# Carborane Complexes of Nickel and Platinum: Synthesis and Protonation Reactions of Anionic Allyl(carborane) Species[†]

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*Received November 24, 1993*[⊗]

Reaction of $Na_2[$*nido*$\text{-}7,8\text{-}Me_2\text{-}7,8\text{-}C_2B_9H_9]$ with $[Ni_2(\mu\text{-}Br)_2(\eta^3\text{-}C_3H_5)_2]$ or $[Pt_2(\mu\text{-}Br)_2(\eta^3\text{-}C_3H_5)_2]$ in thf (tetrahydrofuran) gives the anionic species $[M(\eta^3\text{-}C_3H_5)(\eta^5\text{-}7,8\text{-}Me_2\text{-}7,8\text{-}C_2B_9H_9)]^-$ (M = Ni or Pt) which have been isolated as their $[NEt_4]^+$ and $[N(PPh_3)_2]^+$ salts **1a**–**1d**. In the presence of suitable substrate molecules (L = CO or $CNBu^t$), protonation ($HBF_4{\cdot}Et_2O$) of the reagents **1** at low temperatures gives the neutral compounds $[ML_2(\eta^5\text{-}7,8\text{-}Me_2\text{-}7,8\text{-}C_2B_9H_9)]$ (**2a**, M = Ni, L = CO; **2b**, M = Ni, L = $CNBu^t$; **2c**, M = Pt, L = CO; **2d**, M = Pt, L = $CNBu^t$). Dichloromethane solutions of the dicarbonylnickel complex **2a** slowly decompose through loss of carbon monoxide to give a mixture of the isomeric dimetal species $[Ni_2(CO)_2(\eta^5\text{-}7,8\text{-}Me_2\text{-}7,8\text{-}C_2B_9H_9)_2]$ (**3a**), $[Ni_2(CO)_2(\eta^5\text{-}7,8\text{-}Me_2\text{-}7,8\text{-}C_2B_9H_9)(\eta^5\text{-}2,7\text{-}Me_2\text{-}2,7\text{-}C_2B_9H_9)]$ (**3b**), and $[Ni_2(CO)_2(\eta^5\text{-}2,7\text{-}Me_2\text{-}2,7\text{-}C_2B_9H_9)_2]$ (**3c**). The molecular structure of **3c**, in which the carborane CMe groups of both cages occupy vertices in different layers of the $\eta^5\text{-}C_2B_9$ *nido*-cages, was established by X-ray diffraction. Crystals are monoclinic, space group *C*2/*c* (No. 15), with $a = 21.498(5)$ Å, $b = 7.722(2)$ Å, $c = 14.962(3)$ Å, $\beta = 98.21(2)°$, and $Z = 4$. Each nickel atom is ligated by a terminal carbonyl group and by a $2,7\text{-}Me_2\text{-}2,7\text{-}C_2B_9H_9$ carborane cage, the coordinated $\overline{\mathrm{CBBBB}}$ ring of which displays pronounced nonplanarity. In addition, the metal–metal vector is spanned by two three-center, two-electron $B\text{–}H{\rightharpoonup}Ni$ "agostic" interactions. Treatment of a $CH_2Cl_2$ solution of $[N(PPh_3)_2][Pt(\eta^3\text{-}C_3H_5)(\eta^5\text{-}7,8\text{-}Me_2\text{-}7,8\text{-}C_2B_9H_9)]$ (**1d**) with $HBF_4{\cdot}Et_2O$ at *ca.* –78 °C followed by addition of the alkyne $PhC{\equiv}CH$ affords the dimetal species $[Pt_2\{\mu\text{-}\sigma,\sigma'{:}\eta^4\text{-}C(H)C(Ph)C(H)C(Ph)\}(\eta^5\text{-}7,8\text{-}Me_2\text{-}7,8\text{-}C_2B_9H_9)_2]$ (**4**), the structure of which has been established by X-ray diffraction. Crystals are triclinic, space group $P\bar{1}$ (No. 2) with $a = 13.317(2)$ Å, $b = 16.783(4)$ Å, $c = 17.289(4)$ Å, $\alpha = 64.94(2)°$, $\beta = 83.31(2)°$, $\gamma = 78.58(2)°$, and $Z = 4$. Two alkyne molecules have coupled in a "head-to-tail" manner to give a bridging "$C_4$" moiety that is $\sigma$-bonded to one of the metal centers through the two terminal carbon atoms and $\eta^4$-bound to the second metal center. In addition, each platinum atom is ligated by a $7,8\text{-}Me_2\text{-}7,8\text{-}C_2B_9H_9$ carborane cage bound in a pentahapto manner, with neither cage involved in exopolyhedral bonding. Protonation ($HBF_4{\cdot}Et_2O$) of **1a** in $CH_2Cl_2$ followed by addition of $[Co_2(CO)_8]$ affords the trinuclear metal complex $[Co_2Ni(\mu\text{-}CO)(CO)_5(\eta^5\text{-}7,8\text{-}Me_2\text{-}7,8\text{-}C_2B_9H_9)]$ (**5**), in which the $NiC_2B_9$ metallacarborane cage forms two exopolyhedral $B\text{–}H{\rightharpoonup}Co$ "agostic" interactions. In addition to the X-ray diffraction studies, the new compounds have been characterized by microanalysis, $^1H$, $^{13}C$, and $^{11}B$ NMR spectroscopy, and infrared spectroscopy.

## Introduction

We have described the synthesis of salts of the anionic allyl(carborane)molybdenum and -tungsten complexes $[M(CO)_2(\eta^3\text{-}C_3H_5)(\eta^5\text{-}7,8\text{-}R_2\text{-}7,8\text{-}C_2B_9H_9)]^-$ (M = Mo or W; R = H or Me), and have shown them to be useful reagents for the preparation of novel mononuclear compounds of these group 6 metals.[1] The success of this approach lies in the ease with which the allyl ligand can be released as propene by treating the salts with acid. The coordinatively unsaturated (carborane)metal species thereby generated can be captured by the addition of suitable reagents.

By employing similar methodology we have developed a somewhat general synthetic route to carborane complexes of the group 10 metals. Previous preparative routes to such species have, in general, relied on reactions of the dianions $[$*nido*$\text{-}7,n\text{-}R_2\text{-}7,n\text{-}C_2B_9H_9]^{2-}$ ($n$ = 8 or 9; R = H or Me) with suitable metal–halide complexes[2] and on reactions of zerovalent complexes of the group 10 metals with carboranes.[3] Although these methodologies have led to the characterization of many interesting compounds, the types of species obtained have been somewhat limited by the availability of suitable metal precursors.

## Results and Discussion

Addition of a thf (tetrahydrofuran) solution of $Na_2[$*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} to a solution of $[Ni_2(\mu\text{-}Br)_2(\eta^3\text{-}C_3H_5)_2]$ in the same solvent held at –50 °C, followed by addition of a suitable salt, affords the species $[Y][Ni(\eta^3\text{-}C_3H_5)(\eta^5\text{-}7,8\text{-}Me_2\text{-}7,8\text{-}C_2B_9H_9)]$ [**1a**, Y = $NEt_4$; **1b**, Y = $N(PPh_3)_2$]. The analogous platinum species $[Y][Pt(\eta^3\text{-}C_3H_5)(\eta^5\text{-}7,8\text{-}Me_2\text{-}7,8\text{-}C_2B_9H_9)]$ [**1c**, Y = $NEt_4$; **1d**, Y = $N(PPh_3)_2$] may be similarly obtained from $Na_2[$*nido*$\text{-}7,8\text{-}Me_2\text{-}7,8\text{-}C_2B_9H_9]$ and $[Pt_2(\mu\text{-}Br)_2(\eta^3\text{-}C_3H_5)_2]$. Data characterizing the new metallacarborane salts **1a**–**1d** are given in Tables 1–3. Thus, in the $^1H$ NMR spectrum of **1a**, the methylene hydrogen atoms of the allyl group give rise to two doublet resonances at $\delta$ 2.22 and 2.71, while the methine hydrogen

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[†] 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 polynuclear metal complexes reported. We have therefore chosen to treat the cages as *nido*-11 vertex ligands with numbering as for an icosahedron from which the 12th vertex has been removed.

[⊗] Abstract published in *Advance ACS Abstracts*, March 15, 1994.

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**Table 1.** Physical and Infrared Absorption Data

| compd |  |  |  | anal.[a] |  |  |
|---|---|---|---|---|---|---|
| no. | formula | color | % yield | % C | % H | % N |
| **1a** | $[NEt_4][Ni(\eta^3\text{-}C_3H_5)(\eta^5\text{-}7,8\text{-}Me_2\text{-}7,8\text{-}C_2B_9H_9)]$ | brown | 62 | 44.86 (46.14) | 10.73 (10.33) | 3.60 (3.59) |
| **1d** | $[N(PPh_3)_2][Pt(\eta^3\text{-}C_3H_5)(\eta^5\text{-}7,8\text{-}Me_2\text{-}7,8\text{-}C_2B_9H_9)]$ | brown | 84 | 55.07 (55.23) | 5.66 (5.39) | 1.59 (1.50) |
| **2a** | $[Ni(CO)_2(\eta^5\text{-}7,8\text{-}Me_2\text{-}7,8\text{-}C_2B_9H_9)]$ | brown | *ca.* 78 | 25.25 (26.19) | 5.90 (5.49) |  |
| **2b** | $[Ni(CNBu^t)_2(\eta^5\text{-}7,8\text{-}Me_2\text{-}7,8\text{-}C_2B_9H_9)]$ | green | 51 | 43.85 (43.63) | 8.47 (8.63) | 7.11 (7.27) |
| **2c** | $[Pt(CO)_2(\eta^5\text{-}7,8\text{-}Me_2\text{-}7,8\text{-}C_2B_9H_9)]$ | brown | 64 | 18.52 (17.51) | 3.93 (3.67) |  |
| **2d** | $[Pt(CNBu^t)_2(\eta^5\text{-}7,8\text{-}Me_2\text{-}7,8\text{-}C_2B_9H_9)]$ | yellow | 60 | 32.64 (32.22) | 6.27 (6.37) | 5.13 (5.37) |
| **3** | $[Ni_2(CO)_2(\eta^5\text{-}C_2B_9H_9Me_2)_2]$[b] | green | 18 | 24.21 (24.30) | 6.42 (6.12) |  |
| **4** | $[Pt_2\{\mu\text{-}\sigma,\sigma'\text{:}\eta^4\text{-}C(H)C(Ph)C(H)C(Ph)\}(\eta^5\text{-}7,8\text{-}Me_2\text{-}7,8\text{-}C_2B_9H_9)_2]$ | red | 35 | 31.92 (31.49) | 4.57 (4.62) |  |
| **5** | $[Co_2Ni(\mu\text{-}CO)(CO)_5(\eta^5\text{-}7,8\text{-}Me_2\text{-}7,8\text{-}C_2B_9H_9)]$ | mauve | 39 | 24.28 (23.78) | 3.04 (2.99) |  |

[a] Calculated values in parentheses. [b] Formed as a mixture of three isomers (see text).

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

| compd | $\delta(^1H)$ | $\delta(^{13}C)$[b] |
|---|---|---|
| **1a** | 1.29 [tt, 12 H, NCH$_2$*Me*, *J*(NH) = 2, *J*(HH) = 7], 1.71 (s, 6 H, CMe), 2.22 [d, 2 H, H$_{anti}$, *J*(HH) = 11.5], 2.71 [d, 2 H, H$_{syn}$, *J*(HH) = 6.2], 3.21 [q, 8 H, N*CH$_2$*Me, *J*(HH) = 7], 4.74 [tt, 1 H, H$_m$, *J*(HH) = 6.2, 11.5] | 93.7 (CH), 57.3 (br, *C*Me), 52.9 (br, N*CH$_2$*Me), 52.0 (CH$_2$), 25.9 (C*Me*), 7.6 (NCH$_2$*Me*) |
| **1d** | 1.79 (s, 6 H, CMe), 2.88 [d, 2 H, H$_{anti}$, *J*(HH) = 10.5, *J*(PtH) = 82], 3.76 [tt, 1 H, H$_m$, *J*(HH) = 5.9, 10.5], 4.02 [d, 2 H, H$_{syn}$, *J*(HH) = 5.9, *J*(PtH) = 47], 7.43 to 7.67 (30 H, Ph) | 133.9 [C$^4$(Ph)], 132.3 [vt, C$^2$(Ph), $\lvert J(PC) + J(P'C)\rvert = 11$], 129.6 [vt, C$^3$(Ph), $\lvert J(PC) + J(P'C)\rvert = 13$], 127.4 [d, C$^1$(Ph), *J*(PC) = 109], 89.4 [CH, *J*(PtC) = 12], 64.2 (br, *C*Me), 44.5 [CH$_2$, *J*(PtC) = 255], 25.1 (C*Me*) |
| **2a**[c] | 1.69 (s, CMe) | 185.2 (CO), 77.8 (br, *C*Me), 28.3 (C*Me*) |
| **2b** | 1.48 (s, 18 H, Bu$^t$), 2.28 (s, 6 H, CMe) | 137.1 [t, *C*NC(CH$_3$)$_3$, *J*(NC) = 18], 63.7 [br, CN*C*(CH$_3$)$_3$], 58.6 (br, *C*Me), 30.2 [CNC(*C*H$_3$)$_3$], 28.6 (C*Me*) |
| **2c** | 1.88 (s, CMe) | [c]173.0 [CO, *J*(PtC) = 1506], 65.9 (br, *C*Me), 26.6 (C*Me*) |
| **2d** | 1.54 (s, 18 H, Bu$^t$), 2.28 (s, 6 H, CMe) | 127.7 [t, *C*NC(CH$_3$)$_3$, *J*(NC) = 18, *J*(PtC) = 1450], 82.2 [br, CN*C*(CH$_3$)$_3$, *J*(PtC) = 92], 58.7 (br, *C*Me), 30.4 [CNC(*C*H$_3$)$_3$], 26.3 (C*Me*) |
| **3**[d] | −3.85 (m, 8 H, B–H→Ni), 1.84, 1.87, 1.90, 1.92, 2.35, 2.39, 2.40, 2.44 (s × 8, Me) | 185.2 (br, CO), 184.2 (br, CO), 66.8 (br, *C*Me), 66.5 (br, *C*Me), 66.0 (br, *C*Me), 58.2 (*C*Me), 25.7 (C*Me*), 25.4 (C*Me*), 23.7 (C*Me*), 23.40 (C*Me*), 23.37 (C*Me*) |
| **4** | 1.76 (s, 3 H, CMe), 1.89 (s, 3 H, CMe), 2.56 (s, 3 H, CMe), 2.83 (s, 3 H, CMe), 6.83 [d, 1 H, CH, *J*(HH) = 2.7, *J*(PtH) = 20, 90], 7.46 (m, 3 H, Ph), 7.60 (m, 3 H, Ph), 7.73 [d, 1 H, CH, *J*(HH) = 2.7, *J*(PtH) = 40], 7.74 (m, 2 H, Ph), 7.86 (m, 2 H, Ph) | 144.1 [$\alpha$-*C*Ph, *J*(PtC) = 128, 864], 142.4 [$\beta$-*C*Ph, *J*(PtC) = 36], 133.7 to 126.0 (Ph), 119.3 [$\beta$-CH, *J*(PtC) = 96], 110.6 [$\alpha$-CH, *J*(PtC) = 248, 757], 83.5 [*C*Me, *J*(PtC) = 40], 83.1 (*C*Me), 79.7 [*C*Me, *J*(PtC) = 78], 65.0 [*C*Me, *J*(PtC) = 28], 29.3 [C*Me*, *J*(PtC) = 14], 28.3 [br, C*Me*, *J*(PtC) = 12], 28.1 [C*Me*, *J*(PtC) = 16], 26.2 [C*Me*, *J*(PtC) = 13] |
| **5** | −6.20 (br, 2 H, B–H→Co), 1.97 (s, 3 H, CMe), 2.03 (s, 3 H, CMe) | 234.1 (vbr, CoCO), 195.9 (CoCO), 188.9 (NiCO), 66.0 (br, *C*Me), 60.7 (br, *C*Me), 29.2 (C*Me*), 23.0 (C*Me*) |

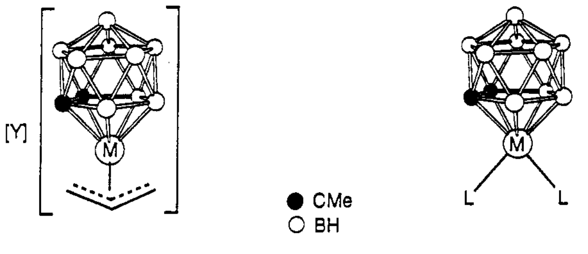
[a] Measurements at ambient temperatures in $CD_2Cl_2$ unless otherwise stated, with *J* values in Hz. [b] Hydrogen-1 decoupled, chemical shifts are positive to high frequency of $SiMe_4$. [c] Measured in $C_6D_6$. [d] Mixture of three isomers (see text).

**Table 3.** Boron-11 NMR Data[a]

| compd | $\delta(^{11}B)$ |
|---|---|
| **1a** | −1.2 (1 B), −14.2 (2 B), −16.0 (1 B), −17.3 (2 B), −18.6 (3 B) |
| **1d** | 3.1 [1 B, *J*(PtB) = 403], −13.1 (4 B), −14.0 (1 B), −18.6 (1 B), −24.2 [2 B, *J*(PtB) = 258] |
| **2a**[b] | 11.8 (1 B), 6.0 (1 B), −0.6 (2 B), −4.8 (4 B), −14.5 (1 B) |
| **2b** | 5.6 (1 B), −4.4 (1 B), −9.2 (4 B), −12.5 (2 B), −14.3 (1 B) |
| **2c**[b] | 15.6 [1 B, *J*(PtB) = 330], 2.6 (3 B), −7.6 (2 B), −13.5 (2 B), −14.9 (1 B) |
| **2d** | 14.1 [1 B, *J*(PtB) = 348], −1.6 (2 B), −5.9 (1 B), −10.7 (2 B), −14.6 (1 B), −21.1 (2 B) |
| **3**[c] | 7.0 [2 B, B–H→Ni, *J*(HB) = 75], −3.2 to −17.3 (16 B, BH) |
| **4** | 5.2 (2 B), 2.7 (1 B), −1.7 (2 B), −5.2 (8 B), −10.6 (4 B), −14.5 (1 B) |
| **5** | 22.0 [1 B, B–H→Co, *J*(HB) = 94], 14.9 [1 B, B–H→Co, *J*(HB) = 98], −8.7 to −11.7 (7 B, BH) |

[a] Measurements at ambient temperatures in $CD_2Cl_2$ unless otherwise stated. Hydrogen-1 decoupled. Chemical shifts (ppm) are positive to high frequency of $BF_3{\cdot}Et_2O$ (external). Coupling constants are in Hz. Resonances ascribed to more than nucleus may result from overlapping signals and do not necessarily indicate symmetry equivalence. [b] Measured in $C_6D_6$. [c] Mixture of three isomers (see text).

(H$_m$) appears as a triplet-of-triplets at $\delta$ 4.74. The two doublet signals can be assigned to the *anti*- and *syn*-protons (H$_{anti}$ and H$_{syn}$), respectively, since the doublet separation of the former [$J(H_{anti}H_m)$ = 11.5 Hz] is larger than that of the latter [$J(H_{syn}H_m)$ = 6.2 Hz].[1,4] In the $^{13}C\{^1H\}$ NMR spectrum of **1a**, signals at $\delta$ 52.0 (CH$_2$) and 93.7 (CH) are due to the $\eta^3$-$C_3H_5$ ligand. The CMe groups of the carborane cage give rise to a singlet resonance at $\delta$ 1.71 in the $^1$H NMR spectrum and two signals at $\delta$ 25.9 (C*Me*) and 57.3 (*C*Me) in the $^{13}C\{^1H\}$ NMR spectrum, as expected. The NMR resonances for **1d** were similarly assigned.



| | M | Y |
|---|---|---|
| **1a** | Ni | NEt$_4$ |
| **1b** | Ni | N(PPh$_3$)$_2$ |
| **1c** | Pt | NEt$_4$ |
| **1d** | Pt | N(PPh$_3$)$_2$ |

| | M | L |
|---|---|---|
| **2a** | Ni | CO |
| **2b** | Ni | CNBu$^t$ |
| **2c** | Pt | CO |
| **2d** | Pt | CNBu$^t$ |

Treatment of carbon monoxide saturated solutions of $[NEt_4][Ni(\eta^3\text{-}C_3H_5)(\eta^5\text{-}7,8\text{-}Me_2\text{-}7,8\text{-}C_2B_9H_9)]$ (**1a**) in $CH_2Cl_2$ at −60 °C with the acid $HBF_4{\cdot}Et_2O$ affords the neutral compound $[Ni(CO)_2(\eta^5\text{-}7,8\text{-}Me_2\text{-}7,8\text{-}C_2B_9H_9)]$ (**2a**). This species is difficult

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(4) Lee, S. S.; Knobler, C. B.; Hawthorne, M. F. *Organometallics* **1991**, *10*, 1054.

to isolate pure due to the lability of the carbonyl ligands which are slowly lost from both solutions of the compound and from the solid material *in vacuo*, as discussed in more detail later. The analogous platinum species [Pt(CO)$_2$($\eta^5$-7,8-Me$_2$-7,8-C$_2$B$_9$H$_9$)] (**2c**) was similarly obtained from **1c**, and is somewhat more stable toward loss of CO. It has been previously prepared and characterized by Graham and Krentz,[5] who obtained it by displacement of cyclo-1,5-octadiene in [Pt(cod)($\eta^5$-7,8-Me$_2$-7,8-C$_2$B$_9$H$_9$)] with CO under pressure, a reaction that is readily reversed, and also by treating [PtCl$_2$(CO)$_2$] under a CO atmosphere with Tl[*closo*-1,2-Me$_2$-3,1,2-TlC$_2$B$_9$H$_9$]. The dicarbonyl species **2a** and **2c** each show two CO absorptions in their infrared spectra (**2a**, 2113 and 2081 cm$^{-1}$; **2c**, 2119 and 2080 cm$^{-1}$) and the $^{13}$C{$^1$H} NMR spectra (Table 2) show a single resonance (with $^{195}$Pt satellite peaks for **2c**) at *ca.* $\delta$ 180 due to the two carbonyl ligands. As expected, the equivalent CMe groups of the carborane cage give rise to two signals in the $^{13}$C{$^1$H} NMR spectra and one resonance in $^1$H NMR spectra (Table 2). The $^{11}$B{$^1$H} NMR spectra (Table 3) consist of five separate signals. The most deshielded signal in the spectrum of **2c** (at $\delta$ 15.6) can be ascribed to the unique $\beta$-boron atom in the open pentagonal face of the carborane cage, $\overline{\text{CCB}\beta\text{B}}$, on the basis of it having the largest coupling to the $^{195}$Pt nucleus. By analogy, the resonance at $\delta$ 11.8 in the spectrum of **2a** is due to the analogous boron atom. Although these signals are relatively deshielded for boron atoms not involved in additional exopolyhedral bonding,[6] this would appear to be a feature common to these neutral species (see Table 3).

Protonation of the reagents **1a** and **1d** at −70 °C, followed by addition of *ca.* 2 molar equiv of CNBu$^t$, gives [Ni(CNBu$^t$)$_2$($\eta^5$-7,8-Me$_2$-C$_2$B$_9$H$_9$)] (**2b**) and [Pt(CNBu$^t$)$_2$($\eta^5$-7,8-Me$_2$-7,8-C$_2$B$_9$H$_9$)] (**2d**), respectively, both of which display two NC absorptions (**2b**, 2197 and 2178 cm$^{-1}$; **2d**, 2207 and 2180 cm$^{-1}$) in their infrared spectrum. Compound **2d** has been synthesized by Graham and Krentz[5] by treating [Pt(cod)($\eta^5$-7,8-Me$_2$-7,8-C$_2$B$_9$H$_9$)] with an excess of CNBu$^t$. The ligated carbon atoms of the CNBu$^t$ ligands of **2b** give rise to a triplet resonance at $\delta$ 137.1 in the $^{13}$C{$^1$H} NMR spectrum due to coupling to the quadrupolar $^{14}$N nucleus [*J*(NC) = 18 Hz].[7] Similarly, a triplet resonance at $\delta$ 127.7 with $^{195}$Pt satellite peaks [*J*(PtC) = 1450 Hz] in the spectrum of **2d** is due to the *C*NBu$^t$ nuclei.

The isomeric palladium complex [Pd(CNBu$^t$)$_2$($\eta^5$-7,9-Me$_2$-7,9-C$_2$B$_9$H$_9$)] has previously been prepared by insertion of the zerovalent palladium complex [Pd(CNBu$^t$)$_2$] into the carborane *closo*-2,3-Me$_2$-2,3-C$_2$B$_9$H$_9$.[8] In this latter species, however, the two carborane CMe vertices in the coordinated pentagonal belt of the cage are separated by a BH vertex.

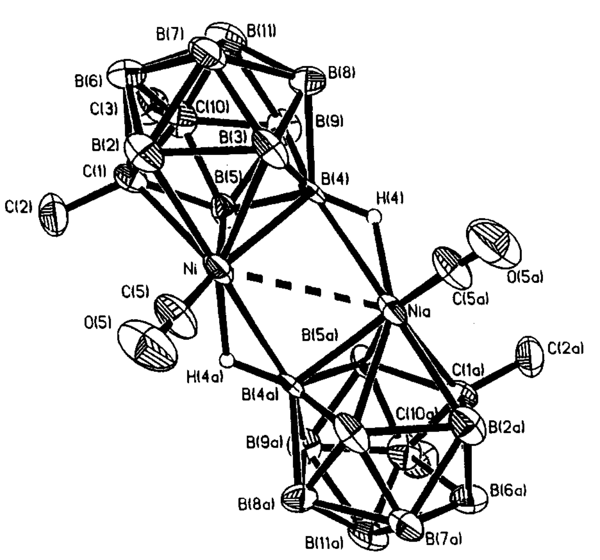
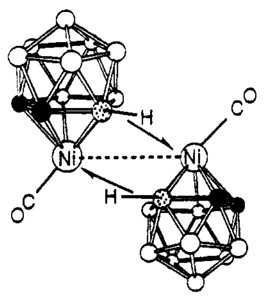
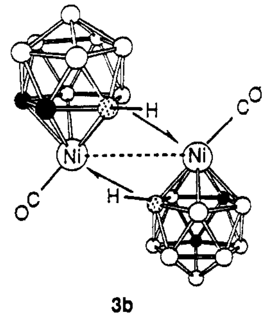


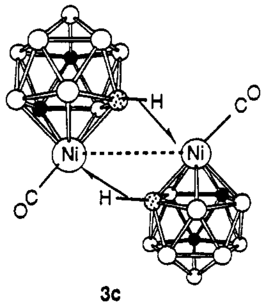
**Figure 1.** Structure of [Ni$_2$(CO)$_2$($\eta^5$-2,7-Me$_2$-2,7-C$_2$B$_9$H$_9$)$_2$] (**3c**). Thermal ellipsoids are shown at 40% probability level.



**3a**



**3b**



**3c**

● CMe ○ BH ◎ B

It is interesting to note that neither of the compounds **2b** and **2d** show any sign of decomposition after prolonged periods in solution under a nitrogen atmosphere or under vacuum. In contrast, carbon monoxide is slowly (days) released from CH$_2$Cl$_2$ solutions of the dicarbonyl complex **2a** to afford an inseparable mixture of the isomeric dimetal species [Ni$_2$(CO)$_2$($\eta^5$-7,8-Me$_2$-7,8-C$_2$B$_9$H$_9$)$_2$] (**3a**), [Ni$_2$(CO)$_2$($\eta^5$-7,8-Me$_2$-7,8-C$_2$B$_9$H$_9$)($\eta^5$-2,7-Me$_2$-2,7-C$_2$B$_9$H$_9$)] (**3b**), and [Ni$_2$(CO)$_2$($\eta^5$-2,7-Me$_2$-2,7-C$_2$B$_9$H$_9$)$_2$] (**3c**). The structures of the species **3** were not fully established until after an X-ray diffraction study on one of the isomers (**3c**) had been carried out. An ORTEP view of the molecular structure is shown in Figure 1 and selected bond distances and bond angles are collected in Table 4. It is immediately apparent that the cage CMe groups present in **3c** do not occupy the same relative positions as in the precursor **2a**, but nevertheless occupy adjacent vertices. The 3,1,2-NiC$_2$B$_9$ polyhedral skeleton present in **2a** has therefore been transformed to a 2,1,4-NiC$_2$B$_9$ arrangement in complex **3c**. The nickel to cage boron atom distances range from 2.083(11) to 2.157(10) Å, but the Ni–C(1) distance [2.325(8) Å] is appreciably longer. Polyhedral distortions of this type where the carbon atoms in the open face of the carborane ligand have moved away from the metal atom and toward the upper pentagonal belt are a common structural feature of electron-rich metallacarboranes.[9] For comparison, the four Pt–B distances in the complex [Pt(PMe$_2$Ph)$_2$($\eta^5$-2,8-Ph$_2$-2,8-C$_2$B$_9$H$_9$)] lie in the range 2.199–2.231 Å, while the platinum to carbon cage distance [2.610(5) Å] is much greater.[2e] The Ni···Ni separation [2.744(2) Å] in **3c** is long and is probably indicative of little if any direct metal–metal bonding. This distance should be compared with those in

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**Table 4.** Selected Internuclear Distances (Å) and Angles (deg) for $[Ni_2(CO)_2(\eta^5\text{-}2,7\text{-}Me_2\text{-}2,7\text{-}C_2B_9H_9)_2]$ (**3c**), with Estimated Standard Deviations in Parentheses

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| Ni–Ni(a) | 2.744(2) | Ni–C(1) | 2.325(8) | Ni–B(2) | 2.098(11) | Ni–B(3) | 2.157(10) |
| Ni–B(4) | 2.083(11) | Ni–B(5) | 2.134(10) | Ni(a)–B(4) | 2.261(11) | C(1)–B(2) | 1.692(14) |
| B(2)–B(3) | 1.918(17) | B(3)–B(4) | 1.775(16) | B(4)–B(5) | 1.845(16) | B(5)–C(1) | 1.675(13) |
| C(10)–B(6) | 1.731(14) | B(6)–B(7) | 1.732(17) | B(7)–B(8) | 1.748(17) | B(8)–B(9) | 1.786(16) |
| B(9)–C(10) | 1.713(15) | Ni(a)–H(4) | 1.71 | B(4)–H(4) | 1.09 | Ni–C(5) | 1.750(10) |
| C(5)–O(5) | 1.163(13) | | | | | | |

| | | | | | |
|---|---|---|---|---|---|
| Ni(a)–Ni–C(1) | 132.1(2) | Ni(a)–Ni–B(2) | 133.4(3) | Ni(a)–Ni–B(3) | 80.7(3) |
| Ni(a)–Ni–B(4) | 53.8(3) | Ni(a)–Ni–B(5) | 89.9(3) | B(4)–H(4)–Ni(a) | 106 |
| Ni(a)–B(4)–H(4) | 46 | Ni–C(5)–O(5) | 175.2(9) | C(5)–Ni–Ni(a) | 107.7(3) |

the compounds $[Ni_2(\mu\text{-}CO)_2(\eta^5\text{-}7,8\text{-}C_2B_9H_{10}\text{-}10\text{-}PPh_3)_2]$ [2.477(2) Å][2c] and $[Ni_2(\mu\text{-}CO)_2(\eta^5\text{-}C_5H_5)_2]$ [2.357(1) Å],[10] both of which have a formal Ni–Ni single bond spanned by two carbonyl ligands. Consideration of the electron count at the metal centers in **3c** would also imply no direct metal–metal bonding, since both metals attain an 18-electron count without the need to invoke a Ni–Ni bond. In addition to the carborane cage, the nickel atoms carry a terminal carbonyl group [Ni–C(5) 1.750(10) Å, Ni–C(5)–O(5) 175.2(9)°]. The two "$(\eta^5\text{-}2,7\text{-}Me_2\text{-}2,7\text{-}C_2B_9H_9)$Ni(CO)" moieties are therefore held together by two B–H⇀Ni "agostic" interactions, which involve boron atoms that are situated $\beta$ to the carbon atom of the $\overline{CB\beta BB}$ face ligating the metal.

The spectroscopic data on the material obtained from this decomposition reaction of the complex **2a** are consistent with the presence of two other species, in addition to **3c**. It seems likely that the formation of **3c** proceeds via loss of a carbon monoxide molecule followed by dimerization of the resultant carborane–nickel–carbonyl fragment, with isomerization of the cage CMe groups occurring after the CO group is lost. We interpret the spectroscopic data as being due to the formation of all three of the isomers possible by combination of the two fragments "$(\eta^5\text{-}7,8\text{-}Me_2\text{-}7,8\text{-}C_2B_9H_9)$Ni(CO)" and "$(\eta^5\text{-}2,7\text{-}Me_2\text{-}2,7\text{-}C_2B_9H_9)$Ni(CO)", namely the symmetric compounds **3c** and $[Ni_2(CO)_2(\eta^5\text{-}7,8\text{-}Me_2\text{-}7,8\text{-}C_2B_9H_9)_2]$ (**3a**), and the asymmetric compound $[Ni_2(CO)_2(\eta^5\text{-}7,8\text{-}Me_2\text{-}7,8\text{-}C_2B_9H_9)(\eta^5\text{-}2,7\text{-}Me_2\text{-}2,7\text{-}C_2B_9H_9)]$ (**3b**). Thus the $^1H$ NMR spectrum of the mixture (Table 2) shows eight signals of equal intensity due to the cage CMe groups of the three isomers and a broad resonance at $\delta$ −3.85 ppm for the protons of the B–H⇀Ni linkages. The methyl groups of the asymmetric compound **3b** will all be in different spatial environments irrespective of which boron atoms are involved in the B–H⇀Ni bonds and hence, four of the methyl resonances are due to this species. Two of the remaining four methyl signals are due to the symmetric species **3c**, having the 2,1,4-$NiC_2B_9$ arrangement, and so the remaining two signals must be due to the other symmetric compound **3a**. This strongly implies that it is the boron atom that is in the site $\alpha$ to the carbon of the $\overline{CC\beta BB}$ ring of the 3,1,2-$NiC_2B_9$ nickelacarborane moiety in **3a** that is involved in the B–H⇀Ni three-center, two-electron interactions. For a structure involving the $\beta$ boron atoms, the four cage CMe groups would be expected to be equivalent and hence give rise to only one methyl group signal. The $^{13}C\{^1H\}$ NMR spectrum of the mixture (Table 2) shows five cage C*Me* resonances because some of the signals are coincident. In addition, two very broad resonances are observed at $\delta$ 184.2 and 185.2 for the carbonyl ligands. These groups give rise to two absorptions at 2100 and 2094 cm$^{-1}$ in the infrared spectrum. In accord with the $^1H$ NMR data, a broad doublet resonance at $\delta$ 7.0 [$J$(HB) = 75 Hz] due to the boron nuclei of the B–H⇀Ni linkages is observed in the proton-coupled $^{11}B$ NMR spectrum (Table 3).

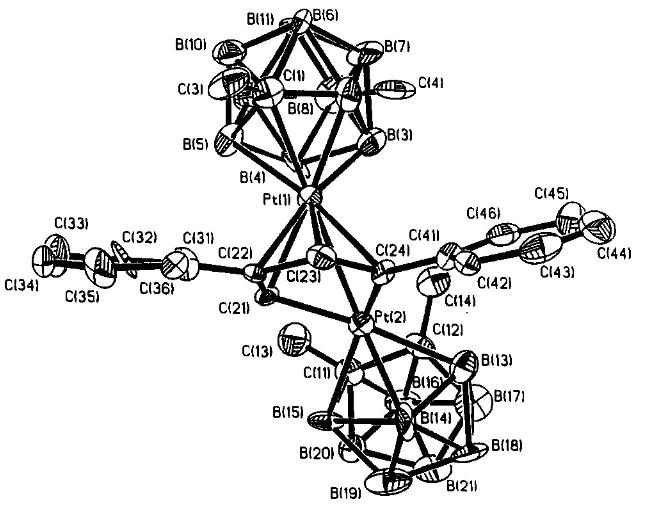
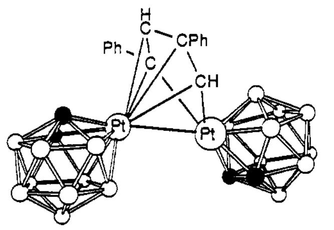


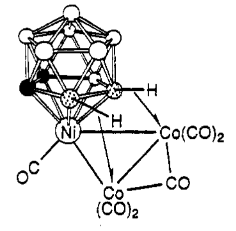
**Figure 2.** Structure of $[Pt_2\{\mu\text{-}\sigma,\sigma':\eta^4\text{-}C(H)C(Ph)C(H)C(Ph)\}(\eta^5\text{-}7,8\text{-}Me_2\text{-}7,8\text{-}C_2B_9H_9)_2]$ (**4**). Thermal ellipsoids are shown at 40% probability level.

Although relatively uncommon, facile polytopal rearrangements of the kind occurring in the transformation of **2a** into **3b** and **3c**, namely 3,1,2-$MC_2B_9$ to 2,1,4-$MC_2B_9$, have been previously observed for the "sandwich" compounds $[M(\eta^5\text{-}7,8\text{-}Me_2\text{-}7,8\text{-}C_2B_9H_9)_2]$ (M = Ni or Pd) and thoroughly studied.[11] It is interesting to note that the ratio of the three isomers of **3** formed in this work (**3a**:**3b**:**3c** = 1:2:1, estimated from relative peak intensities in the $^1H$ NMR spectrum) is independent of the reaction time. This would seem to imply that the cage rearrangement occurs prior to formation of the B–H⇀Ni bonds.

Protonation of the platinum reagent **1d**, followed by addition of one or more mole equivalents of the terminal alkyne PhC≡CH, affords the red crystalline diplatinum complex $[Pt_2\{\mu\text{-}\sigma,\sigma':\eta^4\text{-}C(H)C(Ph)C(H)C(Ph)\}(\eta^5\text{-}7,8\text{-}Me_2\text{-}7,8\text{-}C_2B_9H_9)_2]$ (**4**). Although it was evident from the NMR spectral data for **4** that a diplatinum species had been formed, it was impossible to elucidate how the alkyne was bonded to the two metal centers. Crystals of **4** suitable for study by X-ray diffraction were therefore grown. The molecular structure is shown in Figure 2, and selected bond distances and bond angles are collected in Table 5. The compound crystallized with two crystallographically independent but chemically very similar molecules in the asymmetric unit. Discussion of the structure will therefore be limited to only one of these molecules. Each platinum atom is ligated by a 7,8-Me$_2$-7,8-



**4** ● CMe ○ BH



**5** ● CMe ○ BH ⊚ B

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**Table 5.** Selected Internuclear Distances (Å) and Angles (deg) for $[Pt_2\{\mu\text{-}\sigma,\sigma':\eta^4\text{-}C(H)C(Ph)C(H)C(Ph)\}(\eta^5\text{-}7,8\text{-}Me_2\text{-}7,8\text{-}C_2B_9H_9)_2]$ (**4**) (Molecule 1), with Estimated Standard Deviations in Parentheses

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| Pt(1)–Pt(2) | 2.782(1) | Pt(1)–C(1) | 2.262(21) | Pt(1)–C(2) | 2.241(19) | Pt(1)–B(3) | 2.154(32) |
| Pt(1)–B(4) | 2.194(25) | Pt(1)–B(5) | 2.192(21) | Pt(2)–C(11) | 2.235(20) | Pt(2)–C(12) | 2.328(26) |
| Pt(2)–B(13) | 2.309(30) | Pt(2)–B(14) | 2.160(24) | Pt(2)–B(15) | 2.241(20) | Pt(1)–C(21) | 2.170(16) |
| Pt(1)–C(22) | 2.244(19) | Pt(1)–C(23) | 2.260(18) | Pt(1)–C(24) | 2.330(15) | Pt(2)–C(21) | 2.023(22) |
| Pt(2)–C(24) | 2.062(15) | C(21)–C(22) | 1.401(27) | C(22)–C(23) | 1.474(23) | C(23)–C(24) | 1.441(33) |
| C(22)–C(31) | 1.463(34) | C(24)–C(41) | 1.355(22) | | | | |

| | | | | | |
|---|---|---|---|---|---|
| Pt(1)–C(21)–Pt(2) | 83.1(7) | Pt(1)–C(24)–Pt(2) | 78.3(5) | Pt(1)–C(22)–C(31) | 127.2(12) |
| Pt(1)–C(24)–C(41) | 124.5(13) | Pt(2)–C(21)–C(22) | 116.8(12) | C(21)–C(22)–C(23) | 112.0(19) |
| C(22)–C(23)–C(24) | 116.0(16) | C(23)–C(24)–Pt(2) | 112.2(11) | C(24)–Pt(2)–C(21) | 80.2(7) |
| C(21)–C(22)–C(31) | 125.4(15) | C(23)–C(22)–C(31) | 122.6(17) | C(23)–C(24)–C(41) | 120.3(15) |
| Pt(2)–C(24)–C(41) | 127.3(15) | | | | |

$C_2B_9H_9$ *nido*-cage bound in a pentahapto manner, with the coordinated $\overline{CCBBB}$ faces of the two cages showing much less deviation from planarity than was observed in the structure of the complex **3c**. Interest centers around the bonding of the four-atom carbon fragment spanning the two metal centers. Clearly two PhC≡CH molecules have linked in a "head-to-tail" manner and are bridging the two metal centers. While Pt(1) is bound in a tetrahapto manner to all four of the carbon atoms in the bridging group [Pt(1)–C(21) = 2.170(16) Å, Pt(1)–C(22) = 2.244(19) Å, Pt(1)–C(23) = 2.260(18) Å, and Pt(1)–C(24) = 2.330(15) Å], Pt(2) is bound only to the two terminal atoms C(21) and C(24), and at distances [Pt(2)–C(21) = 2.023(22) Å and Pt(2)–C(24) = 2.062(15) Å] appreciably shorter than those between Pt(1) and these two atoms (Table 5). Furthermore, the four carbon atoms of the bridging group and the metal atom Pt(2) are coplanar [maximum deviation from the plane 0.12 Å for C(21)], with Pt(1) situated in the face of this plane and situated 1.88 Å from it. Within the four-atom chain the bond length between the two central carbon atoms [C(22)–C(23) 1.474(23) Å] is slightly longer than the two other distances [C(21)–C(22) = 1.401(27) Å and C(23)–C(24) = 1.441(33) Å]. The structure of **4** is therefore most closely related to those of the complexes $[Fe_2(\mu\text{-}\sigma,\sigma':\eta^4\text{-}C_4H_4)(CO)_6]$[12] and $[W_2H(\mu\text{-}CPh)(\mu\text{-}\sigma,\sigma':\eta^4\text{-}C_4Me_4)(O\text{-}i\text{-}Pr)_4]$,[13] rather than the dichromium complex $[Cr_2(\mu\text{-}C_4Ph_4)(CO)(\eta^5\text{-}C_5H_5)_2]$.[14] An X-ray diffraction study on the latter revealed that the α-carbon atoms of the $C_4$ chain are essentially symmetrically bonded to the two metal atoms, so that the bridge system is best described as a bis(μ-alkylidene). In both the diiron and the ditungsten species, the $C_4M$ (M = Fe, W) ring is essentially planar, as it is **4**. In contrast, the $C_4Cr$ ring in $[Cr_2(\mu\text{-}C_4Ph_4)(CO)(\eta^5\text{-}C_5H_5)_2]$ is distinctly nonplanar, the chromium atom in the ring being situated 0.51 Å away from the plane defined by the four carbon atoms.[14] The Pt–Pt distance in **4** [2.782(1) Å] is shorter than those observed in the compounds $[Pt_2(\mu\text{-}PhC_2SiMe_3)(cod)_2]$ [2.914(0) Å][15] and $[Pt_3(\mu\text{-}PhC_2Ph)_2(PEt_3)_4]$ [2.904(1) Å],[16] both of which have alkyne ligands transversely bridging the metal centers and little, if any, direct metal–metal bonding. Consideration of the electronic configurations of the Pt atoms in **4** suggests that the Pt(1)–Pt(2) interaction is best viewed as a $Pt^0(d^{10}) \rightarrow Pt^{2+}(d^8)$ unit.

In the $^{13}C\{^1H\}$ NMR spectrum of **4** (Table 2) the signals due to the α-carbon atoms of the $PtC_4$ ring occur at δ 144.1 (CPh) and 110.6 (CH), while those due to the β-carbons occur at δ 142.4 (CPh) and 119.3 (CH). These shifts compare well with those of the structurally related species $[Fe_2\{\mu\text{-}\sigma,\sigma':\eta^4\text{-}C(H)C(Ph)C(H)C(Ph)\}(CO)_6]$, for which the α- and β-carbons of the $FeC_4$ ferracyclopentadiene ring occur at δ 181.1 and 150.1 and at δ 113.2 and 131.6, respectively.[17] The bridging CH groups give rise to two doublet resonances [*J*(HH) = 2.7 Hz] at δ 6.83 and 7.73 in the $^1H$ NMR spectrum. The remainder of the NMR data is as expected.

Having established that the compounds **1** are useful sources of the reactive species "$M(\eta^5\text{-}C_2B_9H_9Me_2)$", it was of interest to see if they could be used to prepare polynuclear metal complexes containing heteronuclear metal–metal bonds. Preliminary studies in this area suggest that this is indeed so. Thus, treatment of a $CH_2Cl_2$ solution of $[NEt_4][Ni(\eta^3\text{-}C_3H_5)(\eta^5\text{-}7,8\text{-}Me_2\text{-}7,8\text{-}C_2B_9H_9)]$ (**1a**) with $HBF_4{\cdot}Et_2O$ at −60 °C, followed by addition of 1 molar equiv of $[Co_2(CO)_8]$, affords the trinuclear metal complex $[Co_2Ni(\mu\text{-}CO)(CO)_5(\eta^5\text{-}7,8\text{-}Me_2\text{-}7,8\text{-}C_2B_9H_9)]$ (**5**), which has been characterized by elemental analysis and infrared and NMR spectroscopy. Thus, the infrared spectrum has a CO absorption at 2086 $cm^{-1}$, which we ascribe to the NiCO group, and a broad absorption at 1833 $cm^{-1}$ due to the carbonyl ligand bridging the Co–Co bond. Other absorptions in the infrared spectrum at 2054, 2047, and 2026 $cm^{-1}$ are assigned to the terminal CoCO groups. The appearance of a sharp signal at δ 188.9 in the $^{13}C\{^1H\}$ NMR spectrum (Table 2) confirms the presence of the terminal carbonyl group bound to nickel. The cobalt carbonyls give rise to two very broad signals at δ 234.1 and 195.9, even at low temperatures, suggesting that these groups are undergoing site exchange at the two cobalt centers. Two relatively deshielded resonances at δ 22.0 [*J*(HB) = 94 Hz] and 14.9 [*J*(HB) = 98 Hz] in the $^{11}B$ NMR spectrum (Table 3) are due to the boron atoms of the B–H⇀Co linkages. Correspondingly, these groups give rise to a broad resonance at δ −6.20 in the $^1H$ NMR spectrum. The remainder of the NMR spectral data is in accord with the postulated structure.

## Conclusions

The new carborane complexes of nickel and platinum described in this paper suggest that the allyl(carborane) metal reagents **1** could prove to be excellent precursors to both mononuclear and polynuclear metallacarborane complexes of the group 10 metals that would be difficult to prepare by existing methods. As far as we are aware, the mode of bonding of the $C_4$ chain present in complex **4** has not previously been observed for the late transition metals. Further studies in this area are underway.

## 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.* 15 cm in length and *ca.* 2 cm in diameter) were packed with either alumina (Brockmann activity II) or silica gel (Aldrich, 70–230 mesh). The compounds $[Pt(\eta^2\text{-}C_7H_{10})_3]$[18] and $[Ni_2(\mu\text{-}Br)_2(\eta^3\text{-}C_3H_5)_2]$[19] were prepared as previously described. The acid $HBF_4{\cdot}Et_2O$ was used as supplied by Aldrich Chemical Co. as an 85% solution in

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**Table 6.** Crystallographic Data[a]

| | **3c** | **4** |
|---|---|---|
| cryst dimens/mm | 0.10 × 0.20 × 0.61 | 0.23 × 0.33 × 0.51 |
| formula | $C_{10}H_{30}B_{18}Ni_2O_2$ | $C_{24}H_{42}B_{18}Pt_2$ |
| $M_r$ | 494.35 | 915.38 |
| cryst color, shape | green rectangle | red prism |
| cryst system | monoclinic | triclinic |
| space group | *C*2/*c* (No. 15) | $P\bar{1}$ (No. 2) |
| *a*/Å | 21.498(5) | 13.317(2) |
| *b*/Å | 7.722(2) | 16.783(4) |
| *c*/Å | 14.962(3) | 17.289(4) |
| $\alpha$/deg | | 64.94(2) |
| $\beta$/deg | 98.21(2) | 83.31(2) |
| $\gamma$/deg | | 78.58(2) |
| *V*/Å$^3$ | 2458.2(9) | 3420.1(12) |
| *Z* | 4 | 4 |
| $d_{calcd}$/g cm$^{-3}$ | 1.338 | 1.778 |
| $\mu$(Mo K$\alpha$)/cm$^{-1}$ | 15.47 | 82.75 |
| *F*(000)/e | 1008 | 1728 |
| 2$\theta$ range/deg | 3–40 | 3–40 |
| *T*/K | 292 | 292 |
| no. of reflcns measd | 2611 | 6734 |
| no. of unique reflcns | 1141 | 6361 |
| no. of obsd reflcns | 1012 | 5527 |
| criterion for obsd *n* [$F_o \geq n\sigma(F_o)$] | $n = 4$ | $n = 4$ |
| $R(R')^b$ | 0.0854 (0.0857) | 0.0588 (0.0707) |
| final electron density diff features (max/min)/eÅ$^{-3}$ | 1.69/−1.16 | 3.37$^c$/−1.95 |
| *S* (goodness-of-fit) | 1.31 | 1.45 |

[a] Data collected on an Enraf Nonius CAD4-F automated diffractometer operating in the $\omega$–2$\theta$ scan mode (*h*, 0 to 20; *k*, 0 to 7; *l*, −14 to 14 for **3c**. *h*, 0 to 12; *k*, −15 to 16; *l*, −16 to 16 for **4**); graphite-monochromated Mo K$\alpha$ X-radiation, $\bar{\lambda}$ = 0.710 73 Å. Refinement was by a block-full-matrix least-squares method on *F* with a weighting scheme of the form $w^{-1} = [\sigma^2(F_o) + g|F_o|^2]$ ($g$ = 0.0064 for **3c**, $g$ = 0.0058 for **4**), where $\sigma_c^2(F_o)$ is the variance in $F_o$ due to counting statistics. [b] $R = \sum||F_o| - |F_c||/\sum|F_o|$, $R' = \sum w^{1/2}||F_o| - |F_c||/\sum w^{1/2}|F_o|$. [c] Located ca. 3 Å from nearest atom.

**Table 7.** Atomic Positional Parameters (Fractional Coordinates × 10$^4$) and Equivalent Isotropic Displacement Parameters (Å$^2$ × 10$^3$) for the Unique Atoms of **3c**

| atom | *x* | *y* | *z* | *U*(eq)[a] |
|---|---|---|---|---|
| Ni | 577(1) | 533(1) | 7209(1) | 33(1) |
| C(1) | 1464(4) | −1181(12) | 7587(5) | 31(3) |
| B(2) | 1496(6) | 948(14) | 7858(8) | 41(4) |
| B(3) | 842(5) | 1592(13) | 8543(7) | 39(4) |
| B(4) | 384(5) | −327(15) | 8460(7) | 41(4) |
| B(5) | 775(5) | −1940(12) | 7820(7) | 32(3) |
| B(6) | 1966(6) | −564(14) | 8531(8) | 49(5) |
| B(7) | 1599(5) | 1018(16) | 9088(7) | 46(4) |
| B(8) | 929(5) | 121(16) | 9446(8) | 38(4) |
| B(9) | 827(5) | −2017(12) | 8993(8) | 37(4) |
| C(10) | 1478(4) | −2355(10) | 8475(7) | 42(3) |
| B(11) | 1583(6) | −1162(16) | 9459(7) | 50(4) |
| C(2) | 1747(4) | −1909(13) | 6801(6) | 51(4) |
| C(3) | 1741(5) | −4188(12) | 8486(8) | 58(4) |
| C(5) | 631(5) | 2420(12) | 6576(7) | 51(4) |
| O(5) | 676(4) | 3736(11) | 6213(5) | 77(3) |

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

$Et_2O$. The NMR spectra were recorded at the following frequencies: $^1H$ at 360.13 MHz, $^{13}C$ at 90.56 MHz, and $^{11}B$ at 115.55 MHz.

**Synthesis of [$Pt_2(\mu\text{-}Br)_2(\eta^3\text{-}C_3H_5)_2$].**[20] In this work the compound was prepared as follows. Allyl bromide (0.20 mL, 2.30 mmol) was added in three portions to a solution of [$Pt(\eta^2\text{-}C_7H_{10})_3$] (0.96 g, 2.01 mmol) in petroleum ether (30 mL), allowing time for the allyl bromide to react before the next addition. After addition of the allyl bromide was complete, the mixture was rapidly stirred for 30 min. The bright yellow precipitate was then allowed to settle, the supernatant liquid was removed with a syringe, and the powder was washed with petroleum ether (2 × 10 mL). Yield 0.60 g (94%).

**Synthesis of the Reagents [Y][$M(\eta^3\text{-}C_3H_5)(\eta^5\text{-}7,8\text{-}Me_2\text{-}7,8\text{-}C_2B_9H_9)$] [Y = $NEt_4$ or $N(PPh_3)_2$; M = Ni or Pt].** (i) A solution of $Na_2$[*nido*-7,8-$Me_2$-7,8-$C_2B_9H_9$] {generated from [$NHMe_3$][7,8-$Me_2$-7,8-$C_2B_9H_{10}$] (0.79 g, 3.60 mmol) and NaH (0.70 g of a 60% dispersion in mineral oil, washed with 2 × 20 mL of thf) at reflux temperature for 12 h} in thf (30 mL) was slowly added to a solution of [$Ni_2(\mu\text{-}Br)_2(\eta^3\text{-}C_3H_5)_2$] (0.70 g, 1.94 mmol) in thf (5 mL) held at −50 °C. After the mixture was vigorously stirred for 1 h, it was warmed to 0 °C and stirring was continued for a further 12 h. Solid [$NEt_4$]Cl·$H_2O$ (0.66 g, 3.6 mmol) was then added and the mixture allowed to warm to room temperature. Volatile materials were removed *in vacuo*, the residue was extracted with $CH_2Cl_2$ (30 mL), and the extracts were filtered through a Celite pad (*ca.* 5 cm depth). The volume of solvent was then reduced *in vacuo* to *ca.* 10 mL. Petroleum ether was added to give a brown precipitate, which was washed with petroleum ether (2 × 15 mL) and dried *in vacuo* for *ca.* 24 h to give [$NEt_4$][$Ni(\eta^3\text{-}C_3H_5)(\eta^5\text{-}7,8\text{-}Me_2\text{-}7,8\text{-}C_2B_9H_9)$] (**1a**) as a very dark brown powder (0.88 g). The [$N(PPh_3)_2$]$^+$ salt is obtained in an identical manner employing [$N(PPh_3)_2$]Cl in place of [$NEt_4$]Cl·$H_2O$.

(ii) Similarly, a thf (25 mL) solution of $Na_2$[*nido*-7,8-$Me_2$-7,8-$C_2B_9H_9$] (2.08 mmol) was slowly added to solid [$Pt_2(\mu\text{-}Br)_2(\eta^3\text{-}C_3H_5)_2$] (0.67 g, 1.06 mmol) at −60 °C. The resulting mixture was rapidly stirred at this temperature for 4 h and then at −10 °C for a further 12 h. Solid [$N(PPh_3)_2$]Cl (1.20 g, 2.09 mmol) was then added, and the mixture was warmed to room temperature over a period of *ca.* 1 h. Solvent was removed *in vacuo*, the residue was extracted with $CH_2Cl_2$ (30 mL), and the extract was filtered through a Celite pad (*ca.* 5 cm depth). The volume of solvent was reduced *in vacuo* to *ca.* 10 mL and petroleum ether (40 mL) was added to give a brown oil from which the solvent was decanted. The oil was washed with $Et_2O$ (2 × 15 mL) and dried *in vacuo* at *ca.* 25 °C for *ca.* 24 h to give [$N(PPh_3)_2$][$Pt(\eta^3\text{-}C_3H_5)(\eta^5\text{-}7,8\text{-}Me_2\text{-}7,8\text{-}C_2B_9H_9)$] (**1d**) as a brown powder (1.64 g). The [$NEt_4$]$^+$ salt was prepared in an identical manner employing [$NEt_4$]Cl·$H_2O$ in place of [$N(PPh_3)_2$]Cl, but is generally obtained as a slightly impure oil.

**Protonation Reactions.** (i) The salt [$NEt_4$][$Ni(\eta^3\text{-}C_3H_5)(\eta^5\text{-}7,8\text{-}Me_2\text{-}7,8\text{-}C_2B_9H_9)$] (**1a**) (0.60 g, 1.54 mmol) was dissolved in $CH_2Cl_2$ (50 mL), and the mixture was cooled to *ca.* −60 °C and saturated with CO gas. The acid $HBF_4$·$Et_2O$ (240 μL, 1.53 mmol) was added, and the resulting solution was rapidly stirred at this temperature for 1 h and then slowly (*ca.* 1.5 h) allowed to warm to room temperature, affording a brown solution. After this was allowed to stand at room temperature for *ca.* 0.5 h, the CO source was removed, volatile materials were removed *in vacuo*, and the residue was extracted with $CH_2Cl_2$–petroleum ether (1:4, 50 mL and then 3 × 10 mL). The extracts were filtered through a Celite pad (*ca.* 5 cm depth) and the solvent volume was reduced *in vacuo* to *ca.* 5 mL to yield a mixture of brown [$Ni(CO)_2(\eta^5\text{-}7,8\text{-}Me_2\text{-}7,8\text{-}C_2B_9H_9)$] (**2a**) and a purple impurity (combined yield 0.33 g). An analytically pure sample of **2a** was obtained by extracting this mixture with cold (*ca.* 0 °C) petroleum ether (2 × 2 mL) and cooling the solution thus obtained at *ca.* −30 °C for *ca.* 16 h. $\nu_{max}$(CO) in *n*-hexane was 2113 vs, 2081 s cm$^{-1}$. This species is unstable both in solution and in the solid-state, decomposing to the aforementioned purple compound and **3**.

(ii) Similarly, a $CH_2Cl_2$ (15 mL) solution of [$NEt_4$][$Pt(\eta^3\text{-}C_3H_5)(\eta^5\text{-}7,8\text{-}Me_2\text{-}7,8\text{-}C_2B_9H_9)$] (**1c**) (0.26 g, 0.50 mmol) was cooled to *ca.* −78 °C and saturated with CO gas. The acid $HBF_4$·$Et_2O$ (76 μL, 0.48 mmol) was added, and the solution was warmed to room temperature over a period of *ca.* 1 h. Volatile materials were removed *in vacuo*, the residue was extracted with $CH_2Cl_2$–petroleum ether (1:4, 20 mL), and the extracts were filtered through a Celite pad (*ca.* 4 cm depth). The resulting solution was evaporated to dryness and the residue was washed with petroleum ether (2 × 2 mL) to remove an orange impurity and leave [$Pt(CO)_2(\eta^5\text{-}7,8\text{-}Me_2\text{-}7,8\text{-}C_2B_9H_9)$] (**2c**) was a brown powder (0.13 g). Recrystallization from cold (*ca.* −30 °C) petroleum ether gave brown *microcrystals.* $\nu_{max}$(CO) in *n*-hexane was 2119 vs, 2080 s cm$^{-1}$.

(iii) The salt [$NEt_4$][$Ni(\eta^3\text{-}C_3H_5)(\eta^5\text{-}7,8\text{-}Me_2\text{-}7,8\text{-}C_2B_9H_9)$] (**1a**) (0.22 g, 0.56 mmol) was dissolved in $CH_2Cl_2$ (15 mL), the solution was cooled to *ca.* −70 °C and treated first with $HBF_4$·$Et_2O$ (90 μL, 0.57 mmol) and then with $CNBu^t$ (130 μL, 1.15 mmol). After the resulting solution was allowed to warm to room temperature, volatile materials were removed *in vacuo*, the residue was extracted with $CH_2Cl_2$–petroleum ether (3:1, 8 mL) and the extracts were transferred to the top of a chromatography column packed with alumina. Eluting the column with the same solvent mixture removed a green solution, the volume of which was reduced *in vacuo* until a green powder precipitated. Solvents were removed with a

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(20) (a) Mann, B. E.; Shaw, B. L.; Shaw, G. *J. Chem. Soc. A* **1971**, 3536. (b) Pietropaolo, R.; Dolcetti, G.; Giustiniani, M.; Belluco, U. *Inorg. Chem.* **1970**, *9*, 549. (c) Lukas, J. H.; Blom, J. E. *J. Organomet. Chem.* **1971**, *26*, C25.

**Table 8.** Atomic Positional Parameters (Fractional Coordinates × $10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for **4**

| molecule 1 | | | | | molecule 2 | | | | |
|---|---|---|---|---|---|---|---|---|---|
| atom | *x* | *y* | *z* | *U*(eq)[a] | atom | *x* | *y* | *z* | *U*(eq)[a] |
| Pt(1) | 2878(1) | 3473(1) | 6822(1) | 32(1) | Pt(3) | 824(1) | 2181(1) | 2157(1) | 28(1) |
| C(1) | 1562(15) | 4086(13) | 7454(12) | 45(3) | C(51) | 2320(17) | 2510(14) | 2304(13) | 56(3) |
| C(2) | 1219(16) | 4073(13) | 6613(12) | 46(3) | C(52) | 2359(15) | 2308(12) | 1481(12) | 41(3) |
| B(3) | 1613(19) | 3006(19) | 6567(16) | 60(3) | B(53) | 1341(15) | 2891(13) | 799(15) | 35(3) |
| B(4) | 2200(17) | 2274(17) | 7598(15) | 51(3) | B(54) | 510(16) | 3639(14) | 1341(14) | 36(3) |
| B(5) | 2257(19) | 2991(14) | 8142(14) | 43(3) | B(55) | 1259(16) | 3301(13) | 2306(14) | 35(3) |
| B(6) | 309(17) | 4117(16) | 7396(13) | 38(3) | B(56) | 3257(19) | 2955(16) | 1450(14) | 50(3) |
| B(7) | 320(20) | 3465(16) | 6848(17) | 62(3) | B(57) | 2530(18) | 3190(16) | 521(15) | 50(3) |
| B(8) | 854(22) | 2390(19) | 7416(18) | 80(3) | B(58) | 1447(18) | 4011(16) | 410(15) | 46(3) |
| B(9) | 1312(18) | 2328(14) | 8396(17) | 64(3) | B(59) | 1375(18) | 4284(17) | 1370(15) | 50(3) |
| B(10) | 946(16) | 3411(13) | 8349(16) | 52(3) | B(60) | 2484(19) | 3579(17) | 2008(14) | 50(3) |
| B(11) | 113(15) | 3026(15) | 7920(13) | 52(3) | B(61) | 2617(20) | 4092(17) | 853(16) | 52(3) |
| C(3) | 1800(17) | 4902(14) | 7530(15) | 61(3) | C(53) | 2815(17) | 1840(15) | 3112(13) | 66(3) |
| C(4) | 1168(15) | 4993(14) | 5799(14) | 61(3) | C(54) | 2869(15) | 1436(14) | 1447(14) | 59(3) |
| C(21) | 4508(12) | 3038(11) | 7034(11) | 28(3) | C(71) | −554(14) | 1984(13) | 2901(11) | 34(3) |
| C(22) | 4318(12) | 3939(12) | 6892(11) | 27(3) | C(72) | 162(14) | 1329(11) | 3448(11) | 32(3) |
| C(31) | 4523(15) | 4292(12) | 7490(12) | 39(3) | C(81) | 377(14) | 1287(11) | 4322(12) | 55(3) |
| C(32) | 4659(15) | 3755(15) | 8354(13) | 54(3) | C(82) | −49(15) | 2035(14) | 4541(14) | 48(3) |
| C(33) | 4916(17) | 4080(15) | 8892(14) | 58(3) | C(83) | 211(17) | 1950(16) | 5336(12) | 56(3) |
| C(34) | 5114(16) | 4936(16) | 8554(13) | 61(3) | C(84) | 779(16) | 1191(12) | 5880(12) | 45(3) |
| C(35) | 5018(16) | 5504(15) | 7719(14) | 52(3) | C(85) | 1165(16) | 488(14) | 5663(14) | 66(3) |
| C(36) | 4663(14) | 5168(14) | 7188(12) | 42(3) | C(86) | 974(12) | 536(10) | 4869(10) | 34(3) |
| Pt(2) | 4491(1) | 2765(1) | 6003(1) | 32(1) | Pt(4) | −989(1) | 1745(1) | 1937(1) | 28(1) |
| C(11) | 5190(15) | 1329(13) | 6423(13) | 45(3) | C(61) | −2499(15) | 2689(13) | 1582(11) | 41(3) |
| C(12) | 4459(14) | 1578(13) | 5649(13) | 44(3) | C(62) | −1963(14) | 2620(12) | 696(11) | 34(3) |
| B(13) | 4664(19) | 2490(16) | 4790(15) | 50(3) | B(63) | −1550(18) | 1496(16) | 886(16) | 49(3) |
| B(14) | 5781(19) | 2811(18) | 5111(14) | 57(3) | B(64) | −1990(20) | 863(16) | 1988(17) | 56(3) |
| B(15) | 6096(16) | 2015(15) | 6237(15) | 46(3) | B(65) | −2561(16) | 1641(17) | 2419(14) | 43(3) |
| B(16) | 5402(18) | 611(16) | 5897(16) | 54(3) | B(66) | −3274(17) | 2954(16) | 730(15) | 42(3) |
| B(17) | 5117(18) | 1381(13) | 4844(18) | 65(3) | B(67) | −2665(16) | 2182(16) | 281(17) | 47(3) |
| B(18) | 5951(16) | 2166(15) | 4470(16) | 57(3) | B(68) | −2739(17) | 1103(15) | 1061(14) | 41(3) |
| B(19) | 6750(21) | 1936(18) | 5321(20) | 73(3) | B(69) | −3334(16) | 1129(13) | 2068(15) | 39(3) |
| B(20) | 6393(18) | 979(16) | 6171(15) | 48(3) | B(70) | −3660(17) | 2390(16) | 1768(14) | 40(3) |
| B(21) | 6351(19) | 1033(15) | 5142(17) | 57(3) | B(71) | −3805(19) | 1942(16) | 1027(16) | 53(3) |
| C(13) | 4889(18) | 779(16) | 7405(15) | 71(3) | C(63) | −2433(16) | 3517(12) | 1719(13) | 48(3) |
| C(14) | 3327(16) | 1337(14) | 5833(14) | 56(3) | C(64) | −1393(16) | 3304(14) | 63(13) | 60(3) |
| C(23) | 3870(13) | 4516(12) | 6055(12) | 34(3) | C(73) | 694(15) | 737(12) | 3105(11) | 34(3) |
| C(24) | 3767(13) | 4075(11) | 5519(10) | 28(3) | C(74) | 314(14) | 832(12) | 2304(11) | 34(3) |
| C(41) | 3319(13) | 4542(9) | 4755(10) | 26(3) | C(91) | 788(12) | 292(12) | 1880(9) | 29(3) |
| C(42) | 3473(13) | 5406(10) | 4280(11) | 43(3) | C(92) | 1151(16) | −643(15) | 2402(14) | 59(3) |
| C(43) | 3049(16) | 5919(14) | 3470(14) | 56(3) | C(93) | 1606(15) | −1283(12) | 2102(12) | 42(3) |
| C(44) | 2450(17) | 5549(16) | 3076(15) | 63(3) | C(94) | 1673(18) | −984(11) | 1243(14) | 70(3) |
| C(45) | 2275(16) | 4711(15) | 3579(11) | 62(3) | C(95) | 1341(16) | −105(10) | 719(13) | 55(3) |
| C(46) | 2707(14) | 4232(14) | 4367(10) | 48(3) | C(96) | 926(14) | 525(12) | 1013(9) | 41(3) |

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

syringe, and the powder was dried *in vacuo* to give $[Ni(CNBu^t)_2(\eta^5\text{-}7,8\text{-}Me_2\text{-}7,8\text{-}C_2B_9H_9)]$ (**2b**) (0.11 g). $\nu_{max}$(NC) in $CH_2Cl_2$ was at 2197 s, 2178 s $cm^{-1}$.

(iv) Employing $[N(PPh_3)_2][Pt(\eta^3\text{-}C_3H_5)(\eta^5\text{-}7,8\text{-}Me_2\text{-}7,8\text{-}C_2B_9H_9)]$ (**1d**) (0.30 g, 0.32 mmol), $HBF_4{\cdot}Et_2O$ (50 $\mu$L, 0.32 mmol), and $CNBu^t$ (75 $\mu$L, 0.66 mmol) gave $[Pt(CNBu^t)_2(\eta^5\text{-}7,8\text{-}Me_2\text{-}7,8\text{-}C_2B_9H_9)]$ (**2d**) (0.10 g) as a yellow powder, after column chromatography on alumina eluting with $CH_2Cl_2$–petroleum ether (1:1). $\nu_{max}$(NC) in $CH_2Cl_2$ was at 2207 s, 2180 s $cm^{-1}$, as found by Graham and Krentz.[5]

(v) A $CH_2Cl_2$ (25 mL) solution containing $[N(PPh_3)_2][Pt(\eta^3\text{-}C_3H_5)(\eta^5\text{-}7,8\text{-}Me_2\text{-}7,8\text{-}C_2B_9H_9)]$ (**1d**) (0.35 g, 0.37 mmol) was cooled to *ca.* −78 °C and treated with $HBF_4{\cdot}Et_2O$ (60 $\mu$L, 0.38 mmol) immediately followed by $PhC_2H$ (50 $\mu$L, 0.46 mmol). The resulting solution was rapidly stirred while being warmed to room temperature, after which the volume of the solvent was reduced *in vacuo* to *ca.* 8 mL. The mixture was then filtered through a short (*ca.* 6 cm) alumina pad. The filtrate was adsorbed onto silica gel (*ca.* 2 g) and transferred to the top of a chromatography column packed with silica gel. Eluting the column with $CH_2Cl_2$–petroleum ether (2:7 increasing in polarity to 1:2) removed a red fraction which was reduced in volume *in vacuo* to *ca.* 5 mL to precipitate a red powder. This was crystallized from $CH_2Cl_2$–petroleum ether (1:2, ca. 6 mL) at 0 °C to give red *crystals* of $[Pt_2\{\mu\text{-}\sigma,\sigma'\text{:}\eta^4\text{-}C(H)C(Ph)C(H)C(Ph)\}(\eta^5\text{-}7,8\text{-}Me_2\text{-}7,8\text{-}C_2B_9H_9)_2]$ (**4**) (0.06 g). Employing 2 molar equiv of the acetylene $PhC_2H$ afforded the same species in approximately the same yield.

(vi) The salt $[NEt_4][Ni(\eta^3\text{-}C_3H_5)(\eta^5\text{-}7,8\text{-}Me_2\text{-}7,8\text{-}C_2B_9H_9)]$ (**1a**) (0.12 g, 0.30 mmol) was dissolved in $CH_2Cl_2$ (15 mL), the solution cooled to −60 °C and then treated with $HBF_4{\cdot}Et_2O$ (48 $\mu$L, 0.31 mmol). The resulting purple solution was kept at this temperature for 5 min, $[Co_2(CO)_8]$ (0.10 g, 0.29 mmol) was then added, and the resulting solution was warmed to room temperature over a period of *ca.* 1 h. After the dark colored solution was rapidly stirred for a further 6 h, solvent was removed *in vacuo*, the residue was extracted with *n*-hexane, and the extracts were transferred to a silica gel chromatography column. Eluting the column with *n*-hexane removed a mauve fraction, which was reduced in volume *in vacuo* to *ca.* 5 mL and then cooled (*ca.* −20 °C) overnight to give mauve *microcrystals* of $[Co_2Ni(\mu\text{-}CO)(CO)_5(\eta^5\text{-}7,8\text{-}Me_2\text{-}7,8\text{-}C_2B_9H_9)]$ (**5**) (0.06 g). $\nu_{max}$(CO) in *n*-hexane was at 2086 s, 2054 vs, 2047 vs, 2026 m, 1833 m $cm^{-1}$.

**Thermal Transformation of $[Ni(CO)_2(\eta^5\text{-}7,8\text{-}Me_2\text{-}7,8\text{-}C_2B_9H_9)]$ (2a).** Freshly prepared $[Ni(CO)_2(\eta^5\text{-}7,8\text{-}Me_2\text{-}7,8\text{-}C_2B_9H_9)]$ (**2a**) (0.25 g, 0.91 mmol) was dissolved in $CH_2Cl_2$ (20 mL), and the resulting brown solution was allowed to stand at *ca.* 25 °C for 3 days. Volatile materials were then removed *in vacuo*, the residue was extracted with $CH_2Cl_2$–petroleum ether (1:2, 6 mL), and the extracts were transferred to a silica gel chromatography column. Eluting the column with the same solvent mixture removed a green solution, the volume of which was reduced *in vacuo* to *ca.* 5 mL. Cooling of this solution at *ca.* −30 °C gave green *microcrystals* of $[Ni_2(CO)_2(\eta^5\text{-}C_2B_9H_9Me_2)_2]$ (0.04 g), formed as a mixture of the three isomers **3a**, **3b**, and **3c**. $\nu_{max}$(CO) in *n*-hexane was at 2100 and 2094 $cm^{-1}$.

**Crystal Structure Determinations and Refinements.** Green rectangular crystals of **3c** were obtained by prolonged cooling (*ca.* −30 °C) of a *n*-hexane solution containing a mixture of **3a**, **3b**, and **3c**. Deep red crystals of **4** were grown by the slow diffusion of petroleum ether into a concentrated $CH_2Cl_2$ solution of the compound at *ca* 0 °C. The crystal data and other experimental parameters are given in Table 6. Final cell dimensions used for the data collection were determined from the setting angle values of 25 accurately centered reflections. The stability of the crystals during the period of the data collections was monitored by measuring the intensities of two standard reflections every 2 h. For compound **4**, a gradual decrease in intensity of the check reflections was observed (4.9% over the period of the data collection), and an appropriate decay correction was therefore applied. No significant decay was observed for **3c**. 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 absorption corrections were based on empirical methods.

The structures were solved by conventional heavy-atom methods to determine the metal atom positions and Fourier difference syntheses were used to locate all other non-hydrogen atoms, which were refined with anisotropic thermal parameters. Compound **4** crystallized with two crystallographically independent but chemically very similar molecules in the asymmetric unit. With the exception of the hydrogen atom H(4) of **3c**, all hydrogen atoms for both **3c** and **4** were included at geometrically calculated positions (C–H = 0.96 Å and B–H = 1.10 Å)[21] 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). The atom H(4) was located in the difference Fourier syntheses and allowed to ride on the boron atom B(4) with a fixed isotropic thermal parameter ($U_{iso}$ = 60 × $10^{-3}$ Å$^2$). All calculations were performed using the SHELXTL-PC package of programs.[22] Atomic scattering factors were taken from ref 23. Final atomic positional parameters for the non-hydrogen atoms of complexes **3c** and **4** are given in Tables 7 and 8, respectively.

**Acknowledgment.** We thank the Robert A. Welch Foundation for support (Grants AA-1201 and 0668).

**Supplementary Material Available:** Complete tables of bond lengths and bond angles, anisotropic thermal parameters, and hydrogen atom parameters for **3c** and **4** (24 pages). Ordering information is given on any current masthead page.

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