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# Monocarbollide Complexes of Rhodium[†]

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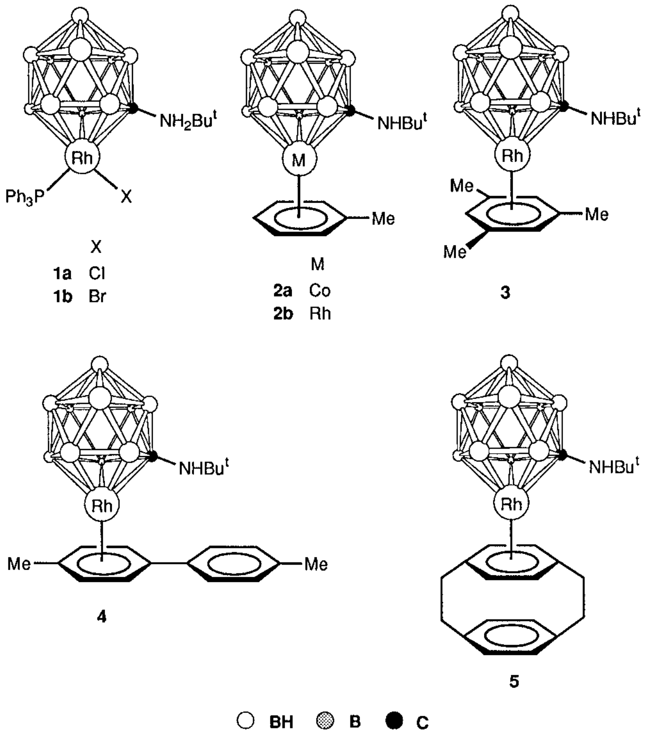
The rhodium sandwich complexes $[Rh(\eta^6\text{-arene})(\eta^5\text{-7-NHBu}^t\text{-7-CB}_{10}H_{10})]$ (arene = $C_6H_5$-Me (**2b**), $C_6H_3Me_3$-1,3,5 (**3**), $MeC_6H_4C_6H_4Me$-4,4′ (**4**), $[2_2](1,4)\text{-}C_{16}H_{16}$ (**5**)) have been prepared from reactions between 1:1 mol mixtures of the arenes and $[RhCl(PPh_3)(\eta^5\text{-7-NH}_2\text{Bu}^t\text{-7-CB}_{10}H_{10})]$ (**1a**) in $CH_2Cl_2$ in the presence of $AgBF_4$. The crystal structures of **3** and **5** have been determined by X-ray diffraction confirming that in these species the rhodium is pentahapto coordinated on one side by the formally three-electron-donor $\text{7-NHBu}^t\text{-7-CB}_{10}H_{10}$ and on the other in the hexahapto manner by a mesitylene molecule and one $C_6H_4$ ring of the cyclophane, respectively. The reaction between **4** and $[Mo(CO)_3(NCMe)_3]$ in THF gave the dirhodium complex $[Rh_2(CO)_2(\eta^5\text{-7-NH}_2\text{Bu}^t\text{-7-CB}_{10}H_{10})_2]$ (**6**), the structure of which has been established by X-ray diffraction. In the molecule two $Rh(CO)(\eta^5\text{-7-NH}_2\text{Bu}^t\text{-7-CB}_{10}H_{10})$ fragments are held together by a Rh−Rh bond which is spanned by two $B{-}H\rightharpoonup Rh$ two-electron three-center bonds employing in each $\overline{\text{CB}\mathit{B}\text{BB}}$ ring ligating a rhodium center a boron atom in one of the β-sites with respect to the carbon vertex. Reactions between **1a** and tris(pyrazolyl)methane in the presence of $TlPF_6$ and between **1a** and $K[HB(pzMe_2\text{-3,5})_3]$ ($HB(pzMe_2\text{-3,5})_3$ = hydrotris(3,5-dimethylpyrazolyl)borate) afforded respectively $[Rh\{HC(pz)_3\}(\eta^5\text{-7-NH}_2\text{Bu}^t\text{-7-CB}_{10}H_{10})][PF_2O_2]$ (**7**) and $[Rh\{HB(pzMe_2\text{-3,5})_3\}(\eta^5\text{-7-NH}_2\text{Bu}^t\text{-7-CB}_{10}H_{10})]$ (**8**). An X-ray diffraction study on **7** confirmed the pentahapto bonding of the charge-compensated $\text{7-NH}_2\text{Bu}^t\text{-7-CB}_{10}H_{10}$ ligand and the tridentate character of the tris(pyrazolyl)methane group and also established the anion as $[PF_2O_2]^-$ formed by hydrolysis of $[PF_6]^-$. The NMR data for the new compounds are reported and discussed.

## Introduction

We have recently reported that the 16-electron complexes $[RhX(PPh_3)(\eta^5\text{-7-NH}_2\text{Bu}^t\text{-7-CB}_{10}H_{10})]$ (X = Cl (**1a**), X = Br (**1b**)) (Chart 1) can be prepared by heating the compounds $[RhX(PPh_3)_3]$ with *nido*-$\text{7-NH}_2\text{Bu}^t\text{-7-CB}_{10}H_{12}$ in toluene.[1] During the course of this work the reaction between $[CoCl(PPh_3)_3]$ and *nido*-$\text{7-NH}_2\text{Bu}^t\text{-7-CB}_{10}H_{12}$ was also investigated. After a prolonged reflux time in toluene the product formed was unexpectedly $[Co(\eta^6\text{-}C_6H_5Me)(\eta^5\text{-7-NHBu}^t\text{-7-CB}_{10}H_{10})]$ (**2a**), rather than $[CoCl(PPh_3)(\eta^5\text{-7-NH}_2\text{Bu}^t\text{-7-CB}_{10}H_{10})]$, a cobalt analog of **1a**. Formation of **2a** is novel and must in the course of the reaction involve conversion of *nido*-$\text{7-NH}_2\text{Bu}^t\text{-7-CB}_{10}H_{12}$ into the three-electron-donor ligand $\eta^5\text{-7-NHBu}^t\text{-7-CB}_{10}H_{10}$. Studies[2] have shown that deprotonation of *nido*-$\text{7-NH}_2\text{Bu}^t\text{-7-CB}_{10}H_{12}$ readily occurs at the $NH_2$-$Bu^t$ group yielding the monoanion $[nido\text{-7-NHBu}^t\text{-7-CB}_{10}H_{12}]^-$.

### Chart 1



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[†] The compounds described in this paper have a rhodium atom incorporated into a *closo*-1-carba-2-rhodadodecaborane structure. However, to avoid a complicated nomenclature for the complexes reported, and to relate them to the many known rhodium species with $\eta^5$-coordinated cyclopentadienyl ligands, we 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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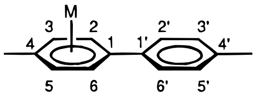
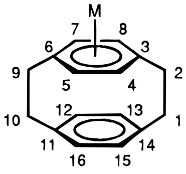
**Table 1. Analytical and Physical Data**

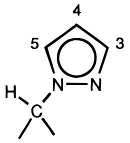
| | | | anal./%[a] | | |
|---|---|---|---|---|---|
| compd | color | yield/% | C | H | N |
| $[Rh(\eta^6\text{-}C_6H_5Me)(\eta^5\text{-}7\text{-}NHBu^t\text{-}7\text{-}CB_{10}H_{10})]$ (**2b**) | yellow | 40 | 36.1 (36.3) | 7.0 (7.1) | 3.4 (3.5) |
| $[Rh(\eta^6\text{-}C_6H_3Me_3\text{-}1,3,5)(\eta^5\text{-}7\text{-}NHBu^t\text{-}7\text{-}CB_{10}H_{10})]$ (**3**) | yellow | 71 | 39.2 (39.5) | 7.4 (7.6) | 3.2 (3.3) |
| $[Rh(\eta^6\text{-}MeC_6H_4C_6H_4Me\text{-}4,4')(\eta^5\text{-}7\text{-}NHBu^t\text{-}7\text{-}CB_{10}H_{10})]$ (**4**) | yellow | 41 | 46.6 (46.8) | 7.0 (7.0) | 2.7 (2.9) |
| $[Rh(\eta^6\text{-}[2_2](1,4)\text{-}C_{16}H_{16})(\eta^5\text{-}7\text{-}NHBu^t\text{-}7\text{-}CB_{10}H_{10})]$ (**5**) | yellow | 45 | 49.0 (49.1) | 7.0 (7.1) | 2.5 (2.7) |
| $[Rh_2(CO)_2(\eta^5\text{-}7\text{-}NH_2Bu^t\text{-}7\text{-}CB_{10}H_{10})_2]$ (**6**)[b] | red | 44 | 21.4 (21.6) | 6.2 (6.3) | 4.1 (4.2) |
| $[Rh\{HC(pz)_3\}(\eta^5\text{-}7\text{-}NH_2Bu^t\text{-}7\text{-}CB_{10}H_{10})][PF_2O_2]$ (**7**) | yellow | 57 | 31.9 (31.8)[c] | 5.6 (5.5) | 14.2 (14.4) |
| $[Rh\{HB(pzMe_2\text{-}3,5)_3\}(\eta^5\text{-}7\text{-}NH_2Bu^t\text{-}7\text{-}CB_{10}H_{10})]$ (**8**) | red | 50 | 39.5 (39.8) | 7.2 (7.2) | 16.1 (16.2) |

[a] Calculated values are given in parentheses. [b] IR spectrum measured in $CH_2Cl_2$, $\nu_{max}$(BH) ca. 2550 m br cm$^{-1}$, $\nu_{max}$(CO) 2056 s, 2036 s cm$^{-1}$. [c] Crystallizes with a molecule of acetone.

**Table 2. Hydrogen-1, Carbon-13, and Boron-11 NMR Data[a]**







| compd | $^1H/\delta$[b] | $^{13}C/\delta$[c] | $^{11}B/\delta$[d] |
|---|---|---|---|
| **2b** | 1.16 (s, 9 H, $Bu^t$), 2.55 (s, 3 H, Me), 3.01 (s br, 1 H, NH), 6.65−6.95 (m, 5 H, Ph) | 119.0 ($CB_{10}$, br), 116.1 ($C^1$(Ph)), 111.7, 110.7 ($C^{2,6}C^{3,5}$(Ph)), 108.9 ($C^4$(Ph)), 55.8 ($CMe_3$), 30.7 ($C\mathit{Me}_3$), 19.8 (Me) | 14.8 (1 B), 10.4 (2 B), 6.1 (2 B), −7.2 (1 B), −9.1 (2 B), −11.9 (2 B) |
| **3** | 1.14 (s, 9 H, $Bu^t$), 2.43 (s, 9 H, $Me_3$-1,3,5), 3.05 (s br, 1 H, NH), 6.29 (s, 3 H, $C_6H_3$) | 123.0 ($C^{1,3,5}(C_6H_3)$), 120.0 ($CB_{10}$, br), 111.2 ($C^{2,4,6}(C_6H_3)$), 55.8 ($CMe_3$), 30.7 ($C\mathit{Me}_3$), 19.4 ($Me_3$-1,3,5) | 13.2 (1 B), 10.6 (2 B), 7.3 (2 B), −7.1 (1 B), −9.0 (2 B), −12.4 (2 B) |
| **4** | 0.97 (s, 9 H, $Bu^t$), 2.45, 2.63 (s × 2, 6 H, $Me_2$-4,4′), 3.66 (s br, 1 H, NH), 6.70, 6.88 ($(AB)_2$, 4 H, $C_6H_4$, $J$(AB) = 7), 7.14, 7.67 ($(AB)_2$, 4 H, $C_6H_4$, $J$(AB) = 8) | 141.9 ($C^{4'}(C_6H_4)$), 130.5, 128.3 ($C^{2',6'}C^{3',5'}(C_6H_4)$), 129.4 ($C^{1'}(C_6H_4)$), 126.9 ($C^4(C_6H_4)$), 124.5 ($C^1(C_6H_4)$), 121.0 ($CB_{10}$, br), 110.4, 108.9 ($C^{2,6}C^{3,5}(C_6H_4)$), 55.7 ($CMe_3$), 30.5 ($C\mathit{Me}_3$), 21.3, 19.5 ($Me_2$-4,4′) | 14.1 (1 B), 11.0 (2 B), 7.0 (2 B), −7.2 (1 B), −9.0 (2 B), −12.0 (2 B) |
| **5** | 1.03 (s, 9 H, $Bu^t$), 3.06 (m, 4 H, $CH_2$), 3.16 (s br, 1 H, NH), 3.30 (m, 4 H, $CH_2$), 5.95, 6.76 (s × 2, 8 H, ArH) | 139.6 ($C^{11,14}(C_{16}H_{16})$), 138.7 ($CB_{10}$, br), 133.8 ($C^{12,13,15,16}(C_{16}H_{16})$), 133.2 ($C^{3,6}(C_{16}H_{16})$), 108.1 ($C^{4,5,7,8}(C_{16}H_{16})$), 55.3 ($CMe_3$), 34.6 ($C^{1,10}(C_{16}H_{16})$), 33.5 ($C^{2,9}(C_{16}H_{16})$), 30.7 ($C\mathit{Me}_3$) | 13.9 (1 B), 8.9 (2 B), 5.2 (2 B), −7.9 (1 B), −10.0 (2 B), −12.6 (2 B) |
| **6** | −6.38 (q br, 2 H, B−H⇀Rh, $J$(BH) = 76), 1.60 (s, 18 H, $Bu^t$), 6.01, 7.51 (s br × 2, 4 H, $NH_2$) | 189.1 (CO, d, $J$(RhC) = 78), 75.4 ($CB_{10}$, br), 68.2 ($CMe_3$), 28.7 ($C\mathit{Me}_3$) | 23.5 (1 B, B−H⇀Rh, $J$(HB) = 76), 2.8 (1 B), −2.9 (1 B), −8.8 (2 B), −10.3 (3 B), −19.2 (1 B), −21.2 (1 B) |
| **7** | 1.64 (s, 9 H, $Bu^t$), 6.76 (d, 2 H, $H^3$, $J(H^4H^3)$ = 3), 7.39 (d, 1 H, $H^3$, $J(H^4H^3)$ = 3), 8.27−8.41 (m, 3 H, $H^4$), 9.12 (d, 2 H, $H^5$, $J(H^4H^5)$ = 4), 9.13 (d, 1 H, $H^5$, $J(H^4H^5)$ = 4), 9.29 (s br, 2 H, $NH_2$), 10.36 (s, 1 H, CH)[e] | 149.0, 148.1, 137.2, 137.0, 111.1, 110.9 ($N_2C_3H_3$), 78.0 ($CB_{10}$, d br, $J$(RhC) = 14), 70.0 (CH), 56.7 ($CMe_3$), 33.7 ($C\mathit{Me}_3$)[e] | 13.3 (1 B), 12.1 (2 B), 8.1 (2 B), −0.3 (1 B), −10.0 (2 B), −12.1 (2 B)[f] |
| **8** | 1.22 (s, 9 H, $Bu^t$), 2.13 (s br, 18 H, $N_2C_3H\mathit{Me}_2$-3,5), 5.83 (s, 3 H, $N_2C_3\mathit{H}Me_2$-3,5), 11.40 (s br, 2 H, $NH_2$)[e] | 143.3 (vbr, $C^{3,5}(N_2\mathit{C}_3HMe_2\text{-}3,5)$), 103.9 ($C^4(N_2\mathit{C}_3HMe_2\text{-}3,5)$), 54.3 ($CMe_3$), 30.4 ($C\mathit{Me}_3$), 11.5 (br, $N_2C_3H\mathit{Me}_2$-3,5)[e,g] | 12.1 (1 B), 7.4 (2 B), 4.0 (2 B), −7.8 (1 B), −12.9 (2 B), −15.7 (3 B)[f] |

[a] Chemical shifts in ppm, coupling constants in Hz, and measurements in $CD_2Cl_2$ unless otherwise stated at room temperature. [b] Resonances for terminal BH protons occur as broad unresolved signals in the range $\delta$ ca. −2 to 3. [c] Hydrogen-1 decoupled; chemical shifts are positive to high frequency of $SiMe_4$. [d] Hydrogen-1 decoupled; chemical shifts are positive to high frequency of $BF_3{\cdot}Et_2O$ (external). B−H⇀Rh assignment made from fully coupled $^{11}B$ spectrum. [e] Measured in DMSO-$d_6$. [f] Measured in acetone-$d_6$. [g] Signal due to $\mathit{C}B_{10}$ nucleus not observed.

As far as we are aware, only two species structurally related to **2a** have been reported: $[Co(\eta^6\text{-}C_{10}H_{10})(CB_{10}H_{11})]$[3] and $[Co(\eta^6\text{-}C_6H_5Me)(\eta^5\text{-}7\text{-}CH(SiMe_3)_2\text{-}7\text{-}CB_{10}H_{10})]$.[4] The former was obtained in ca. 9% yield as an unexpected product of treating $Na[Co(\eta^5\text{-}C_5H_5)(\eta^5\text{-}CB_{10}H_{11})]$ with sodium naphthalide in tetrahydrofuran, followed by addition of $NaC_5H_5$ and $NiBr_2$ with air oxidation of the mixture. The latter was prepared in ca. 6% yield by reacting *nido*-7-$CH(SiMe_3)_2$-9-$SMe_2$-7-$CB_{10}H_{11}$ in toluene with cobalt vapor. In the three cobalt compounds monocarbon ligands, formally $\eta^5$-7-R-7-$CB_{10}H_{10}$, are bound to Co(III).

A rhodium analog $[Rh(\eta^6\text{-}C_6H_5Me)(\eta^5\text{-}7\text{-}NHBu^t\text{-}7\text{-}CB_{10}H_{10})]$ (**2b**) of the cobalt species **2a** is not formed by prolonged heating of the compounds **1** in toluene. Since monocarbon rhodacarborane compounds are relatively rare,[5] but are likely to have a role in further syntheses, we have devised a method for preparing **2b** and related complexes.

## Results and Discussion

Compound **1a** with toluene or mesitylene in $CH_2Cl_2$ on treatment with $AgBF_4$ affords the complexes $[Rh(\eta^6\text{-}C_6H_5Me)(\eta^5\text{-}7\text{-}NHBu^t\text{-}7\text{-}CB_{10}H_{10})]$ (**2b**) and [Rh($\eta^6$-$C_6H_3$-

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**Table 3. Selected Internuclear Distances (Å) and Angles (deg) for $[Rh(\eta^6\text{-}C_6H_3Me_3\text{-}1,3,5)(\eta^5\text{-}7\text{-}NHBu^t\text{-}7\text{-}CB_{10}H_{10})]$ (3) with Estimated Standard Deviations in Parentheses**

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| Rh−C(1) | 2.198(2) | Rh−B(2) | 2.168(2) | Rh−B(3) | 2.184(2) | Rh−B(4) | 2.183(2) |
| Rh−B(5) | 2.151(2) | Rh−C(6) | 2.323(2) | Rh−C(7) | 2.324(2) | Rh−C(8) | 2.349(2) |
| Rh−C(9) | 2.308(2) | Rh−C(10) | 2.298(2) | Rh−C(11) | 2.265(2) | C(1)−N(1) | 1.434(2) |
| N(1)−C(2) | 1.487(2) | N(1)−H(1) | 0.73(2) | C(2)−C(3) | 1.538(3) | C(2)−C(4) | 1.531(3) |
| C(2)−C(5) | 1.522(3) | C(6)−C(7) | 1.413(3) | C(6)−C(11) | 1.411(3) | C(6)−C(60) | 1.501(3) |
| C(7)−C(8) | 1.413(3) | C(8)−C(9) | 1.413(3) | C(8)−C(80) | 1.495(3) | C(9)−C(10) | 1.416(3) |
| C(10)−C(11) | 1.423(3) | C(10)−C(100) | 1.504(3) | | | | |

| | | | | | |
|---|---|---|---|---|---|
| B(5)−Rh−B(2) | 84.61(8) | B(5)−Rh−B(4) | 50.36(8) | B(2)−Rh−B(4) | 85.57(8) |
| B(5)−Rh−B(3) | 85.73(8) | B(2)−Rh−B(3) | 50.11(8) | B(4)−Rh−B(3) | 49.51(8) |
| B(5)−Rh−C(1) | 48.56(7) | B(2)−Rh−C(1) | 47.26(8) | B(4)−Rh−C(1) | 83.82(6) |
| B(3)−Rh−C(1) | 83.13(7) | C(11)−Rh−C(10) | 36.32(8) | C(11)−Rh−C(9) | 64.24(7) |
| C(10)−Rh−C(9) | 35.81(7) | C(11)−Rh−C(6) | 35.81(7) | C(10)−Rh−C(6) | 64.80(8) |
| C(9)−Rh−C(6) | 75.32(6) | C(11)−Rh−C(7) | 63.76(7) | C(10)−Rh−C(7) | 75.52(7) |
| C(9)−Rh−C(7) | 63.16(6) | C(6)−Rh−C(7) | 35.40(7) | C(11)−Rh−C(8) | 75.58(7) |
| C(10)−Rh−C(8) | 64.28(7) | C(9)−Rh−C(8) | 35.31(7) | C(6)−Rh−C(8) | 63.84(7) |
| C(7)−Rh−C(8) | 35.20(7) | C(1)−N(1)−C(2) | 127.9(2) | C(1)−N(1)−H(1) | 106(2) |
| C(2)−N(1)−H(1) | 110(2) | C(11)−C(6)−C(7) | 118.3(2) | C(11)−C(6)−Rh | 69.89(11) |
| C(7)−C(6)−Rh | 72.33(10) | C(6)−C(7)−C(8) | 121.9(2) | C(6)−C(7)−Rh | 72.26(11) |
| C(8)−C(7)−Rh | 73.38(10) | C(9)−C(8)−C(7) | 118.3(2) | C(9)−C(8)−Rh | 70.76(10) |
| C(7)−C(8)−Rh | 71.42(10) | C(8)−C(9)−C(10) | 121.9(2) | C(8)−C(9)−Rh | 73.93(10) |
| C(10)−C(9)−Rh | 71.73(10) | C(9)−C(10)−C(11) | 117.9(2) | C(9)−C(10)−Rh | 72.47(10) |
| C(11)−C(10)−Rh | 70.58(10) | C(6)−C(11)−C(10) | 121.8(2) | C(6)−C(11)−Rh | 74.31(10) |
| C(10)−C(11)−Rh | 73.10(11) | | | | |

$Me_3$-1,3,5)($\eta^5$-7-NHBu$^t$-7-$CB_{10}H_{10}$)] (**3**), respectively. These arene complexes were isolated after column chromatography and characterized by the data given in Tables 1 and 2. Since the charge-compensated precursor **1a** contains the four-electron-donor $\eta^5$-7-$NH_2$Bu$^t$-7-$CB_{10}H_{10}$ and the neutral products **2b** and **3** contain the three-electron-ligand $\eta^5$-7-NHBu$^t$-7-$CB_{10}H_{10}$, deprotonation of the *nido*-carborane has occurred with elimination of AgCl and presumably $[PHPh_3][BF_4]$. As mentioned above, deprotonation of the $\eta^5$-7-$NH_2$Bu$^t$-7-$CB_{10}H_{10}$ group has been observed previously in the formation of **2a**. Moreover, if **1a** is treated with an excess of CNBu$^t$ a similar conversion of the 7-$NH_2$Bu$^t$-7-$CB_{10}H_{10}$ group into 7-NHBu$^t$-7-$CB_{10}H_{10}$ occurs affording either [Rh(CNBu$^t$)($PPh_3$)($\eta^5$-7-NHBu$^t$-7-$CB_{10}H_{10}$)] or [Rh(CNBu$^t$)$_2$($PPh_3$)($\eta^5$-7-NHBu$^t$-7-$CB_{10}H_{10}$)].[1]

In order to establish fully the structure of **3** a single-crystal X-ray diffraction study was undertaken. Selected bond distances and angles are given in Table 3, and the molecule is shown in Figure 1. The rhodium atom is coordinated on one side by the $C_6H_3Me_3$-1,3,5 group in the expected $\eta^6$-bonding mode and on the other by the open face of the *nido*-7-NHBu$^t$-7-$CB_{10}H_{10}$ cage in the $\eta^5$-manner. The distances from the Rh atom to the atoms of the CBBBB ring (Rh−C(1) = 2.198(2), Rh−B(2) = 2.168(2), Rh−B(3) = 2.184 (2), Rh−B(4) = 2.183(2), Rh−B(5) = 2.151(2) Å) are very similar to the corresponding distances in [Rh(CNBu$^t$)($PPh_3$)($\eta^5$-7-NHBu$^t$-7-$CB_{10}H_{10}$)] (Rh−C(1) = 2.103(3), Rh−B(2) = 2.200(3), Rh−B(3) = 2.204(4), Rh−B(4) = 2.218(3), Rh−B(5) = 2.171(3) Å).[1] The position of H(1) was located and refined with N(1)−H(1) = ca. 0.73(2) Å, to be compared with ca. 0.83(4) Å in [Rh(CNBu$^t$)($PPh_3$)($\eta^5$-7-NHBu$^t$-7-$CB_{10}H_{10}$)]. The C(1)−N(1) distance in the latter (1.413(4) Å) is also comparable with that in **3** (1.434(2) Å).

The NMR spectra of **3** are in agreement with the structure established by X-ray diffraction. Thus the $^1$H NMR spectrum of **3** shows a broad peak corresponding in intensity to one proton at $\delta$ 3.05 as expected for the NH group. The corresponding resonance in [Rh(CNBu$^t$)($PPh_3$)($\eta^5$-7-NHBu$^t$-7-$CB_{10}H_{10}$)] is at $\delta$ 3.15 whereas the $NH_2$ protons in **1a** resonate at $\delta$ 8.30.[1] In the $^{13}C\{^1H\}$ NMR spectrum of **3** a signal at $\delta$ 120.0 is assigned to the cage carbon. In the spectrum of [Rh(CNBu$^t$)($PPh_3$)($\eta^5$-7-NHBu$^t$-7-$CB_{10}H_{10}$)] the corresponding peak is at $\delta$ 118.7. The resonances for the cage carbon nuclei in complexes with $\eta^5$-7-$NH_2$Bu$^t$-7-$CB_{10}H_{10}$ ligands are considerably more shielded, *e.g.*, that for **1a** is at $\delta$ 75.8.[1] Other peaks in the $^1$H and $^{13}C\{^1H\}$ NMR spectra of **3** are as expected. The $^{11}B\{^1H\}$ NMR spectrum (Table 2) shows a pattern of six peaks of relative intensities 1:2:2:1:2:2 as anticipated for the local symmetry of the cage. The NMR data for **2b** are similar and thus in agreement with its formulation.

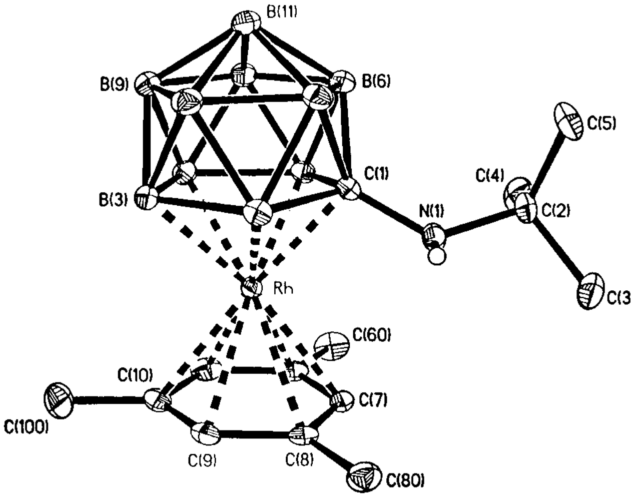

**Figure 1.** Structure of [Rh($\eta^6$-$C_6H_3Me_3$-1,3,5)($\eta^5$-7-NHBu$^t$-7-$CB_{10}H_{10}$)] (**3**), showing the crystallographic labeling scheme. Hydrogen atoms, except H(1), are omitted for clarity, and thermal ellipsoids are shown at the 40% probability level.

The reaction between **1a** and 4,4′-$MeC_6H_4C_6H_4Me$ in the presence of $AgBF_4$ was next investigated. The complex [Rh($\eta^6$-$MeC_6H_4C_6H_4Me$-4,4′)($\eta^5$-7-NHBu$^t$-7-$CB_{10}H_{10}$)] (**4**) was obtained and characterized by the data given in Tables 1 and 2. Resonances in the NMR spectra were as expected. The signal at $\delta$ 121.0 in the $^{13}C\{^1H\}$ NMR spectrum is attributable to the cage $CB_{10}$ nucleus, and in the $^1$H NMR spectrum the peak at $\delta$ 3.66 is due to the NH group. In the $^{13}C\{^1H\}$ NMR spectrum (Table

**Table 4. Selected Internuclear Distances (Å) and Angles (deg) for $[Rh(\eta^6\text{-}[2_2](1,4)\text{-}C_{16}H_{16})(\eta^5\text{-}7\text{-}NHBu^t\text{-}7\text{-}CB_{10}H_{10})]$ (5) with Estimated Standard Deviations in Parentheses**

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| Rh−C(1) | 2.213(2) | Rh−B(2) | 2.155(3) | Rh−B(3) | 2.180(3) | Rh−B(4) | 2.164(3) |
| Rh−B(5) | 2.166(3) | Rh−C(6) | 2.503(2) | Rh−C(7) | 2.307(2) | Rh−C(8) | 2.239(2) |
| Rh−C(9) | 2.386(2) | Rh−C(10) | 2.274(2) | Rh−C(11) | 2.323(2) | C(1)−N | 1.429(3) |
| N−C(2) | 1.492(3) | N−H(1) | 0.81(3) | C(2)−C(3) | 1.539(3) | C(2)−C(4) | 1.533(3) |
| C(2)−C(5) | 1.531(3) | C(6)−C(7) | 1.410(3) | C(6)−C(11) | 1.413(4) | C(6)−C(12) | 1.503(3) |
| C(7)−C(8) | 1.411(3) | C(8)−C(9) | 1.414(3) | C(9)−C(10) | 1.412(3) | C(9)−C(14) | 1.507(3) |
| C(10)−C(11) | 1.403(3) | C(12)−C(13) | 1.592(3) | C(13)−C(16) | 1.516(4) | C(14)−C(15) | 1.586(3) |
| C(15)−C(19) | 1.518(4) | C(16)−C(17) | 1.394(4) | C(16)−C(21) | 1.399(4) | C(17)−C(18) | 1.387(4) |
| C(18)−C(19) | 1.404(4) | C(19)−C(20) | 1.393(4) | C(20)−C(21) | 1.388(4) | | |

| | | | | | |
|---|---|---|---|---|---|
| B(2)−Rh−B(4) | 85.63(11) | B(2)−Rh−B(5) | 84.08(10) | B(4)−Rh−B(5) | 51.16(10) |
| B(2)−Rh−B(3) | 49.69(10) | B(4)−Rh−B(3) | 50.02(10) | B(5)−Rh−B(3) | 86.24(10) |
| B(2)−Rh−C(1) | 48.08(9) | B(4)−Rh−C(1) | 83.93(10) | B(5)−Rh−C(1) | 47.20(9) |
| B(3)−Rh−C(1) | 83.63(9) | C(8)−Rh−C(10) | 64.47(9) | C(8)−Rh−C(7) | 36.13(8) |
| C(10)−Rh−C(7) | 74.85(9) | C(8)−Rh−C(11) | 75.28(9) | C(10)−Rh−C(11) | 35.50(8) |
| C(7)−Rh−C(11) | 62.47(8) | C(8)−Rh−C(9) | 35.41(8) | C(10)−Rh−C(9) | 35.16(8) |
| C(7)−Rh−C(9) | 62.87(8) | C(11)−Rh−C(9) | 62.55(8) | C(8)−Rh−C(6) | 62.05(8) |
| C(10)−Rh−C(6) | 61.42(8) | C(7)−Rh−C(6) | 33.78(8) | C(11)−Rh−C(6) | 33.79(8) |
| C(9)−Rh−C(6) | 71.15(8) | C(1)−N−C(2) | 127.0(2) | C(1)−N−H(1) | 111(2) |
| C(2)−N−H(1) | 110(2) | C(7)−C(6)−C(11) | 116.5(2) | C(7)−C(6)−C(12) | 122.2(2) |
| C(11)−C(6)−C(12) | 120.5(2) | C(7)−C(6)−Rh | 65.44(13) | C(11)−C(6)−Rh | 66.10(13) |
| C(12)−C(6)−Rh | 149.8(2) | C(6)−C(7)−C(8) | 120.9(2) | C(6)−C(7)−Rh | 80.78(14) |
| C(8)−C(7)−Rh | 69.33(13) | C(7)−C(8)−C(9) | 120.2(2) | C(7)−C(8)−Rh | 74.53(13) |
| C(9)−C(8)−Rh | 77.98(14) | C(10)−C(9)−C(8) | 116.9(2) | C(10)−C(9)−C(14) | 120.8(2) |
| C(8)−C(9)−C(14) | 121.8(2) | C(10)−C(9)−Rh | 68.08(13) | C(8)−C(9)−Rh | 66.61(13) |
| C(14)−C(9)−Rh | 144.3(2) | C(11)−C(10)−C(9) | 120.7(2) | C(11)−C(10)−Rh | 74.16(14) |
| C(9)−C(10)−Rh | 76.77(14) | C(10)−C(11)−C(6) | 120.8(2) | C(10)−C(11)−Rh | 70.34(13) |
| C(6)−C(11)−Rh | 80.11(14) | C(6)−C(12)−C(13) | 110.2(2) | C(16)−C(13)−C(12) | 112.6(2) |
| C(9)−C(14)−C(15) | 110.2(2) | C(19)−C(15)−C(14) | 112.8(2) | C(17)−C(16)−C(21) | 116.9(2) |
| C(17)−C(16)−C(13) | 120.9(2) | C(21)−C(16)−C(13) | 120.8(2) | C(18)−C(17)−C(16) | 121.1(2) |
| C(17)−C(18)−C(19) | 120.6(2) | C(20)−C(19)−C(18) | 116.6(2) | C(20)−C(19)−C(15) | 121.9(2) |
| C(18)−C(19)−C(15) | 120.1(2) | C(21)−C(20)−C(19) | 121.3(2) | C(20)−C(21)−C(16) | 120.6(2) |

2) assignments of the resonances due to the $C_6H_4C_6H_4$ nuclei are made on the basis that the shifts for carbons in the ring ligating the metal would be expected to be to lower frequency than those of the uncoordinated ring.[6,7]

There is current interest in cyclophanes as ligands[8] and so a 1:1 mol equiv mixture of **1a** and $[2_2](1,4)$-cyclophane in $CH_2Cl_2$ was treated with $AgBF_4$. After column chromatography the complex $[Rh(\eta^6\text{-}[2_2](1,4)\text{-}C_{16}H_{16})(\eta^5\text{-}7\text{-}NHBu^t\text{-}7\text{-}CB_{10}H_{10})]$ (**5**) was isolated, data for which are given in Tables 1 and 2. However, before discussion of the NMR spectra, the results of an X-ray diffraction study are presented. The molecule is shown in Figure 2 and selected bond distances and angles are given in Table 4.

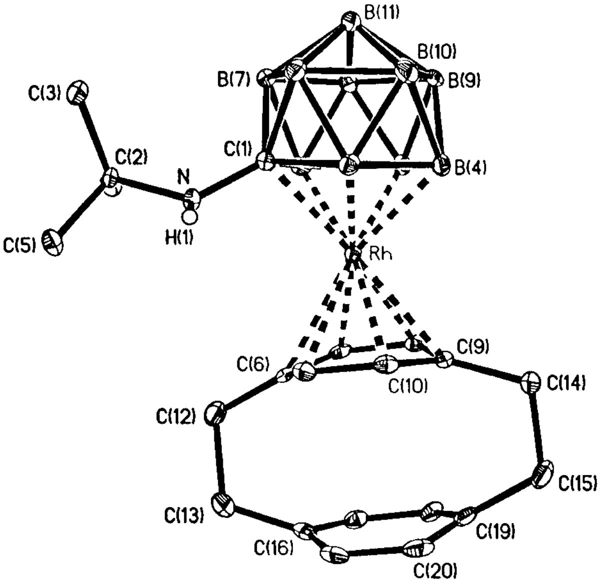

**Figure 2.** Structure of $[Rh(\eta^6\text{-}[2_2](1,4)\text{-}C_{16}H_{16})(\eta^5\text{-}7\text{-}NHBu^t\text{-}7\text{-}CB_{10}H_{10})]$ (**5**), showing the crystallographic labeling scheme. Hydrogen atoms, except H(1), are omitted for clarity, and thermal ellipsoids are shown at the 40% probability level.

The metal atom is $\eta^6$-coordinated on one side by one of the $C_6H_4$ rings of the cyclophane and on the other in the usual $\eta^5$-manner by the $7\text{-}NHBu^t\text{-}7\text{-}CB_{10}H_{10}$ group. Comparison of the data in Table 4 with that in Table 3 reveals that the distances between the rhodium atoms and the $CB_4$ rings in the species **5** and **3** are very similar. Moreover, the C−C bond distances within the ligating arene rings are essentially the same. In both free and $\eta^6$-$C_6$ rings of $[2_2](1,4)$-cyclophanes there is normally deviation from planarity toward a boat conformation, with four carbon atoms coplanar and the two carbons bound to the $CH_2CH_2$ linkages bent out of this plane. This is indeed observed for the free ring in **5**, but the deviation in the coordinated ring appears to be more severe with Rh−C(6) = 2.503(2) and Rh−C(9) = 2.386(2) Å. The remaining four Rh−C(arene) bond distances lie in the range 2.239(2)−2.323(2) Å, with Rh−C(8) and Rh−C(10) the shortest of these. This is seen to correspond to an additional deformation in the form of a partial "slippage" of the rhodium atom toward the carbon atoms C(8), C(9), and C(10) of the coordinated ring. The cause of this additional strain is uncertain, although crystal packing forces may play an important role. The atom H(1) of the $NHBu^t$ group in **5** was located and its position refined, the N−H(1) distance (ca. 0.81(3) Å) being comparable with that for **3** (ca. 0.73(2) Å). Interestingly, **5** is isolobal with the cation of the

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salt [Rh($\eta^5$-$C_5Me_5$)($\eta^6$-[$2_2$](1,4)-$C_{16}H_{16}$)][$BF_4$]$_2$ reported by Plitzko and Boekelheide.[9]

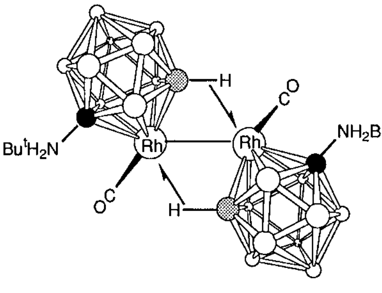
With the structure of **5** having been established, the NMR spectra are readily interpretable. The $^1$H NMR spectrum shows a diagnostic broad peak for the N*H*Bu$^t$ group at $\delta$ 3.16. The $CH_2$ protons appear as two multiplet resonances at $\delta$ 3.06 and 3.30. In the $^{13}$C-{$^1$H} NMR spectrum the resonance for the cage carbon nucleus is observed as a broad peak at $\delta$ 138.7, while the signals for the carbons of the $C_6H_4$ ring ligating the rhodium are assigned to the arene peaks at lower frequency ($\delta$ 133.2 and 108.1) than those for the uncoordinated ring ($\delta$ 139.6 and 133.8). In the $^{13}$C NMR spectrum of [Rh($\eta^5$-$C_5Me_5$)($\eta^6$-[$2_2$](1,4)-$C_{16}H_{16}$)][$BF_4$]$_2$ resonances at $\delta$ 141.3 and 102.4 were assigned to the coordinated $C_6H_4$ ring and peaks at $\delta$ 142.7 and 135.7 to the uncoordinated ring.[9] The number of signals for the arene rings in the $^{13}$C{$^1$H} NMR spectra of both these compounds correspond to local $C_{2v}$ symmetry of the cyclophane ligands. This is easily achieved by rapid spinning of the arene about the axis through the rhodium and the arene ring centroids; however, it is not unknown for cages in metallacarboranes to also spin about a similar axis.[10] In the $^{11}$B{$^1$H} NMR spectrum of **5** (Table 2) the pattern and relative intensities of the peaks observed (1:2:2:1:2:2) conform with the mirror symmetry of the cage.

A major objective for the synthesis of compounds **4** and **5** was to establish whether the arene rings in these species which are not coordinated to the rhodium would bind another metal−ligand fragment. Accordingly, **5** was treated with **1a** and $AgBF_4$ in attempt to obtain a product in which both $C_6H_4$ rings of the cyclophane formed a bridge between two Rh($\eta^5$-7-NHBu$^t$-7-$CB_{10}H_{10}$) moieties. The desired reaction did not occur, and in this context it is interesting to note that it was found that the fragment [Co($\eta^5$-$C_5Me_5$)]$^{2+}$, isolobal with the group Rh($\eta^5$-7-NHBu$^t$-7-$CB_{10}H_{10}$), did not complex with the free arene rings in the complexes [Co($\eta^5$-$C_5Me_5$)($\eta^6$-[$2_n$]-(1,4)-$C_{16}H_{16}$)][$BF_4$]$_2$.[9]

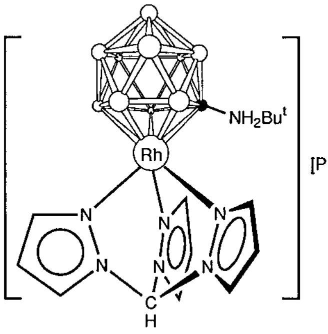
In an attempt to add a metal ligand fragment to complex **4** the latter was treated with [Mo(CO)$_3$-(NCMe)$_3$] in THF at room temperature. A reaction occurred, but the desired product [MoRh(CO)$_3$($\eta^6$,$\eta^6$-$MeC_6H_4C_6H_4Me$-4,4′)($\eta^5$-7-NHBu$^t$-7-$CB_{10}H_{10}$)] in which both $C_6H_4$ rings are hexahapto bonded to the rhodium and molybdenum centers, respectively, was not obtained. The new compound was identified as [$Rh_2$-(CO)$_2$($\eta^5$-7-$NH_2Bu^t$-7-$CB_{10}H_{10}$)$_2$] (**6**) (Chart 2) only after a single-crystal X-ray diffraction study. The results are listed in Table 5 with the molecule shown in Figure 3.

Hence the compound is a dirhodium species, with two B−H⇀Rh groups bridging the metal−metal bond, a structural feature previously found in several dimetal complexes formed by dimerization of ML($\eta^5$-$C_2B_9H_9R_2$) (L = phosphine or CO, R = H or Me, M = Co,[11] Rh,[12] or Ni[13]) fragments. However, **6** appears to be the first monocarbollide complex of this type. Both H(4) and H(24) were located from the difference Fourier maps. The Rh(1)−Rh(2) separation (2.6993(4) Å) may be compared with those found in [$Rh_2$($PPh_3$)$_2$($\eta^5$-7,8-$C_2B_9H_{11}$)$_2$] (2.763(1) Å) and [$Rh_2$($PPh_3$)$_2$($\eta^5$-7-Ph-7,8-$C_2B_9H_{10}$)$_2$] (2.791(1) Å).[12b] In **6** both B−H⇀Rh bonds involve boron atoms $\beta$ to the carbon atom in the $\overline{\mathrm{CB}\mathit{B}\mathrm{BB}}$ rings ligating the rhodium centers, with both the cage carbon atoms lying in positions *anti* to the CO ligands (C(6)−Rh(1)−C(1) = 122.12(9), C(7)−Rh(2)−C(21) = 119.48(9)°), a feature consistently found in similar structures.[11−13] The stereospecific formation of this particular isomer is intriguing as a maximum of ten are possible (three each for the αα- and $\beta\beta$-cage configurations and four for the α$\beta$-cage systems). In reality this number may be less as there is no structural precedent for a cage carbon atom lying *syn* to the noncage ligand on the same metal atom. Interestingly, [$Rh_2$($PPh_3$)$_2$($\eta^5$-7,8-$C_2B_9H_{11}$)$_2$] is also formed as a single isomer out of a possible six.[12b] It is less symmetric than **6** because one cage employs a $B_\alpha$−H⇀Rh linkage of the $\overline{\mathrm{CC}\mathit{B}\mathrm{BB}}$ ring

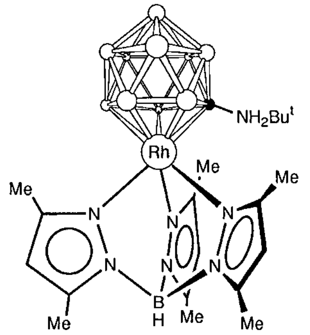
**Chart 2**



**6**



**7**



**8**

○ BH ◎ B ● C

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**Table 5. Selected Internuclear Distances (Å) and Angles (deg) for [$Rh_2(CO)_2(\eta^5$-7-$NH_2Bu^t$-7-$CB_{10}H_{10})_2$] (6) with Estimated Standard Deviations in Parentheses**

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| Rh(1)−C(6) | 1.916(2) | Rh(1)−B(3) | 2.183(3) | Rh(1)−B(4) | 2.194(3) | Rh(1)−B(2) | 2.197(3) |
| Rh(1)−B(5) | 2.219(3) | Rh(1)−C(1) | 2.280(2) | Rh(1)−B(24) | 2.336(3) | Rh(1)−Rh(2) | 2.6993(4) |
| Rh(1)−H(24) | 1.74(3) | Rh(2)−C(7) | 1.943(2) | Rh(2)−B(24) | 2.182(3) | Rh(2)−B(23) | 2.188(3) |
| Rh(2)−B(25) | 2.192(3) | Rh(2)−B(22) | 2.208(3) | Rh(2)−C(21) | 2.260(2) | Rh(2)−B(4) | 2.319(3) |
| Rh(2)−H(4) | 1.74(3) | C(1)−N(1) | 1.519(3) | N(1)−C(2) | 1.506(5) | N(1)−C(2′) | 1.580(7) |
| N(1)−H(1A) | 0.87(2) | N(1)−H(1B) | 0.87(2) | N(1)−H(1A′) | 0.87(2) | N(1)−H(1B′) | 0.87(2) |
| B(4)−H(4) | 1.22(3) | C(21)−N(2) | 1.516(3) | N(2)−C(22) | 1.552(3) | N(2)−H(2A) | 0.78(3) |
| N(2)−H(2B) | 0.94(3) | B(24)−H(24) | 1.22(3) | C(6)−O(6) | 1.138(3) | C(7)−O(7) | 1.132(3) |

| | | | | | |
|---|---|---|---|---|---|
| C(6)−Rh(1)−B(3) | 96.12(10) | C(6)−Rh(1)−B(4) | 139.17(10) | C(6)−Rh(1)−B(2) | 89.38(10) |
| C(6)−Rh(1)−B(5) | 166.91(10) | C(6)−Rh(1)−C(1) | 122.12(9) | C(6)−Rh(1)−B(24) | 92.85(9) |
| C(6)−Rh(1)−Rh(2) | 104.03(7) | B(3)−Rh(1)−Rh(2) | 81.90(7) | B(4)−Rh(1)−Rh(2) | 55.42(7) |
| B(2)−Rh(1)−Rh(2) | 131.93(7) | B(5)−Rh(1)−Rh(2) | 89.04(7) | C(1)−Rh(1)−Rh(2) | 132.07(6) |
| B(24)−Rh(1)−Rh(2) | 50.74(6) | C(6)−Rh(1)−H(24) | 90.7(8) | B(3)−Rh(1)−H(24) | 162.5(9) |
| B(4)−Rh(1)−H(24) | 116.1(8) | B(2)−Rh(1)−H(24) | 145.9(9) | B(5)−Rh(1)−H(24) | 92.1(8) |
| C(1)−Rh(1)−H(24) | 108.7(8) | B(24)−Rh(1)−H(24) | 30.6(8) | Rh(2)−Rh(1)−H(24) | 80.8(8) |
| C(7)−Rh(2)−B(24) | 143.56(10) | C(7)−Rh(2)−B(23) | 100.57(10) | C(7)−Rh(2)−B(25) | 164.01(10) |
| C(7)−Rh(2)−B(22) | 89.91(10) | C(7)−Rh(2)−C(21) | 119.48(9) | C(7)−Rh(2)−B(4) | 91.10(10) |
| C(7)−Rh(2)−Rh(1) | 105.99(7) | B(24)−Rh(2)−Rh(1) | 55.97(7) | B(23)−Rh(2)−Rh(1) | 82.56(7) |
| B(25)−Rh(2)−Rh(1) | 89.61(7) | B(22)−Rh(2)−Rh(1) | 131.95(7) | C(21)−Rh(2)−Rh(1) | 133.55(6) |
| B(4)−Rh(2)−Rh(1) | 51.16(6) | C(7)−Rh(2)−H(4) | 87.5(9) | B(24)−Rh(2)−H(4) | 116.7(9) |
| B(23)−Rh(2)−H(4) | 163.7(9) | B(25)−Rh(2)−H(4) | 91.4(9) | B(22)−Rh(2)−H(4) | 145.4(9) |
| C(21)−Rh(2)−H(4) | 108.0(9) | B(4)−Rh(2)−H(4) | 31.1(9) | Rh(1)−Rh(2)−H(4) | 81.6(9) |
| C(2)−N(1)−C(1) | 131.5(2) | C(1)−N(1)−C(2′) | 124.8(3) | C(21)−N(2)−C(22) | 127.6(2) |
| O(6)−C(6)−Rh(1) | 175.6(2) | O(7)−C(7)−Rh(2) | 176.4(2) | | |

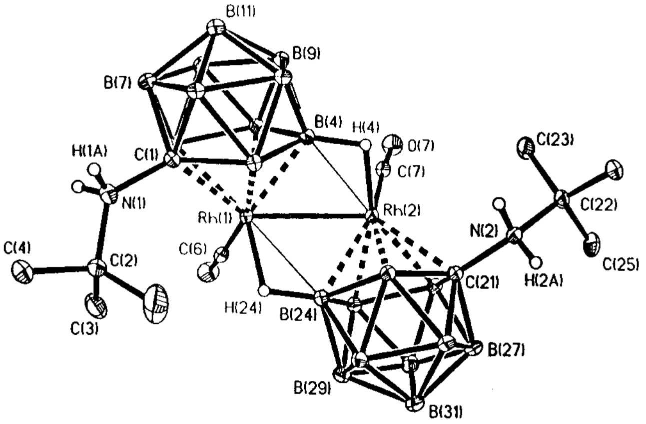

**Figure 3.** Structure of [$Rh_2(CO)_2(\eta^5$-7-$NH_2Bu^t$-7-$CB_{10}H_{10})_2$] (**6**), showing the crystallographic labeling scheme. Hydrogen atoms shown were either located (H(2A), H(2B), H(4), and H(24)) or included in calculated positions (H(1A) and H(1B)). Thermal ellipsoids are shown at the 40% probability level.

coordinated to the metal and the other forms a $B_\beta-H\rightharpoonup Rh$ bridge from the $\overline{CCBBB}$ ring. In [$Rh_2(PPh_3)_2(\eta^5$-7-Ph-7,8-$C_2B_9H_{10})_2$], however, both $B-H\rightharpoonup Rh$ interactions involve $B_\beta-H\rightharpoonup Rh$ bridges. A recently determined structure of an isomer of [$Co_2(CO)_2(\eta^5$-7,8-$C_2B_9H_{11})_2$][11] revealed that both three-center two-electron bonds in this molecule were of the type $B_\alpha-H\rightharpoonup Co$. Evidently dimerization of metallacarborane fragments can occur employing a variety of different $B-H\rightharpoonup M$ bridging modes. The influence of changing R from H to Me in $M(\eta^5$-7,8-$R_2$-7,8-$C_2B_9H_9)$ systems has led to the observation that the $B_\beta-H$ bond is further activated toward formation of exopolyhedral $B-H\rightharpoonup M$ and B−M bonds.[14] However, much less is known about the comparative reactivity of $B_\alpha-H$ and $B_\beta-H$ bonds in $M(\eta^5$-7-$NR_3$-7-$CB_{10}H_{10})$ groups, and further studies with regard to this are in progress.

The NMR data for **6** (Table 2) are in agreement with the results of the X-ray diffraction study. In the $^1H$ NMR spectrum broad singlets at $\delta$ 6.01 and 7.51 with relative intensities corresponding to two protons each are attributable to the $NH_2$ groups. It is noteworthy that these chemical shifts are to appreciably higher frequency than those of the NH groups in the species **2b**−**5**, in agreement with previous results.[1] A diagnostic quartet resonance is seen for the $B-H\rightharpoonup Rh$ bridge systems at $\delta$ −6.38 with $J(BH) = 76$ Hz. Correspondingly, in the $^{11}B\{^1H\}$ NMR spectrum there is a peak at $\delta$ 23.5 for these groups which in a fully coupled $^{11}B$ spectrum becomes a doublet with a $^1H-^{11}B$ coupling of 76 Hz.[14a] The molecule possesses axial $C_2$ symmetry with the rotation axis bisecting the Rh(1)−Rh(2) bond. This results in the appearance of only one resonance for the bridge systems in these spectra.

The pathway by which compound **6** is formed from **4** is not known. Perhaps reaction proceeds initially by attack of the nitrogen lone pair in **4** on the molybdenum atom of [$Mo(CO)_3(NCMe)_3$], displacing a MeCN molecule. Coordination of such a lone pair to another metal center has precedent in the dimeric complex [$N(PPh_3)_2$][$Rh_2(\mu$-Br)$(\mu$-$\sigma,\eta^5$-7-$NH_2$-7-$CB_{10}H_{10})_2(PPh_3)_2$].[15] In the current situation, it would bring the Mo atom in close proximity to the free ring of the biphenyl ligand, and from there, possible formation of the desired complex [$MoRh(CO)_3(\eta^6,\eta^6$-$MeC_6H_4C_6H_4Me$-4,4′)$(\eta^5$-7-$NHBu^t$-7-$CB_{10}H_{10})$] might occur. Being very unstable, a CO molecule could transfer from molybdenum to the rhodium center, as the biphenyl ring is displaced from the latter metal. Loss of a $Mo(CO)_x(\eta^6$-$MeC_6H_4C_6H_4Me$-4,4′) moiety might then follow, although no such species was identified. A complicating feature of the reaction is the conversion of the 7-$NHBu^t$-7-$CB_{10}H_{10}$ group in **4** into the 7-$NH_2Bu^t$-7-$CB_{10}H_{10}$ ligand in **6** arising through protonation at the nitrogen atom of the cage $NHBu^t$ substituent. The proton source is almost certainly water present during the procedure, despite rigorous

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**Table 6. Selected Internuclear Distances (Å) and Angles (deg) for $[Rh\{HC(pz)_3\}(\eta^5\text{-}7\text{-}NH_2Bu^t\text{-}7\text{-}CB_{10}H_{10})][PF_2O_2]$ (7) with Estimated Standard Deviations in Parentheses**

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| Rh(1)−N(6) | 2.118(4) | Rh(1)−B(2) | 2.143(5) | Rh(1)−B(5) | 2.150(5) | Rh(1)−C(1) | 2.169(4) |
| Rh(1)−B(3) | 2.170(5) | Rh(1)−B(4) | 2.184(5) | Rh(1)−N(4) | 2.237(3) | Rh(1)−N(2) | 2.244(4) |
| C(1)−N(1) | 1.519(5) | C(1)−B(6) | 1.718(6) | C(1)−B(7) | 1.726(6) | C(1)−B(2) | 1.743(6) |
| C(1)−B(5) | 1.766(6) | N(1)−C(2) | 1.561(6) | N(1)−H(1A) | 0.80(5) | N(1)−H(1B) | 0.94(5) |
| C(2)−C(5) | 1.521(7) | C(2)−C(4) | 1.523(7) | C(2)−C(3) | 1.524(7) | P(1)−O(1) | 1.415(4) |
| P(1)−O(2) | 1.425(5) | P(1)−F(2) | 1.534(4) | P(1)−F(1) | 1.545(5) | O(1)···H(1A) | 1.985 |

| | | | | | |
|---|---|---|---|---|---|
| N(6)−Rh(1)−B(2) | 131.0(2) | N(6)−Rh(1)−B(5) | 122.9(2) | B(2)−Rh(1)−B(5) | 84.8(2) |
| N(6)−Rh(1)−C(1) | 168.59(14) | B(2)−Rh(1)−C(1) | 47.7(2) | B(5)−Rh(1)−C(1) | 48.3(2) |
| N(6)−Rh(1)−B(3) | 89.1(2) | B(2)−Rh(1)−B(3) | 50.2(2) | B(5)−Rh(1)−B(3) | 85.7(2) |
| C(1)−Rh(1)−B(3) | 83.3(2) | N(6)−Rh(1)−B(4) | 85.8(2) | B(2)−Rh(1)−B(4) | 85.5(2) |
| B(5)−Rh(1)−B(4) | 49.4(2) | C(1)−Rh(1)−B(4) | 82.8(2) | B(3)−Rh(1)−B(4) | 49.9(2) |
| N(6)−Rh(1)−N(4) | 82.48(13) | B(2)−Rh(1)−N(4) | 142.2(2) | B(5)−Rh(1)−N(4) | 90.0(2) |
| C(1)−Rh(1)−N(4) | 103.37(14) | B(3)−Rh(1)−N(4) | 166.5(2) | B(4)−Rh(1)−N(4) | 118.6(2) |
| N(6)−Rh(1)−N(2) | 82.95(14) | B(2)−Rh(1)−N(2) | 86.3(2) | B(5)−Rh(1)−N(2) | 151.3(2) |
| C(1)−Rh(1)−N(2) | 107.53(14) | B(3)−Rh(1)−N(2) | 109.0(2) | B(4)−Rh(1)−N(2) | 156.3(2) |
| N(4)−Rh(1)−N(2) | 80.50(13) | C(1)−N(1)−C(2) | 125.7(3) | C(1)−N(1)−H(1A) | 107(4) |
| C(2)−N(1)−H(1A) | 104(4) | C(1)−N(1)−H(1B) | 105(3) | C(2)−N(1)−H(1B) | 107(3) |
| H(1A)−N(1)−H(1B) | 106(4) | O(1)−P(1)−O(2) | 121.1(3) | O(1)−P(1)−F(2) | 109.8(2) |
| O(2)−P(1)−F(2) | 114.3(4) | O(1)−P(1)−F(1) | 107.2(3) | O(2)−P(1)−F(1) | 105.6(5) |
| F(2)−P(1)−F(1) | 95.2(2) | | | | |

drying of solvents, and it is noteworthy that the X-ray diffraction study revealed water in part of the crystal lattice. Interestingly, compound **6** was not formed by treating solutions of **4** with CO.

In the $^{13}C\{^1H\}$ NMR spectrum of **6** the resonance for the cage-carbon nuclei occurs at $\delta$ 75.4. This is at an appreciably lower frequency than the corresponding signals in the spectra of **2b**−**5**. This result, like the relative chemical shifts for NH and $NH_2$ groups in the $^1H$ NMR spectra discussed above, correlates with the ligand in **6** being the charge-compensated group $7\text{-}NH_2Bu^t\text{-}7\text{-}CB_{10}H_{10}$ rather than $7\text{-}NHBu^t\text{-}7\text{-}CB_{10}H_{10}$.[1] A characteristic doublet is observed at $\delta$ 189.1 ($J(RhC) = 78$ Hz) for the equivalent CO ligands, the presence of which is also revealed by bands in the IR spectrum at 2056 and 2036 $cm^{-1}$. Other peaks in the $^{13}C\{^1H\}$ NMR spectrum (Table 2) are as expected.

Isolation of the compounds **2a**−**5** raised the possibility as to whether complexes could be similarly prepared from **1a** in which rhodium is ligated on one side by a monocarbon carborane cage and on the other by tris(pyrazolyl)methane or hydrotris(pyrazolyl)borate groups. It was of particular interest to establish whether any sandwich complexes formed were species with three-electron-donor $\eta^5\text{-}7\text{-}NHBu^t\text{-}7\text{-}CB_{10}H_{10}$ ligands or molecules with charge compensated four-electron-donor $\eta^5\text{-}7\text{-}NH_2Bu^t\text{-}7\text{-}CB_{10}H_{10}$ groups.

A THF solution of **1a** and $HC(pz)_3$ after treatment with $TlPF_6$ gave yellow crystals of the salt $[Rh\{HC(pz)_3\}(\eta^5\text{-}7\text{-}NH_2Bu^t\text{-}7\text{-}CB_{10}H_{10})][PF_2O_2]$ (**7**). Although the NMR data for this product quickly identified the two ligands in the cation, the nature of the anion was puzzling until the results of an X-ray diffraction study became available. This study revealed that the anion was unexpectedly $[PF_2O_2]^-$, probably formed during crystallization of the salt from acetone. There is ample precedent in metal complex chemistry for the partial hydrolysis of $[PF_6]^-$ anions to give $[PF_2O_2]^-$, particularly with acetone as solvent.[16−18]

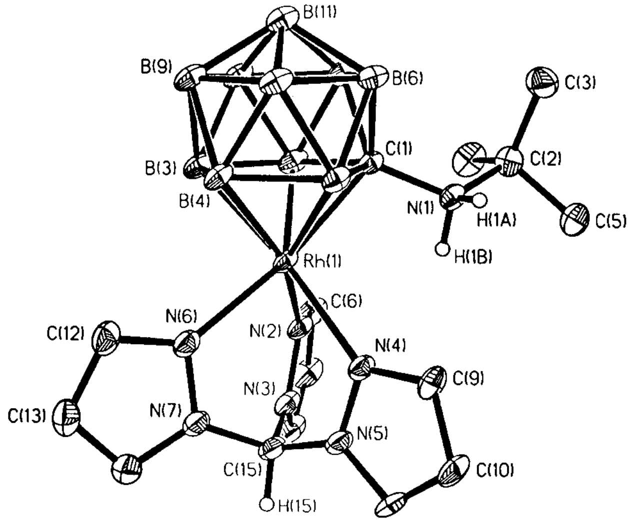

**Figure 4.** Structure of the cation of $[Rh\{HC(pz)_3\}(\eta^5\text{-}7\text{-}NH_2Bu^t\text{-}7\text{-}CB_{10}H_{10})][PF_2O_2]$ (**7**), showing the crystallographic labeling scheme. Hydrogen atoms shown were either located (H(1A) and H(1B)) or included in a calculated position (H(15)). Thermal ellipsoids are shown at the 40% probability level.

The structure of the cation is shown in Figure 4, and selected bond distances and angles are listed in Table 6. The rhodium atom is coordinated by the $7\text{-}NH_2Bu^t\text{-}7\text{-}CB_{10}H_{10}$ group as it is in the species **1**. The hydrogen atoms H(1A) and H(1B) of the $NH_2$ group were located from the difference Fourier maps with N(1)−H(1A) = ca. 0.80(5) Å and N(1)−H(1B) = ca. 0.94(5) Å. Interestingly, probable hydrogen bonding was detected between H(1A) and an oxygen atom of the anion (O(1)−H(1A) = 1.985 Å). The distances between the rhodium and the atoms of the $\overline{CBBBB}$ ring in **7** (Rh(1)−C(1) = 2.169(4), Rh(1)−B(2) = 2.143(5), Rh(1)−B(3) = 2.170(5), Rh(1)−B(4) = 2.184(5), Rh(1)−B(5) = 2.150(5) Å) are similar to those found in **1b** (Rh(1)−C(1) = 2.240(5), Rh(1)−B(2) = 2.129(6), Rh(1)−B(3) = 2.182(6), Rh(1)−B(4) = 2.179(6), Rh(1)−B(5) = 2.131(6) Å).[1]

The tris(pyrazolyl)methane ligand is coordinated to the rhodium via the three nitrogen atoms in the usual tridentate manner.[19] The Rh(1)−N(6) distance (2.118(4) Å) is somewhat shorter than the Rh(1)−N(2) (2.244-

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(4) Å) and Rh(1)−N(4) (2.237(3) Å) separations. This feature may be due to the N(6) atom lying transoid to the cage-carbon atom C(1) (N(6)−Rh(1)−C(1) = 168.6 (1)°) carrying the bulky $NH_2Bu^t$ substituent whereas pyrazolyl rings containing N(2) and N(4) are closer to the latter.

The NMR data (Table 2) for **7** are in agreement with the structure established in the solid state. The atoms N(1), C(1), Rh(1), N(6), and N(7) lie in a plane of symmetry, with two of the pyrazolyl rings, those containing N(2)N(3) and N(4)N(5), lying symmetrically on either side of this plane. The cage is evidently unable to rotate about the rhodium atom in solution at ambient temperatures. In accord with this local symmetry, in the $^{13}C\{^1H\}$ NMR spectrum the ring carbons give rise to six resonances at $\delta$ 149.0, 148.1, 137.2, 137.0, 111.1, and 110.9. A diagnostic signal for the cage-carbon occurs at $\delta$ 78.0, a doublet with $J(RhC) = 14$ Hz, and having a chemical shift in the region expected for a species with a zwitterionic $7\text{-}NH_2Bu^t\text{-}7\text{-}CB_{10}H_{10}$ group. A resonance at $\delta$ 70.0 is assigned to the $H\mathit{C}(pz)_3$ carbon. The signal for the proton bound to this carbon is seen in the $^1H$ NMR spectrum at $\delta$ 10.36, and that for the $NH_2$ group is observed at $\delta$ 9.29, in the region characteristic for this group. Signals for the protons of the pz rings occur in a 2:1:3:2:1 relative intensity pattern (Table 2). On the basis of the local symmetry of the $HC(pz)_3$ group, discussed above, a 2:1:2:1:2:1 pattern would be expected. However, the resonance corresponding to three protons was a multiplet at $\delta$ 8.27−8.41 and is assigned to an overlap of two signals due to the $H^4$ nuclei.

The reaction between **1a** and $K[HB(pzMe_2\text{-}3,5)_3]$ in THF gave the neutral complex $[Rh\{HB(pzMe_2\text{-}3,5)_3\}(\eta^5\text{-}7\text{-}NH_2Bu^t\text{-}7\text{-}CB_{10}H_{10})]$ (**8**). A similar methodology has been used previously in the synthesis of the species $[Rh\{HB(pz)_3\}(\eta^5\text{-}7,n\text{-}C_2B_9H_{11})]$ ($n$ = 8 or 9) from $[RhCl(PPh_3)_2(\eta^5\text{-}7,n\text{-}C_2B_9H_{11})]$ and $K[HB(pz)_3]$.[20] The monocarbon and dicarbon rhodacarborane species are isolobal.

The presence of the $7\text{-}NH_2Bu^t\text{-}7\text{-}CB_{10}H_{10}$ ligand in **8** was clearly revealed by the NMR spectra. In the $^1H$ NMR spectrum a characteristic peak for the $NH_2$ group protons is seen at $\delta$ 11.40. The $^{11}B\{^1H\}$ NMR spectrum had six signals with a relative intensity pattern 1:2:2:1:2:3, corresponding as expected to the presence of 11 boron nuclei. This is consistent with the local symmetry of the cage and with the resonance for the $H\mathit{B}(pzMe_2\text{-}3,5)_3$ group at $\delta$ 12.1 or −7.8 or coincident with a peak for two cage-borons at $\delta$ −15.7.[20]

Interest focuses on the $^1H$ and $^{13}C\{^1H\}$ resonances for the $pzMe_2$-3,5 rings in **8**. If the group $[HB(pzMe_2\text{-}3,5)_3]^-$ functions as a tridentate ligand and the cage does not rotate rapidly about the rhodium atom, then a mirror plane of symmetry would encompass the rhodium atom, the $C_3N_2$ atoms of one ring, and the cage-carbon atom and its N substituent. Two $pzMe_2$-3,5 groups would lie symmetrically on opposite sides of this plane. This would lead to two peaks of 1:2 relative intensity for the methine protons and four signals of relative intensity 3:3:6:6 for the $Me_2$-3,5 groups in the $^1H$ NMR spectrum indicating two chemically equivalent $pzMe_2$-3,5 rings and one unique.[21] Correspondingly, the $^{13}C\{^1H\}$ NMR spectrum should show four peaks for the Me groups and six for the $\mathit{C}_3N_2$-ring nuclei. However, the $^1H$ and $^{13}C\{^1H\}$ NMR spectra of **8** measured at ambient temperatures displayed appreciably fewer resonances than expected. Thus in the $^1H$ NMR spectrum only one resonance ($\delta$ 2.13), integrating to 18 protons, was seen for the $Me_2$-3,5 groups and one ($\delta$ 5.83) for the three methine protons of the pyrazolyl rings. The former signal was clearly broad in comparison to the signal for the $Bu^t$ methyl protons, and therefore, a variable-temperature NMR experiment was conducted. Upon cooling of the sample to −90 °C, a $^1H$ NMR spectrum revealed that the peak due to the pyrazolyl methyls had split into two very broad peaks at $\delta$ 2.27 and 1.59, integrating 12:6, and the signal due to the methine protons had also broadened significantly. The low-temperature limit could not be reached, and had it been possible to measure this spectrum at a lower temperature, we suspect that these broad signals would have split further into the expected number of peaks discussed above. Evidently a dynamic process is occurring in solution at temperatures above −90 °C as has also been observed in many poly(pyrazolyl)borate transition metal complexes.[22] Sharp resonances in the $^1H$ NMR spectra of $[Rh\{HB(pz)_3\}(\eta^5\text{-}7,n\text{-}C_2B_9H_{11})]$ attributable to three equivalent pyrazolyl rings indicates stereochemical nonrigidity in solution for these species also.[20] It was suggested that the dynamic process likely involves a dissociation of one of the metal−nitrogen bonds. In this pathway the hydrotris(pyrazolyl)borate group would in the intermediate become bidentate (16-electron rhodium complex) rather than tridentate (18-electron rhodium complex) as in the ground state. Although rapid rotation of the cage at higher temperatures cannot be ruled out, the steric demands of the methyl groups in the pyrazolyl rings of **8** may promote destabilization of the tridentate bonding mode. The $^1H$ and $^{13}C\{^1H\}$ NMR spectra of **8** were measured at 90 °C in DMSO-$d_6$. The signal due to the pyrazolyl methyl protons in the former spectrum sharpened up considerably compared with the room-temperature spectrum but did not split into two signals as one might expect, this possibly being due to fortuitous coincidence of resonances. In the latter spectrum, the signals due to the $C^3$ and $C^5$ carbon nuclei of the pyrazolyl rings, and that due to the pyrazolyl methyls, while slightly sharper than at room temperature, were still noticeably broader than the remaining signals in this spectrum. This may again be due to separate resonances which are merely close in chemical shift not being resolved, but this spectrum may not provide reliable data as the onset of decomposition was evident after prolonged heating.

## Conclusions

As far as we are aware the neutral molecules **2b**−**5** are the first mixed-sandwich complexes of rhodium with arenes and a monocarbon carborane ligand. All contain the formally three-electron-donor $\eta^5\text{-}7\text{-}NHBu^t\text{-}7\text{-}CB_{10}H_{10}$ and are isolobal with the several previously known[23] cationic cyclopentadienyl complexes [Rh(arene)($\eta^5$-

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**Table 7. Data for X-ray Crystal Structure Analyses**

| | **3** | **5** | **6** | **7** |
|---|---|---|---|---|
| cryst dimens/mm | 0.45 × 0.45 × 0.48 | 0.10 × 0.18 × 0.40 | 0.10 × 0.25 × 0.60 | 0.20 × 0.25 × 0.50 |
| formula | $C_{14}H_{32}B_{10}NRh$ | $C_{21}H_{36}B_{10}NRh$ | $C_{12}H_{42}B_{20}N_2O_2Rh_2\cdot0.39H_2O$ | $C_{15}H_{31}B_{10}F_2N_7O_2PRh\cdot(CH_3)_2CO$ |
| $M_r$ | 425.42 | 513.52 | 675.52 | 679.53 |
| cryst color, shape | yellow, cube | yellow, needle | red, plate | yellow, prism |
| cryst system | orthorhombic | orthorhombic | monoclinic | monoclinic |
| space group | $P2_12_12_1$ | *Pbca* | $P2_1/c$ | $P2_1/n$ |
| $T$/K | 138 | 138 | 138 | 173 |
| $a$/Å | 15.595(1) | 12.020(2) | 22.217(4) | 11.152(2) |
| $b$/Å | 15.925(2) | 17.588(5) | 10.108(2) | 14.713(3) |
| $c$/Å | 8.369(2) | 22.922(5) | 13.689(2) | 18.993(5) |
| $\beta$/deg | | | 107.13(2) | 103.10(2) |
| $V$/Å$^3$ | 2078.4(6) | 4846(2) | 2937.7(7) | 3035.3(12) |
| Z | 4 | 8 | 4 | 4 |
| $d_{calcd}$/g cm$^{-3}$ | 1.360 | 1.408 | 1.527 | 1.487 |
| $\mu$(Mo K$\alpha$)/mm$^{-1}$ | 0.819 | 0.716 | 1.143 | 0.663 |
| $F$(000)/e | 872 | 2112 | 1352 | 1384 |
| 2$\theta$ range/deg | 5.1−50.1 | 4.5−50.0 | 4.5−50.1 | 4.7−50.1 |
| data frame collcn time (per frame/s, overall/h) | 10, ca. 6 | 30, ca. 13 | 20, ca. 10 | 10, ca. 6 |
| no. rflns measd | 9841 | 21300 | 13311 | 13832 |
| no. indep rflns | 3641 | 4257 | 5063 | 5319 |
| refinement method | full-matrix least-squares on all $F^2$ data | full-matrix least-squares on all $F^2$ data | full-matrix least-squares on all $F^2$ data | full-matrix least-squares on all $F^2$ data |
| final residuals | wR2 = 0.036[a] (R1 = 0.014)[b] | wR2 = 0.060[a] (R1 = 0.025)[b] | wR2 = 0.056[a] (R1 = 0.022)[b] | wR2 = 0.135[a] (R1 = 0.048)[b] |
| weighting factors | $a$ = 0.0190; $b$ = 0.5468[a] | $a$ = 0.0188; $b$ = 7.4217[a] | $a$ = 0.0244; $b$ = 3.6121[a] | $a$ = 0.0609; $b$ = 8.8003[a] |
| goodness of fit on $F^2$ | 1.137 | 1.090 | 1.097 | 1.152 |
| final electron density diff features (max/min)/e Å$^{-3}$ | 0.21, −0.28 | 0.31, −0.32 | 0.46, −0.44 | 1.75, −0.90 |

[a] Structure was refined on $F_o^2$ using all data: $wR2 = [\sum[w(F_o^2 - F_c^2)^2]/\sum w(F_o^2)^2]^{1/2}$, where $w^{-1} = [\sigma^2(F_o^2) + (aP)^2 + bP]$ and $P = [\max(F_o^2,0) + 2F_c^2]/3$. [b] The value in parentheses is given for comparison with refinements based on $F_o$ with a typical threshold of $F_o > 4\sigma(F_o)$ and $R1 = \sum||F_o| - |F_c||/\sum|F_o|$ and $w^{-1} = [\sigma^2(F_o) + gF_o^2]$.

$C_5R_5)]^{2+}$. The mode of formation of **2b**−**5** further indicates the readiness with which the $\eta^5$-7-$NH_2Bu^t$-7-$CB_{10}H_{10}$ group deprotonates at the exopolyhedral N atom. However, the deprotonation is clearly reversible as indicated by the formation of **6** from **4**, and the syntheses of complexes **7** and **8** indicate that the fragment Rh($\eta^5$-7-$NH_2Bu^t$-7-$CB_{10}H_{10}$) is capable of existing in a stable system, without subsequent deprotonation.

## Experimental Section

**General Considerations.** All experiments were conducted under an atmosphere of dry nitrogen using Schlenk tube techniques. Solvents were freshly distilled under nitrogen from appropriate drying agents before use. Light petroleum refers to that fraction of boiling point 40−60 °C. Chromatography columns (ca. 60 cm long and 1 cm in diameter) were packed with silica gel (Aldrich, 70−230 mesh). The NMR measurements were recorded at the following frequencies: $^1$H at 360.13, $^{13}$C at 90.56, and $^{11}$B at 115.55 MHz. The reagent [RhCl($PPh_3$)($\eta^5$-7-$NH_2Bu^t$-7-$CB_{10}H_{10}$)] (**1a**) was made as previously described.[1]

**Syntheses of the Complexes [Rh(arene)($\eta^5$-7-$NHBu^t$-7-$CB_{10}H_{10}$)].** (i) A $CH_2Cl_2$ (10 mL) solution of **1a** (60 mg, 0.10 mmol) and toluene (1.0 mL, 9.4 mmol) were combined, and the solution and was treated with $AgBF_4$ (20 mg, 0.10 mmol) and stirred for 10 h. After filtration, solvent was reduced in volume *in vacuo* to ca. 2 mL and chromatographed. Elution with $CH_2Cl_2$−light petroleum (4:1) removed a yellow band from the column. Evaporation of solvent from the eluate and crystallization of the residue from $CH_2Cl_2$−light petroleum (5 mL, 1:9) gave yellow microcrystals of [Rh($\eta^6$-$C_6H_5Me$)($\eta^5$-7-$NHBu^t$-7-$CB_{10}H_{10}$)] (**2b**) (16 mg).

(ii) Using a similar procedure, a mixture of 1,3,5-$C_6H_3Me_3$ (2.1 mL, 15 mmol) and **1a** (120 mg, 0.20 mmol) dissolved in $CH_2Cl_2$ (15 mL) was treated with $AgBF_4$ (39 mg, 0.20 mmol). After the reagents were stirred for 5 h, filtration followed by reduction in volume of solvent and chromatography gave a yellow eluate from which [Rh($\eta^6$-$C_6H_3Me_3$-1,3,5)($\eta^5$-7-$NHBu^t$-7-$CB_{10}H_{10}$)] (**3**) (60 mg) was obtained.

(iii) Similarly, **1a** (120 mg, 0.20 mmol) and 4,4′-$MeC_6H_4C_6H_4$-Me (37 mg, 0.20 mmol) in $CH_2Cl_2$ (15 mL) with $AgBF_4$ (40 mg, 0.20 mmol) after stirring the mixture for 5 h gave [Rh($\eta^6$-$MeC_6H_4C_6H_4Me$-4,4′)($\eta^5$-7-$NHBu^t$-7-$CB_{10}H_{10}$)] (**4**) (40 mg).

(iv) Likewise, **1a** (180 mg, 0.30 mmol) and [$2_2$](1,4)-$C_{16}H_{16}$ (63 mg, 0.30 mmol) in $CH_2Cl_2$ (15 mL) treated with $AgBF_4$ (60 mg, 0.30 mmol) after stirring for 12 h gave yellow microcrystals of [Rh($\eta^6$-[$2_2$](1,4)-$C_{16}H_{16}$)($\eta^5$-7-$NHBu^t$-7-$CB_{10}H_{10}$)] (**5**) (70 mg) after workup in the usual manner.

**Synthesis of [$Rh_2(CO)_2$($\eta^5$-7-$NH_2Bu^t$-7-$CB_{10}H_{10}$)$_2$].** A THF (15 mL) solution of **4** (50 mg, 0.10 mmol) was treated with [Mo$(CO)_3$(NCMe)$_3$] (30 mg, 0.10 mmol) and the mixture stirred for 16 h. Solvent was reduced in volume *in vacuo* to ca. 2 mL and the mixture chromatographed. Elution with THF−$CH_2Cl_2$ (1:10) yielded a red fraction which after removal of solvent *in vacuo* and crystallization from $CH_2Cl_2$−light petroleum (10 mL, 1:8) gave red microcrystals of [$Rh_2(CO)_2$($\eta^5$-7-$NH_2Bu^t$-7-$CB_{10}H_{10}$)$_2$] (**6**) (15 mg).

**Synthesis of [Rh{HC(pz)$_3$}($\eta^5$-7-$NH_2Bu^t$-7-$CB_{10}H_{10}$)][$PF_2O_2$].** A THF (15 mL) solution containing **1a** (60 mg, 0.10 mmol) and HC(pz)$_3$ (22 mg, 0.10 mmol) was treated with $TlPF_6$ (35 mg, 0.10 mmol) and the mixture stirred for 12 h. After filtration the solvent was removed *in vacuo* and the residue crystallized from acetone−light petroleum (5 mL, 1:9) to afford yellow microcrystals of [Rh{HC(pz)$_3$}($\eta^5$-7-$NH_2Bu^t$-7-$CB_{10}H_{10}$)][$PF_2O_2$] (**7**) (35 mg).

**Synthesis of [Rh{HB(pzMe$_2$-3,5)$_3$}($\eta^5$-7-$NH_2Bu^t$-7-$CB_{10}H_{10}$)].** A THF (15 mL) solution of **1a** (60 mg, 0.10 mmol) was treated with K[HB(pzMe$_2$-3,5)$_3$] (34 mg, 0.10 mmol) and the mixture stirred for 24 h. Solvent was reduced in volume *in vacuo* to ca. 3 mL and the mixture chromatographed. Elution with THF−$CH_2Cl_2$ (1:2) gave a red fraction, which after removal of solvent *in vacuo* afforded red microcrystals of [Rh{HB(pzMe$_2$-3,5)$_3$}($\eta^5$-7-$NH_2Bu^t$-7-$CB_{10}H_{10}$)] (**8**) (30 mg).

**Crystal Structure Determinations and Refinements.** Crystals of **3**, **5**, and **6** were grown by diffusion of light

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(23) Sharp, P. R. In *Comprehensive Organometallic Chemistry II*; Abel, E. W., Stone, F. G. A., Wilkinson, G., Eds.; Pergamon Press: Oxford, U.K., 1995; Vol. 8 (Atwood, J. D., Ed.), Chapter 2.

petroleum into $CH_2Cl_2$ solutions of the complexes. Crystals of **7** were grown by diffusion of light petroleum into an acetone solution of the complex. Low-temperature data sets were collected with the crystals mounted on glass fibers. Compound **6** crystallized with 0.39 of a molecule of water per molecule of complex. Compound **7** crystallized with one molecule of acetone per molecule of complex.

Data were collected on a Siemens SMART CCD area-detector 3-circle diffractometer using Mo Kα X-radiation $\bar{\lambda} = 0.710\,73$ Å. For three settings of $\phi$, narrow data "frames" were collected for 0.3° increments in $\omega$. In all cases 1321 frames of data were collected affording rather more than a hemisphere of data. The substantial redundancy in data allows empirical absorption corrections to be applied using multiple measurements of equivalent reflections. The data frames were integrated using SAINT,[24] and the structures were solved by conventional direct methods. The structures were refined by full-matrix least-squares on all $F^2$ data using Siemens SHELXTL 5.03[24] and with anisotropic thermal parameters for all non-hydrogen atoms.

Hydrogen atoms in **3** and **5** were included in calculated positions (except for the hydrogen atoms H(1)) and allowed to ride on the parent boron or carbon atoms with isotropic thermal parameters ($U_{\rm iso} = 1.2U_{\rm iso\ equiv}$ of the parent atom except for methyl protons where $U_{\rm iso} = 1.3U_{\rm iso\ equiv}$). The NH hydrogen atoms H(1) in both **3** and **5** were located in final electron density difference syntheses and their positions and isotropic thermal parameters refined. For **6** the agostic hydrogen atoms H(4) and H(24) and the $NH_2Bu^t$ hydrogens H(2A) and H(2B) were located in electron density difference syntheses and their positions and isotropic thermal parameters refined. Positional disorder of the other $NH_2Bu^t$ group was found to have occurred about the pivotal nitrogen atom N(1). The nitrogen N(1) and two methyl carbon atoms C(4) and C(5) had a 100% site occupation, while the quaternary carbon atom C(2) and the methyl carbon C(3) were found, after site occupancy refinement, to occupy the positions shown in Figure 3, in only 61% of the lattice. In the remaining 39% of the lattice these two carbon atoms were disposed in the opposite direction (C(2′) and C(3′)), with a water molecule occupying the hole subsequently generated. Hence the oxygen atom O(99) of the water molecule was also refined with a site occupation of 39%. No hydrogen atoms could be located or calculated for O(99), but they were assigned in calculated positions for the $NH_2Bu^t$ group carbon and nitrogen atoms, with both possible disordered positions taken into account, *i.e.* four hydrogen atom positions for the $NH_2$ group (H(1A) and H(1B) at 61% and H(1A′) and H(1B′) at 39%, with $U_{\rm iso} = 1.2U_{\rm iso\ equiv}$ of the parent nitrogen atom), three each for carbon atoms C(3) and C(3′), and six each for carbons C(4) and C(5), with $U_{\rm iso} = 1.3U_{\rm iso\ equiv}$ of the parent carbon atoms. All remaining hydrogen atoms (cage B−H hydrogens and methyl hydrogens of the nondisordered $Bu^t$ group) were included in calculated positions and allowed to ride on the parent boron or carbon atoms with isotropic thermal parameters ($U_{\rm iso} = 1.2U_{\rm iso\ equiv}$ of the parent boron atoms or $U_{\rm iso} = 1.5U_{\rm iso\ equiv}$ of the parent carbon atoms). Hydrogen atoms in **7** (excluding H(1A) and H(1B)) were included in calculated positions and allowed to ride on the parent boron or carbon atoms with isotropic thermal parameters ($U_{\rm iso} = 1.2U_{\rm iso\ equiv}$ of the parent atom except for methyl protons where $U_{\rm iso} = 1.3U_{\rm iso\ equiv}$). The $NH_2$ hydrogen atoms H(1A) and H(1B) were located in final electron density difference syntheses and their positions and isotropic thermal parameters refined. Large residual peaks (maximum 1.75 e Å$^{-3}$) were located close to the rhodium atom Rh(1) and are attributed to poor crystal quality. All calculations were carried out on Silicon Graphics Iris, Indigo, or Indy computers.

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**Supporting Information Available:** Tables of complete atomic coordinates and *U* values, bond lengths and angles, and anisotropic thermal parameters and an ORTEP diagram for **3** and **5**−**7** (49 pages). Ordering information is given on any current masthead page.

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[24] Siemens X-ray Instruments, Madison, WI.