# Synthesis of Carborane Palladium Complexes: Examples of Low-Temperature Polytopal Rearrangements†

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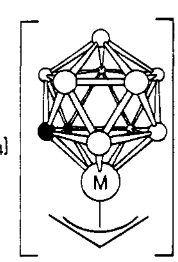
Treatment of $[Pd_2(\mu\text{-}Cl)_2(\eta^3\text{-}C_3H_5)_2]$ with $Na_2[nido\text{-}7,8\text{-}Me_2\text{-}7,8\text{-}C_2B_9H_9]$ in thf (tetrahydrofuran), followed by addition of $[NEt_4]Cl$, gives the complex $[NEt_4][Pd(\eta^3\text{-}C_3H_5)(\eta^5\text{-}7,8\text{-}Me_2\text{-}7,8\text{-}C_2B_9H_9)]$ (**1c**). Protonation of $CH_2Cl_2$ solutions of this species with $HBF_4{\cdot}Et_2O$ in the presence of CO at low temperatures affords a neutral but very unstable dicarbonyl complex $[Pd(CO)_2(\eta^5\text{-}Me_2C_2B_9H_9)]$ (**2c**). Reaction between $[PdCl_2(cod)]$ (cod = cycloocta-1,5-diene) and $Tl[closo\text{-}1,2\text{-}Me_2\text{-}3,1,2\text{-}TlC_2B_9H_9]$ in thf yields as the principal product (75%) $[Pd(cod)(\eta^5\text{-}7,8\text{-}Me_2\text{-}7,8\text{-}C_2B_9H_9)]$ (**3a**), together with small quantities of the polytopal isomer $[Pd(cod)(\eta^5\text{-}2,7\text{-}Me_2\text{-}2,7\text{-}C_2B_9H_9)]$ (**3b**) and the sandwich compound $[Pd(\eta^5\text{-}2,7\text{-}Me_2\text{-}2,7\text{-}C_2B_9H_9)_2]$ (**4**). The structure of **3b** was established by X-ray diffraction. Crystals are monoclinic, space group $P2_1/c$ (No. 14), with $a = 10.030(1)$ Å, $b = 14.197(2)$ Å, $c = 12.524(3)$ Å, and $\beta = 103.98(1)°$, $Z = 4$. In this molecule one of the CMe groups has migrated from the open pentagonal bonding face of the carborane ligand to the next pentagonal belt, while still occupying a vertex adjacent to the other CMe group. Treatment of $CH_2Cl_2$ solutions of **3a** with CO displaces the cod group, giving **2c**, but attempts to isolate the latter in the presence of cod afforded **3b**. A similar polytopal rearrangement of **3a** into **3b** occurs either on heating solutions of the former, or in room-temperature reactions with PhC≡CH or $[W(\equiv CC_6H_3Me_2\text{-}2,6)(CO)_2(\eta^5\text{-}C_5Me_5)]$. Protonation of **1c** in $CH_2Cl_2$ in the presence of $CNBu^t$ gave $[Pd(CNBu^t)_2(\eta^5\text{-}7,8\text{-}Me_2\text{-}7,8\text{-}C_2B_9H_9)]$ (**5a**), which was also prepared from $[PdCl_2(CNBu^t)_2]$ and $Tl[closo\text{-}1,2\text{-}Me_2\text{-}3,1,2\text{-}TlC_2B_9H_9]$. The tmen (tetramethylethylenediamine) complex $[Pd(tmen)(\eta^5\text{-}7,8\text{-}Me_2\text{-}7,8\text{-}C_2B_9H_9)]$ (**6**) is obtained from $[PdCl_2(tmen)]$ and $Tl[closo\text{-}1,2\text{-}Me_2\text{-}3,1,2\text{-}TlC_2B_9H_9]$ and reacts with CO to give initially **2c** followed by **4**. The latter is also the product from the reaction between **6** and butadiene in the presence of $BF_3{\cdot}Et_2O$, this reagent being used to remove tmen as the adduct $(BF_3)_2{\cdot}$tmen. A similar reaction of **6** with cod gives a mixture of the two isomers **3a** and **3b**. The complex $[Pd(PMe_2Ph)_2(\eta^5\text{-}7,8\text{-}Me_2\text{-}7,8\text{-}C_2B_9H_9)]$ (**7**) is formed from $[PdCl_2(PMe_2Ph)_2]$ and $Tl[closo\text{-}1,2\text{-}Me_2\text{-}3,1,2\text{-}TlC_2B_9H_9]$, and by displacement of cod from **3a** with $PMe_2Ph$. In contrast with **2c** or **3a**, the complexes **5a**, **6**, and **7**, having a *closo*-3,1,2-$PdC_2B_9$ cage topology, show no tendency at room temperature or below to convert to products having the *closo*-2,1,4-$PdC_2B_9$ architecture. In addition to the X-ray diffraction study on **3b**, the new compounds were characterized by microanalysis, $^1H$, $^{13}C\{^1H\}$, and $^{11}B\{^1H\}$ NMR spectroscopy, and infrared spectroscopy.

## Introduction

We have recently reported the synthesis of the nickel and platinum salts $[NEt_4][M(\eta^3\text{-}C_3H_5)(\eta^5\text{-}7,8\text{-}Me_2\text{-}7,8\text{-}C_2B_9H_9)]$ (**1a**, M = Ni; **1b**, M = Pt) which we prepared as precursors to complexes containing $M(\eta^5\text{-}7,8\text{-}Me_2\text{-}7,8\text{-}C_2B_9H_9)$ fragments.[1] Thus treatment of CO-saturated solutions of **1a** or **1b** in $CH_2Cl_2$ with $HBF_4{\cdot}Et_2O$ releases propene and yields the dicarbonyl species $[M(CO)_2(\eta^5\text{-}7,8\text{-}Me_2\text{-}7,8\text{-}C_2B_9H_9)]$ (**2a**, M = Ni; **2b**, M = Pt). In this paper we describe the palladium compound $[NEt_4][Pd(\eta^3\text{-}C_3H_5)(\eta^5\text{-}7,8\text{-}Me_2\text{-}7,8\text{-}C_2B_9H_9)]$ (**1c**). As with **1a** and **1b**, protonation of solutions of **1c** in the presence of CO gives a dicarbonyl metal complex, but the thermal instability of this product prompted us to search for alternative routes to complexes with an icosahedral *closo*-3,1,2-$PdC_2B_9$ cage framework and with the metal center carrying exopolyhedral donor ligands.

[NEt4]



● CMe ○ BH

| | M |
|---|---|
| 1a | Ni |
| 1b | Pt |
| 1c | Pd |

## Results and Discussion

In thf (tetrahydrofuran) at *ca.* −60 °C the reaction between $[Pd_2(\mu\text{-}Cl)_2(\eta^3\text{-}C_3H_5)_2]$ and $Na_2[nido\text{-}7,8\text{-}Me_2\text{-}7,8\text{-}C_2B_9H_9]$ {generated *in situ* from $[NHMe_3][7,8\text{-}Me_2\text{-}7,8\text{-}C_2B_9H_{10}]$ and NaH}, followed by addition of $[NEt_4]Cl$, affords **1c** in good yield. This product was fully characterized by microanalysis and by its NMR spectra, which are similar to those of **1a** and **1b**. Thus in the $^1H$ NMR spectrum (Table 1) the equivalent cage CMe groups give rise to one signal at $\delta$ 1.77, while the methylene hydrogens of the allyl group are seen as doublet resonances at $\delta$ 3.81 and 3.18. These two doublet signals can be assigned to

† In the compounds described in this paper $[nido\text{-}7,8\text{-}Me_2\text{-}7,8\text{-}C_2B_9H_9]^{2-}$ anions form *closo*-1,2-dicarba-3- and *closo*-1,4-dicarba-2-metallacarborane structures. Use of this numbering scheme, however, results in a complex and confusing nomenclature for the palladium complexes reported. We have therefore chosen to treat the cages as *nido* 11-vertex ligands with numbering as for an icosahedron from which the twelfth vertex has been removed.

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**Table 1.** Hydrogen-1 and Carbon-13 NMR Data[a]

| compd | $\delta(^{1}H)$ | $\delta(^{13}C)^{b}$ |
|---|---|---|
| **1c** | 1.31 [tt, 12 H, $NCH_2Me$, $J$(NH) = 2, $J$(HH) = 7], 1.77 (s, 6 H, CMe), 3.18 [d, 2 H, $H_{anti}$, $J$(HH) = 12], 3.21 [q, 8 H, $NCH_2Me$, $J$(HH) = 7], 3.81 [d, 2 H, $H_{syn}$, $J$(HH) = 7], 4.82 [tt, 1 H, $H_m$, $J$(HH) = 7, 12) | 7.8 ($NCH_2$*Me*), 25.7 (C*Me*), 53.1[c] (br, $CHCH_2$ and $NCH_2Me$), 58.0 (br, *C*Me), 103.3 (*C*H) |
| **3a** | 2.36 (s, 6 H, CMe), 2.63 (br m, 8 H, $CH_2$), 5.59 (br m, 4 H, CH) | 26.6 (C*Me*), 30.2 ($CH_2$), 82.1 (br, *C*Me), 113.8 (*C*H) |
| **3b** | 1.96 (s, 3 H, CMe), 2.31 (s, 3 H, CMe), 2.55−2.65 (br m, 8 H, $CH_2$), 5.60−5.75 (br m, 4 H, CH) | 23.6, 25.3 (C*Me*), 30.1, 31.1 ($CH_2$), 60.5 (br, *C*Me), 110.5−111.9 (br, *C*H) |
| **5a** | 1.51 (s, 18 H, Bu$^t$), 2.28 (s, 6 H, CMe) | 26.8 (C*Me*), 30.4 ($CNCMe_3$), 57.9 (br, *C*Me), 81.5 (br, $CNCMe_3$, 134.5 [t, $CNCMe_3$, $J$(NC) = 28] |
| **6** | 2.06 (s, 6 H, CMe), 2.61 (br s, 12 H, NMe), 2.72 (br s, 4 H, $CH_2$) | 24.7 (C*Me*), 50.0 (br, $NCH_2$), 60.5 (NMe), 79.8 (*C*Me) |
| **7**[d] | 1.51 [br t, 12 H, CMe and PMe, $J$(PH) = 5], 2.11 [t, 6 H, PMe, $J$(PH) = 3], 7.35−7.42 (br m, 10 H, Ph) | 16.5, 16.6 (br, P*Me*), 26.2 (C*Me*), 74.6 (*C*Me), 129.1 [(AXX′), $C^{\alpha}$(Ph), $N$ = 9], 130.6 [s, $C^{\gamma}$(Ph)], 130.9 [(AXX′), $C^{\beta}$(Ph), $N$ = 12], 135.8 [(AXX′), $C^{ipso}$(Ph), $N$ = 41][e] |

[a] Measurements at ambient temperatures in $CD_2Cl_2$ unless otherwise stated, with $J$ values in hertz. [b] Hydrogen-1 decoupled, chemical shifts are positive to high frequency of $SiMe_4$. [c] Signal for $CH_2$ group of allyl ligand is coincident with those of the cation. [d] Signals for the cage C*Me* protons in the $^{1}H$ spectrum are partially obscured by those for PMe (confirmed by integration). [e] Insufficient resolution prevents full analysis of coupling constants; $N = |J(AX) + J(AX')|$.

the *anti*- and *syn*-protons ($H_{anti}$ and $H_{syn}$), respectively, since the doublet separation of the former [$J(H_{anti}H_m)$ = 12 Hz] is larger than that of the latter [$J(H_{syn}H_m)$ = 7 Hz].[1−3] The methine hydrogen ($H_m$) of the allyl group is revealed as a triplet of triplets at $\delta$ 4.82 [$J(H_mH_{anti})$ = 12, $J(H_mH_{syn})$ = 7 Hz)]. The $^{13}C\{^{1}H\}$ NMR spectrum is as expected, with one signal being observed for the two cage *C*Me vertices at $\delta$ 58.0. The allyl ligand gives only two observable signals, one a broad peak at $\delta$ 53.1, assigned to the two methylene carbons, and the other at $\delta$ 103.3 a peak for the methine carbon.

Addition of $HBF_4{\cdot}Et_2O$ to a CO-saturated solution of **1c** in $CH_2Cl_2$ at −78 °C caused a change in the color of the solution from dark orange to brown. At this point, the reaction mixture was sampled and the IR spectrum showed two CO bands at 2020 and 1995 cm$^{-1}$, indicating the formation of a species of type $[Pd(CO)_2(\eta^5\text{-}Me_2C_2B_9H_9)]$ (**2c**) containing two terminal carbonyl ligands. However, the product decomposed rapidly either on warming solutions to room temperature or on removal of solvent and so could not be characterized other than by its IR spectrum. As a result of the previous isolation of the dicarbonyl complexes **2a** [$\nu_{max}$(CO) 2113 and 2081 cm$^{-1}$] and **2b** [$\nu_{max}$(CO) 2119 and 2080 cm$^{-1}$],[1] the new palladium(II) complex **2c** was initially formulated as $[Pd(CO)_2(\eta^5\text{-}7,8\text{-}Me_2\text{-}7,8\text{-}C_2B_9H_9)]$ with a *closo*-3,1,2-$PdC_2B_9$ cage topology. However, the facile polytopal rearrangements described below make this presumption unsafe, and **2c** may be the isomer $[Pd(CO)_2(\eta^5\text{-}2,7\text{-}Me_2\text{-}2,7\text{-}C_2B_9H_9)]$ having a *closo*-2,1,4-$PdC_2B_9$ core structure, or the dicarbonyl product formed may perhaps be a mixture of the *closo*-3,1,2- and *closo*-2,1,4-$PdC_2B_9$ isomers.

The instability of **2c** suggested that the cycloocta-1,5-diene (cod) complex $[Pd(cod)(\eta^5\text{-}7,8\text{-}Me_2\text{-}7,8\text{-}C_2B_9H_9)]$ (**3a**) might by virtue of easy displacement of the cod ligand serve as an alternative source of the $Pd(\eta^5\text{-}7,8\text{-}Me_2\text{-}7,8\text{-}C_2B_9H_9)$ fragment for synthesis. It has been previously observed[4] that treatment of the platinum complex $[Pt(cod)(\eta^5\text{-}7,8\text{-}Me_2\text{-}7,8\text{-}C_2B_9H_9)]$ with CO under pressure affords **2b**, and we have noted that this reaction is partially reversed at room temperature.[1] Since $[Pt(cod)(\eta^5\text{-}7,8\text{-}Me_2\text{-}7,8\text{-}C_2B_9H_9)]$[4] is readily obtained by treating $[PtCl_2(cod)]$ with Tl[*closo*-1,2-$Me_2$-3,1,2-$TlC_2B_9H_9$][5,6] in thf, it was reasonable to anticipate that the palladium analog could be obtained in a similar manner.

**Table 2.** Boron-11 NMR Data[a]

| compd | $\delta(^{11}B)$ |
|---|---|
| **1c** | 2.7 (1 B), −12.9 (2 B), −13.9 (3 B), −21.5 (1 B), −22.4 (2 B) |
| **3a** | 18.7 (1 B), −0.6 (2 B), −2.7 (1 B), −8.0 (2 B), −10.2 (2 B), −13.9 (1 B) |
| **3b** | 8.2 (1 B), −2.3 (2 B), −4.8 (1 B), −5.8 (1 B), −9.9 (1 B), −10.6 (1 B), −17.1 (1 B), −19.8 (1 B) |
| **5a** | 17.7 (1 B), 0.0 (2 B), −3.3 (1 B), −10.3 (2 B), −15.3 (3 B) |
| **6** | 21.5 (1 B), −0.4 (2 B), −6.9 (1 B), −11.7 (2 B), −16.0 (1 B), −21.2 (2 B) |
| **7** | 18.1 (1 B), −0.5 (2 B), −7.3 (1 B), −8.9 (2 B), −12.7 (1 B), −16.2 (2 B) |

[a] Measurements at ambient temperatures in $CD_2Cl_2$. Hydrogen-1 decoupled, chemical shifts (ppm) are positive to high frequency of $BF_3{\cdot}Et_2O$ (external). Resonances ascribed to more than one nucleus may result from overlapping signals and do not necessarily indicate symmetry equivalence.

The reaction between $[PdCl_2(cod)]$ and Tl[*closo*-1,2-$Me_2$-3,1,2-$TlC_2B_9H_9$] in thf produced a very dark solution along with a grayish precipitate apparently consisting of a mixture of TlCl and Pd metal. Column chromatography allowed the separation of three products from this reaction. By far the major product was the expected complex **3a**, isolated as a purple powder in *ca.* 75% yield. It was fully characterized by elemental analysis and NMR spectroscopy (Tables 1 and 2). The $^{1}H$ and $^{13}C\{^{1}H\}$ spectra are fully consistent with the formulation. The $^{1}H$ spectrum is very similar to that obtained by Graham and Krentz[4] for the platinum analog $[Pt(cod)(\eta^5\text{-}7,8\text{-}Me_2\text{-}7,8\text{-}C_2B_9H_9)]$. The $^{11}B\{^{1}H\}$ spectrum (Table 2) consists of six overlapping signals, one of which, corresponding in intensity to a single boron nucleus, is appreciably shifted downfield ($\delta$ 18.7). This signal is unusually deshielded for a boron atom not involved in exopolyhedral bonding,[7] but may be ascribed to the unique $\beta$-boron CCB*B*B in the open pentagonal face of the carborane cage coordinated to the palladium. This phenomenon has been observed previously.[8,9] In a study of the $^{11}B\{^{1}H\}$ NMR spectra of the related complex $[Pd(cod)(\eta^5\text{-}7,8\text{-}C_2B_9H_{11})]$ a low-field doublet was observed at $\delta$ 17.67 and was assigned to the boron $\beta$ to the carbons of the ligating CCB*B*B ring.[9] This deshielding is considered diagnostic for structures in which there is a degree of distortion resulting from "slippage" of the metal center across the pentagonal $C_2B_3$ face away from the two carbon atoms and toward the $\beta$-boron. It has been proposed[9] that the $\pi$-acceptor

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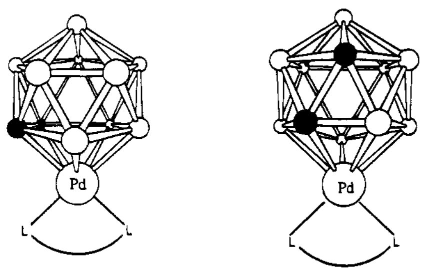
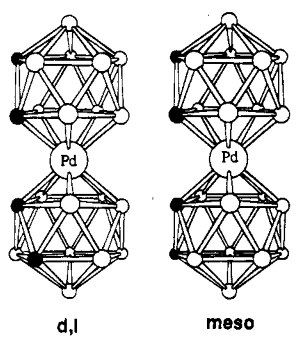
ability of the ligand may influence the degree of distortion present in the structure. With ligands possessing the ability to accept $\pi$ electron density, the formal electron density at the metal center decreases, and in compensation the metal-to-cage bonding becomes stronger, thereby causing less distortion from an $\eta^5$ bonding mode. As cycloocta-1,5-diene is considered only a moderate $\pi$-acceptor ligand, it is probable that the structures of **3a** and [Pd(cod)($\eta^5$-7,8-$C_2B_9H_{11}$)] are indeed of the "slipped" variety, thereby accounting for the relatively deshielded $^{11}B\{^1H\}$ signals at $\delta$ 18.7 and 17.67, respectively.



| | L | | L |
|---|---|---|---|
| **3a** | cod | **3b** | cod |
| **6** | tmen | | |



**d,l** **meso**

**4**

● CMe ○ BH

One of the minor products formed in the reaction between [$PdCl_2$(cod)] and Tl[*closo*-1,2-$Me_2$-3,1,2-$TlC_2B_9H_9$] was the Pd(IV) sandwich compound [Pd($\eta^5$-2,7-$Me_2$-2,7-$C_2B_9H_9$)$_2$] (**4**) in which one of the carbon atoms in each of the carborane cages has migrated from the open pentagonal $\overline{CCBBB}$ face to the next pentagonal belt, while still occupying an adjacent vertex to the carbon atom remaining in the lower pentagonal belt. This complex has been previously reported by Warren and Hawthorne[10] who obtained it by oxidizing the Pd(II) salt [$NMe_4$]$_2$[Pd($\eta^5$-7,8-$Me_2$-7,8-$C_2B_9H_9$)$_2$] with $I_2$ in $CH_2Cl_2$. As was the case in the previous work, the compound was formed as a mixture of *meso* and *d,l* isomers. It was characterized by us by its mass spectrum and NMR spectra. The mass spectrum displayed a parent peak at mass 427.3 amu (calculated 427.3 amu), along with peaks at 266 and 159 amu, corresponding to loss of one of the carborane cages followed by loss of Pd. The $^{11}B\{^1H\}$ NMR spectrum measured at 115.3 MHz consisted of eight overlapping resonances ranging from $\delta$ 15.8 to −9.06, consistent with a *closo*-metallacarborane structure, the large number of peaks resulting from the asymmetry in the system. The $^1H$ NMR spectrum consists of two sets of resonances for the CMe protons, one set each for the *meso* isomer and the *d,l* racemate. These pairs of peaks are observed at $\delta$ 2.37 and 2.38 and at $\delta$ 2.09 and 2.10 The $^{13}C\{^1H\}$ NMR spectrum was also informative, showing the expected four distinct signals at $\delta$ 24.7, 24.8, 27.6, and 27.8 for the inequivalent C*Me* carbons present in a mixture of *d,l* and *meso* forms of **4**.[10] Correspondingly, there were four peaks in the spectrum at $\delta$ 70.0, 70.3, 84.3, and 84.4 for the four inequivalent *C*Me atoms. It is of interest to note that in our studies complex **4** was also obtained as the sole metal-containing species from the reaction between [$PdCl_2$($NCPh$)$_2$] and Tl[*closo*-1,2-$Me_2$-3,1,2-$TlC_2B_9H_9$] in thf. Thus in this reaction also there is a facile intramolecular rearrangement of cage CMe vertices under mild conditions, as was first observed by Warren and Hawthorne[8,10] for certain icosahedral *C,C'*-dialkyl $PdC_2B_9$ compounds.

(10) Warren, L. F.; Hawthorne, M. F. *J. Am. Chem. Soc.* **1970**, *92*, 1157.

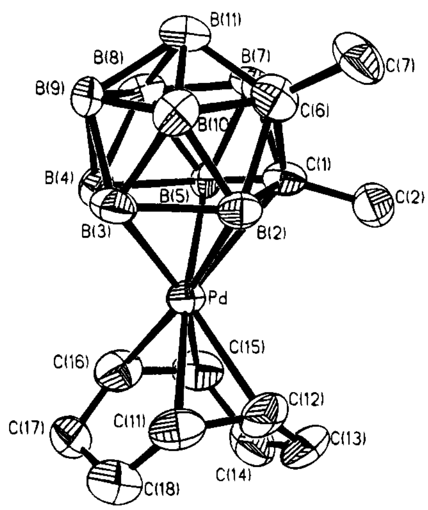



**Figure 1.** Molecular structure of [Pd(cod)($\eta^5$-2,7-$Me_2$-2,7-$C_2B_9H_9$)] (**3b**). Thermal ellipsoids are shown at the 40% probability level.

The formulation of the third product isolated from the reaction between [$PdCl_2$(cod)] and Tl[*closo*-1,2-$Me_2$-3,1,2-$TlC_2B_9H_9$] was only elucidated after a crystal structure determination. It was identified as [Pd(cod)($\eta^5$-2,7-$Me_2$-2,7-$C_2B_9H_9$)] (**3b**), an isomer of **3a** resulting from a CMe vertex migration similar to that observed in the formation of **4**. The molecular structure is shown in Figure 1, and selected connectivities and angles are presented in Table 3.

Apart from the obvious difference in structure resulting from the cage-carbon migration, it is of interest to note the positioning of the metal center with respect to the carborane cage. In **3b** the metal atom is nearly equidistant from the four boron atoms [Pd−B(2) to B(5), 2.184(7)−2.282(8) Å] in the open pentagonal ring of the *nido*-$C_2B_9$ cage and only slightly further from the remaining carbon atom in the pentagonal belt [Pd−C(1), 2.467(6) Å]. These bond lengths indicate more symmetrical bonding between the carborane cage and the metal center than perhaps exists for **3a**. Support for this view is evidenced from the $^{11}B\{^1H\}$ NMR spectrum (Table 2) where the lowest field resonance ($\delta$ 8.2) assigned to a boron atom in the $CB_4$ ring coordinated to the palladium is shifted upfield by over 10 ppm compared with the peak ($\delta$ 18.7) for the $\overline{CCBBB}$ nucleus in **3a**. As discussed elsewhere,[10] this shift is in the direction expected if the $CB_4$ bonding face contributes more electron density to the metal atom than the unrearranged $C_2B_3$ face.

The $^1H$ and $^{13}C\{^1H\}$ NMR data for **3b** are in accord with the structure established by X-ray analysis. In the $^1H$ NMR spectrum, broad diagnostic multiplets for the cod ligand are seen at $\delta$ 2.55−2.65 for the $CH_2$ groups and at $\delta$ 5.60−5.75 for the CH moieties, corresponding in their intensities to eight and four protons, respectively. The inequivalent cage CMe groups give rise to two signals at $\delta$ 1.96 and 2.31, each corresponding in intensity to three protons. The $^{13}C\{^1H\}$ NMR spectrum displays resonances for the cod ligand at $\delta$ 30.1 and 31.1 ($CH_2$) and at $\delta$ 110.5 and 111.9 (CH). The nonequivalent cage C*Me* nuclei are revealed by peaks at $\delta$ 23.6 and 25.3. However, only one

**Table 3.** Selected Internuclear Distances (Å) and Angles (deg) For [Pd(cod)($\eta^5$-2,7-$Me_2$-2,7-$C_2B_9H_9$)] (**3b**), with Estimated Standard Deviations in Parentheses

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| Pd—C(1) | 2.467(6) | Pd—B(2) | 2.184(7) | Pd—B(3) | 2.282(8) | Pd—B(4) | 2.267(9) |
| Pd—B(5) | 2.208(7) | Pd—C(11) | 2.275(8) | Pd—C(12) | 2.266(10) | Pd—C(15) | 2.290(7) |
| Pd—C(16) | 2.270(8) | C(1)—B(2) | 1.715(11) | C(1)—B(5) | 1.652(10) | C(1)—C(6) | 1.626(9) |
| C(1)—B(7) | 1.670(11) | C(1)—C(2) | 1.534(10) | B(2)—B(3) | 1.858(12) | B(2)—C(6) | 1.806(11) |
| B(2)—B(10) | 1.779(11) | B(3)—B(4) | 1.761(12) | B(3)—B(9) | 1.767(11) | B(3)—B(10) | 1.757(9) |
| B(4)—B(5) | 1.922(10) | B(4)—B(8) | 1.746(11) | B(4)—B(9) | 1.770(10) | B(5)—B(7) | 1.799(9) |
| B(5)—B(8) | 1.785(12) | C(6)—B(7) | 1.677(12) | C(6)—B(10) | 1.759(11) | C(6)—B(11) | 1.687(12) |
| C(6)—C(7) | 1.487(10) | B(7)—B(8) | 1.801(13) | B(7)—B(11) | 1.745(12) | B(8)—B(9) | 1.799(12) |
| B(8)—B(11) | 1.817(12) | B(9)—B(10) | 1.789(12) | B(9)—B(11) | 1.762(11) | B(10)—B(11) | 1.807(12) |
| C(11)—C(12) | 1.380(12) | C(11)—C(18) | 1.501(10) | C(12)—C(13) | 1.497(12) | C(13)—C(14) | 1.480(13) |
| C(14)—C(15) | 1.522(13) | C(15)—C(16) | 1.369(12) | C(16)—C(17) | 1.499(11) | C(17)—C(18) | 1.485(12) |

| | | | | | |
|---|---|---|---|---|---|
| C(1)—Pd—B(2) | 42.7(3) | C(1)—Pd—B(5) | 40.9(2) | C(1)—Pd—C(11) | 133.2(2) |
| C(1)—Pd—B(3) | 78.1(2) | Pd—C(15)—C(16) | 71.7(4) | C(1)—Pd—C(12) | 105.1(3) |
| C(1)—Pd—B(4) | 78.0(2) | Pd—C(16)—C(15) | 73.3(4) | C(11)—Pd—C(12) | 35.4(3) |
| Pd—C(11)—C(18) | 108.1(5) | Pd—C(16)—C(17) | 104.9(5) | C(15)—Pd—C(16) | 34.9(3) |
| C(11)—Pd—C(16) | 80.4(3) | C(12)—Pd—C(15) | 79.2(3) | C(14)—C(15)—C(16) | 122.0(7) |
| C(15)—C(16)—C(17) | 127.8(8) | C(16)—C(17)—C(18) | 115.6(7) | C(11)—C(18)—C(17) | 117.7(7) |

broad resonance ($\delta$ 60.5) is observed for the *C*Me vertices due evidently to overlapping signals.

The conversion of **3a** into **3b** can be affected by mild heating. When a thf solution of **3a** was heated at 60 °C for 1 h, there appeared to be about a 40% conversion to **3b**; however, some decomposition occurred as metallic palladium was observed precipitating from solutions. Heating at higher temperatures accelerated this decomposition process.

Alternative methods for preparing **3a** were attempted in hopes of forming the product in the absence of **3b** and **4**. These included adding cycloocta-1,5-diene to [$PdCl_2$(cod)] before addition of Tl[*closo*-1,2-$Me_2$-3,1,2-$C_2B_9H_9$)] in thf and reacting [$Pd_2(\mu\text{-}Cl)_2(cod)_2$][$BF_4$]$_2$ with Tl[*closo*-1,2-$Me_2$-3,1,2-$TlC_2B_9H_9$)]. However, neither of these modifications gave a better yield of **3a** than the original method.

In earlier work,[1] it was observed that the nickel dicarbonyl species **2a** slowly releases CO to afford a mixture of three isomers, [$Ni_2(CO)_2$($\eta^5$-7,8-$Me_2$-7,8-$C_2B_9H_9$)$_2$], [$Ni_2(CO)_2$($\eta^5$-7,8-$Me_2$-7,8-$C_2B_9H_9$)($\eta^5$-2,7-$Me_2$-2,7-$C_2B_9H_9$)], and [$Ni_2(CO)_2$($\eta^5$-2,7-$Me_2$-2,7-$C_2B_9H_9$)$_2$], two of which contain cages with the *closo*-2,1,4-$NiC_2B_9$ topology. The dicarbonylpalladium compound **2c** is less stable than **2a**, precluding any structural studies. Thus as mentioned above, the topology of the *closo*-$PdC_2B_9$ cage in **2c** is unresolved. When solutions of **3a** in $CH_2Cl_2$ are saturated with CO at room temperature, the IR spectrum of the mixture shows the presence of **2c**. However, within a short time, it was observed that metallic palladium was deposited on the reaction vessel and that the color of the solution changed to a reddish-orange color. After workup, **3b** was isolated, evidently formed by displacement of carbonyl ligands from Pd by free cod, with overall a polytopal rearrangement from **3a** to **3b** taking place. The displacement of the CO groups by the cod molecules in the solution is not unexpected since in the synthesis of [Pt(CO)$_2$($\eta^5$-7,8-$Me_2$-7,8-$C_2B_9H_9$)] by treating [Pt(cod)($\eta^5$-7,8-$Me_2$-7,8-$C_2B_9H_9$)] with CO, complete conversion to the dicarbonyl is never attained due to back reaction with liberated cod.[1,4]

Since the reaction of **3a** with CO produced **3b**, it was envisioned that reactions with other substrate molecules might also induce this polytopal rearrangement. No reaction of **3a** with ethylene occurred. However, treatment of **3a** with phenylacetylene gave **3b** in *ca.* 45% yield as the only metal-containing species. On the basis of the knowledge that alkynes are isolobal with the species [W($\equiv$CR)(CO)$_2$($\eta^5$-$C_5R'_5$)] (R = $C_6H_4Me$-4, R′ = H, and R = $C_6H_3Me_2$-2,6, R′ = Me) and that these alkylidyne tungsten compounds displace cod groups from metal centers to afford complexes with metal—metal bonds,[7b,11] reactions between these reagents and **3a** were investigated. With [W($\equiv$CC$_6H_4$Me-4)(CO)$_2$($\eta^5$-$C_5H_5$)], complex **3a** afforded several products, but no stable palladium complex could be isolated. In contrast, [W($\equiv$CC$_6H_3Me_2$-2,6)(CO)$_2$($\eta^5$-$C_5Me_5$)] with **3a** catalyzed isomerization of the latter to **3b**.

These results lead us to suggest that the polytopal rearrangement of the cage of **3a** in the various reactions occurs upon dissociation of ligands from unstable intermediates, and that this process is followed by recoordination of the cod group. In the reaction with phenylacetylene, labile species of the type [Pd(PhC$\equiv$CH)$_n$($\eta^5$-7,8-$Me_2$-7,8-$C_2B_9H_9$)] ($n$ = 1 or 2) might form; rearrangement could then occur followed by attack of free cod so as to generate **3b**. In the case of [W($\equiv$CC$_6H_3Me_2$-2,6)(CO)$_2$($\eta^5$-$C_5Me_5$)], the steric bulk of the $CC_6H_3Me_2$-2,6 and $\eta^5$-$C_5Me_5$ ligands may allow formation of an $\eta^2$-C$\equiv$W bound Pd intermediate with the requisite instability for dissociation, polytopal rearrangement, and recoordination of cod.

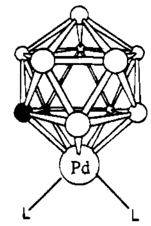
Further protonation reactions of **1c** were next investigated. Addition of 2 equiv of CNBu$^t$ to **1c** in $CH_2Cl_2$ at −78 °C, followed by $HBF_4{\cdot}Et_2O$, gave [Pd(CNBu$^t$)$_2$($\eta^5$-7,8-$Me_2$-7,8-$C_2B_9H_9$)] (**5a**) as orange microcrystals. This species displays two NC absorptions in its IR spectrum at 2202 and 2184 cm$^{-1}$, frequencies which compare well with those reported[1] for the nickel and platinum analogs [M(CNBu$^t$)$_2$($\eta^5$-7,8-$Me_2$-7,8-$C_2B_9H_9$)] [**5b**, M = Ni, $\nu_{max}$(NC) at 2197, 2178 cm$^{-1}$; **5c**, M = Pt, $\nu_{max}$(NC) at 2207, 2180 cm$^{-1}$]. An isomer of **5a** was reported several years ago.[12] Treatment of [*closo*-2,3-$Me_2$-2,3-$C_2B_9H_9$] with [Pd(CNBut)$_2$] results in a polyhedral expansion reaction yielding [Pd(CNBu$^t$)$_2$($\eta^5$-7,9-$Me_2$-7,9-$C_2B_9H_9$)], with the two CMe groups lying in the open pentagonal belt of the carborane but separated by one BH vertex.

Although **5a** was produced from **1c** in good yield by the above route, it was subsequently found that the reaction of [$PdCl_2$(CNBu$^t$)$_2$], generated *in situ* by adding 2 equiv of CNBu$^t$ to [Pd(NCPh)$_2Cl_2$], with Tl[*closo*-1,2-$Me_2$-3,1,2-$TlC_2B_9H_9$)] gave **5a** in even higher yield (70%). The $^1$H spectrum (Table 1) of **5a** is as expected, with one resonance at $\delta$ 1.51 for the equivalent CNBu$^t$ protons, and one resonance at $\delta$ 2.28 for the cage CMe protons. In the $^{13}$C{$^1$H} NMR spectrum the C*Me* groups of the carborane cage are evidenced by a singlet at $\delta$ 26.8, and the carbons of the C*Me*$_3$ groups are revealed by a peak at $\delta$ 30.4, while the signal corresponding to the *C*Me nuclei of the cage is seen as a broad peak at $\delta$ 57.9. The peak representing the ligated carbon of the *C*NBu$^t$ ligand is observed as a triplet at $\delta$ 134.5 [$J$(NC) = 28 Hz]. It should be noted that in neither of these methods for preparing **5a** was there any evidence of formation of the isomer [Pd(CNBu$^t$)$_2$($\eta^5$-2,7-$Me_2$-

(11) Carr, N.; Mullica, D. F.; Sappenfield, E. L.; Stone, F. G. A.; Went, M. J. *Organometallics* **1993**, *12*, 4350. Stone, F. G. A. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 89.

(12) Green, M.; Spencer, J. L.; Stone, F. G. A.; Welch, A. J. *J. Chem. Soc., Dalton Trans.* **1975**, 179.

2,7-$C_2B_9H_9$)]. Moreover, no polytopal rearrangement of **5a** was observed on heating solutions of the complex.



| | L |
|---|---|
| **5a** | CNBu$^t$ |
| **7** | PMe$_2$Ph |

● CMe  ○ BH

Since the literature contains numerous examples of palladium compounds containing bridging isocyanide ligands, it was thought that **5a** might form polynuclear metal complexes when treated with metal species containing labile ligands. For this reason, the following experiments were performed. When [Pt(cod)$_2$] was added to a $CH_2Cl_2$ solution of **5a**, no immediate reaction was evident; however, the IR spectrum of the solution indicated after some minutes the disappearance of **5a** and the formation of a product displaying NC absorbances at 2207 and 2180 cm$^{-1}$. After workup and separation of the products, it became evident that the latter species was the previously reported platinum compound **5c**,[1] while the other product formed was **3a**; these compounds resulted from ligand-exchange processes. Reactions between **5a** and either [$Co_2(CO)_8$] or [$Fe_2(CO)_9$] in thf gave as the only palladium-containing product the "sandwich" compound **4** and palladium metal.

An attempt to protonate the isocyanide ligands in **5a** with $HBF_4$·$Et_2O$ to yield an alkylidene complex was unsuccessful. Again the product of this reaction was the Pd(IV) complex **4**, together with unidentified nonmetallic products. Since the reaction with acid caused decomposition, it was speculated that reaction with $Me^+$ might be more profitable; however, no reaction was observed between **5a** and $CF_3SO_3Me$.

Previous workers[9] have shown that the complex [Pd(tmen)($\eta^5$-7,8-$C_2B_9H_{11}$)] (tmen = tetramethylethylenediamine) can be employed as a precursor to compounds containing the Pd($\eta^5$-7,8-$C_2B_9H_{11}$) group. The tmen ligand may be removed with anhydrous HCl as the hydrochloride salt [tmenH]Cl, a process yielding, in the presence of donor ligands, species such as [Pd(cod)($\eta^5$-7,8-$C_2B_9H_{11}$)] mentioned above. Anticipating that this methodology could be applied to our systems, the complex [Pd(tmen)($\eta^5$-7,8-$Me_2$-7,8-$C_2B_9H_9$)] (**6**) was prepared by addition of Tl[*closo*-1,2-$Me_2$-3,1,2-$TlC_2B_9H_9$)] to a thf solution of [$PdCl_2$(tmen)], the latter being prepared *in situ* by the reaction of [$PdCl_2(NCPh)_2$] with tetramethylethylenediamine.

Compound **6** was characterized by microanalysis and by NMR spectroscopy (Tables 1 and 2). Although the signals in the $^1$H NMR spectrum were very broad, possibly due to the presence of quadrupolar $^{14}$N, the resonances were readily assigned. There is a diagnostic singlet peak for the cage CMe protons at $\delta$ 2.06 and resonances at $\delta$ 2.61 and 2.72 which may be assigned to the NMe and $CH_2$ groups, respectively, of the tmen ligand. The peaks in the $^{13}C\{^1H\}$ spectrum were also somewhat broad but are fully consistent with the proposed formulation. The appearance of two signals at $\delta$ 79.8 (*C*Me) and 24.7 (C*Me*) indicated the equivalence of the cage CMe groups, the complex thus retaining the *closo*-3,1,2-$PdC_2B_9$ cage architecture. The $^{11}B\{^1H\}$ NMR spectrum of **6** exhibits six resonances, some of which were overlapping. However, one signal at $\delta$ 21.5, corresponding in intensity to a single boron nucleus, was shifted significantly downfield, as was noted for the CCB*B*B atom in the $^{11}B\{^1H\}$ NMR spectrum of **3a**. This is as expected if the appearance of the downfield resonance is due to "slippage" from an $\eta^5$-$C_2B_3$ bonding mode with the metal center toward an $\eta^3$-$C_2B_3$ interaction, resulting from the inability of tmen, a classical $\sigma$-donor, to remove electron density from the palladium by $\pi$-acceptor bonding. It is noteworthy that the $^{11}B\{^1H\}$ NMR spectrum of [Pd(tmen)($\eta^5$-7,8-$C_2B_9H_{11}$)] also displays a deshielded resonance ($\delta$ 20.04) for the boron in the $\beta$ site in the pentagonal ring CCB*B*B ligating the palladium.[9] Moreover, an X-ray diffraction determination of the structure of this molecule revealed very appreciable slippage of the metal center away from the two carbons toward the unique $\beta$-B atom so that the palladium is more closely associated with the three boron atoms of the $C_2B_3$ ring.

In order to study the reactivity of **6**, several reactions were investigated. Use of **6** rather than **3a** as the source of the *closo*-3,1,2-$PdC_2B_9$ fragment might be advantageous since complications of having free cod present in the solutions would be avoided. A $CH_2Cl_2$ solution of **6** was saturated with CO, and 1 equiv of HCl was added. As in the carbonylation of **3a**, the dicarbonyl species **2c** was detected in the solution by IR, but upon removal of solvent it decomposed, yielding **4** as the only isolable metal-containing product. As an alternative to the use of HCl, the tmen ligand in **6** can be removed with $BF_3$·$Et_2O$ as the insoluble Lewis acid/base adduct $(BF_3)_2$·tmen. This is convenient if the presence of the protonic acid in solutions of the reactants would be undesirable. Treatment of **6** in thf for several hours with $BF_3$·$OEt_2$ in the presence of cycloocta-1,5-diene, followed by removal of the solvent and separation of the products by chromatography, gave a mixture of the isomers **3a** and **3b** formed in an approximately 3:1 ratio, respectively. Increasing the temperature increased the rate of reaction and also the proportion of **3b** produced, but the amount of overall decomposition also increased.

Prompted by the existence of the cyclobutadiene species [Pd($\eta^4$-$C_4Ph_4$)($\eta^5$-7,8-$Me_2$-7,8-$C_2B_9H_9$)],[13] we attempted to prepare a Pd(II) butadiene complex [Pd($\eta^4$-$C_4H_6$)($\eta^5$-7,8-$Me_2$-7,8-$C_2B_9H_9$)] from **6** and butadiene, using $BF_3$·$Et_2O$ to remove tmen. Unfortunately, after workup the only metal-containing species present was the ubiquitous Pd(IV) sandwich compound **4**, probably formed as a decomposition product from the desired diene complex.

During the course of the work described herein, the complex [Pd($PMe_2Ph$)$_2$($\eta^5$-7,8-$Me_2$-7,8-$C_2B_9H_9$)] (**7**) was prepared by reacting **3a** with 2 equiv of $PMe_2Ph$ and also by treating [$PdCl_2(PMe_2Ph)_2$] in thf with Tl[*closo*-1,2-$Me_2$-3,1,2-$TlC_2B_9H_9$)]. In both reactions there was no evidence for a polytopal rearrangement leading to the isomer [Pd($PMe_2Ph$)$_2$($\eta^5$-2,7-$Me_2$-2,7-$C_2B_9H_9$)]. Compound **7** was fully characterized by the data in Tables 1 and 2.

The $^1$H spectrum displays two triplet signals for the two $PMe_2$ groups. Within each group the Me moieties are nonequivalent. The four Me groups give rise to two signals by virtue of a plane of symmetry which can be generated through the Pd atom, the $\beta$-B atom CCB*B*B, and the mid-point of the C—C connectivity. The couplings [$^2J$(PH) = 3 and 5 Hz] in this case have been arbitrarily assigned (Table 1) . Unfortunately, the resonance for the equivalent cage CMe protons is obscured by the signals for the $PMe_2$ groups, but its presence was confirmed by peak integration. The resonances for the phenyl protons are observed

(13) Hawthorne, M. F.; Young, D. C.; Andrews, T. D.; Howe, D. V.; Pilling, R. L.; Pitts, A. D.; Reintjes, M.; Warren, L. F.; Wegner, P. A. *J. Am. Chem. Soc.* **1968**, *90*, 879.

as a multiplet at $\delta$ 7.35–7.42. In the $^{13}C\{^1H\}$ spectrum of **7**, the peaks for the inequivalent $PMe_2$ carbons occur as signals at $\delta$ 16.5 and 16.6, with some broadening apparently due to unresolved $^{31}P$ coupling. A peak for the two cage C*Me* nuclei is observed at $\delta$ 26.2, and the resonance for the two carbons of the ligating *nido*-$C_2B_9$ fragment is seen at $\delta$ 74.6, thus establishing a *closo*-3,1,2-$PdC_2B_9$ cage framework. The resonances for the carbon atoms of the phenyl groups are seen in the expected region, with $C^{ipso}$ appearing at $\delta$ 135.8 and displaying a typical one-bond $^{31}P-^{13}C$ coupling (41 Hz). The $C^{\alpha}$ and $C^{\beta}$ nuclei of the $C_6H_5$ rings give rise to resonances at $\delta$ 129.1 and 130.9, while $C^{\gamma}$ is observed as a singlet at $\delta$ 130.6.

The $^{31}P\{^1H\}$ NMR spectrum of **7** displays a singlet at $\delta$ −5.6, indicating equivalence of the two cis phosphine groups, further confirming that this complex does not have a *closo*-2,1,4-$PdC_2B_9$ core architecture, a structure which would would render the two phosphines inequivalent. The $^{11}B\{^1H\}$ NMR spectrum (Table 2) again consists of six peaks, with one of these peaks shifted significantly downfield ($\delta$ 18.1). This argues for the occurrence of an appreciable lateral slip of the $Pd(PMe_2Ph)_2$ moiety across the $C_2B_3$ face even though the $PMe_2Ph$ ligand is considered to be a good $\pi$-acceptor. The resonance for the CCB*B*B boron nucleus in the related complex $[Pd(PMe_3)_2(\eta^5\text{-}7,8\text{-}C_2B_9H_{11})]$ is much less deshielded, occurring at $\delta$ 6.68.[9] X-ray diffraction studies on $[Pd(PMe_3)_2(\eta^5\text{-}7,8\text{-}C_2B_9H_{11})]$ and on $[Pd(tmen)(\eta^5\text{-}7,8\text{-}C_2B_9H_{11})]$ revealed a good correlation between slippage of the $PdL_2$ moieties in these molecules and the resonances for the CCB*B*B nuclei.[9] The palladium atom is much less symmetrically positioned with respect to the centroid of the $C_2B_3$ ring in the tmen complex. In agreement, as mentioned earlier, the resonance for the $\beta$-B atom in the tmen complex ($\delta$ 20.04) is considerably more deshielded than that in the phosphine complex ($\delta$ 6.68). The $^{11}B\{^1H\}$ NMR data for **7**, with $B^{\beta}$ at $\delta$ 18.1, would appear to argue against the thesis that the degree of ring slippage is solely related to the acceptor ability of the ligand or ligands (phosphines *versus* tmen). However, steric factors may play a role in determining the degree of asymmetry. The $PMe_2Ph$ ligand is relatively bulky (cone angle of 122°),[14] and thus the two $PMe_2Ph$ groups could possibly interact with the CMe groups in the open face of the carborane cage, causing the complex to distort and assume a more "slipped" structure than that in $[Pd(PMe_3)_2(\eta^5\text{-}7,8\text{-}C_2B_9H_{11})]$, which has an unsubstituted cage. Indeed, it has been demonstrated that if steric demands in the face of a *nido*-$C_2B_9$ ligand become appreciable a polyhedral rearrangement is induced under mild conditions, as observed in the ready conversion of $[Pt(PMe_2Ph)_2(\eta^5\text{-}7\text{-}Ph\text{-}7,8\text{-}C_2B_9H_{10}]$ into a mixture of isomers with *closo*-1-Ph-3,1,11-$PtC_2B_9$ and *closo*-11-Ph-3,1,11-$PtC_2B_9$ cage architectures.[15]

## Conclusions

Several synthetic routes have been developed to yield Pd(II) complexes containing *C*-methyl-substituted icosahedral *closo*-$PdC_2B_9$ fragments and in which the palladium carries donor ligands (CO, $CNBu^t$, $PMe_2Ph$, cod, and tmen). Under mild conditions the cod complex $[Pd(cod)(\eta^5\text{-}7,8\text{-}Me_2\text{-}7,8\text{-}C_2B_9H_9)]$ (**3a**), with a *closo*-3,1,2-$PdC_2B_9$ cage structure, readily affords a variety of products in which the cage transforms to species having the *closo*-2,1,4-$PdC_2B_9$ architecture, an intramolecular rearrangement apparently promoted by dissociation of the cod group. The complexes **5a**, **6**, and **7**, with the more strongly bound $CNBu^t$, tmen, and $PMe_2Ph$ ligands, do not undergo a similar polytopal rearrangement at ambient temperatures, although removal of the tmen ligand from **6** with $BF_3{\cdot}Et_2O$ can lead to cage isomerization. From $^{11}B\{^1H\}$ NMR measurements there is further evidence supporting the proposal that ring slippage in Pd(II) complexes is reduced by coordination of good $\pi$-acceptor ligands, although this may be negated by other factors such as steric effects.

## Experimental Section

**General Considerations.** Solvents were distilled from appropriate drying agents under nitrogen prior to use. Petroleum ether refers to that fraction of boiling point 40–60 °C. All reactions were carried out under an atmosphere of dry nitrogen using Schlenk-line techniques. Chromatography columns (*ca.* 8 cm in length and 2 cm in diameter) were packed with alumina (Brockmann activity III). The acid $HBF_4{\cdot}Et_2O$ was used as an 85% solution in $Et_2O$ as supplied by Aldrich Chemical Co. The compounds $Tl[closo\text{-}1,2\text{-}Me_2\text{-}3,1,2\text{-}TlC_2B_9H_9)]$,[5] $[Pd_2(\mu\text{-}Cl)_2(\eta^3\text{-}C_3H_5)_2]$,[16] $[PdCl_2(cod)]$,[17] $[PdCl_2(NCPh)_2)]$,[18] and $[Pt(cod)_2]$[19] were prepared by literature methods. NMR spectra were recorded at the following frequencies: $^1H$ at 360.13 MHz, $^{13}C\{^1H\}$ at 90.57 MHz, and $^{11}B\{^1H\}$ at 115.3 MHz.

**Synthesis of $[NEt_4][Pd(\eta^3\text{-}C_3H_5)(\eta^5\text{-}7,8\text{-}Me_2\text{-}7,8\text{-}C_2B_9H_9)]$.** A solution of $Na_2[nido\text{-}7,8\text{-}Me_2\text{-}7,8\text{-}C_2B_9H_9]$ {generated from $[NHMe_3][7,8\text{-}Me_2\text{-}7,8\text{-}C_2B_9H_{10}]$ (0.40 g, 1.8 mmol) and NaH (0.40 g of a 60% dispersion in mineral oil, washed with 2 × 20 mL of thf) at reflux temperature for 4 h} in thf (40 mL) was added slowly over a period of 15 min to a solution of $[Pd_2(\mu\text{-}Cl)_2(\eta^3\text{-}C_3H_5)_2]$(0.33 g, 0.09 mmol) in thf (40 mL) held at −60 °C. After the solution was stirred for 1 h, the reactants were warmed to −30 °C, and stirring was continued for 12 h. The salt $[NEt_4]Cl{\cdot}H_2O$ (0.33 g, 1.8 mmol) was added and the mixture warmed to room temperature over a period of 4 h. Volatile materials were removed *in vacuo*, and the residue was extracted with benzene–$CH_2Cl_2$ (50 mL, 4:1) and filtered through a Celite pad (*ca.* 8 × 2 cm). The solution was then evaporated *in vacuo* to dryness, and the residue obtained was dissolved in a minimum of $CH_2Cl_2$ (2 mL). Diethyl ether (15 mL) was added, giving $[NEt_4][Pd(\eta^3\text{-}C_3H_5)(\eta^5\text{-}7,8\text{-}Me_2\text{-}7,8\text{-}C_2B_9H_9)]$ (**1c**) (0.52 g, 66%) as rust-colored microcrystals. Anal. Calcd for $C_{15}H_{40}B_9NPd$: C, 41.1; H, 9.2. Found: C, 41.6; H, 9.0.

**Synthesis of $[Pd(cod)(\eta^5\text{-}7,8\text{-}Me_2\text{-}7,8\text{-}C_2B_9H_9)]$ (3a).** The reagent $[PdCl_2(cod)]$ (0.10 g, 0.04 mmol) was suspended in 40 mL of thf and treated with 1 equiv of solid $[Tl(closo\text{-}1,2\text{-}Me_2\text{-}3,1,2\text{-}TlC_2B_9H_9)]$ (0.2 g, 0.04 mmol). The reactants were stirred for 2 h, and the resulting black mixture was then filtered through a Celite plug (4 × 2 cm) to remove precipitated TlCl. All volatile material was removed *in vacuo*, leaving a dark-colored oil. The latter was dissolved in a minimum of $CH_2Cl_2$ (*ca.* 4 mL) and transferred to the top of a chromatography column. The column was eluted with 3:1 petroleum ether–$CH_2Cl_2$, giving first a small yellow band found to contain (*ca.* 0.01 g) the sandwich compound $[Pd(\eta^5\text{-}2,7\text{-}Me_2\text{-}2,7\text{-}C_2B_9H_9)_2]$ (**4**). Further elution with 1:1 $CH_2Cl_2$–petroleum ether developed a broad band containing two orange and purple components. The eluate was pumped to dryness and the resulting solid washed with diethyl ether to remove a small amount of orange $[Pd(cod)(\eta^5\text{-}2,7\text{-}Me_2\text{-}2,7\text{-}C_2B_9H_9)]$ (**3b**) (*ca.* 0.014 g), leaving the isomer $[Pd(cod)(\eta^5\text{-}7,8\text{-}Me_2\text{-}7,8\text{-}C_2B_9H_9)]$ (**3a**) (0.10 g, 74%) as purple microcrystals. Anal. Calcd for $C_{12}H_{27}B_9Pd$: C, 38.4; H, 7.3. Found: **3a**, C, 37.6; H, 7.1. **3b**, C, 38.7; H, 7.4.

**Carbonylation.** Carbon monoxide was bubbled through a $CH_2Cl_2$ (20 mL) solution of **3a** (0.10 g, 0.03 mmol) for 30 min. During this time it was observed that the color of the solution changed from purple to orange-red and that metallic palladium precipitated from the solution. Filtration of the mixture through a short Florisil pad (2 × 2 cm) gave a clear orange-red solution. Removal of solvent *in vacuo* gave orange microcrystals of $[Pd(cod)(\eta^5\text{-}2,7\text{-}Me_2\text{-}2,7\text{-}C_2B_9H_9)]$ (**3b**) (0.03 g, 30%).

**Synthesis of $[Pd(CNBu^t)_2(\eta^5\text{-}7,8\text{-}Me_2\text{-}7,8\text{-}C_2B_9H_9)]$.** The reagent $^tBuNC$ (0.45 mL, 2 equiv) was added to a stirred solution of $[PdCl_2(NCPh)_2]$ (0.76 g, 1.97 mmol) in $CH_2Cl_2$ (30 mL), giving a colorless solution. After the mixture was stirred for 30 min, solvent

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**Table 4.** Crystallographic Data for **3b**[a]

| | |
|---|---|
| cryst dimens (mm) | 0.12 × 0.34 × 0.34 |
| formula | $C_{12}H_{27}B_9Pd$ |
| $M_r$ | 375.1 |
| cryst color, shape | red, parallelpiped |
| cryst system | monoclinic |
| space group | $P2_1/c$ (No. 14) |
| $a$ (Å) | 10.030(1) |
| $b$ (Å) | 14.197(2) |
| $c$ (Å) | 12.524(3) |
| $\beta$ (deg) | 103.98(1) |
| $V$ (Å$^3$) | 1730.5(5) |
| $Z$ | 4 |
| $d_{calcd}$ (g cm$^{-3}$) | 1.439 |
| $\mu$(Mo Kα) (cm$^{-1}$) | 10.44 |
| $F(000)$ (e) | 760 |
| $2\theta$ range (deg) | 3−40 |
| $T$ (K) | 292 |
| no. of reflcns measd | 1824 |
| no. of unique reflcns | 1607 |
| no. of obsd reflcns | 1441 |
| criterion for obsd $n$ [$F_o \geq n\sigma(F_o)$] | $n = 4$ |
| $R$ ($R'$)[b] | 0.0325 (0.0429) |
| final electron density diff features (max/min) (e Å$^{-3}$) | 0.51/−0.46 |
| $S$ (goodness-of-fit) | 1.35 |

[a] Data collected on an Enraf Nonius CAD4-F automated diffractometer operating in the $\omega-2\theta$ scan mode ($h$, 0−9; $k$, 0−13; $l$ −11 to 12; graphite-monochromated Mo Kα X-radiation, $\lambda$ = 0.710 73 Å. Refinement was by a full-matrix least squares method on $F$ with a weighting scheme of the form $w^{-1} = [\sigma^2(F_o) + g|F_o|^2]$ ($g$ = 0.0024); where $\sigma_c^2(F_o)$ is the variance in $F_o$ due to counting statistics. [b] $R = \sum||F_o| - |F_c||/\sum|F_o|$, $R' = \sum w^{1/2}||F_o| - |F_c||/\sum w^{1/2}|F_o|$.

was removed *in vacuo*, leaving a white, sticky solid. This material was washed with petroleum ether (2 × 10 mL) and dried, giving [$PdCl_2(CNBu^t)_2$] as a white powder which was then dissolved in 50 mL of $CH_2Cl_2$. To this solution was added 1 equiv of Tl[*closo*-1,2-$Me_2$-3,1,2-$TlC_2B_9H_9$] (1.12 g, 1.97 mmol), and the mixture was stirred for 4 h. The dark brown solution was then filtered through a Celite plug (4 × 2 cm), and the volatiles were removed *in vacuo*. The residue was dissolved in a small amount (*ca.* 3 mL) of $CH_2Cl_2$ and chromatograped. Elution of the column with 3:1 $CH_2Cl_2$−petroleum ether produced an orange-colored band, which after removal of solvent gave [Pd($CNBu^t)_2$($\eta^5$-7,8-$Me_2$-7,8-$C_2B_9H_9$)] (**5a**) (0.60 g, 70%) as orange microcrystals. Anal. Calcd for $C_{14}H_{33}B_9N_2Pd$: C, 38.8; H, 7.7. Found: C, 39.4; H, 8.1.

**Synthesis of [Pd(tmen)($\eta^5$-7,8-Me$_2$-7,8-C$_2$B$_9$H$_9$)].** A thf (40 mL) solution of [$PdCl_2$(tmen)] (0.33 g, 1.12 mmol) prepared by treating [$PdCl_2(NCPh)_2$] with tmen in $CH_2Cl_2$ was treated with the reagent Tl[*closo*-1,2-$Me_2$-3,1,2-$TlC_2B_9H_9$] (0.64 g, 1.12 mmol), giving a brown solution. After being stirred for 2 h, the mixture was filtered through a Celite plug (4 × 2 cm) and the volatiles were removed *in vacuo*, leaving a dark brown solid. The solid was dissolved in 4 mL of $CH_2Cl_2$ and chromatographed. Elution with $CH_2Cl_2$−petroleum ether (1:1) brought down a brown band, which upon removal of solvent yielded [Pd(tmen)($\eta^5$-7,8-$Me_2$-7,8-$C_2B_9H_9$)] (**6**) (0.24 g, 56%) as a brown powder. Anal. Calcd for $C_{10}H_{31}B_9N_2Pd$: C, 31.4; H, 8.1. Found: C, 31.5; H, 8.1.

**Synthesis of [Pd(PMe$_2$Ph)$_2$($\eta^5$-7,8-Me$_2$-7,8-C$_2$B$_9$H$_9$)].** A solution of [$PdCl_2(PMe_2Ph)_2$] (0.21 g, 0.46 mmol) in thf (40 mL) was treated with Tl[*closo*-1,2-$Me_2$-3,1,2-$TlC_2B_9H_9$] (0.27 g, 0.47 mmol) and the mixture stirred for 1 h. The mixture was then filtered through a Celite pad (4 × 2 cm), and the solvent was removed, producing a dark brown, oily solid. The latter was dissolved in 3 mL of $CH_2Cl_2$ and transferred to the top of a chromatography column. Elution with $CH_2Cl_2$−petroleum ether (1:3) produced an orange-red band, which upon solvent removal *in vacuo* gave [Pd($PMe_2Ph)_2$($\eta^5$-7,8-$Me_2$-7,8-$C_2B_9H_9$)] (**7**) (0.20 g, 79%) as a maroon powder. Anal. Calcd for $C_{12}H_{26}B_9P_2Pd$: C, 44.2; H, 6.9. Found: C, 45.1; H, 7.0.

**Table 5.** Atomic Positional Parameters (Fractional Coordinates × 10$^4$) and Equivalent Isotropic Displacement Parameters (Å$^2$ × 10$^3$) for the Unique Atoms of **3b**

| atom | $x$ | $y$ | $z$ | $U$(eq)[a] |
|---|---|---|---|---|
| Pd | 10429(1) | 3927(1) | 2609(1) | 34(1) |
| C(1) | 8413(6) | 3126(4) | 1444(5) | 36(1) |
| B(2) | 8844(8) | 4241(6) | 1121(7) | 39(2) |
| B(3) | 8866(7) | 5123(6) | 2222(6) | 44(2) |
| B(4) | 8707(8) | 4432(5) | 3352(7) | 37(2) |
| B(5) | 8573(7) | 3168(5) | 2787(6) | 29(1) |
| C(6) | 7127(8) | 3760(5) | 785(6) | 48(2) |
| B(7) | 6928(8) | 3071(6) | 1823(7) | 49(2) |
| B(8) | 7147(9) | 3825(6) | 3010(8) | 43(2) |
| B(9) | 7251(7) | 5015(5) | 2542(7) | 39(1) |
| B(10) | 7394(8) | 4954(5) | 1148(6) | 38(2) |
| B(11) | 6223(8) | 4200(6) | 1645(7) | 43(2) |
| C(2) | 8809(7) | 2262(5) | 852(6) | 53(2) |
| C(7) | 6485(7) | 3534(6) | −386(6) | 60(2) |
| C(11) | 12284(7) | 4660(6) | 2239(6) | 54(2) |
| C(12) | 12086(9) | 3821(6) | 1664(7) | 62(2) |
| C(13) | 12835(8) | 2913(6) | 1981(8) | 77(2) |
| C(14) | 13092(8) | 2679(6) | 3165(7) | 73(2) |
| C(15) | 11951(7) | 2932(5) | 3723(6) | 52(2) |
| C(16) | 11942(8) | 3766(6) | 4269(7) | 55(2) |
| C(17) | 12912(7) | 4579(6) | 4340(6) | 58(2) |
| C(18) | 13325(8) | 4810(7) | 3309(7) | 76(2) |

[a] Equivalent isotropic $U$ defined as one-third of the trace of the orthogonalized $U_{ij}$ tensor.

**Crystal Structure Determination and Refinement.** Orange parallelpiped crystals of **3b** were obtained by slow diffusion of petroleum ether into a concentrated $CH_2Cl_2$ solution of the compound at *ca.* −40 °C. The crystal and other experimental data are given in Table 4. Final cell dimensions used for the data collection were determined from the setting angle values of 25 accurately centered reflections. The stability of the crystal during the period of the data collection was monitored by measuring the intensities of three standard reflections every 2 h, and no significant decay was observed. After deletion of the check intensity data as well as the systematic absences, averaging of duplicate and equivalent measurements was performed and the data were corrected for Lorentz, polarization, and X-ray absorption effects, the latter based on empirical methods.

The Pd atom and several of the B and C atoms were initially located using direct methods, and Fourier difference syntheses were used to locate all remaining non-hydrogen atoms, which were refined with anisotropic thermal parameters. All hydrogen atoms were included at geometrically calculated positions (C−H = 0.96 Å and B−H = 1.10 Å[20]) and allowed to ride on the parent carbon or boron atom with fixed isotropic thermal parameters ($U_{iso}$ = 80 and 60 × 10$^{-3}$ Å$^2$, respectively). All calculations were performed using the SHELTXL-PC package of programs.[21] Atomic scattering factors were taken from ref 22. Final atomic positional parameters for the non-hydrogen atoms of **3b** are listed in Table 5.

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**Supplementary Material Available:** Complete tables of bond lengths and bond angles, anisotropic thermal parameters, and hydrogen atom parameters for **3b** (8 pages). Ordering information is given on any current masthead page.

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