Synthesis of a Metallaborane Complex Containing Pd(III) and the First Doubly Charge Compensated Ollide Ion. X-ray Crystal Structure of $1,4\text{-Br}_2\text{-}1,2,5\text{-(PMe}_2\text{Ph)}_3\text{-}closo\text{-}1\text{-PdB}_{11}\text{H}_8$

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The reaction of $[\text{Me}_3\text{NH}][nido\text{-B}_{11}\text{H}_{14}]$ with 4 equiv of lithium alkyl in THF at 5 °C generated the putative ollide ion, $\text{Li}_4[\text{B}_{11}\text{H}_{11}]$, which was not isolated. This was treated in situ with $(\text{PMe}_2\text{Ph})_2\text{PdBr}_2$ to yield the metallaborane $1,4\text{-Br}_2\text{-}1,2,5\text{-(PMe}_2\text{Ph)}_3\text{-}closo\text{-}1\text{-PdB}_{11}\text{H}_8$. This metallaborane contains the first doubly charge compensated ollide ion. It was isolated in low yield from the reaction mixture by chromatography. Characterization of this air-stable palladium ollide complex by magnetic susceptibility, EPR, and CV confirmed that it contains Pd(III) and is paramagnetic. It was also characterized by an X-ray diffraction study of a single crystal. The sample consisted of rust-colored crystals of monoclinic space group $P2_1/c$, with $a = 9.749(13)$ Å, $b = 16.30(2)$ Å, $c = 21.65(3)$ Å, $\beta = 97.21(4)°$, and $Z = 4$. The structure was determined by conventional heavy-atom methods and refined to a final value of $R = 0.0730$ (5172 reflections), $R_w = 0.0620$.

Introduction

In the past few years, we have investigated the use of the *nido*-borane cage ligand $[\text{B}_{11}\text{H}_{11}]^{4-}$ to support unusually high formal oxidation states of transition metals, such as Ni(IV) in $[\text{Ni}(\text{B}_{11}\text{H}_{11})_2]^{4-}$ and Cu(V) in $[\text{Cu}(\text{B}_{11}\text{H}_{11})_2]^{3-}$.[1] These complexes, along with the earlier $[(\text{C}_5\text{H}_5)\text{Ni}(\text{B}_{11}\text{H}_{11})]^-$ anion,[2] represent the only reported examples in which a *nido*-$[\text{B}_{11}\text{H}_{11}]^{4-}$ ligand bonds η^5 to a transition metal.

In our continuing investigation of $\eta^5\text{-M}(\text{B}_{11}\text{H}_{11})$ species, we attempted to synthesize the closo anion $[(\text{PMe}_2\text{Ph})_2\text{Pd}^{\text{II}}(\text{B}_{11}\text{H}_{11})]^{2-}$ from $[\text{B}_{11}\text{H}_{11}]^{4-}$ and $(\text{PMe}_2\text{Ph})_2\text{PdBr}_2$. Instead, this reaction led to the synthesis, isolation, and characterization of an air-stable Pd(III) complex which incorporates a B_{11} borane cage ligand.

Mononuclear palladium(III) complexes are relatively uncommon;[3] the two most well-characterized examples are $[\text{Pd}([9]\text{aneS}_3)_2]^{3+}$ ($[9]\text{aneS}_3$ = 1,4,7-trithiacyclononane)[4] and $[\text{Pd}([9]\text{aneN}_3)_2]^{3+}$ ($[9]\text{aneN}_3$ = 1,4,7-triazacyclononane),[5] for which X-ray structures have been determined. Several others have been generated electrochemically or otherwise studied in situ, but not isolated, including $[\text{Pd}(\text{B}_9\text{C}_2\text{H}_{11})_2]^-$ ($\text{B}_9\text{C}_2\text{H}_{11}{}^{2-}$ = 7,8-dicarbollide),[6] $[\text{Pd}(\text{B}_9\text{C}_2\text{Me}_2\text{H}_9)_2]_9{}^{2-}$ = 7,8-dimethyl-7,8-dicarbollide),[7] $[\text{Pd}(\text{mnt})_2]^-$ (mnt = maleonitriledithiolate),[8] $[\text{Pd}(\text{dmi-t})_2]^-$ (dmi-t = isotrithionedithiolate),[8] $[\text{Pd}(\text{xdt})_2]^-$ (xdt = *o*-xylenedithiolate),[8] $[\text{Pd}([18]\text{aneN}_2\text{S}_4)]^{3+}$ ($[18]\text{aneN}_2\text{S}_4$ = 1,4,10,13-tetrathia-7,16-diazacyclooctadecane),[9] $[\text{Pd}([10]\text{aneS}_3)_2]^{3+}$ ($[10]\text{aneS}_3$ = 1,4,7-trithiacyclodecane),[10] and $[\text{Pd}([9]\text{aneNS}_2)_2]^{3+}$ ($[9]\text{aneNS}_2$ = 1,4-dithia-7-azacyclononane).[11]

Results and Discussion

Deprotonation of the three acidic hydrogens of *nido*-$\text{B}_{11}\text{H}_{14}{}^-$ with 3 equiv of lithium alkyl generates $\text{B}_{11}\text{H}_{11}{}^{4-}$, the so-called "ollide" ion,[12] eq 1 (see Figure 1a). Subsequent addition of

$$[\text{Me}_3\text{NH}][\text{B}_{11}\text{H}_{14}] + 4\text{RLi} \rightarrow \text{Li}_4[\text{B}_{11}\text{H}_{11}] + 4\text{RH} + \text{Me}_3\text{N} \quad (1)$$

this ligand to the complex $(\text{PMe}_2\text{Ph})_2\text{PdBr}_2$ resulted in a complex multistep reaction to form the complex $1,4\text{-Br}_2\text{-}1,2,5\text{-(PMe}_2\text{Ph)}_3\text{-}closo\text{-}1\text{-PdB}_{11}\text{H}_8$, which was isolated in low yield by chromatography of the reaction mixture. In this complex, the ollide ion is pentahapto to palladium, and it has been triply substituted to achieve a $[\text{B}_{11}\text{H}_8(\text{PMe}_2\text{Ph})_2\text{Br}]^{2-}$ fragment that complexes with a $[(\text{PMe}_2\text{Ph})\text{PdBr}]^{2+}$ fragment (see Figure 1b). This is the first metallaborane complex containing a doubly charge compensated ollide ligand.

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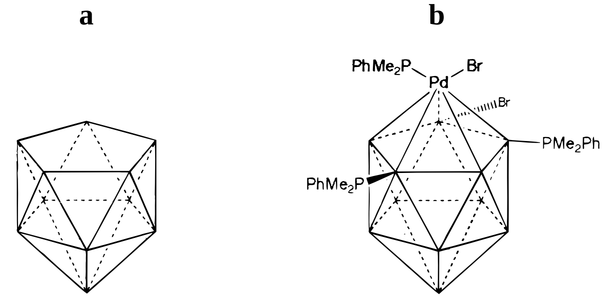

Figure 1. Idealized structures of (a) the ollide ion, *nido*-$B_{11}H_{11}^{4-}$ (left), and (b) the title complex, 1,4-Br_2-1,2,5-$(PMe_2Ph)_2$-*closo*-1-$PdB_{11}H_8$ (right).

Table 1. Selected Bond Distances (Å) for 1,4-Br_2-1,2,5-$(PMe_2Ph)_3$-*closo*-1-$PdB_{11}H_8$

(i) To the Pd			
Pd(1)−B(2)	2.211(22)	Pd(1)−B(6)	2.169(24)
Pd(1)−B(3)	2.220(25)	Pd(1)−Br(13)	2.499(4)
Pd(1)−B(4)	2.249(23)	Pd(1)−P(14)	2.389(7)
Pd(1)−B(5)	2.236(26)		
(ii) Interboron			
B(2)−B(3)	1.80(3)	B(6)−B(10)	1.76(3)
B(2)−B(6)	1.84(3)	B(6)−B(11)	1.78(3)
B(2)−B(7)	1.76(3)	B(7)−B(8)	1.76(3)
B(2)−B(11)	1.77(3)	B(7)−B(11)	1.77(3)
B(3)−B(4)	1.82(3)	B(7)−B(12)	1.78(3)
B(3)−B(7)	1.79(3)	B(8)−B(9)	1.76(3)
B(3)−B(8)	1.73(4)	B(8)−B(12)	1.76(3)
B(4)−B(5)	1.76(3)	B(9)−B(10)	1.74(4)
B(4)−B(8)	1.77(3)	B(9)−B(12)	1.82(3)
B(4)−B(9)	1.72(3)	B(10)−B(11)	1.76(3)
B(5)−B(6)	1.77(3)	B(10)−B(12)	1.79(3)
B(5)−B(9)	1.73(4)	B(11)−B(12)	1.79(3)
B(5)−B(10)	1.70(3)		
(iii) Other			
B(2)−Br(32)	1.996(22)	B(5)−P(23)	1.956(27)
B(3)−P(33)	1.926(25)		

The particular substitution pattern of the ligand, namely, $[2\text{-Br-}3,5\text{-}(PMe_2Ph)_2B_{11}H_8]^{2-}$ (or its equally probable $[2\text{-Br-}4,6\text{-}(PMe_2Ph)_2B_{11}H_8]^{2-}$ enantiomer), was not achieved due to application of rational synthetic methods. Nonetheless, one would expect just such a pattern on the basis of steric arguments and previous results on related closo metallaheteroboranes. The order of chemical events that led to the Pd(III)−ollide complex is unknown. However, palladium-mediated substitution of *nido*-7,8-$C_2B_9H_{12}^-$ with $(PMe_2Ph)_2PdCl_2$ to yield *nido*-7,8-$C_2B_9H_{11}$-(PMe_2Ph) complexes is known.[13] Thus, phosphine and/or bromine substitution of the free *nido*-$B_{11}H_{11}4^-$ ion (or a protonated form) is possible. Equally probable is palladium-mediated substitution of a closo metallaborane complex. We have reported recently palladium-mediated substitution reactions of the closo $B_{10}H_{10}^{2-}$ and $B_{12}H_{12}^{2-}$ anions[14] as well as certain closo metallaheteroboranes such as 1,1-$(PMe_2Ph)_2$-*closo*-1,4,3-$PdAs_2B_9H_9$.[15] It should be noted that, in the substitution studies of the metallaheteroboranes, ligand substitution (phosphine or halogen) was observed only on boron cage atoms adjacent to the transition metal as has been observed with the Pd(III)−ollide complex reported here.

In the solid state under a nitrogen atmosphere, the Pd(III) complex seems to be stable, with little or no decomposition over approximately 1.5 years. Solution stability is less assured, and no attempt to quantify it has been made.

Table 2. Selected Bond Angles (deg) for 1,4-Br_2-1,2,5-$(PMe_2Ph)_3$-*closo*-1-$PdB_{11}H_8$

B(2)−Pd(1)−B(3)	48.1(9)	B(4)−Pd(1)−B(5)	46.3(9)
B(2)−Pd(1)−B(6)	49.7(9)	B(5)−Pd(1)−B(6)	47.3(9)
B(3)−Pd(1)−B(4)	48.0(8)	Br(13)−Pd(1)−P(14)	86.43(19)
B(3)−B(2)−B(6)	105.6(16)	B(8)−B(7)−B(11)	106.2(16)
B(2)−B(3)−B(4)	108.7(16)	B(7)−B(8)−B(9)	110.3(18)
B(3)−B(4)−B(5)	107.6(16)	B(8)−B(9)−B(10)	106.0(17)
B(4)−B(5)−B(6)	109.6(18)	B(9)−B(10)−B(11)	109.6(18)
B(2)−B(6)−B(5)	108.4(17)	B(7)−B(11)−B(10)	107.9(17)

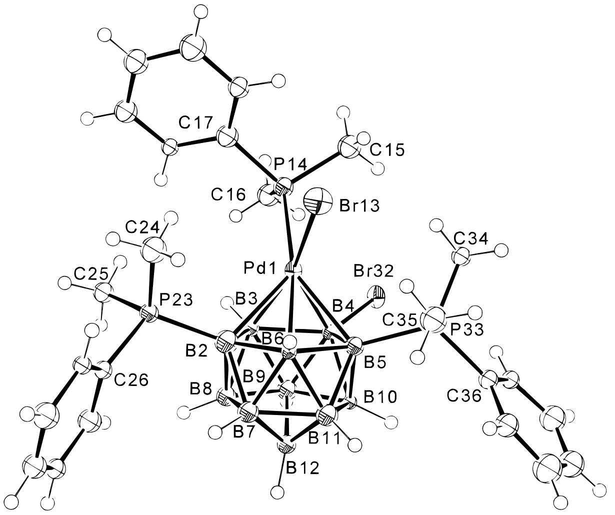

Figure 2. ORTEP diagram of 1,4-Br_2-1,2,5-$(PMe_2Ph)_3$-*closo*-1-$PdB_{11}H_8$.

NMR spectra were generally unattainable for the Pd(III) complex, due to its paramagnetism. When attempts were made, the ^{11}B NMR spectra obtained for this complex had poor signal-to-noise, despite the use of concentrated samples, and generally consisted of an unreproducible forest of peaks. It may be that some or all of these peaks were due to diamagnetic impurities.

We attempted to find paramagnetically shifted signals in either the $^{31}P\{^1H\}$ or ^1H room-temperature NMR spectra, but no definitive NMR data were obtained in either case. After the infrared spectrum revealed a sharp B−H stretch at 2519 cm^{-1}, an X-ray structural determination was undertaken.

The bromide and two phosphine cage substituents appear to cause no significant distortion of the cage framework. Indeed, all of the Pd−B (average 2.217 Å) and B−B (average 1.77 Å) distances are approximately the same, within the 3σ criterion (see Tables 1 and 2); thus, the PdB_{11} cage framework approximates C_{5v} symmetry (see Figure 2). The two B−P distances, 1.926(25) and 1.956(27) Å, agree fairly well with the range of values established for similar phosphines bound exo to a borane cage cluster, 1.886(11)−1.945(9) Å.[14,16]

EPR. An X-band EPR spectrum was recorded at 298 K on a toluene solution of the complex. A strong, near-isotropic signal with $g_{av} = 2.02$ was observed (see Figure 3). At 100 K, some anisotropy in the signal was evident, perhaps indicative of unresolved hyperfine coupling. Coupling to $^{105}Pd^{III}$ (22%, $I = {}^5/_2$) has been observed before, but only with poor resolution.[4a,9a] Delocalization of the unpaired electron over several of the spin-active nuclei (^{31}P, ^{79}Br, ^{81}Br, ^{11}B, ^{10}B) may not be absolutely

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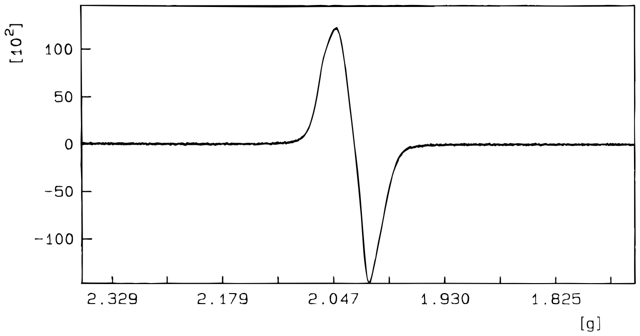

Figure 3. X-band EPR spectrum of d^7 1,4-Br_2-1,2,5-$(PMe_2Ph)_3$-*closo*-1-$PdB_{11}H_8$ in toluene at 298 K: one scan; microwave power = 6.3 mW; receiver frequency modulation = 100 kHz.

ruled out; however, the *g* value indicates that the unpaired electron is primarily at the metal center and is not a ligand radical.

The *g* value is also similar to those previously observed for the Pd(III) species $[Pd([18]aneN_2S_4)]^{3+}$, $[Pd([9]aneS_3)_2]^{3+}$, $[Pd([9]aneN_3)_2]^{3+}$, $[Pd([10]aneS_3)_2]^{3+}$, and $[Pd([9]aneNS_2)_2]^{3+}$, which are in the range 2.005−2.123.[4,5,9−11]

Magnetic Susceptibility. Palladium(III) in this complex may be considered to be pentacoordinate, because the bonding of the PdB_{11} cage cluster is isolobal with a ML_3 fragment.[17] As such, palladium is expected to be low spin d^7; i.e., it should have one unpaired electron. To determine the veracity of this, the magnetic susceptibility was determined on a solid sample. The following equations were used for mass susceptibility χ_g, measured molar susceptibility (χ_m), and effective magnetic moment (μ_{eff}):

$$\chi_g = cl(R - R_0)/10^9 m \tag{2}$$

where c = instrument constant, l = sample length (cm), R = reading obtained for tube + sample, R_0 = reading obtained for empty tube, and m = sample mass;

$$\chi_m = \chi_g(\text{mol wt of sample}) \tag{3}$$

$$\chi_{para} = \chi_m - \chi_{dia} \tag{4}$$

$$\mu_{eff} = 2.828(\chi_{para}T)^{1/2} \tag{5}$$

where T = temperature (K); and

$$\mu_{eff} = g[S(S + 1)]^{1/2} \tag{6}$$

where g = isotropic shift found by EPR and S = spin angular momentum quantum number.

Using eqs 2 and 3, the experimentally determined magnetic susceptibility χ_m was 1.1×10^{-3} (cgs units) for the Pd^{3+} complex. In determining χ_{dia}, the sum of Pascal's constants gave $\chi_{dia(1)} = -4.86 \times 10^{-4}$. The experimentally determined diamagnetic susceptibility for $[Me_3NH][B_{11}H_{14}]$ was -1.7×10^{-4}, which when added to the appropriate remaining Pascal's constants gave $\chi_{dia(2)} = -4.93 \times 10^{-4}$. Thus, $\chi_{dia(1)} \approx \chi_{dia(2)}$, and plugging either into eq 4 gives $\chi_{para} = 1.6 \times 10^{-3}$ for the Pd^{3+} complex. Using the spin-only formula (eq 6) gives $\mu_{eff} = 2.0\ \mu_B$, which corresponds to S = 0.59, or 1.18 unpaired electrons, reasonably close to the expectation. For comparison, the magnetic susceptibility of $[Pd(B_9C_2H_{11})_2]^-$ was determined to be 1.68 μ_B.[6]

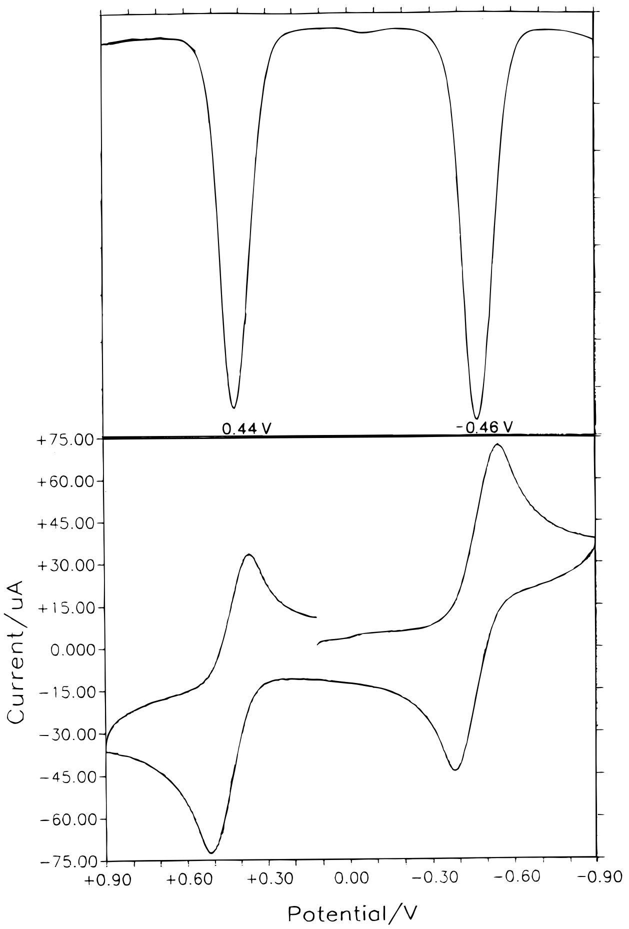

Figure 4. Differential pulse voltammogram (top) and cyclic voltammogram (bottom) of 1,4-Br_2-1,2,5-$(PMe_2Ph)_3$-*closo*-1-$PdB_{11}H_8$ in CH_2Cl_2. The indicated potentials are given versus the SCE measured under the same conditions.

Electrochemical Studies. The Pd^{3+} complex displays a reversible reduction and a reversible oxidation when investigated by cyclic voltammetry (CV) at 20 °C in 0.1 M $[Bu_4N][PF_6]$ CH_2Cl_2 solution under an Ar atmosphere (see Figure 4). The potentials, all versus SCE, are at $E_{1/2} = -0.46$ V ($\Delta E_p = 161$ mV at a scan rate of 300 mV/s, $i_{pa}/i_{pc} = 0.94$) for the Pd^{2+}/Pd^{3+} couple, and $E_{1/2} = +0.44$ V ($\Delta E_p = 150$ mV at a scan rate of 300 mV/s, $i_{pa}/i_{pc} = 0.91$) for the Pd^{3+}/Pd^{4+} couple. The ratio i_{pa}/i_{pc} equals unity for a reversible redox couple.[18] Plots of i_p vs (scan rate)$^{1/2}$ for both redox couples are nearly linear, which indicates diffusion control.[19] Least-squares fits of those plots have linear correlation coefficients R^2 ranging from 0.975 to 0.992.

The potential of the Pd^{2+}/Pd^{3+} couple in the CV is similar to that determined for a similar palladadicarbollide, $[Pd(B_9C_2H_{11})_2]^-$ (−0.56 V). However, the potential of the Pd^{3+}/Pd^{4+} couple is considerably more positive, +0.44 V for this complex vs −0.14 V for the palladadicarbollide. In contrast, most of the Pd^{2+}/Pd^{3+} couples in the $[Pd(\text{heterocycloalkane})]^{n+}$ series are more positive than the Pd^{3+}/Pd^{4+} couple in this complex; the Pd^{3+}/Pd^{4+} couples in that series are even more positive, or else not accessible or not reversible. This indicates that the palladaborane cage complexes are generally easier to

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oxidize than the [Pd(heterocycloalkane)]$^{n+}$ complexes, which supports our contention that borane and heteroborane ligands are particularly well-suited to the stabilization of high metal oxidation states.

In addition, an irreversible reduction is observed at -0.10 V after reduction from Pd^{4+} to Pd^{3+}. This peak seems to be more readily observed when the cathodic sweep has first cycled through the Pd^{3+}/Pd^{4+} couple (all sweeps were initiated at $i = 0$, $E = 118$ mV), which suggests that it is due to irreversible reduction of some decomposition product from the perhaps metastable +4 species. Differential pulse voltammetry (DPV) studies confirm that the irreversible reduction at -0.10 V occurs only upon sweeping from $+0.90$ to -0.90 V, and not in the reverse direction.

Since the CV indicates a reversible Pd^{2+}/Pd^{3+} couple, an attempt was made to reduce the Pd^{3+} complex with sodium/mercury amalgam. If successful, this would be expected to result in a diamagnetic Pd^{2+} species that would exhibit a ^{11}B NMR spectrum with 11 signals. However, no ^{11}B NMR spectrum was observed. The addition of naphthalene to the solution, intended as an electron-transfer reagent, resulted in decolorization of the solution after it was stirred overnight. Some gray solids were also observed, which suggests that decomposition of the complex occurred. We do not rule out the possibility that a Pd^{2+} complex may be accessible by controlled potential electrolysis.

If the free ligand [*nido*-$(PMe_2Ph)_2B_{11}H_9]^{2-}$ could be made, it may form a series of transition metal complexes similar to those already known for dicarbollide dianions. This may have the advantage of being a more accessible starting ligand, since it would be made from *nido*-$B_{11}H_{14}^-$, which is easily made in high yield from $NaBH_4$ and $BF_3{\cdot}OEt_2$;[20] by contrast, $B_9C_2H_{11}^{2-}$ comes from *o*-carborane, which requires handling of $B_{10}H_{14}$ and C_2H_2 to synthesize. It is possible that different reaction conditions may yield less extensively substituted palladium complexes, and a study of this type is underway.

Experimental Section

Physical Measurements. The infrared spectrum was obtained as a KBr pellet on a Nicolet 510P Fourier transform spectrometer. EPR measurements were performed at X-band frequencies (9.45 GHz) on a Bruker ESP 300 spectrometer with a Hewlett-Packard 5350B microwave frequency counter.

Magnetic susceptibility measurements were made on solid samples (average of 5 trials) at room temperature using a Johnson Matthey Evans type magnetic susceptibility balance. Two different methods were used to estimate the diamagnetic correction χ_{dia} for the complex, which was subtracted from the experimental susceptibility to give the molar paramagnetic susceptibility χ_m. In one method, Pascal's constants[21] were added up to determine the correction factor ($\chi_{dia(1)}$). In the second method, the diamagnetic susceptibility of the free ligand $[Me_3NH][B_{11}H_{14}]$ was experimentally determined, and this value was used in tandem with appropriate remaining Pascal's constants to determine the correction factor ($\chi_{dia(2)}$).

Cyclic voltammograms were recorded with a BAS CV-50W voltammetric analyzer using a standard three-electrode assembly consisting of a glassy carbon working electrode, SCE reference electrode, and Pt wire auxiliary electrode. The complex was 0.36 mM in previously distilled CH_2Cl_2 solution that included 0.1 M $[Bu_4N][PF_6]$ as the supporting electrolyte.

Materials. This reaction was performed under an atmosphere of prepurified nitrogen. Tetrahydrofuran (THF) was freshly distilled from sodium benzophenone ketyl. Dichloromethane (CH_2Cl_2) was distilled from P_2O_5. Trimethylammonium *nido*-undecaborane, $[Me_3NH][B_{11}H_{14}]$, was prepared by the method of Dunks et al.[20] Bis(dimethylphenylphosphine)palladium(II) bromide was prepared by the method of Wild et al.[22] All other commercially available reagents were used as purchased.

Table 3. Crystallographic Data for $1,4\text{-}Br_2\text{-}1,2,5\text{-}(PMe_2Ph)_3$-*closo*-$1,PdB_{11}H_8$

a, Å	9.749(13)	space group	$P2_1/c$
b, Å	16.30(2)		
c, Å	21.65(3)	λ, Å	0.710 69
β, deg	97.21(4)	ρ_{calcd}, g/cm^{-3}	1.572
V, Å^3	3413.45	μ(Mo $K\alpha$), cm^{-1}	30.112
Z	4	*R*	0.0730
fw	807.63	R_w	0.0620

Synthesis of $1,4\text{-}Br_2\text{-}1,2,5\text{-}(PMe_2Ph)_3$-*closo*-$1\text{-}PdB_{11}H_8$. In a two-neck round-bottom flask equipped with a septum and nitrogen inlet was placed $[Me_3NH][B_{11}H_{14}]$ (386 mg, 2.00 mmol). Dry THF (20 mL) was added via syringe, and an ice bath was added around the flask. When the solution temperature equilibrated, methyllithium (8.5 mmol = 4.2 equiv) in ether solution was added dropwise via syringe, until gas evolution ceased. Then, $(PMe_2Ph)_2PdBr_2$ (907 mg, 1.67 mmol) in THF/CH_2Cl_2 solution was placed in a pressure-equalizing addition funnel and added dropwise to the borane solution over a period of 0.5 h. The resulting solution quickly turned green and then changed to brown as it reacted for 2.5 days. The reaction mixture was filtered on a medium-porosity fritted funnel, and the THF filtrate was rotary evaporated. These solids were redissolved in CH_2Cl_2, and 2 g of silica gel (Merck grade 60, 230−400 mesh, 60 Å) was added. The CH_2Cl_2 was removed under reduced pressure, and the solids were packed on a 40 cm × 2.4 cm silica gel chromatography column and eluted with 1:1 (v/v) toluene−CH_2Cl_2, followed by CH_2Cl_2. The principal band was amber with $R_f = 0.8$ by TLC (CH_2Cl_2 mobile phase, Ag^+ development). Recrystallization from CH_2Cl_2/pentane at 5 °C yielded rust-colored crystals (90 mg, 5.6% yield based on $B_{11}H_{14}^-$). IR (cm^{-1}): ν_{max} 3440 (w, br), 3058 (w), 2990 (w), 2913 (w), 2519 (vs), 1489 (w), 1437 (s), 1412 (m), 1302 (m), 1287 (m), 1194 (w), 1111 (m), 1019 (m), 965 (m), 947 (s), 912 (vs), 870 (w), 856 (m), 802 (m), 743 (vs), 691 (s), 484 (s), and 413 (w).

X-ray Crystal Structure Determination. The diffractometer utilized for data collection was designed and constructed locally. A Picker four-circle goniostat equipped with a Furnas monochromator (HOG crystal) was modified by addition of stepping motors (slo-syn) on each of the four axes, and a fifth motor drives a 20-position filter/attenuator wheel. The latter allows top/bottom−left/right alignment of reflections. All motors are driven by a locally designed ISA board in an IBM-PC compatible computer. The computer also has a timer/scaler board, which is used to accumulate the counts from the scintillation counter used with the goniostat. The control software, PCPS.EXE, is the Picker software written by W. E. Streib of the IUMSC. The software for structure solution and refinement includes SHELXTL-PC and other versions of SHELX, as well as the XTEL program library.

Data were collected using a continuous $\theta-2\theta$ scan technique with fixed backgrounds at each extreme of the scan. A small, slightly split (as evidenced by ω scans: the ω half-width varied from 0.28° to 0.85°) fragment with the dimensions 0.15 × 0.20 × 0.30 mm was affixed to the end of a glass fiber using silicone grease and transferred to the goniostat, where it was cooled to −174 °C for characterization and data collection. A systematic search of a limited hemisphere of reciprocal space located a set of diffraction maxima with symmetry and systematic absences corresponding to the unique monoclinic space group $P2_1/c$. Subsequent solution and refinement confirmed this choice. The structure was solved by direct methods (MULTAN78) and standard Fourier techniques. Several of the boron and carbon atoms diverged to nonpositive definite thermal parameters when an attempt was made to refine them anisotropically. This is probably due to the fact that less than half of the data was observed based on the 2.33σ criteria.

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Although many hydrogen atoms were readily located in a difference Fourier phased on the non-hydrogen atoms, no attempt was made to refine their positions, and they were placed in idealized fixed positions for the final cycles of refinement. A final difference Fourier map was essentially featureless, the largest peak being 1.04 e/Å^3, located at the metal site. Additional information may be obtained from the Molecular Structure Center by reference to Report No. 94285. See also Table 3.

Conclusions

This work presents characterization of a relatively uncommon example of a mononuclear palladium(III) complex. We have shown that it is possible to form transition metal complexes with *nido*-B_{11} type cages. The $B_{11}H_{11}^{4-}$ ligand has the ability to coordinate η^5 to a transition metal, apparently in the same manner in which the well-known and isoelectronic dicarbollide ligand $B_9C_2H_{11}^{4-}$ does so. The $B_{11}H_{11}^{4-}$ ligand has shown a tendency to support high metal oxidation states as demonstrated by this work and previous Ni(IV) and Cu(V) work. However, by charge-compensating the ligand, many more transition metal complexes with “typical” formal oxidation states may become synthetically accessible.

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Supporting Information Available: Tables of anisotropic thermal parameters, bond distances, and intramolecular angles (4 pages). Ordering information is given on any current masthead page.

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