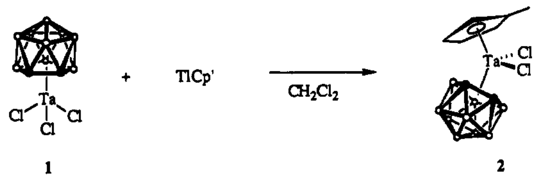
Table IV. Selected Bond Distances (Å) and Angles (deg) for $Cp'(C_2B_9H_{11})TaCl_2$ (2)

	Bond Distances		
Ta–Cl1	2.369 (1)	Ta–Cl2	2.365 (1)
Ta–C1	2.491 (3)	Ta–C2	2.445 (3)
Ta–C3	2.426 (3)	Ta–C4	2.382 (3)
Ta–C5	2.391 (3)	Ta–B1	2.465 (4)
Ta–B2	2.502 (4)	Ta–B3	2.448 (4)
Ta–CB4	2.471 (3)	Ta–CB5	2.487 (3)
Ta–C0[a]	2.109	Ta–B0[b]	2.011
C1–C2	1.414 (5)	C1–C5	1.409 (5)
C2–C3	1.420 (5)	C3–C4	1.389 (6)
C4–C5	1.433 (5)	C1–C6	1.497 (5)
B1–B2	1.771 (5)	B1–CB5	1.687 (6)
B1–B8	1.809 (6)	B1–B9	1.814 (5)
B2–B3	1.765 (6)	B2–B7	1.792 (5)
B2–B8	1.793 (4)	B3–CB4	1.684 (5)
B3–B6	1.785 (5)	B3–B7	1.780 (6)
CB4–CB5	1.578 (5)	CB4–B6	1.709 (6)
CB4–B10	1.728 (5)	CB5–B9	1.690 (6)
CB5–B10	1.722 (6)	B6–B7	1.759 (7)
B6–B10	1.780 (8)	B6–B11	1.777 (7)
B7–B8	1.778 (6)	B7–B11	1.771 (5)
B8–B9	1.769 (6)	B8–B11	1.771 (6)
B9–B10	1.762 (9)	B9–B11	1.795 (7)
B10–B11	1.764 (8)		
	Bond Angles		
Cl1–Ta–Cl2	92.05 (3)	Cl1–Ta–C0	102.38
Cl1–Ta–B0	108.54	Cl2–Ta–C0	103.23
Cl2–Ta–B0	109.37	C0–Ta–B0	133.48

[a] C0 denotes the centroid of the Cp′ ligand. [b] B0 denotes the centroid of the dicarbollide ligand.

relative to B.[22] The structure of 1 is analogous to that of isoelectronic $CpTiCl_3$, although in this case the centroid–Ti–Cl angles are nearly equal (114.3–117.2°).[23]

Synthesis of $(C_5H_4R)(C_2B_9H_{11})TaCl_2$ (2, R = Me; 3, R = H). Two routes to $(C_2B_9H_{11})Ta$ analogues of group 4 Cp_2MX_2 bent-metallocene complexes were developed. Reaction of 1 with TlCp′ (Cp′ = C_5H_4Me) in CH_2Cl_2 solution produces $Cp'(C_2B_9H_{11})TaCl_2$ (2) in 83% isolated yield (eq 2). Complex 2 is a sublimable yellow solid which is air-stable in the solid state and in solution. The NMR data for 2 are consistent with the presence of η^5-Cp′ and η^5-$C_2B_9H_{11}$ ligands and with a bent-metallocene structure of effective C_s symmetry. Assignment of the ^{11}B NMR resonances by [^{11}B–^{11}B]COSY experiments was inconclusive. The analogous C_5H_5 complex $Cp(C_2B_9H_{11})TaCl_2$ (3) was prepared by reaction of $CpTaCl_4$ with $Li_2C_2B_9H_{11}$ (eq 3).



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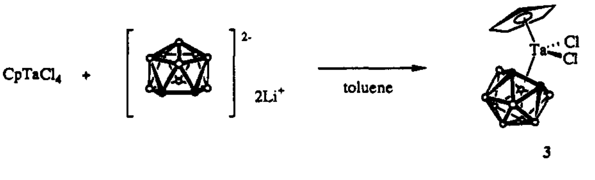

3 (3)

Table V. Positional Parameters and *B* Values for $Cp'(C_2B_9H_{11})TaCl_2$ (2)

atom	*x*	*y*	*z*	*B*,[a] Å^2
Ta	0.95179 (1)	0.73440 (1)	0.73973 (1)	2.300 (2)
Cl1	0.89851 (9)	0.86345 (7)	0.9711 (1)	3.95 (2)
Cl2	0.85990 (9)	0.59248 (7)	0.8697 (1)	4.20 (2)
C1	0.7588 (4)	0.8294 (3)	0.5126 (5)	3.51 (6)
C2	0.6853 (3)	0.7363 (3)	0.5444 (5)	3.49 (6)
C3	0.7337 (4)	0.6471 (3)	0.4526 (6)	4.09 (7)
C4	0.8430 (4)	0.6826 (3)	0.3774 (5)	4.13 (7)
C5	0.8606 (4)	0.7967 (3)	0.4175 (4)	3.69 (6)
C6	0.7259 (5)	0.9411 (3)	0.5556 (7)	5.5 (1)
B1	1.1826 (4)	0.8520 (3)	0.7892 (6)	3.60 (6)
B2	1.1626 (4)	0.7394 (3)	0.6025 (5)	3.20 (6)
B3	1.1535 (4)	0.6282 (3)	0.7264 (6)	3.27 (6)
CB4	1.1820 (3)	0.6773 (3)	0.9725 (5)	3.67 (6)
CB5	1.2005 (4)	0.8030 (3)	1.0076 (5)	3.92 (7)
B6	1.3308 (5)	0.6280 (4)	0.9237 (7)	4.79 (9)
B7	1.3245 (4)	0.6710 (3)	0.6925 (6)	3.62 (7)
B8	1.3454 (4)	0.8125 (3)	0.7344 (6)	3.88 (7)
B9	1.3631 (5)	0.8564 (4)	0.9917 (7)	4.85 (9)
B10	1.3596 (5)	0.7430 (6)	1.1109 (7)	5.4 (1)
B11	1.4496 (4)	0.7431 (4)	0.9285 (7)	4.6 (1)
H2	0.618 (4)	0.732 (3)	0.614 (6)	4.3 (9)*
H3	0.682 (5)	0.576 (3)	0.445 (6)	5(1)*
H4	0.897 (5)	0.642 (3)	0.310 (6)	5(1)*
H5	0.917 (6)	0.838 (4)	0.387 (7)	8 (1)*
H6A	0.658 (6)	0.967 (4)	0.411 (8)	7 (1)*
H6B	0.822 (7)	0.992 (4)	0.601 (9)	10 (2)*
HB1	1.138 (4)	0.927 (3)	0.772 (6)	4.2 (9)*
HB2	1.132 (4)	0.740 (3)	0.437 (5)	3.5 (8)*
HB3	1.103 (5)	0.550 (3)	0.682 (7)	6 (1)*
HB4	1.147 (5)	0.641 (3)	1.047 (6)	5 (1)*
HB5	1.176 (4)	0.846 (3)	1.117 (6)	4.0 (8)*
HB6	1.355 (7)	0.553 (5)	0.975 (8)	10 (2)*
HB7	1.366 (4)	0.626 (2)	0.580 (5)	3.0 (7)*
HB8	1.388 (5)	0.856 (3)	0.650 (6)	5 (1)*
HB9	1.425 (6)	0.918 (4)	1.100 (8)	7 (1)*
HB10	1.387 (5)	0.743 (3)	1.261 (6)	4.2 (9)*
HB11	1.579 (4)	0.744 (3)	0.968 (6)	4.9 (9)*

[a] Starred values denote atoms refined isotropically. Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as: $^4/_3[a^2B_{11} + b^2B_{22} + c^2B_{33} + ab(\cos\gamma)B_{12} + ac(\cos\beta)B_{13} + bc(\cos\alpha)B_{23}]$.

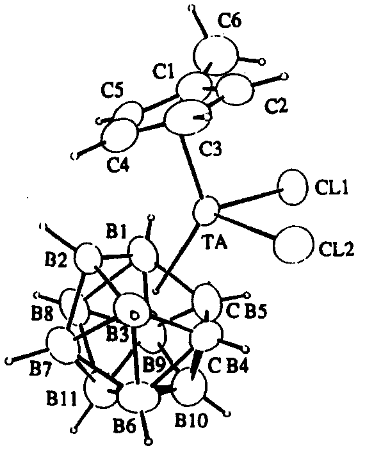

Figure 3. Structure of $Cp'(C_2B_9H_{11})TaCl_2$ (2).

Structure of 2. The solid-state structure of 2 has been determined by X-ray crystallography. Metrical parameters and atomic coordinates are listed in Tables IV and V. As Figure 3 illustrates, 2 adopts a monomeric bent-metallocene structure with η^5-Cp′ and η^5-$C_2B_9H_{11}$ ligands. The (dicarbollide centroid)–Ta–(Cp′ centroid) angle (133.5°) and Cl–Ta–Cl angle (92.1°) are in the range normally observed for d^0 Cp_2MX_2 complexes.[24] The

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[22] (a) For a similar effect in a Mn carborane complex see: Cowie, J.; Hamilton, E. J. M.; Laurie, J. C. V.; Welch, A. J. *J. Organomet. Chem.* **1990**, *394*, 1. (b) For MO analyses of $C_2B_9H_{11}^{2-}$ see refs 2b,c and 4c,d, and: Goursot, A.; Penigault, E.; Chermette, H.; Fripiat, J. G. *Can. J. Chem.* **1986**, *64*, 1752.

[23] (a) Structure of $CpTiCl_3$: Engelhardt, L. M.; Papasergio, R. I.; Raston, C. L.; White, A. H. *Organometallics* **1984**, *3*, 18. (b) Structure of (η^5-C_5Me_4Et)$TiCl_3$: Alcock, N. W.; Toogood, G. E.; Wallbridge, M. G. H. *Acta Crystallogr.* **1984**, *C40*, 598.

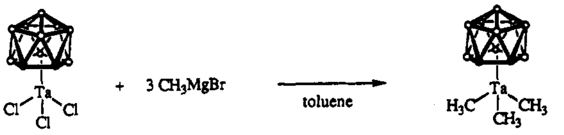
[24] Prout, K.; Cameron, T. S.; Forder, R. A.; Critchley, S. R.; Denton, B.; Rees, G. V. *Acta Crystallogr.* **1974**, *B30*, 2290.

methyl group roughly eclipses Cl1, destroying the C_s symmetry in the solid state; presumably Cp′ ring rotation is rapid in solution. The Ta–dicarbollide distances are slightly (ca. 0.06 Å) longer than those in 1, with Ta–B and Ta–C distances ranging from 2.502 (Ta–B2) to 2.448 Å (Ta–B3). The carbons in the dicarbollide ligand were distinguished from the borons by their longer bond distances. The C–B bond lengths on the η^5 face (1.684, 1.687 Å) are slightly shorter than the other C–B bonds (1.690–1.728 Å), and the B–B distances are fairly uniform (1.780(16) Å).

All hydrogen atoms were located and refined isotropically. Except for the hydrogen on B2, the B–H and C–H hydrogens on the η^5 dicarbollide face are bent toward Ta with (centroid)–B/C–H angles of 158–154°, which are nearly ideal for icosahedral geometry. The angle at B2, however, is flattened out to 170°, probably due to crowding involving the Cp′ ligand. This is consistent with the longer Ta–B2 distance noted above. A nonbonding contact of 2.31 Å is estimated between the B2 hydrogen and the C4 hydrogen of the Cp′ ring.

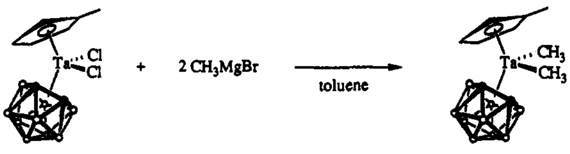
The Ta–(dicarbollide centroid) distance (2.011 Å) is significantly shorter than the Ta–(Cp′ centroid) distance (2.109 Å), consistent with the expected stronger donor ability of $C_2B_9H_{11}^{2-}$ vs Cp'^{-}.[1,2] Cone angles of 133 and 152° for Cp′ and dicarbollide, respectively, are estimated from the metrical data for 2. The larger dicarbollide cone angle is due to the shorter Ta–dicarbollide distance, the larger size of the B_3C_2 ring, and the bending of the η^5 face hydrogens toward Ta, which contributes about 8° to the cone angle. The larger dicarbollide cone angle is reflected in the (Cp′ centroid)–Ta–Cl (103°) and (dicarbollide centroid)–Ta–Cl (109°) angles. The dicarbollide cone angle in 2 is slightly smaller than that in 1 (158°) due to the slightly longer Ta–dicarbollide distances for 2 and is consistent with greater electronic unsaturation and decreased steric demand in 1.

Synthesis of ($C_2B_9H_{11}$)Ta Alkyl Complexes. Alkylation of 1 with 3 equivalents of MeMgBr in toluene produces ($C_2B_9H_{11}$)$TaMe_3$ (4) as a white solid in 89% isolated yield (eq 4). Complex 4 was also prepared by reaction of $TaMe_3Cl_2$ with $Li_2C_2B_9H_{11}$. The $^{11}B\{^1H\}$ NMR spectrum of 4 consists of six resonances in a 1:1:1:2:2:2 ratio, shifted to higher field than 1 by an average of 5 ppm, and consistent with an η^5-bonded dicarbollide ligand. The ^1H and $^{13}C\{^1H\}$ NMR spectra of 4 include singlets (δ 1.14, 86.0) for the Ta–CH_3 groups. Reaction of 1 with MeMgBr in ether solution yielded the monoetherate 4·Et_2O, from which the Et_2O could not be removed under high vacuum (72 °C, 3 h).[25]



1 4 (4)

Alkylation of 2 with MeMgBr in toluene solution produces Cp′($C_2B_9H_{11}$)$TaMe_2$ (5) in 71% isolated yield (eq 5). The ^1H NMR and ^{13}C NMR spectra of 5 contain singlets for the Ta–Me groups at δ –0.05 and 62.4. The ^{11}B NMR resonances of 5 are shifted upfield from those of 2 by an average of 4 ppm. The reaction of 2 with $LiCH_2{}^tBu$ did not give identifiable Ta(V) alkyl products under a variety of conditions; most of the products were insoluble in toluene. Reaction of 2 with $LiCH_2SiMe_3$ did yield Cp′($C_2B_9H_{11}$)Ta(CH_2SiMe_3)$_2$ as the major product in an NMR-tube reaction.[26]



2 5 (5)

Discussion

Simple halide metathesis routes to the prototypical Ta(V) dicarbollide complexes (η^5-$C_2B_9H_{11}$)$TaCl_3$ (1) and (C_5H_4R)(η^5-$C_2B_9H_{11}$)$TaCl_2$ (2, R = Me; 3, R = H) have been developed. Alkylation of 1 and 2 with MeMgBr yields the corresponding methyl derivatives 4 and 5. The complexes presented here are analogous to group 4 metal $CpMX_3$ and Cp_2MX_2 complexes and are one ligand more unsaturated than corresponding group 5 metal $CpMX_4$ and Cp_2MX_3 systems. Like group 4 $CpMX_3$ complexes,[27] 1 and 4 are both potent Lewis acids; 1 rapidly polymerizes THF, and 4 strongly coordinates Et_2O. The bent-metallocene complexes 2, 3, and 5 are stable 16-electron species analogous to the well-studied group 4 Cp_2MX_2 systems.[28]

The (η^5-$C_2B_9H_{11}$)Ta fragment in compounds 1–5 is closely comparable to a (η^5-Cp*)Ti fragment. The electronic and steric properties of the $C_2B_9H_{11}^{2-}$ ligand are similar to those of anionic Cp^{*-},[1,2] and the effective ionic radii of Ti(IV) and Ta(V) in comparable coordination spheres are essentially equal (0.74 Å, eight-coordinate geometry).[29] The effective ionic radii of Hf(IV) and Zr(IV) are 0.1 Å larger, which makes a comparison with Ti(IV) more appropriate. The mono(dicarbollide) Ta complex 1 is sublimable, soluble, and monomeric, as is Cp*$TiCl_3$. In contrast, Cp*$ZrCl_3$ is ologiomeric in solution, and $CpZrCl_3$ is polymeric in the solid state, as a result of the larger Zr(IV) radius.[23a,30] The structure of 2 is is almost identical with that of the mixed-ring complex CpCp*$TiCl_2$ (6).[31] The Cl–Ti–Cl (94.8°) and (centroid)–Ti–(centroid) angles (130°) of 6 are within 3° of the corresponding angles in 2, and the M–Cl distances in both complexes are identical (6, 2.334, 2.323 Å; 2, 2.369, 2.365 Å). Also, an out-of-plane, sterically induced, bending distortion of a Cp* methyl is present which is similar to the bending of B(2)–H in 2.[32]

We are currently studying the chemistry of alkyl complexes 4 and 5 to determine the extent to which the structural similarity of ($C_2B_9H_{11}$)Ta and Cp*Ti systems is reflected in their chemical reactivity. It is anticipated that reactive ($C_2B_9H_{11}$)Ta alkyl complexes analogous to

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[25] ^1H NMR (toluene-d_8): δ 3.45 (br s, 4 H), 2.50 (br s, 2 H), 1.25 (br s, 9 H), 0.91 (br s, 6 H).

[26] ^1H NMR data for Cp′($C_2B_9H_{11}$)Ta(CH_2SiMe_3)$_2$ (300 MHz, C_6D_6): δ 5.95 (m, 2 H, C_5H_4Me), 5.86 (m, 2 H, C_5H_4Me), 4.15 (br s, 2 H, $C_2H_2B_9H_9$), 2.15 (s, C_5H_4Me), 0.92 (d, J = 9.6 Hz, 2 H, $CHHSiMe_3$), 0.36 (d, J = 9.6 Hz, $CHHSiMe_3$), 0.01 (s, 18 H, $SiMe_3$).

[27] For a recent review of mono-Cp metal–halide chemistry of d- and f-block elements, see: Poli, R. *Chem. Rev.* **1991**, *91*, 509.

[28] Cardin, D. J.; Lappert, M. F.; Raston, C. L. *Chemistry of Organo-Zirconium and -Hafnium Compounds*; Wiley: New York, 1986.

[29] Shannon, R. D. *Acta Crystallogr.* **1976**, *A32*, 751.

[30] Solution molecular weight studies establish that (Cp*$ZrCl_3$)$_x$ is oligomeric in benzene solution (x = 2.4): Uhrhammer, R.; Jordan, R. F. Unpublished observations. Also see: Wolczanski, P. T.; Bercaw, J. E. *Organometallics* **1982**, *1*, 793.

[31] Khotsyanova, T. L.; Kuznetsov, S. I. *J. Organomet. Chem.* **1973**, *57*, 155.

[32] Permethylated Cp*$_2TiCl_2$ (8) is also structurally similar to 2. The Cl–Ti–Cl angle of 8 (92.9°) is in close agreement with that of 2; however, greater steric interactions between the Cp* ligands result in larger methyl group bending distortions, a longer (Cp* centroid)–Ti distance, and a larger (centroid)–Ti–(centroid) angle (137.4°) than observed for 2: McKenzie, T. C.; Sanner, R. D.; Bercaw, J. E. *J. Organomet. Chem.* **1975**, *102*, 457.

group 4 metal $Cp^*M(R)_2(L)_n^+$ and $Cp_2M(R)L^+$ derivatives[5,33] can be prepared and studied.

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Supplementary Material Available: Complete listings of bond distances, bond angles, H atom positional parameters, and anisotropic thermal parameters for 1 and 2 (13 pages). Ordering information is given on any current masthead page.

OM920160M

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[33] Crowther, D. J.; Jordan, R. F.; Baenziger, N. C. *Organometallics* 1990, *9*, 2574.

Reactivity of $Cp^*W(O)_2(CH_2SiMe_3)$ toward *p*-Tolyl Isocyanate: Cycloaddition Reactions of Tungsten–Oxo and –Imido Linkages[1,2]

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Treatment of $Cp^*W(O)_2(CH_2SiMe_3)$ with *p*-tolyl isocyanate under appropriate experimental conditions leads to the formation of $Cp^*W(O)(NC_6H_4\text{-}p\text{-}Me)(CH_2SiMe_3)$ (1), $Cp^*W(NC_6H_4\text{-}p\text{-}Me)_2(CH_2SiMe_3)$ (2), or $Cp^*\overline{W(NC_6H_4\text{-}p\text{-}Me)[N(C_6H_4\text{-}p\text{-}Me)C(O)N}(C_6H_4\text{-}p\text{-}Me)](CH_2SiMe_3)$ (3). Each of the complexes 1–3 is derived in a sequential manner from its precursor by incorporation of an additional *p*-tolyl isocyanate fragment or molecule. The spectroscopic properties of these organometallic imido complexes are consistent with their possessing three-legged (1 and 2) and four-legged (3) piano-stool molecular structures. These conclusions have been confirmed by single-crystal X-ray crystallographic analyses of 2 and 3. Crystal data for 2: triclinic, $a = 15.095$ (3) Å, $b = 18.583$ (4) Å, $c = 10.828$ (2) Å, $\alpha = 95.01$ (2)°, $\beta = 107.01$ (2)°, $\gamma = 89.02$ (2)°, $Z = 4$, space group $P\bar{1}$, $R_F = 0.033$, $R_{wF} = 0.031$ for 5463 reflections with $I \geq 3\sigma(I)$. Crystal data for 3: monoclinic, $a = 14.5279$ (11) Å, $b = 10.447$ (7) Å, $c = 11.6482$ (13) Å, $\beta = 105.170$ (6)°, $Z = 2$, space group $P2_1$, $R_F = 0.058$, $R_{wF} = 0.081$ for 2479 reflections with $I \geq 3\sigma(I)$. The formation of complex 3 involves the *net* [2 + 2] cycloaddition of the N=C bond of *p*-tolyl isocyanate across one of the tungsten–imido links of complex 2, $Cp^*W(NC_6H_4\text{-}p\text{-}Me)_2(CH_2SiMe_3)$.

Introduction

The study of transition-metal imido complexes and other compounds having metal–ligand multiple bonds is currently in a period of rapid growth.[3-5] Imido complexes are of particular interest both as new reagents[6] and as heterogeneous or homogeneous catalysts for various organic conversions. For instance, metal–imido species have been invoked as intermediates during the ammoxidation of propylene.[7-9] Such species also appear to be involved in the catalytic cycles of a variety of metalloenzymes.[3,4] In light of the versatile reactivity exhibited by transition-metal–imido complexes, determination of their characteristic properties in various chemical environments is warranted.

We have previously described the synthesis, characterization, and some reactivity of metal–dioxo and metal–alkylidene–oxo complexes of the types A and B.[10] It was, therefore, of interest to us to determine whether the analogous metal–imido complexes (type C) could also be prepared.[11,12]

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[1] Organometallic Oxo Chemistry. 4. Part 3: Reference 10.

[2] Taken in part from: (a) Phillips, E. C. Ph.D. Dissertation, The University of British Columbia, 1989. (b) Yee, V. C. Ph.D. Dissertation, The University of British Columbia, 1990.

[3] Nugent, W. A.; Haymore, B. L. *Coord. Chem. Rev.* 1980, *31*, 123.

[4] Nugent, W. A.; Mayer, J. M. *Metal-Ligand Multiple Bonds*; Wiley-Interscience: New York, 1988.

[5] For recent examples of the synthesis and chemistry of imido complexes see: (a) Walsh, P. J.; Hollander, F. J.; Bergman, R. G. *J. Am. Chem. Soc.* 1988, *110*, 8729. (b) Cummins, C. C.; Baxter, S. M.; Wolczanski, P. D. *J. Am. Chem. Soc.* 1988, *110*, 8731. (c) Glueck, D. S.; Hollander, F. J.; Bergman, R. G. *J. Am. Chem. Soc.* 1989, *111*, 2719. (d) Burns, C. J.; Smith, W. H.; Huffman, J. C.; Sattelberger, A. P. *J. Am. Chem. Soc.* 1990, *112*, 3237. (e) Williams, D. S.; Schofield, M. H.; Anhaus, J. T.; Schrock, R. R. *J. Am. Chem. Soc.* 1990, *112*, 6728. (f) Luan, L.; White, P. S.; Brookhart, M.; Templeton, J. L. *J. Am. Chem. Soc.* 1990, *112*, 8190. (g) Michelman, R. I.; Andersen, R. A.; Bergman, R. G. *J. Am. Chem. Soc.* 1991, *113*, 5100. (h) Glueck, D. S.; Wu, Jianxin, Hollander, F. J.; Bergman, R. G. *J. Am. Chem. Soc.* 1991, *113*, 2041.

[6] The synthetic utility of imido complexes as stoichiometric reagents has been described. For example, see: Chong, A. O.; Oshima, K.; Sharpless, K. B. *J. Am. Chem. Soc.* 1977, *99*, 3420 and references therein.

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[9] Chan, D. M.-T.; Fultz, W. C.; Nugent, W. A.; Roe, D. C.; Tulip, T. H. *J. Am. Chem. Soc.* 1985, *107*, 251.

[10] Legzdins, P.; Phillips, E. C.; Sánchez, L. *Organometallics* 1989, *8*, 940 and references therein.

[11] We have previously synthesized one such imido oxo complex, namely $CpW(O)(N\text{-}o\text{-}tolyl)(o\text{-}tolyl)$, by exposure of its diaryl nitrosyl precursor $CpW(NO)(o\text{-}tolyl)_2$ as a solid to deaerated water vapor.[12] To date, this conversion remains unique.

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