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Notes

Anionic Tantalum(V) Bis(dicarbollide) Complexes with Bent-Metallocene Structures

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Introduction

Bis(dicarbollide) complexes $(\eta^5\text{-}C_2B_9H_{11})_2M$ which adopt ferrocene-type metallocene structures are well-known.[1] However, $(\eta^5\text{-}C_2B_9H_{11})_2MX_n$ species with bent metallocene structures are comparitively rare and to our knowledge are limited to the f-block metals. Key examples include Raymond's dianionic U(IV) complex $(\eta^5\text{-}C_2B_9H_{11})_2UCl_2^{2-}$ [2] and a series of lanthanide complexes $(\eta^5\text{-}C_2B_9H_{11})_2Ln(THF)_2^-$ (Ln = Sm, Yb) prepared by Hawthorne.[3] Recently, Hosmane has characterized a series of $\{\eta^5\text{-}2\text{-}(SiMe_3)\text{-}3\text{-}(R)\text{-}2,3\text{-}C_2B_4H_4\}_2M(Cl)(THF)^{n-}$ (n = 2, Y; n = 1, Zr, Hf) complexes which adopt bent-metallocene structures.[4] For several years we have been investigating the possibility of exploiting carborane ligands in the construction of electrophilic early transition metal alkyl systems,[5] and we have reported on a series of mixed-ring bent-metallocene $(C_5Me_5)(C_2B_9H_{11})M(R)$ (M = Zr, Hf) and $(C_5H_4R)(C_2B_9H_{11})TaX_2$ (R = H, Me) species.[6,7] During the course of this work we prepared a series of anionic tantalum(V) bis(dicarbollide) complexes, $(\eta^5\text{-}C_2B_9H_{11})_2TaX_2^-$ (X = Cl (**1**), Me (**2**), F (**3**)), which adopt bent-metallocene structures. The synthesis and characterization of these compounds are discussed in this contribution.

Experimental Section

General Procedures. All manipulations were performed on a high-vacuum line or in a glovebox N_2 atmosphere. Toluene and pentane were distilled from sodium/benzophenone ketyl. CH_2Cl_2 was distilled from CaH_2 and stored over molecular sieves. $C_2D_2Cl_4$ and C_6D_5Cl were dried over molecular sieves, and CD_2Cl_2 was dried over P_2O_5. $TaCl_5$ (CERAC) was sublimed before use.

NMR spectra were recorded on Bruker AMX-360 and AC-300 spectrometers in flame-sealed or Teflon-valved (J. Young) tubes. ^1H and ^{13}C NMR chemical shifts are reported vs Me_4Si and were determined by reference to the residual ^1H and ^{13}C NMR solvent peaks. $^{11}B\{^1H\}$ NMR spectra are referenced to external $BF_3\cdot Et_2O$ (δ 0, C_6D_6). The numbering system used in the ^{11}B NMR assignments is based on that in Figure 1. Assignments are based on $^{11}B-^{11}B$ COSY data.[8] In some cases (noted below) expected $^{11}B-^{11}B$ COSY correlations involving B nuclei which flank the carborane C nuclei were not observed; this phenomenon has been noted previously and has been ascribed to diversion of s electron density away from B−B bonds to B−C bonds.[9] ^{19}F NMR spectra are referenced to external CCl_3F (δ 0, CD_2Cl_2). Elemental analyses were performed by E & R Microanalytical Laboratory, Inc. $(C_2B_9H_{11})TaCl_3$ [7] and $[PPN][Tl(C_2B_9H_{11})]$ [10] were prepared by literature methods.

$[PPN][(C_2B_9H_{11})_2TaCl_2]$ (1). A slurry of $(C_2B_9H_{11})TaCl_3$ (336 mg, 0.800 mmol) and $[PPN][Tl(C_2B_9H_{11})]$ (700 mg, 0.800 mmol) in CH_2Cl_2 (100 mL) was prepared at −78 °C. The mixture was warmed to 23 °C and stirred for 1 h. The slurry was filtered through an E porosity Schlenk frit, and the residue on the frit was washed with CH_2Cl_2 (2 × 10 mL). The combined filtrate and wash was evaporated to dryness and dried overnight under vacuum yielding **1** (0.824 g, 99%) as a red-brown oily solid. This material may be purified by dissolution in CH_2Cl_2 and reprecipitation with pentane. ^1H NMR (360 MHz, CD_2Cl_2): δ 7.67 (m, 6 H, PPN), 7.48 (m, 24 H, PPN), 3.64 (s, 4 H, CH), 4.0−1.5 (br m, 18 H, BH). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 134.0, 132.4 (vir t, J = 6 Hz), 129.8 (vir t, J = 7 Hz), 127.3 (dd, J = 109, 1.8 Hz), 62.1 ($C_2B_9H_{11}$). $^{11}B\{^1H\}$ NMR (CD_2Cl_2): δ 26.7 (B2), 2.9 (B6, B7), −4.7 (B5, B8), −5.6 (B1, B3), −11.8 (B4), −14.4 (B9). $^{11}B-^{11}B$ COSY (CD_2Cl_2) (correlations observed): B2−(B1, B3) s; B2−(B6, B7) m; (B1, B3)−(B5, B8) m; (B6, B7)−(B5, B8) w; (B6, B7)−(B9) m; (B5, B8)−B9 w.[11] Anal. Calcd for $C_{40}H_{52}B_{18}Cl_2NP_2Ta$: C, 45.53; H, 4.97; Cl, 6.72; N, 1.33. Found: C, 45.33; H, 5.03; Cl, 6.90; N, 1.38.

$[PPN][(C_2B_9H_{11})_2TaMe_2]$ (2). Method A. A solution of MeLi in Et_2O (0.27 mL, 1.4 M, 0.38 mmol, Aldrich) was added dropwise via syringe to a solution of $[PPN][(C_2B_9H_{11})_2TaCl_2]$ (200 mg, 0.189 mmol) in toluene (40 mL). The mixture was stirred at 23 °C for 2 h. The resulting yellow slurry was centrifuged, and the residue was extracted with toluene (200 mL) until the remaining residue was off-white in color. The combined extract was concentrated to 125 mL and cooled to −32 °C for 6 h. Filtration yielded 135 mg of **2** as yellow crystals. The filtrate was concentrated to 25 mL and stored at −32 °C overnight, yielding an additional 45 mg of **2**. Total yield: 77%.

Method B. A solution of MeLi in Et_2O (0.14 mL, 1.4 M, 0.19 mmol, Aldrich) was added dropwise via syringe to a solution of $[PPN][(C_2B_9H_{11})_2TaCl_2]$ (100 mg, 0.195 mmol) in toluene (40 mL). The mixture was stirred at 23 °C for 2 h. The resulting slurry was evaporated to dryness under vacuum. The crude product was dissolved in CH_2Cl_2 (10 mL), and the mixture was filtered through a frit covered with Celite. The Celite was washed with CH_2Cl_2 (2 × 10 mL). The combined filtrate and wash was quickly evaporated to dryness under

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(11) Expected B4−(B3, B5, B9) and (B1, B3)−(B6, B7) correlations not observed.

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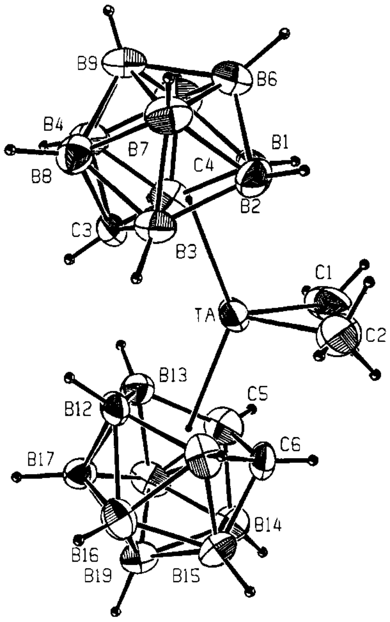

Figure 1. ORTEP view of the $(\eta^5\text{-}C_2B_9H_{11})_2TaMe_2^-$ anion of **2**.

vacuum. The residue was recrystallized from toluene/pentane yielding **2** (69 mg, 72%). Traces of toluene in **2** can be removed by (i) dissolution of **2** in CH_2Cl_2 followed by solvent removal and drying under vacuum at 23 °C for 15 h or (ii) drying under vacuum at 65 °C for 44 h. ^1H NMR (CD_2Cl_2): δ 7.65 (m, 6 H, PPN), 7.50 (m, 24 H, PPN), 4.25 (s, 4 H, CH), 3.0−0.5 (br m, 18 H, BH), 1.38 (s, 6 H, Me). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 134.1, 132.5 (vir t, J = 6 Hz), 129.8 (vir t, J = 6 Hz), 127.4 (d, J = 109 Hz), 78.4 (Me), 60.8 ($C_2B_9H_{11}$). $^{11}B\{^1H\}$ NMR (CD_2Cl_2): 12.9 (B2), 0.1 (B1, B3, B6, B7), −8.7 (B9), −11.1 (B5, B8), −14.4 (B4). $^{11}B-^{11}B$ COSY (115 MHz, CD_2Cl_2) (correlations observed): B2−(B6, B7) w; B2−(B1, B3) s; (B6, B7)−(B5, B8) m; (B6, B7)−(B9) m; (B5, B8)−B9 vw.[12] Anal. Calcd for $C_{42}H_{58}B_{18}NP_2Ta$: C, 49.73; H, 5.76; N, 1.36. Found: C, 49.64; H, 5.54; N, 1.36.

[PPN][$(C_2B_9H_{11})_2TaF_2$] (3). A mixture of **1** (292 mg, 0.276 mmol) and Ag[PF_6] (140. mg, 0.554 mmol) in CH_2Cl_2 (50 mL) was stirred at 23 °C for 24 h and then heated at 50 °C for 30 h. The resulting yellow slurry was filtered, and the precipitate was washed with CH_2Cl_2 (2 × 10 mL). The combined filtrate and wash was evaporated to dryness and dried overnight yielding a yellow oily solid **3** (285 mg, 98%). Attempts to recrystallize this material were unsuccessful. ^1H NMR (CD_2Cl_2): δ 7.67 (m, 6H, PPN), 7.50 (m, 24 H, PPN), 3.81 (s, 4 H, CH), 4.00−0.50 (br m, 18 H, BH). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 134.1, 132.5 (vir t, J = 6 Hz), 129.8 (vir t, J = 6 Hz), 127.4 (d, J = 109 Hz), 69.0 ($C_2B_9H_{11}$). ^{19}F NMR (CD_2Cl_2): δ 14.6. $^{11}B\{^1H\}$ NMR (CD_2Cl_2): δ 13.2 (B2), 1.5 (B6, B7), 0.4 (B1, B3), −7.6 (B5, B8), −10.5 (B4), −10.6 (B9). $^{11}B-^{11}B$ COSY (CD_2Cl_2) (correlations observed): B2−(B1, B3) s; B2−(B6, B7) vw, (B1, B3)−(B6, B7) m; (B6, B7)−(B5, B8) m; (B6, B7)−(B9) m; (B5, B8)−(B4) w, (B5, B8)−B9 vw.[13] Anal. Calcd for $C_{40}H_{52}B_{18}F_2NP_2Ta$: C, 46.99; H, 5.13; N, 1.37; F, 3.72. Found: C, 46.74; H, 4.90; N, 1.18; F, 3.62.

X-ray Diffraction Analysis of 2. Single crystals of **2**·CH_2Cl_2 suitable for X-ray diffraction were grown by cooling a CH_2Cl_2/pentane solution of **2** at −32 °C and 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.[14] Crystallographic details are summarized in Table 1.

Table 1. Summary of Crystallographic Data for [PPN][$(C_2B_9H_{11})_2TaMe_2$] (**2**)

empirical formula	$C_{42}H_{58}B_{18}NP_2Ta{\cdot}CH_2Cl_2$
fw	1099.36
cryst size (mm)	0.36 × 0.37 × 0.23
cryst color	yellow
T (K)	295
space group	$P\bar{1}$
a (Å)	15.012(5)
b (Å)	14.777(5)
c (Å)	12.117(6)
α (deg)	90.31(4)
β (deg)	96.03(4)
γ (deg)	79.96(3)
V (Å^3)	2632.(3)
Z	2
d_{calcd} (g/cm^3)	1.39
cell dimen determination	24 reflns; $19 < 2\theta < 28$
λ (Mo Kα radiation, Å)	0.7107
scan ratio (ω/θ)	1
scan limit (deg)	$2 < \theta < 25$
scan speed (deg/min)	1.5−5.0
ω scan range (deg)	0.75 + tan θ
data collected h; k; l	−17, 17; −17, 17; −14, 8
no. of tot. reflns	12 804
no. of unique reflns	9194
no. of reflns used, $I < 2\sigma(I)$	5863
R_{int}	0.047
max decay cor factor	1.175
μ, cm^{-1}	14.3
empirical abs cor range	1.00−1.32
structure soln method	Patterson/Fourier
refinement^a	all non-H anisotropic, H isotropic
tot. no. of params	688
R	0.059
R_w	0.080
weighting coeff: P, Q^b	0.04, 0.0
SDOUW^c	1.478
max shift/esd	0.24
max resid density (e/Å^3)	4.34^d

^{a} Non-dicarbollide H atoms were fixed at theoretical positions with $B_H = 1.1(B_C)_{eq}$. ^{b} $w = [\sigma_F^2 + (PF)^2 + Q]^{-1}$. ^{c} *S*tandard *D*eviation of *U*nit *W*eight. ^{d} Near Ta atom and due to absorption.

Results and Discussion

Synthesis of [PPN][$(C_2B_9H_{11})_2TaCl_2$] (1). The reaction of $(C_2B_9H_{11})TaCl_3$ and [PPN][$Tl(C_2B_9H_{11})$] in CH_2Cl_2 (23 °C, 1 h) yields [PPN][$(C_2B_9H_{11})_2TaCl_2$] (**1**, >95%) as an air sensitive, oily red-brown solid (Scheme 1). Compound **1** is also formed by the reaction of $TaCl_5$ with 2 equiv of [PPN][$Tl(C_2B_9H_{11})$] though in lower isolated yield. The ^{11}B NMR spectrum of **1** contains a single set of B−H resonances in a 1,2,2,2,1,1 intensity pattern, indicating that the two dicarbollide ligands are equivalent and that the sides of each dicarbollide ligand are equivalent. This is confirmed by the observation of single ^1H (δ 3.64) and ^{13}C (δ 62.1) NMR resonances for the dicarbollide C−H units. The ^{11}B chemical shifts are similar to those for the mixed-ring bent metallocene species $(C_5H_5R)(\eta^5\text{-}C_2B_9H_{11})TaCl_2$ (R = H, Me), with the exception of the B2 resonance (see Figure 1 for numbering system), which is shifted downfield by ca. 20 ppm to δ 26.7. Collectively, these data are consistent with the C_{2v}-symmetric bent-metallocene structure exhibited in Scheme 1.

Complex **1** is soluble and stable in THF, CH_2Cl_2, and chlorobenzene. It is also moderately soluble in toluene, which is an effective solvent for extraction of **1** from the TlCl coproduct in its synthesis. However, this species is susceptible to loss of a carborane ligand upon reaction with Bronsted or Lewis acids. Complex **1** reacts rapidly with H_2O or HCl to

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[12] Expected B4−(B5, B8, B9) and (B1, B3)−(B5, B6, B7, B8) correlations not observed.

[13] Expected (B1, B3)−(B5, B8) correlation not observed. B4 and B9 resonances insufficiently resolved to observe correlation.

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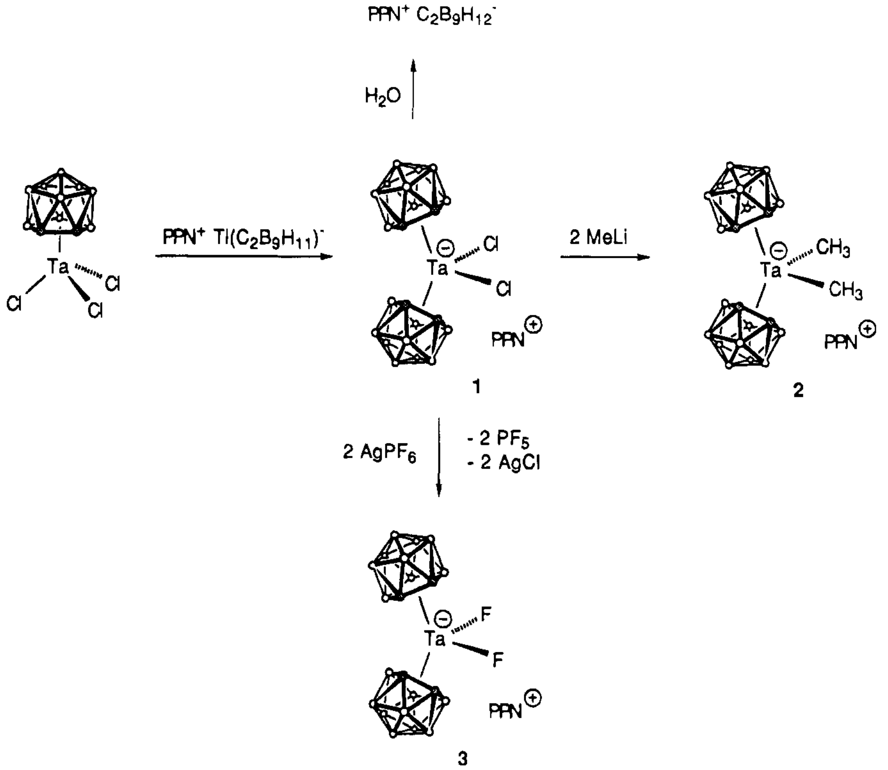
Scheme 1



yield $C_2B_9H_{12}^-$ as the principal boron-containing product[15] and is thus highly moisture sensitive. The reaction of **1** with $AlCl_3$ in $C_2D_2Cl_4$ is complex. NMR analysis establishes that $(C_2B_9H_{11})TaCl_3$ is a major (and the only identifiable) product after 24 h, indicating that abstraction of a dicarbollide ligand occurs.[16]

Synthesis and Properties of [PPN][$(C_2B_9H_{11})_2TaMe_2$] (2). Alkylation of **1** with 2 equiv of CH_3Li or CH_3MgBr in toluene produces [PPN][$(C_2B_9H_{11})_2TaMe_2$] (**2**, 77%, Scheme 1), which is isolated as a yellow crystalline solid by recrystallization from toluene. Compound **2** is also formed by the reaction of **1** with $AlMe_3$ but less cleanly. The ^{11}B NMR spectrum of **2** contains a single set of B—H resonances in a 1,4,1,2,1 intensity pattern, and single ^1H and ^{13}C NMR resonances are observed for the carborane C—H units and the Ta—Me groups. These NMR data are consistent with a C_{2v}-symmetric bent-metallocene structure analogous to that proposed above for **1**. This has been confirmed by X-ray crystallography.

Crystals of **2**·CH_2Cl_2 were obtained by slow crystallization of **2** from CH_2Cl_2/pentane. Compound **2** crystallizes as discrete cations and anions. The anion structure is shown in Figure 1, and crystallographic details are summarized in Tables 1−3. The $(C_2B_9H_{11})_2TaMe_2^-$ anion adopts a distorted tetrahedral, bent-metallocene structure containing two η^5-dicarbollide ligands arranged in a staggered orientation. This structure is comparable to those of sterically similar d^0 Cp_2MX_2 complexes.[17] The centroid—Ta—centroid angle (137.2°) is similar to those in $(C_5Me_5)_2Ta^V$ complexes (e.g., $(C_5Me_5)_2Ta(OH)(CH_3)^+$, 137.3°; $(C_5Me_5)_2Ta(OH)_2^+$, 138.4°)[18] in which steric interactions are expected to be similar due to the similarity in $C_5Me_5^-$ and $C_2B_9H_{11}^{2-}$ cone angles.[19] Similar centroid—Ti—centroid angles are observed in $(C_5Me_5)_2Ti^{IV}$ complexes (e.g., $(C_5Me_5)_2TiCl_2$, 137.4°; $(C_5Me_5)_2Ti(CH_3)(THF)^+$, 137.8°)[20] in which steric interactions also are expected to be similar to those in **2** due to the nearly identical ionic radii of Ti(IV) and Ta(V).[21] The B11—C6 dicarbollide ligand of **2** is bound in a very symmetrical fashion (Ta—C/B distances 2.51 ± 0.01 Å), and the C/B—H bonds on the η^5-face point toward Ta as normally observed

Table 2. Selected Bond Distances (Å) and Bond Angles (deg) for [PPN][$(C_2B_9H_{11})_2TaMe_2$][a]

Ta—C1	2.20(1)	Ta—B1	2.58(1)
Ta—C2	2.22(2)	Ta—B2	2.51(1)
Ta—C3	2.47(1)	Ta—B3	2.43(1)
Ta—C4	2.50(1)	Ta—B11	2.52(1)
Ta—C5	2.57(1)	Ta—B12	2.51(1)
Ta—C6	2.52(1)	Ta—B13	2.51(1)
Ta—Ctd1	2.05	Ta—Ctd2	2.08
av B—C	1.69(1)	ave B—B	1.76(1)
C3—C4	1.59(1)	C5—C6	1.57(2)
N—P1	1.58(1)	av P1—C	1.81(1)
N—P2	1.57(1)	av P2—C	1.80(1)
C1—Ta—C2	82.5(7)	Ctd1—Ta—Ctd2	137.2
Ctd1—Ta—C1	106.9	Ctd1—Ta—C2	108.2
Ctd2—Ta—C1	103.6	Ctd2—Ta—C2	104.7
ave N—P1—C	111.8	ave N—P2—C	111.5
P1—N—P2	143.2(5)		

[a] Ctd1 and Ctd2 are the centroids of the B1—C4 and B11—C6 η^5-faces of the dicarbollide ligands.

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Table 3. Positional Parameters and Thermal Parameters (Å^2) for [PPN][($C_2B_9H_{11}$)$_2$TaMe$_2$]

atom	*x*	*y*	*z*	B^a	atom	*x*	*y*	*z*	B^a
Ta	0.65144(3)	0.09238(3)	0.22675(4)	4.422(9)	Ctd2	0.7903	0.0933	0.2345	
Cl1	0.4944(4)	0.5614(4)	0.1540(5)	12.2(2)	C45	−0.3531(8)	0.4906(7)	0.4904(9)	5.1(3)
Cl2	0.5887(4)	0.7116(4)	0.1973(7)	14.5(2)	C46	−0.3155(7)	0.4458(7)	0.5878(9)	4.5(2)
P1	0.0195(1)	0.3194(1)	0.7347(2)	2.63(4)	C51	−0.2319(6)	0.2201(6)	0.7183(8)	3.5(2)
P2	−0.1807(1)	0.3210(1)	0.7146(2)	2.72(4)	C52	−0.3269(7)	0.2257(6)	0.704(1)	4.7(2)
N	−0.0757(5)	0.2874(5)	0.7136(6)	3.7(2)	C53	−0.3634(7)	0.1478(8)	0.706(1)	5.9(3)
C1	0.6445(9)	−0.0490(8)	0.277(2)	9.4(5)	C54	−0.3104(9)	0.0649(7)	0.729(1)	7.1(4)
C2	0.6146(9)	0.041(1)	0.059(1)	9.0(4)	C55	−0.219(1)	0.0586(8)	0.746(2)	9.9(5)
C3	0.5932(6)	0.2357(6)	0.3219(8)	3.7(2)	C56	−0.1789(7)	0.1361(6)	0.739(1)	6.1(3)
C4	0.5658(7)	0.1527(7)	0.3858(8)	4.5(2)	C61	−0.2130(6)	0.3923(5)	0.8316(8)	3.2(2)
C5	0.8124(7)	0.0152(7)	0.3038(9)	4.8(2)	C62	−0.2377(7)	0.3528(7)	0.9247(8)	4.3(2)
C6	0.8036(7)	0.0148(6)	0.1736(9)	4.6(2)	C63	−0.2595(9)	0.4077(8)	1.0175(8)	5.8(3)
C11	0.0146(6)	0.4420(5)	0.7482(6)	2.8(2)	C64	−0.2568(9)	0.5004(8)	1.0120(9)	5.9(3)
C12	0.0358(7)	0.4815(6)	0.8465(8)	4.0(2)	C65	−0.2320(8)	0.5380(6)	0.923(1)	5.9(3)
C13	0.0239(8)	0.5761(7)	0.8555(9)	5.2(3)	C66	−0.2077(7)	0.4846(6)	0.8288(8)	4.1(2)
C14	−0.0071(8)	0.6307(6)	0.7643(9)	4.8(2)	C100	0.510(1)	0.662(2)	0.107(1)	13.3(7)
C15	−0.0285(9)	0.5919(7)	0.6629(9)	5.4(3)	B1	0.4978(7)	0.0989(8)	0.307(1)	4.7(3)
C16	−0.0172(8)	0.4964(6)	0.6549(8)	4.5(2)	B2	0.4846(9)	0.1508(9)	0.178(1)	4.9(3)
C21	0.0827(6)	0.2652(5)	0.8598(6)	2.7(2)	B3	0.5510(8)	0.2388(8)	0.189(1)	4.3(3)
C22	0.0377(6)	0.2262(7)	0.9345(7)	3.9(2)	B4	0.5145(9)	0.2652(9)	0.415(1)	5.3(3)
C23	0.0875(8)	0.1824(7)	1.0283(8)	5.0(2)	B5	0.4514(9)	0.181(1)	0.402(1)	5.4(3)
C24	0.1787(8)	0.1802(7)	1.0484(8)	5.1(3)	B6	0.3984(8)	0.1788(9)	0.268(1)	5.1(3)
C25	0.2236(7)	0.2158(7)	0.9735(9)	4.8(2)	B7	0.4330(8)	0.2670(9)	0.192(1)	4.5(3)
C26	0.1767(7)	0.2596(6)	0.8780(8)	4.1(2)	B8	0.5054(9)	0.3208(8)	0.284(1)	4.4(3)
C31	0.0874(6)	0.2830(6)	0.6233(7)	2.9(2)	B9	0.4092(8)	0.2848(9)	0.332(1)	4.8(3)
C32	0.1629(7)	0.3210(7)	0.6072(8)	4.8(2)	B11	0.7778(8)	0.1193(8)	0.116(1)	4.3(3)
C33	0.2185(8)	0.2859(9)	0.5275(9)	5.7(3)	B12	0.7696(70	0.1937(6)	0.230(1)	3.5(2)
C34	0.1980(8)	0.2139(9)	0.4648(90	5.8(3)	B13	0.7882(8)	0.1234(8)	0.349(1)	3.9(2)
C35	0.1221(8)	0.1750(7)	0.4791(8)	4.7(2)	B14	0.9113(8)	−0.0120(8)	0.243(1)	4.5(3)
C36	0.0673(6)	0.2101(6)	0.5575(7)	3.2(2)	B15	0.8889(9)	0.0568(9)	0.122(1)	4.9(3)
C41	−0.2315(6)	0.3856(6)	0.5923(7)	3.3(2)	B16	0.8706(8)	0.1717(8)	0.160(1)	4.2(2)
C42	−0.1888(8)	0.3722(7)	0.4957(9)	4.8(2)	B17	0.8784(7)	0.1752(8)	0.3077(9)	3.8(2)
C43	−0.228(1)	0.4181(8)	0.397(1)	6.1(3)	B18	0.9022(8)	0.0618(8)	0.355(1)	4.5(3)
C44	−0.3092(9)	0.4776(7)	0.3957(9)	5.9(3)	B19	0.9529(8)	0.0915(8)	0.243(1)	4.1(2)
Ctd1	0.5385	0.1754	0.2763						

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

(angles from C_2B_3 plane 15−26°). However, there is some asymmetry in the bonding of the B1—C4 dicarbollide ligand. There is greater variation in the Ta—B/Ta—C distances (2.43(1)−2.58(1) Å) and the B2—H, C3—H, and C4—H bonds project toward Ta to a much lesser extent than normally observed (angles from C_2B_3 plane 5, 10, and < 0°, respectively). The most unusual feature of the (η^5-$C_2B_9H_{11}$)TaMe$_2^-$ structure is the acute Me—Ta—Me angle (82.5(7)°), which is ca. 15° smaller than the X—M—X angles (94−100°) generally observed in d^0 Cp$_2$MX$_2$ complexes.[17] The nonsymmetrical Ta/B1—C4 dicarbollide bonding and the acute Me—Ta—Me angle most likely result from steric interactions involving the dicarbollide and methyl ligands in this crowded species. Several close H—H contacts (2.0−2.4 Å) and short C—B/C—C distances are present and would be reinforced if the methyl ligands were moved further back into the metallocene wedge.[22] For comparison, the O—Sm—O angle of ($C_2B_9H_{11}$)$_2$Sm(THF)$_2^-$ is also acute (79.5°),[3] and the Cl—U—Cl angle in ($C_2B_9H_{11}$)$_2$UCl$_2^{2-}$ is 90.3(5)°.[2]

The PPN$^+$ cation of **2** adopts a "transoid" conformation with a staggered arrangement of phenyl groups. This differs from the commonly observed eclipsed ("cisoid") conformation in which two phenyl groups on different phosphorus centers within the same cation adopt a parallel arrangement.[23] The difference can be traced to inter-cation π-stacking interactions involving phenyl groups on neighboring PPN$^+$ cations, as shown in the packing diagram in Figure 2.[24]

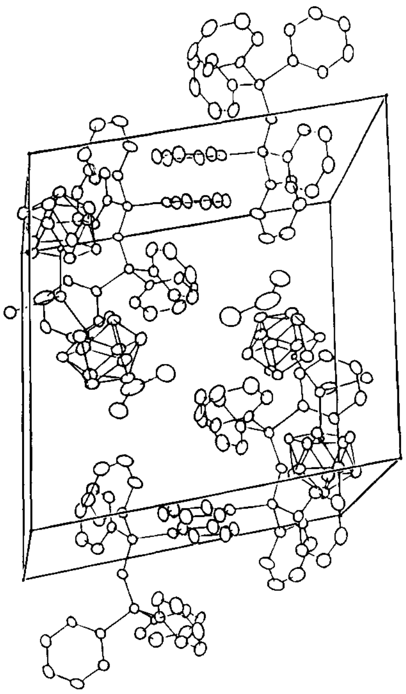

Figure 2. Packing diagram for [PPN][(η^5-$C_2B_9H_{11}$)$_2$TaMe$_2$]·CH$_2$Cl$_2$ (**2**·CH$_2$Cl$_2$).

Compex **2** is thermally stable in toluene, THF, and chlorinated solvents but like **1** undergoes facile hydrolysis with release of

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(22) Close H—H contacts in ($C_2B_9H_{11}$)$_2$TaMe$_2^-$ (Å): HC2A—HB2, 2.04; HC2B—HC6, 2.23; HC2C—HB11, 2.18; HC1A—HC5, 2.36; HC1B—HC5, 2.27; HC1B—HC6, 2.29; HC1C—HB1, 2.15; HC3—HB12, 2.21; HB3—HB12, 2.38. Close C—B and C—C contacts (Å): C2—B2, 2.83; C2—B11, 2.91; C2—C6, 2.98; C1—B1, 2.87; C1—C5, 2.83.

$C_2B_9H_{12}^-$. Attempts to convert **2** to the as yet unknown species $(C_2B_9H_{11})_2TaMe$ via Ta—Me bond protonolysis or Me^- abstraction by Lewis acids have thus far been unsuccessful. The reaction of **2** with Bronsted acids yields $C_2B_9H_{12}^-$ as the only identifiable product, and reactions with Lewis acids yield as yet unidentified mixtures of products.

Synthesis of [PPN][$(C_2B_9H_{11})_2TaF_2$] (3). In an attempt to prepare $(C_2B_9H_{11})_2TaCl$ by chloride abstraction from **1** with 1 equiv of Ag[PF_6] in $C_2D_2Cl_4$, the difluoride complex [PPN][$(C_2B_9H_{11})_2TaF_2$] (**3**) was obtained in ca. 50% yield. When 2 equiv of Ag[PF_6] was used in this reaction, **3** was obtained in 98% yield (Scheme 1). A colorless gas identified as PF_5 (^{19}F and ^{31}P NMR and GC-MS) and an off-white precipitate identified as AgCl (solubility) are also produced in this reaction. The reaction of **1** with 2 equiv of LiF in $C_2D_2Cl_4$ did not produce **3** even after heating at 80 °C for 13 h. Thus the formation of **3** likely proceeds via sequential abstraction of Cl^- from **1** by Ag^+, followed by F^- transfer from PF_6^- to Ta. This suggests that $(\eta^5\text{-}C_2B_9H_{11})_2TaX$ (X = Cl, F) species are highly electrophilic, as expected for 14-electron bent-metallocene species.[5]

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Supplementary Material Available: Tables of bond distances and angles, anisotropic thermal parameters, hydrogen atom coordinates, and least squares planes and related atomic deviations and dihedral angles for **2** (13 pages). Ordering information is given on any current masthead page.

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(23) Selected examples: (a) Handy, L. B.; Ruff, J. K.; Dahl, L. F. *J. Am. Chem. Soc.* **1970**, *92*, 7327. (b) Ruff, J. K.; White, R. P., Jr.; Dahl, L. F. *J. Am. Chem. Soc.* **1971**, *93*, 2159. (c) Goldfield, S. A.; Raymond, K. N. *Inorg. Chem.* **1974**, *13*, 770. (d) Garner, C. D.; Mabbs, F. E.; Richens, D. T. J. *Chem. Soc., Chem. Commun.* **1979**, 415. (e) Bryce, M. R.; Ahmad, M. M.; Friend, R. H.; Obertelli, D.; Fairhurst, S. A.; Winter, J. N. *J. Chem. Soc., Perkin Trans. 2* **1988**, 1151. (f) Glidewell, C.; Lambert, R. J.; Hursthouse, M. B.; Motevalli, M. *J. Chem. Soc., Dalton Trans.* **1989**, 2061. (g) Swartz, W. E.; Ruff, J. K.; Hercules, D. M. *J. Am. Chem. Soc.* **1972**, *94*, 5227.

(24) For a somewhat similar case see: Chivers, T.; Edelmann, F.; Richardson, J. F.; Schmidt, K. J. *Can. J. Chem.* **1986**, *64*, 1509.