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# TANTALUM-BOROLLIDE ALKYL COMPLEXES*

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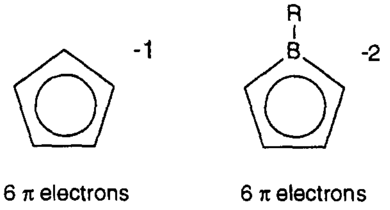
**Abstract**—Reaction of $Me_3TaCl_2$ with $Li_2[C_4H_4BN(CHMe_2)_2](THF)$ produces $[\eta^5\text{-}C_4H_4BN(CHMe_2)_2]Me_2Ta[\mu\text{-}\eta^5\text{-}C_4H_4BN(CHMe_2)_2]TaMe_4$ (**1**) which is an extremely deficient (24 electron) triple decker complex. Similarly, mononuclear $[\eta^5\text{-}C_4H_4BN(CHMe_2)_2]TaMe_3(PMe_3)$ (**2**) is obtained when $Me_3TaCl_2(PMe_3)$ is used as the metal source. Compound **2** undergoes clean migratory insertion chemistry with 2,6-dimethylisocyanide. The product of the reaction of **2** with three equivalents of isocyanide is the metallabicyclic complex $[\eta^5\text{-}C_4H_4BN(CHMe_2)_2]Ta[\eta^2\text{-}MeCN(2,6\text{-}Me_2\text{-}C_6H_3)][\eta^3\text{-}(2,6\text{-}Me_2C_6H_3)NCHCH_2C(Me)N(2,6\text{-}Me_2\text{-}C_6H_3)]$ which has been structurally characterized.

The formal replacement of the cyclopentadienyl (Cp) monoanion by a dianionic 6π electron ligand should, in principle, result in complexes with similar electronic and structural characteristics but different molecular charge. Hawthorne's classic $Cp[C_2B_9H_{11}]Fe^{III}$, a neutral analog of the ferrocenium cation, illustrates this concept by use of the dianionic dicarbollide ligand.[1] Moreover, this strategy may also be exploited in the design and preparation of isoelectronic molecules containing different metal and ligand formulations. For example, $(TMM)Cp^*ZrCl_2Li(TMEDA)$ ($Cp^* = C_5Me_5$, TMM = trimethylenemethane dianion) is similar in molecular geometry and reactivity to bis-cyclopentadienyl complexes of group 3 metals.[2] Comparative studies of transformations mediated by compounds related in this manner provide a means to better delineate how the intrinsic properties of the metal site and the ligands cooperate in determining overall reactivity.

Boron containing heterocycles constitute an attractive class of ligands for this type of study.[3] The borollide dianion, which contains only one boron atom, is the closest structural relative to the cyclopentadienyl anion and is conveniently free of the problematic B—H functionality known to attenuate the reactivity of dicarbollide early-metal complexes.[4]



Several borollide complexes have been prepared and structurally characterized. Most of these molecules are late-metal compounds, such as *cis*-$Cr(CO)_2[C_4H_4BN(CHMe_2)]_2$ with elongated metal–boron distances, in which the borollide–metal bonding has been described as akin to that of a cyclic diolefin.[5] Additionally, boron heterocycles tend to form low valent triple decker complexes like $(\mu\text{-}\eta^5\text{-}C_4H_4BPh)[V(CO)_4]_2$.[6] In contrast, only one report exists regarding electrophilic borollide early-metal complexes, and in these the borollide ligand appears to bind in a fashion intermediate between that characteristic of a diolefin and a fully delocalized 6π electron dianion.[7]

In this paper, we report the synthesis, characterization and some simple reactions of borollide-tantalum alkyl complexes. The intermediate reduction potential of tantalum makes it ideal to study bonding issues pertaining to the borollide

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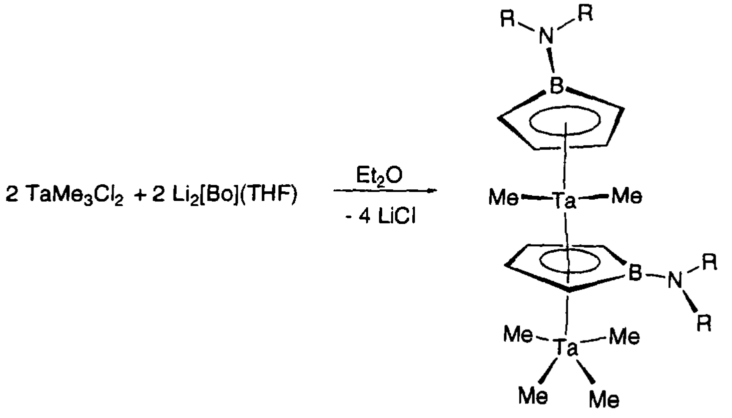
* Dedicated with deep respect to Professor John E. Bercaw (EPV), a scholar and friend, on the occasion of his 50th birthday.

† Author to whom correspondence should be addressed.



(1)

**(1)**

ligand. Moreover, comparison of the chemistry of the borollide-Ta fragment to the reactivity of the isoelectronic group 4 CpZr function is of interest in view of the extensive chemistry supported by this molecular fragment. We have focused our efforts on the use of Herberich's aminoborollide dianion $[C_4H_4BN(CHMe_2)]^{2-}$, primarily because of the ease of preparation of its dilithium salt.[8]

## RESULTS

Addition of one equivalent of $Li_2[C_4H_4BN(CHMe_2)_2](THF)$ ($Li_2[Bo](THF)$) to $Me_3TaCl_2$ in ether followed by filtration of LiCl and crystallization from pentane yields a bright green solid in 60% yield. Elemental analyses of the product agree with the expected formulation "$[Bo]TaMe_3$". However, both $^1H$ and $^{13}C$ NMR spectroscopy could only be consistent with an asymmetric molecule with two inequivalent but symmetric borollide ligands and two types of methyl groups in a two to four ratio. An X-ray diffraction study (Fig. 1, with selected bond distances and angles in Table 1) revealed that **1** is a bimetallic dimer of overall composition $[\eta^5\text{-}C_4H_4BN(CHMe_2)_2]Me_2Ta[\mu\text{-}\eta^5\text{-}C_4H_4BN(CHMe_2)_2]TaMe_4$ (**1**, eq. 1) in which one borollide is simultaneously bound in an $\eta^5$-fashion to two tantalum atoms on opposite sides of the ring plane. Two independent molecules are present in the unit cell, and since the two molecules do not differ significantly, only one is discussed here. The $[\eta^5\text{-}C_4H_4B\text{-}N(CHMe_2)_2]Ta(Me)_2[\mu\text{-}\eta^5\text{-}C_4H_4BN(CHMe_2)_2]$ half of the dimer [$C_4B_{cent}$—Ta(3)—$C_4B_{cent}$ = 138(1)°, Me—Ta(3)—Me = 87.7(8)°] is similar in geometry to bent-sandwich molecules of the type $Cp_2MMe_2$ (M = Zr, Hf).[9] Indeed, the structural features of this fragment are consistent with those which would be expected for the hypothetical $([\eta^5\text{-}C_4H_4BN(CHMe_2)_2]_2TaMe_2)^-$ anion. The $(\mu\text{-}\eta^5\text{-}C_4H_4BN(CHMe_2)_2)TaMe_4$ portion of the dimer adopts the "four-legged piano-stool" geometry (square pyramid)

Table 1. Selected bond lengths (Å) and angles (°) for **1**

| | | | |
|---|---|---|---|
| Ta(3)—B(3) | 2.68(2) | Ta(4)—C(49) | 2.16(2) |
| Ta(3)—B(4) | 2.70(2) | Ta(4)—C(50) | 2.18(2) |
| Ta(3)—C(27) | 2.38(2) | Ta(4)—C(51) | 2.24(2) |
| Ta(3)—C(28) | 2.34(2) | Ta(4)—C(52) | 2.20(2) |
| Ta(3)—C(29) | 2.37(2) | B(3)—N(3) | 1.42(3) |
| Ta(3)—C(30) | 2.41(2) | B(4)—N(4) | 1.45(3) |
| Ta(3)—C(37) | 2.20(2) | Ta(4)—C(40) | 2.44(2) |
| Ta(3)—C(38) | 2.23(2) | Ta(4)—C(41) | 2.45(2) |
| Ta(3)—C(39) | 2.45(2) | Ta(4)—C(42) | 2.46(2) |
| Ta(3)—C(40) | 2.33(2) | C(38)—TA(3)—C(37) | 87.7(8) |
| Ta(3)—C(41) | 2.43(2) | C(31)—N(3)—C(34) | 113(2) |
| Ta(3)—C(42) | 2.59(2) | C(46)—N(4)—C(43) | 115(1) |
| Ta(4)—B(4) | 2.50(2) | | |
| Ta(4)—C(39) | 2.45(2) | | |

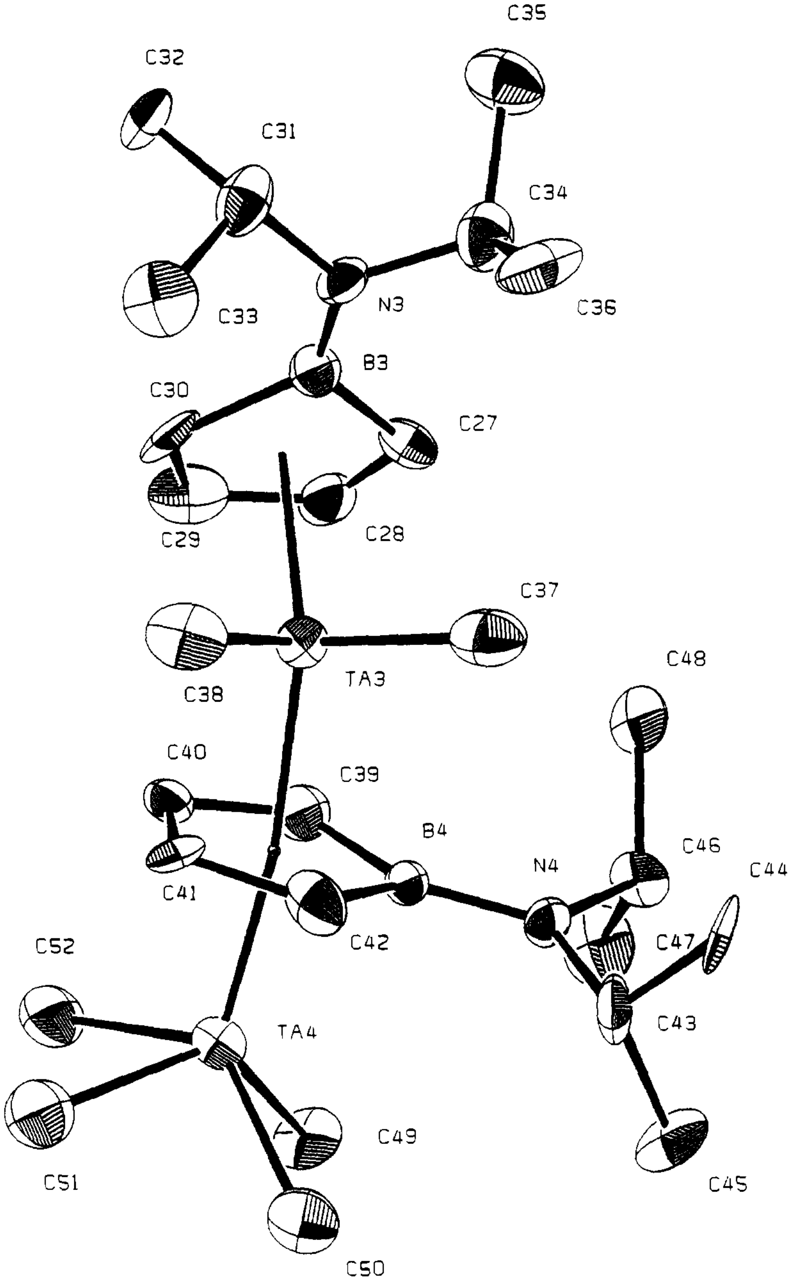
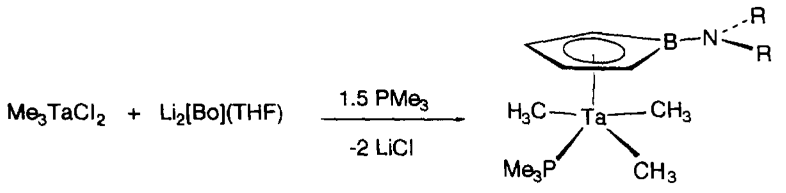
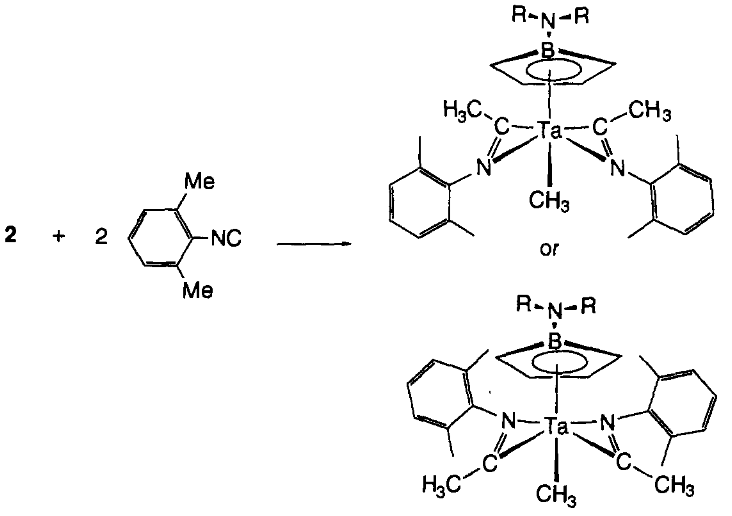


Fig. 1. An ORTEP drawing of **1** with 50% probability ellipsoids.



(2)

**(2)**



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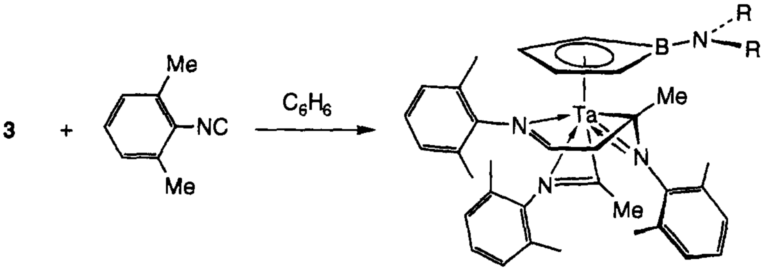


(4)

(4)

typical of $CpML_4$ complexes and contains normal Ta(4)—Me distances.[10,11] Intracyclic bond distances and angles are similar in both borollide rings. However, the $C_4H_4B(3)N(3)^iPr_2$ ring deviates from planarity considerably more [13(1)°] than the "sandwiched" $C_4H_4B(4)N(4)^iPr_2$ ring [1(1)°]. These data therefore describe **1** as a remarkably electron deficient (24 electron) triple decker complex.[12] Compound **1** reacts quickly but non-selectively to yield mixtures of non-isolable complexes with a variety of protic reagents, hydrogen and molecules capable of insertion such as carbon monoxide and isocyanides. However, no reaction is observed upon heating **1** in the presence of $PMe_3$.

Since **1** did not react cleanly, we sought a synthetic entry into mononuclear reagents. Thus, pretreating an ether solution of $Me_3TaCl_2$ with a slight excess of trimethylphosphine followed by reaction with $Li_2$[Bo](THF) produces red [Bo] $TaMe_3(PMe_3)$ which can be purified by recrystallization from pentane (**2**, eq. 2) in 65% yield. The $^1H$ NMR spectrum (25°C, $C_6D_6$) of **2** displays two sets of broad methyl signals in a one to two ratio, together with a doublet ($J_{PH} = 10$ Hz) attributed to tantalum-bound $PMe_3$. The geometry of **2** is likely to be square pyramidal, similar to that of $Cp^*TaMe_4$.[13] Heating a sample of **2** in $d^8$-toluene to 100°C averages the methyl signals which retain $J_{PH}$ coupling at the high temperature limit. These data are consistent with an intramolecular fluxional process which permutes the methyl ligands, probably via a trigonal bipyramidal intermediate, and rule out a dissociative pathway. Solution molecular weight measurements ($580 \pm 90$ g $mol^{-1}$) correlate better with a monomeric species (465.2 g $mol^{-1}$) than a dimer.[14]

It is of interest to note that **2** is obtained even when a large excess of $PMe_3$ is added to the reaction mixture. Furthermore, addition of $PMe_3$ to **2** in $C_6D_6$ only broadens the signals due to bound $PMe_3$ leaving those characteristic of the methyl and Bo ligands unperturbed. Hence, it appears that, unlike the reaction of $Cp^*ZrMe_3$ with $PMe_3$,[15] only phosphine exchange occurs and not the formation of a stable bis phosphine adduct.

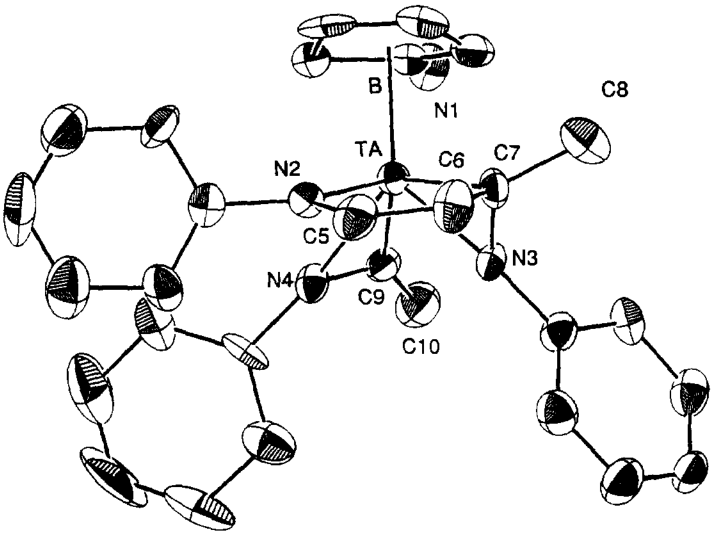


Fig. 2. An ORTEP drawing of **4** with 50% probability ellipsoids. The isopropyl groups on the exocyclic nitrogen atom and the methyl substituents on the aromatic rings have been omitted for clarity.

Table 2. Selected bond lengths (Å) and angles (°) for **4**

| | | | |
|---|---|---|---|
| Ta—C(1) | 2.489(9) | C(5)—N(2) | 1.30(1) |
| Ta—C(2) | 2.398(9) | C(7)—N(3) | 1.47(1) |
| Ta—C(3) | 2.31(1) | B—N(1) | 1.46(1) |
| Ta—C(4) | 2.35(1) | C(17)—N(2)—C(5) | 117.0(9) |
| Ta—B | 2.68(2) | N(2)—C(5)—C(6) | 123(1) |
| Ta—N(2) | 2.293(7) | C(8)—C(7)—C(6) | 112(1) |
| Ta—N(3) | 1.980(7) | C(5)—C(6)—C(7) | 112.5(9) |
| Ta—N(4) | 2.214(8) | | |
| Ta—C(7) | 2.21(1) | | |
| Ta—C(9) | 2.13(1) | | |

Treatment of **2** with one equivalent of 2,6-dimethylphenylisocyanide results in a product containing two inserted isocyanide moieties (50%), unreacted **2** (50%) and free trimethylphosphine. Reaction with two equivalents of isocyanide results in quantitative formation (by $^1$H NMR spectroscopy) of the doubly inserted product (**3**, eq. 3). $^1$H and $^{13}$C NMR data establish that the product must contain a mirror plane of symmetry, therefore we propose, in analogy to CpTa Me(PhCCPh)(MeCN$^t$Bu),[16] that **3** exists as *one* of the two isomers shown in equation 3. Two signals are observed for the aryl methyl substituents. Consequently, rotation of these rings is slow on the NMR timescale as would be expected in a sterically constrained pentagonal pyramidal arrangement. We have observed broadening of these signals upon warming but attempts to obtain an accurate determination of the energetics of ring rotation were frustrated by the thermal instability of **3**.

A third equivalent of isocyanide reacts quickly with **3** to afford a red, air and moisture stable product (**4**, *vide infra*) which by $^1$H NMR analysis contains four non-equivalent borollide ring protons, three different aromatic functions and, excluding the isopropyl groups, *eight* unique methyl resonances. The spectrum was further complicated by a complex aromatic region and the presence of two strongly coupled doublets at 3.73 and 2.50 ppm ($J_{HH} = 26$ Hz, typical of geminate coupling). Although samples of **4** are typically oily in nature, X-ray quality crystals of **4**, grown by slow evaporation of a toluene solution, enabled its structural elucidation (Fig. 2; selected bond distances and angles are given in Table 2). Molecule **4** contains a borollide ring, a normal Ta$^V$ iminoacyl function, resulting from isocyanide insertion into a Ta—Me bond,[17] and a metallabicyclic ligand bound to tantalum via one $sp^3$ hybridized carbon and two $sp^2$ hybridized nitrogen atoms with very different

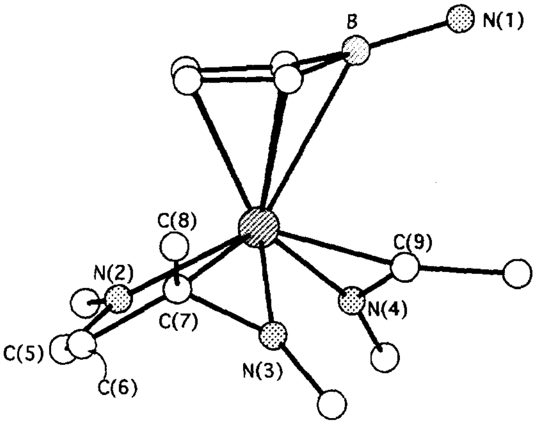


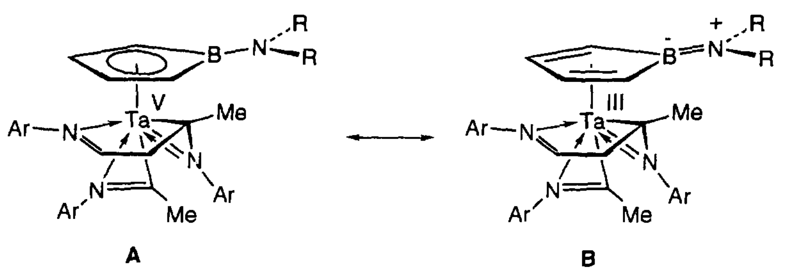
Fig. 3. Partial structure of **4** highlighting the tantalaaziridine functionality and the weak Ta—B interaction.

Ta—N bond lengths. The Ta—C(7) distance corresponds to a regular Ta—C single bond while the Ta—N(3) distance is consistent with an amido ligand that contains considerable $Ta_d$—$N_p\pi$ overlap.[18] The second tantalum–nitrogen interaction arising from the bicyclic ligand [Ta—N(2) = 2.293(7) Å] appears weaker and matches well with distances observed in $Ta^V$ nitrogen adducts. In addition, the short N(2)—C(5) distance of 1.30(1) Å together with the non-bonding distance between Ta and C(5) of 3.05(1) Å, describes this Ta—N(2) interaction as that of a simple imine–Ta adduct.[19] We therefore view the product as containing a metallaaziridine ligand with a tethered imine capable of coordinating to the metal center as a simple dative adduct (eq. 4). The solid-state data are entirely consistent with the solution $^1H$ NMR spectrum in which the two doublets described above can be assigned to the two geminal hydrogens on C(6).

Figure 3 highlights the molecular features described above as well as the long Ta—B distance [2.68(2) Å] and the short B—N bond length [1.46(1) Å]. These details provide convincing structural evidence that both the borollide–$Ta^V$ (**A**) and the diolefin–$Ta^{III}$ (**B**) resonance structures contribute significantly to the bonding description of **4**.[20]

## DISCUSSION

Although the borollide salt $Li_2[Bo](THF)$ is known to be a strong reducing agent,[21] the use of $Me_3TaCl_2$ as a metal source effectively eliminates electron transfer problems and facilitates a clean entry to borollide-supported tantalum-alkyl chemistry. The stoichiometric reaction of the two reagents results in the formation of the unusually electron deficient triple decker **1** which to the best of our knowledge is the first example of this type of molecule containing alkyl ligands. The reaction sequence by which **1** forms is not known at the present time. One plausible route is via disproportionation of an initially formed $[Bo]TaMe_3$, forced by the electron deficiency at Ta, a sterically restricted coordination ability of the exo-cyclic nitrogen and the extra electron density present on the borollide ring (*vide infra*). It is obvious that **1** is extremely reactive, especially towards substrates such as CO and isocyanides that are capable of insertion chemistry. Unfortunately, these reactions are not clean, and we have failed to identify any of the ensuing products. The evidence accumulated thus far indicates that the bimetallic integrity nature of **1** is rather tenuous and easily disrupted after an initial insertion step, leading to a variety of metal containing species. Mononuclear **2** is a more logical starting material from which to explore Bo—Ta chemistry. Formation of **2** (eq. 2) almost certainly proceeds via initial formation of $Me_3TaCl_2(PMe_3)$ followed by halide exchange with $Li_2[Bo](THF)$. It is interesting to note here that, unlike the isoelectronic and more sterically protected $Cp^*ZrMe_3(PMe_3)$, which readily forms $Cp^*ZrMe_3(PMe_3)_2$, **2** does not coordinate a second equivalent of $PMe_3$. Therefore, even though they are both formally 14 electron species, $Cp^*ZrMe_3$ is more electrophilic (at least towards $PMe_3$) than "$BoTaMe_3$". Furthermore, since there is no similar reaction with $Cp^*ZrMe_3$, the formation of **1** from $BoTaMe_3$ would seem to depend strongly on the dianionic nature of the borollide ligand. The greater electron density on the five-membered ring makes Bo a better bridging ligand than Cp (or Cp*) and as a consequence **1** is formed.



**A** **B**

The migratory insertion of isocyanides into metal–carbon bonds has been of interest for quite some time because of its relationship to carbon monoxide chemistry and consequently, several industrially relevant processes.[22] As would be predicted from previous observations on Cp*Zr and Cp*Ta supported alkyls, **2** reacts readily with 2,6-dimethylphenylisocyanide (eq. 3). The mono-inserted product was never observed, even when an excess of **2** was used. Instead, the 16-electron, doubly inserted product, **3** was obtained in all experiments. We assume that a monoinserted product does form initially, probably via an associative pathway (a dissociative mechanism would necessitate the 12-electron intermediate $BoTaMe_3$). If the resulting 16-electron $[BoTaMe_2(MeCNAr)(PMe_3)]$ loses $PMe_3$ (recall that **2** does not bind $PMe_3$) to form $BoTaMe_2(MeCNAr)$ for which isocyanide insertion is favored relative to **2**, then only **3** should form, as is observed experimentally.

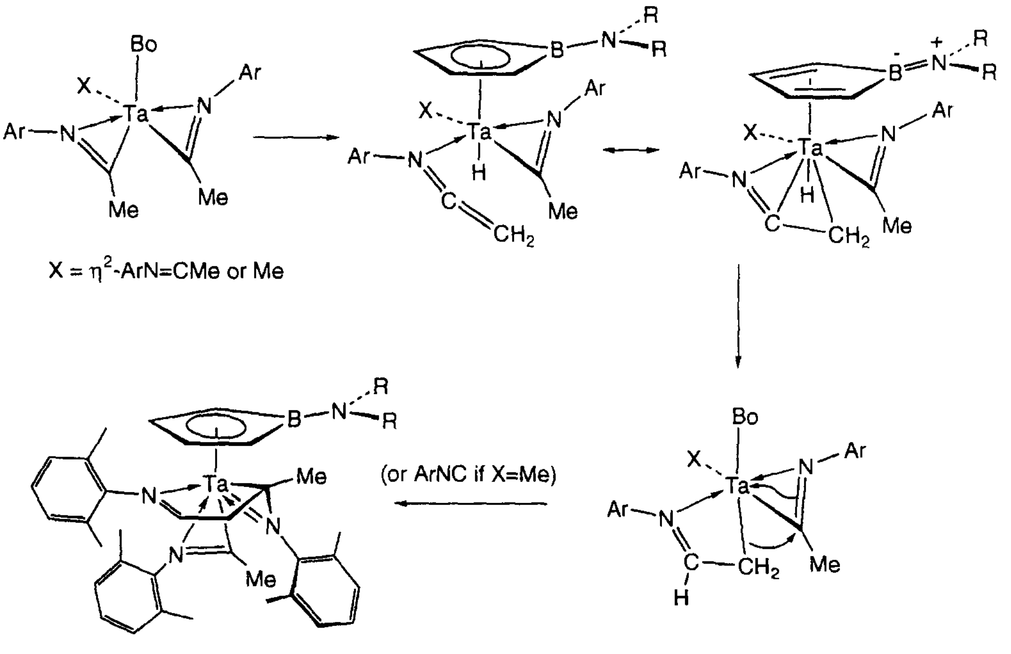
Formation of **4** from **3** and ArNC involves a novel iminoacyl coupling reaction that must involve C—H activation. We propose that the metallabicyclic functionality forms according to the sequence in Scheme 1. The key transformation in this sequence is a $\beta$-hydrogen elimination step from one of two vicinal iminoacyls to generate a coordinated ketenimine hydride intermediate. It is possible that at this stage the diolefinic nature of the borollide ligand becomes important in stabilizing the keteneimine ligand by permitting a stronger tantalum olefin interaction as shown in Scheme 1. Hydride transfer to $C_\beta$ of the keteneimine generates the $\sigma$-bound imine. Finally, migration of the resulting alkyl to the vicinal iminoacyl ultimately results in the metallabicyclic connectivity observed in **4**.[23] It is unclear whether the rearrangement shown in Scheme 1 is driven by initial formation of the tris iminoacyl $BoTa(MeCNAr)_3$, or it occurs in **3** and trapped by the third equivalent of isocyanide.

In summary, the results disclosed herein represent the first examples of borollide complexes containing alkyl ligands. We have shown that the reactivity and properties of these molecules differ substantially from those of their cyclopentadienylzirconium relatives. Ongoing work is aimed at understanding and exploiting these differences in other metal mediated processes, in particular homogeneous Ziegler–Natta polymerization.

## EXPERIMENTAL

### *General considerations*

All manipulations were carried out using either high-vacuum or glovebox techniques as described earlier.[24] $^1$H and $^{13}$C NMR spectra were recorded on a Bruker AMX-400 NMR spectrometer at 400.1 and 100.6 MHz, respectively. Toluene, pentane, diethyl ether and tetrahydrofuran were distilled from benzophenone ketyl and then vacuum distilled from titanocene prior to use.[25] Trimethylphosphine (Aldrich) was used as received and $TaCl_5$ (Aldrich)



X = $\eta^2$-ArN=CMe or Me

Scheme 1.

was purified by sublimation before use. The preparations of $Li_2(C_4H_4BN^iPr_2)\cdot THF$[8] and $TaMe_3Cl_2$[26] are available in the literature.

### $[\eta^5\text{-}C_4H_4BN(CHMe_2)_2](Me)_2Ta[\mu\text{-}\eta^5\text{-}C_4H_4BN(CHMe_2)_2]Ta(Me)_4$ (**1**)

To a cold ($-30$°C) solution of $TaMe_3Cl_2$ (588 mg, 2 mmol) in ether (20 $cm^3$) was added dropwise but quickly one equivalent of $Li_2(C_4H_4BN^iPr_2)\cdot THF$ (500 mg, 2 mmol) in ether (5 $cm^3$). The resulting green solution was allowed to warm up to room temperature and stirred an additional 2 h. The solvent was removed *in vacuo*, the resulting solids extracted with pentane and filtered through Celite. Recrystallization at $-30$°C over a period of 3 days gave **1** as dark green crystals (520 mg, 67%): $^1H$ NMR ($C_6D_6$) $\delta$ 5.76 (dd, 2, BC*H*), 5.64 (m, 2, BC*H*), 3.61 (m, 2, C*H*CHB), 3.55 (sept, 2, C*H*$Me_2$), 3.49 (m, 2, C*H*CHB), 3.32 (sept, 2, C*H*$Me_2$), 1.24 (s, 12, Ta*Me*$_4$), 1.20 (d, 6, CH*Me*$_2$), 1.01 (d, 6, CH*Me*$_2$), 0.62 (s, 6, Ta*Me*$_2$); $^{13}C$ NMR ($C_6D_6$) $\delta$ 107.4 (*C*HCHB), 105.4 (*C*HCHB), 85.2 (b, *C*HB), 83.4 (b, *C*HB), 71.9 (Ta(*C*$H_3$)$_4$), 45.8 (*C*H$Me_2$), 45.7 (Ta(*C*$H_3$)$_2$), 41.2 (*C*H$Me_2$), 18.5 (overlapping signals, CH(*C*$H_3$)$_2$). Found: C, 40.05; H, 6.72; N, 3.15; calc. for $Ta_2C_{26}H_{54}B_2N_2$: C, 40.13; H, 6.99; N, 3.

### *X-Ray structure of* **1**

A green irregular crystal of $Ta_2C_{26}H_{50}B_2N_2$ (**1**) having approximate dimensions of 0.488 × 0.225 × 0.150 mm was mounted on a glass fiber under a stream of nitrogen.[27] Cell constants and an orientation matrix for data collection, obtained from a least-squares refinement using the setting angles of 25 carefully centered reflections in the range $4.00 < 2\theta < 50.00°$ corresponded to a triclinic cell with dimensions: $a = 10.726(4)$ Å, $b = 17.388(8)$ Å, $c = 17.910(4)$ Å, $\alpha = 98.78(3)°$, $\beta = 107.37(2)°$, $\gamma = 107.81(3)°$, $V = 2924(5)$ Å$^3$. Other relevant data are $F_{000} = 1504$, $\mu(\text{Mo-}K_\alpha) = 74.07\ cm^{-1}$, $\lambda = 0.71069$ Å. For $Z = 4$ and F.W. = 774.21, the calculated density is 1.759 g $cm^{-3}$. Based on packing considerations, a statistical analysis of intensity distribution, and the successful solution and refinement of the structure, the space group was determined to be $P(\bar{1})$ (#2). Of the 7624 reflections which were collected, 7154 were unique ($R_{int} = 0.075$). The linear absorption coefficient for Mo-$K_\alpha$ is 74.1 $cm^{-1}$. An empirical absorption correction, using the program DIFABS,[28] was applied which resulted in transmission factors ranging from 0.74 to 1.29. The data were corrected for Lorentz and polarization effects.

The structure was solved by direct methods.[29] With the exception of C39, C51, B2, B3 and B4, which were refined isotropically, all non-hydrogen atoms were refined anisotropically. Hydrogen atoms were not used in the final refinement. The final cycle of full-matrix least-squares refinement[30] was based on 4732 observed reflections [$I \geqslant 3.00\sigma(I)$] and 552 variable parameters and converged (largest parameter shift was 0.17 times its esd) with unweighted and weighted agreement factors of $R = 0.048$, and $R_w = 0.055$. The standard deviation of an observation of unit weight[31] was 1.71. The weighting scheme was based on counting statistics and included a factor ($p = 0.03$) to downweight the intense reflections. Plots of $\Sigma\ w\ (|F_o| - |F_c|)^2$ *vs* $|F_o|$, reflection order in data collection, sin $\theta/\lambda$, and various classes of indices showed no unusual trends. The maximum and minimum peaks on the final difference Fourier map corresponded to 1.32 and $-1.63$ e$^-$ Å$^{-3}$, respectively.

### $[\eta^5\text{-}C_4H_4BN(CHMe_2)_2]Ta(Me)_3(PMe_3)$ (**2**)

A cold ($-30$°C) solution of $TaMe_3Cl_2$ (5.0 g, 16.8 mmol) in ether (150 $cm^3$) was treated with a slight excess of $PMe_3$ (1.9 g, 25 mmol) (caution! exothermic) and stirred for 15 min. After recooling to $-30$°C the resulting solution was reacted (dropwise addition) with one equivalent of $Li_2(C_4H_4BN^iPr_2)\cdot THF$ (4.2 g, 16.8 mmol) in ether (25 $cm^3$) causing an immediate coloration of the reaction mixture. After stirring for an additional hour at room temperature the solvent was removed *in vacuo*, the resulting solids extracted with pentane and filtered through Celite. The product can be obtained as a dark microcrystalline solid by recrystallization from pentane at $-30$°C over a period of several days (5.0 g, 65%): $^1H$ NMR ($d^8$-toluene) $\delta$ 5.37 (b, 2, BC*H*), 3.71 (sept, 2, C*H*$Me_2$), 3.38 (m, 2, C*H*CHB), 1.44 (b, 3, Ta$Me_2$*Me*), 1.40 (d, 6, CH*Me*Me), 1.38 (d, 6, CH*Me*Me), 0.80 (d, 9, TaP*Me*$_3$, $J_{PH} = 7$ Hz), 0.47 (broad doublet, 6, Ta*Me*$_2$Me, $J_{PH} = 9$ Hz); $^{13}C$ NMR ($d^8$-toluene) $\delta$ 108.8 (*C*HCHB), 83.1 (b, *C*HB), 69.1 (Ta*C*$H_3$), 54.5 (Ta*C*$H_3$), last two signals average out upon heating, 47.2 (*C*H$Me_2$), 23.1 (CH*Me*Me), 21.9 (CHMe*Me*), 13.0 (P*Me*$_3$, $J_{PC} = 20$ Hz). Found: C, 41.66; H, 7.86; N, 3.06; calc. for $TaC_{16}H_{36}BNP$: C, 41.31; H, 7.80; N, 3.01.

### $[\eta^5\text{-}C_4H_4BN(CHMe_2)_2]Ta(Me)[\eta^2\text{-}MeCN(2,6\text{-}Me_2C_6H_3)]_2$ (**3**)

Reaction of **2** with two equivalents of 2,6-dimethylphenylisocyanide in $C_6D_6$ produces quantitatively **3**. Scale up the reaction yields **3** as an orange oil with identical spectroscopic characteristics. Thermal instability of this compound prevents accurate elemental analysis. NMR data: $^1$H NMR ($C_6D_6$) $\delta$ 6.98–6.82 (m, 6, aromatic), 5.48 (m, 2, BC*H*), 3.73 (sept, 2, C*H*Me$_2$), 2.94 (m, d, C*H*CHB), 2.39 (s, 6, *Me*CN), 1.75 and 1.59 (s, 6 each, Ar*Me*), 1.46 (d, 12, CH*Me*$_2$), 0.95 (s, 3, TaC*H*$_3$); $^{13}$C NMR ($C_6D_6$) $\delta$ 258.4 (MeCN), 142.7, 129.8, 129.1, 128.9, 125.9, 125.6 (aromatic Cs), 115.0 (*C*HB), 103.7 (*C*HCHB), 47.5 (*C*HMe$_2$), 23.8, 22.7, 19.2, 18.2, 17.7 (methyl Cs).

### $[\eta^5\text{-}C_4H_4BN(CHMe_2)_2]Ta[\eta^2\text{-}MeCN(2,6\text{-}Me_2C_6H_3)][\eta^3\text{-}(2,6\text{-}Me_2C_6H_3)NCHCH_2C(Me)N(2,6\text{-}Me_2C_6H_3)]$ (**4**)

A solution of **3** in toluene was reacted with one equivalent of 2,6-dimethylphenylisocyanide for a period of 1 h. Removal of the solvent typically provides oily samples of the product in good yield. The reaction is quantitative by $^1$H NMR spectroscopy. NMR data: $^1$H NMR ($C_6D_6$) 7.11–6.67 (aromatic, 8), 6.47 (s, 1, NC*H*CH$_2$), 6.41 (m, 1, C*H*B), 6.36 (t, 1, aromatic), 6.08 (m, 1, C*H*B), 3.72 (b, 1, C*H*Me$_2$), 3.73 (d, 1, NCHC*H*H, $J_{HH}$ = 26 Hz), 3.45 (b, 1, C*H*Me$_2$), 3.43 (m, 1, C*H*CHB), 2.66 (s, 3, *Me*), 2.65 (s, 3, *Me*), 2.50 (d, 1, NCHCH*H*, $J_{HH}$ = 26 Hz), 2.20 (m, 1, C*H*CHB), 2.13 (s, 3, *Me*), 1.81 (s, 3, *Me*), 1.72 (s, 3, *Me*), 1.39 (s, 3, *Me*), 1.38 (s, 3, *Me*), 1.30 (b, 6, CH*Me*$_2$), 1.25 (b, 6, CH*Me*$_2$), 1.00 (s, 3, *Me*); $^{13}$C NMR ($C_6D_6$) $\delta$ 256.2 (Me*C*N), 150.2 (CH$_2$C(Me)N*C*$_6$H$_3$, *ipso*), 143.5–124.3 (aromatic Cs), 114.3 and 113.2 (*C*HB), 104.2 and 102.5 (*C*HCHB), 97.2 (N*C*HCH$_2$), 89.2 [CH$_2$*C*(Me)N], 45.2 (*C*HMe$_2$), 29.7 (*C*H$_2$C(Me)N), 27.5, 24.2, 22.4, 22.1, 21.5, 20.2, 19.3, 18.7, 17.5, 16.9 (methyl Cs).

### *X-Ray structure of* **4**

A red fragment of a crystal of $TaC_{40}H_{54}BN_4$ (**2**) having approximate dimensions of 0.413 × 0.600 × 0.375 mm was mounted on a glass fiber. Cell constants and an orientation matrix for data collection, obtained from a least-squares refinement using the setting angles of 25 carefully centered reflections in the range $4.00 < 2\theta < 50.00^\circ$ corresponded to an orthorhombic cell with dimensions: $a = 11.841(4)$ Å, $b = 13.653(6)$ Å, $c = 26.28(1)$ Å, $V = 4249(5)$ Å$^3$. Other relevant data are $F_{000} = 1600$, $\mu(\text{Mo-}K_\alpha) = 25.82$ cm$^{-1}$, $\lambda = 0.71069$ Å. For $z = 4$ and F.W. = 782.65, the calculated density is 1.223 g cm$^{-3}$. Based on the systematic absences of *h*00 (*h* odd), 0*k*0 (*k* odd), 00*l* (*l* odd) and the successful solution and refinement of the structure, the space group was determined to be $P2_12_12_1$ (# 19).

A total of 3332 reflections were collected. The linear absorption coefficient for Mo-$K_\alpha$ is 25.8 cm$^{-1}$. An empirical absorption correction, using the program DIFABS,[28] was applied which resulted in transmission factors ranging from 0.82 to 1.13. The data were corrected for Lorentz and polarization effects.

The structure was solved by direct methods.[29] The non-hydrogen atoms were refined anisotropically. With the exception of the ring hydrogens on the borole ligand, which were not used, hydrogen atoms were calculated from idealized positions and used in the final refinements. The final cycle of full-matrix least-squares refinement was based on 2884 observed reflections $[I \geqslant 3.00\sigma(I)]$ and 478 variable parameters and converged (largest parameter shift was 0.21 times its esd) with unweighted and weighted agreement factors of $R = 0.031$ and $R_w = 0.035$. The standard deviation of an observation of unit weight[30] was 1.32. The weighting scheme was based on counting statistics and included a factor ($p = 0.03$) to downweight the intense reflections. Plots of $\Sigma\, w\,(|F_o| - |F_c|)^2$ *vs* $|F_o|$, reflection order in data collection, $\sin\theta/\lambda$, and various classes of indices showed no unusual trends. The maximum and minimum peaks on the final difference Fourier map corresponded to 0.47 and $-0.49$ e$^-$ Å$^{-3}$, respectively.

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