Inorg. Chem. **2005**, *44*, 8135–8144

Inorganic Chemistry

Article

Synthesis of Nickel–Monocarbollide Complexes by Oxidative Insertion

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Received July 5, 2005

Treatment of the 11-vertex carborane anion [*closo*-2-$CB_{10}H_{11}$]$^-$ with Ni(0) reagents in tetrahydrofuran (THF) affords—via oxidative insertion reactions—12-vertex Ni(II) complexes, isolated as the salts [$N(PPh_3)_2$][2,2-L_2-*closo*-2,1-$NiCB_{10}H_{11}$] (L = CO (**1a**), $CNBu^t$ (**1b**), and CNXyl (**1c**; Xyl = $C_6H_3Me_2$-2,6); L_2 = cod (**1d**; cod = 1,2:5,6-η-*cyclo*-octa-1,5-diene)). One CO ligand in **1a** is readily replaced by donors L′ in the presence of Me_3NO to give the species [$N(PPh_3)_2$][2-CO-2-L′-*closo*-2,1-$NiCB_{10}H_{11}$] (L′ = PEt_3 (**1e**), PPh_3 (**1f**), $CNBu^t$ (**1g**), and CNXyl (**1h**)). The anionic complexes themselves readily react with hydride abstracting reagents in the presence of donor ligands to yield zwitterionic complexes in which boron vertexes bear substituents that are bound through C, N, or O atoms. Thus, for example, **1c** with H^+ and CNXyl gives [2,2,7-$(CNXyl)_3$-*closo*-2,1-$NiCB_{10}H_{10}$] (**2b**), while **1f** with Me^+ in the presence of OEt_2 affords [2-CO-2,11-{μ-$PPh_2(C_6H_4$-*o*)}-7-OEt_2-*closo*-2,1-$NiCB_{10}H_9$] (**4**), in which an additional cycloboronation of one phosphine phenyl ring has occurred. In contrast, **1f** with Me^+ in the presence of NCMe gives a mixture of the isomers [2-CO-2-PPh_3-7-{(*X*)-N(Me)=C(H)Me}-*closo*-2,1-$NiCB_{10}H_{10}$] (*X* ≡ *E* (**5c**) and *Z* (**5d**)). X-ray diffraction analyses of compounds **1a**, **2b**, **4**, and **5c** confirmed their important structural features.

Introduction

The area of carbametallaborane chemistry was initiated almost 40 years ago by the discovery that the dicarbollide ligand [*nido*-7,8-$C_2B_9H_{11}$]$^{2-}$ could form π complexes with transition metals.[1] It was subsequently shown that the monocarbollide ligand [*nido*-7-$CB_{10}H_{11}$]$^{3-}$ had similar ligating properties.[2] Like the isolobal cyclopentadienide ligand [C_5H_5]$^-$, these di- and monocarbollide ligands behave as pentahapto 6π-electron donors to transition element centers, but they have, in addition, a higher negative charge that leads to often pronounced differences in behavior.[3,4] However, whereas cyclopentadienide–metal complexes have played a central role in the development of modern organometallic chemistry,[5] there has been far less study of the corresponding carbollide species:[3,4] this is particularly so in the case of the monocarbollide derivatives. In an attempt to constructively address this imbalance,[4] we continue to prepare and study the reactivity of “piano stool” complexes in which a metal center is bonded on one side by a monocarbollide ligand and on the other by CO groups, the latter often in combination with isocyanides or phosphines.[6−10]

Thus far, the 12-vertex parent species [2,2,2,2-$(CO)_4$-*closo*-2,1-$MCB_{10}H_{11}$]$^-$ (M = Mo[8] and W[10]) and [2,2,2-$(CO)_3$-*closo*-2,1-$MCB_{10}H_{11}$]$^{n-}$ (n = 2, M = Re;[7] n = 1, M = Fe,[8] Ru,[9] and Os[9]) have all been reported and their chemistry has been explored.[7−14] In seeking to extend this series to encompass

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10.1021/ic051115c CCC: $30.25

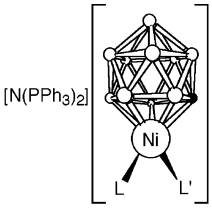
elements further to the right of the periodic table, we have described the cobalt−nitrosyl complex [2-CO-2-NO-*closo*-2,1-$CoCB_{10}H_{11}$]$^{-}$,[15] an analogue of the hitherto elusive dicarbonyl species [2,2-$(CO)_2$-*closo*-2,1-$CoCB_{10}H_{11}$]$^{2-}$. We now report upon the synthesis and reactivity of the corresponding dicarbonyl nickel anion [2,2-$(CO)_2$-*closo*-2,1-$NiCB_{10}H_{11}$]$^{-}$, along with several analogues, which extends the series of carbonyl−metal−monocarbollide complexes into group 10.

Results and Discussion

Previously, the monocarbollide−metal−carbonyl complexes [2-$(CO)_x$-*closo*-2,1-$MCB_{10}H_{11}$]$^{n-}$ have been prepared via two major routes: namely, treatment of a suitable metal carbonyl reagent with the sodium salt of the carborane trianion [*nido*-7-$CB_{10}H_{11}$]$^{3-}$, followed by oxidation where necessary,[7,8,10] or interaction of a metal carbonyl with [*nido*-7-$CB_{10}H_{13}$]$^{-}$ at elevated temperatures, in which case the metal center is oxidized by the concomitant reduction of two face-bridging protons from the carborane and their elimination as H_2.[8,9] For our target nickel−monocarbollide complex, [2,2-$(CO)_2$-*closo*-2,1-$NiCB_{10}H_{11}$]$^{-}$ the former route appeared somewhat unattractive, as it would either involve the presumed formal intermediate [2-CO-*closo*-2,1-$NiCB_{10}H_{11}$]$^{3-}$ or require a reagent such as [$NiCl_2(CO)_2$]. However, an alternative route also presents itself. Some three decades ago, it was discovered that zerovalent d^{10} metal centers could oxidatively insert into *closo*-carboranes, with the resulting net two-electron transfer opening the cluster to afford a *nido*-carborane ligand which complexed with the divalent metal fragment so formed.[16] Indeed, the potential of this “oxidative insertion” approach has already successfully been demonstrated for the reaction of M^0 reagents (M = Ni, Pd, and Pt) with {*closo*-2-CB_{10}} fragments to give species with a {*closo*-2,1-MCB_{10}} architecture.[17]

It was recognized that extending this methodology to use [$Ni(CO)_4$] as the Ni^0 reagent could provide an entry into carbonyl−nickel−monocarbollide chemistry, provided that the nickel reagent is sufficiently nucleophilic. Thus, treatment of [NMe_4][*closo*-2-$CB_{10}H_{11}$] with [$Ni(CO)_4$] (conveniently prepared in situ[18] from [$Ni(cod)_2$] and CO) in THF, followed by addition of [$N(PPh_3)_2$]Cl and chromatographic workup, afforded the desired parent species [$N(PPh_3)_2$][2,2-$(CO)_2$-*closo*-2,1-$NiCB_{10}H_{11}$] (**1a**) in good yields (see Chart 1 for the structure). Note that the aforementioned species [$N(PPh_3)_2$]-[2-CO-2-NO-*closo*-2,1-$CoCB_{10}H_{11}$], formally isoelectronic with **1a**, was similarly prepared using [$Co(CO)_3(NO)$] as the metal reagent.[15] Two bis(isocyanide) analogues of **1a**, namely [$N(PPh_3)_2$][2,2-$(CNR)_2$-*closo*-2,1-$NiCB_{10}H_{11}$] (R = Bu^t (**1b**) and Xyl (**1c**)), could likewise be obtained from [NMe_4][*closo*-2-$CB_{10}H_{11}$] and [$Ni(CNR)_2(cod)$], with the latter being prepared in situ from [$Ni(cod)_2$] and CNR, followed by addition of [$N(PPh_3)_2$]Cl. Moreover, the Ni^{II}−diene complex [$N(PPh_3)_2$][2,2-(cod)-*closo*-2,1-$NiCB_{10}H_{11}$] (**1d**) was synthesized analogously using [$Ni(cod)_2$] itself as the zerovalent nickel source. Although the anion of **1b**, isolated as the [NMe_4]$^{+}$ salt, was prepared in a similar fashion in the original study upon this system,[17] its NMR spectroscopic properties are reported fully here for the first time.

Chart 1



	L	L'
1a	CO	CO
1b	$CNBu^t$	$CNBu^t$
1c	CNXyl	CNXyl
1d	$^1/_2$ cod	$^1/_2$ cod
1e	CO	PEt_3
1f	CO	PPh_3
1g	CO	$CNBu^t$
1h	CO	CNXyl

● CH ○ BH

Compound **1a** is surprisingly stable. Analogous dicarbollide species [1,2-Me_2-3,3-$(CO)_2$-*closo*-3,1,2-$NiC_2B_9H_9$][19] and [2,2-$(CO)_2$-*closo*-2,1,7-$NiC_2B_9H_{11}$][20] have been prepared and found to be somewhat unstable, particularly with respect to carbonyl ligand loss. In contrast, **1a** is essentially unchanged after many months at room temperature in the solid state; compounds **1b**−**d** are similarly robust. The anion of **1d** is itself also noteworthy as a rare example of an anionic Ni(II)−olefin complex.[21]

Data characterizing all of the compounds **1a**−**d** are presented in Tables 1−3. The CO and CN stretching frequencies of anionic **1a** and **b** may be compared with those of their neutral dicarbollide analogues. For **1a**, the IR spectrum shows two strong bands in the CO region at 2035 and 2084 cm^{-1}, whereas for the corresponding {*closo*-NiC_2B_9} derivatives the comparable frequencies are 2081 and 2093 cm^{-1} (3,1,2-isomer)[19] and 2098 and 2130 cm^{-1} (2,1,7-isomer).[20] Similarly, compound **1b** shows CN stretches at 2132 and 2163 cm^{-1}, compared with 2178 and 2197 cm^{-1} (both the 3,1,2- and 2,1,7-isomers).[19,20] These differences are readily understood in terms of the greater electron density at nickel in the anionic species than that in the neutral ones and, hence, the stronger metal-to-ligand back-bonding. In

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Table 1. Analytical and Physical Data

compd	color	yield (%)	IR ν_{max}[a] (cm^{-1})	anal[b] C	H	N
[N(PPh$_3$)$_2$][2,2-(CO)$_2$-*closo*-2,1-NiCB$_{10}$H$_{11}$] (**1a**)	orange	68	2084 s, 2035 s	60.3 (60.2)[c]	5.3 (5.5)	1.9 (1.8)
[N(PPh$_3$)$_2$][2,2-(CNBu^t)$_2$-*closo*-2,1-NiCB$_{10}$H$_{11}$] (**1b**)	orange	40	2163* m, 2132* m	63.2 (63.1)	6.4 (6.6)	4.2 (4.7)
[N(PPh$_3$)$_2$][2,2-(CNXyl)$_2$-*closo*-2,1-NiCB$_{10}$H$_{11}$] (**1c**)	orange	82	2142* m, 2107* m	62.8 (62.5)[d]	5.6 (5.7)	4.0 (3.9)
[N(PPh$_3$)$_2$][2,2-(cod)-*closo*-2,1-NiCB$_{10}$H$_{11}$] (**1d**)	brick red	51		64.7 (64.6)	6.4 (6.4)	1.8 (1.7)
[N(PPh$_3$)$_2$][2-CO-2-PEt$_3$-*closo*-2,1-NiCB$_{10}$H$_{11}$] (**1e**)	yellow-orange	64	2004 s	60.0 (60.4)	6.5 (6.5)	1.6 (1.6)
[N(PPh$_3$)$_2$][2-CO-2-PPh$_3$-*closo*-2,1-NiCB$_{10}$H$_{11}$] (**1f**)	orange-red	79	2016 s	62.0 (62.0)[d]	5.3 (5.3)	1.3 (1.3)
[N(PPh$_3$)$_2$][2-CO-2-CNXyl-*closo*-2,1-NiCB$_{10}$H$_{11}$] (**1h**)	orange	36	2147* m, 2034 m	61.0 (61.3)[d]	5.6 (5.5)	3.0 (3.0)
[2,2,7-(CNBu^t)$_3$-*closo*-2,1-NiCB$_{10}$H$_{10}$] (**2a**)	orange-red	11	2250* m, 2181* s, 2160* s	44.0 (43.9)	8.4 (8.5)	9.6 (9.6)
[2,2,7-(CNXyl)$_3$-*closo*-2,1-NiCB$_{10}$H$_{10}$] (**2b**)	orange-red	42	2225* m, 2159* s, 2134* s	52.6 (52.2)[d]	6.0 (5.9)	6.4 (6.3)
[2-CO-2-PEt$_3$-7-OEt$_2$-*closo*-2,1-NiCB$_{10}$H$_{10}$] (**3a**)	yellow	36	2022 s	35.0 (35.2)	8.5 (8.6)	
[2-CO-2,11-{μ-PPh$_2$(C$_6$H$_4$-*o*)}-7-OEt$_2$-*closo*-2,1-NiCB$_{10}$H$_9$] (**4**)	orange	50	2032 s	49.6 (49.6)[e]	5.9 (5.8)	
[2-CO-2-PPh$_3$-7-{N(Me)═C(H)Me}-*closo*-2,1-NiCB$_{10}$H$_{10}$] (**5c**, **5d**)	red-orange	39	2032 s	48.7 (48.8)	5.7 (5.8)	2.4 (2.4)

[a] Measured in CH$_2$Cl$_2$; CO or *CN stretching frequencies; in addition, the spectra of all compounds show a broad, medium-intensity band at ca. 2500−2550 cm^{-1} due to B−H absorptions. [b] Calculated values are given in parentheses. [c] Crystallizes with 0.25 equiv of C$_5$H$_{12}$. [d] Crystallizes with 1.0 equiv of CH$_2$Cl$_2$. [e] Crystallizes with 0.5 equiv of CH$_2$Cl$_2$.

Table 2. ^{1}H and ^{13}C NMR Data[a]

compd	^{1}H[b] (δ)	^{13}C[c] (δ)
1a	7.69−7.46 (m, 30H, Ph), 2.34 (br s, 1H, cage CH)	194.2 (CO), 134.0−126.7 (Ph), 47.5 (br, cage C)
1b	7.69−7.46 (m, 30H, Ph), 2.01 (br s, 1H, cage CH), 1.43 (s, 18H, Bu^t)	150.1 (C≡N), 134.0−126.7 (Ph), 56.6 (*C*Me$_3$), 42.4 (br, cage C), 30.5 (Me)
1c	7.69−7.46 (m, 30H, Ph), 7.12 (m, 2H, C$_6$H$_3$), 7.06 (m, 4H, C$_6$H$_3$), 2.43 (s, 6H, Me), 2.31 (br s, 1H, cage CH)	163.7 (C≡N), 135.0, 127.9, 127.8 (C$_6$H$_3$), 134.0−126.7 (Ph), 43.8 (br, cage C), 18.8 (Me)
1d	7.69−7.46 (m, 30H, Ph), 5.13 (br m, 4H, ═CH), 2.75 (br s, 1H, cage CH), 2.58 (m, 4H, CH$_2$), 2.23 (m, 4H, CH$_2$)	134.0−126.7 (Ph), 100.9 (═CH), 46.4 (br, cage C), 30.7 (CH$_2$)
1e	7.69−7.46 (m, 30H, Ph), 2.04 (br s, 1H, cage CH), 1.82 (dq, J(HH) = J(PH) = 8, 6H, CH$_2$), 1.13 (dt, J(PH) = 16, 9H, CH$_3$)	198.5 (d, J(PC) = 21, CO), 134.0−126.7 (Ph), 45.1 (br, cage C), 17.8 (d, J(PC) = 27, CH$_2$), 8.0 (br, CH$_3$)
1f	7.75−7.38 (m, 45H, Ph), 2.33 (br s, 1H, cage CH)	197.3 (d, J(PC) = 18, CO), 134.9−126.7 (Ph), 47.2 (br, cage C)
1g	7.69−7.46 (m, 30H, Ph), 2.18 (br s, 1H, cage CH), 1.48 (s, 9H, Bu^t)	196.5 (CO), 145.9 (t, J(NC) = 17, C≡N), 134.0−126.7 (Ph), 66.2 (*C*Me$_3$), 45.0 (br, cage C), 30.3 (Me)
1h	7.69−7.46 (m, 30H, Ph), 7.16−7.07 (m, 3H, C$_6$H$_3$), 2.42 (s, 6H, Me), 2.35 (br s, 1H, cage CH)	160.3 (C≡N), 135.4, 128.6, 128.1 (C$_6$H$_3$), 134.0−126.7 (Ph), 45.7 (br, cage C), 19.0 (Me)
2a	2.46 (br s, 1H, cage CH), 1.58 (s, 9H, B−CNBu^t), 1.50 (s, 18H, Ni−CNBu^t)	144.1 (t, J(NC) = 17, Ni−CN), 128.1 (br q, J(BC) ≈ 55, B−CN), 60.0 (B−CN*C*Me$_3$), 57.8 (Ni−CN*C*Me$_3$), 48.3 (br, cage C), 30.5 (Ni−CNC*Me*$_3$), 29.8 (B−CNC*Me*$_3$)
2b	7.32−7.11 (m, 9H, C$_6$H$_3$), 2.78 (br s, 1H, cage CH), 2.42 (s, 12H, Ni−CNC$_6$H$_3$*Me*$_2$), 2.37 (s, 6H, B−CNC$_6$H$_3$*Me*$_2$)	157.2 (Ni−CN), ca. 141.0 (br, B−CN), 136.7, 136.5, 131.4, 129.3, 128.8, 128.4 (C$_6$H$_3$), 50.6 (br, cage C), 18.9 (Ni−CNC$_6$H$_3$*Me*$_2$), 18.4 (B−CNC$_6$H$_3$*Me*$_2$)
3a	4.62, 4.50 (br m × 2, 2H × 2, OCH$_2$), 2.10 (br, 1H, cage CH), 1.90 (dq, J(PH) = J(HH) = 8, 6H, PC*H$_2$*CH$_3$), 1.46 (vt, J(HH) = 7, 6H, OCH$_2$C*H$_3$*), 1.14 (dt, J(PH) = 15, 9H, PCH$_2$C*H$_3$*)	195.6 (d, J(PC) = 22, CO), 78.8 (OCH$_2$), 43.5 (br, cage C), 18.1 (d, J(PC) = 28, PCH$_2$), 13.3 (OCH$_2$*C*H$_3$), 8.2 (br, PCH$_2$*C*H$_3$)
4	7.87−7.23 (m, 14H, Ph and C$_6$H$_4$), 4.41 (q × 2, J(HH) = 7, 2H × 2, OCH$_2$ × 2), 2.26 (br s, 1H, cage CH), 1.27 (t, J(HH) = 7, 6H, CH$_3$)	193.4 (d, J(PC) = 21, CO),[d] 134.1−126.3 (Ph and C$_6$H$_4$), 77.7 (CH$_2$), 42.7 (br, cage C), 13.1 (CH$_3$)
5a	7.82 (br, 1H, ═CH), 3.70 (d, ^4J(HH) = 1, 1H, NMe), 2.54 (d, ^3J(HH) = 6, 3H, ═CMe), 2.33 (br s, 1H, cage CH), 1.89 (dq, ^2J(PH) = 9, ^3J(HH) = 8, PCH$_2$), 1.12 (dt, ^3J(PH) = 16, PCH$_2$C*H$_3$*)	195.2 (d, J(PC) ≈ 20, CO), 173.8 (N═C), 53.7 (NMe), 47.2 (br, cage C), 20.8 (═C*Me*), 18.2 (d, J(PC) = 29, PCH$_2$), 8.3 (br, PCH$_2$*C*H$_3$)
5b	2.63 (s, 3H, NCMe), 2.28 (br, 1H, cage CH), 1.91 (dq, ^2J(PH) = 9, ^3J(HH) = 8, PCH$_2$), 1.15 (dt, ^3J(PH) = 16, PCH$_2$C*H$_3$*)	190.0 (br, CO), 110.2 (N≡C), 47.3 (br, cage C), 18.3 (d, J(PC) = 29, PCH$_2$), 8.3 (d, J(PC) = 3, PCH$_2$*C*H$_3$), 4.6 (NC*C*H$_3$)
5c	7.76 (br, 1H, ═CH), 7.53−7.16 (m, 15H, Ph), 3.70 (br, 3H, NMe), ca. 2.52 (sh, 1H, cage CH), 2.39 (d, ^3J(HH) = 5, 3H, ═CMe)	193.1 (d, J(PC) = 21, CO), 173.6 (N═C), 53.5 (NMe), 48.0 (br, cage C), 20.8 (═C*Me*)
5d	7.94 (br, 1H, ═CH), 7.53−7.16 (m, 15H, Ph), 3.43 (br, 3H, NMe), ca. 2.52 (sh, 1H, cage CH), 2.48 (d, ^3J(HH) = 5, 3H, ═CMe)	ca. 193.1 (d, J(PC) ≈ 20, CO), 174.3 (N═C), 54.1 (NMe), 48.0 (br, cage C), 20.9 (═C*Me*)

[a] Chemical shifts (δ) in ppm, coupling constants (J) in Hertz, measurements taken at ambient temperatures in CD$_2$Cl$_2$. [b] Resonances for terminal BH protons occur as broad unresolved signals in the range δ ca. −1 to +3. [c] ^{1}H-decoupled chemical shifts are positive to high frequency of SiMe$_4$. [d] The signal for B−C could not be located.

practical terms, this manifests itself as stronger bonding of these ligands to the nickel center, so that **1a** is much more stable than the dicarbonylnickel−dicarbollide species with respect to CO loss.

Table 3. ^{11}B and ^{31}P NMR Data[a]

compd	^{11}B[b] (δ)	^{31}P[c] (δ)
1a	4.5, 0.0 (2B), −4.3, −9.0 (2B), −11.9 (2B) −17.1 (2B)	
1b	ca. −4.0 (sh) −4.5 (2B), −6.6, −14.5 (2B), −17.1 (2B), −19.9 (2B)	
1c	−2.0 (sh), −3.0 (2B), −6.0, −12.8 (2B), −15.7 (2B), −19.1 (2B)	
1d	1.5 (2B), −1.9, −5.4, −8.3 (2B), −14.5 (2B), −18.0 (2B)	
1e	−1.5 (sh), −2.3 (2B), −6.2, −11.9 (2B), −14.9 (2B), −19.0 (2B)	26.6
1f	−0.2 (sh), −1.4 (2B), −5.9, −10.9 (2B), −14.3 (2B), −18.6 (2B)	37.3
1g	0.2, −2.2 (2B), −5.5, −11.6 (2B), −14.4 (2B), −18.5 (2B)	
1h	1.1, −1.6 (2B), −5.2, −11.0 (2B), −13.9 (2B), −18.2 (2B)	
2a	−2.4, −3.4, −7.7, −11.4, −15.2 (2B), −16.1 (2B), −19.1 (B−CN + 1B)	
2b	−0.2, −1.5, −7.1, −9.5, −13.7 (2B), −14.7 (2B), −18.2 (B−CN + 1B)	
3a	22.9 (B−OEt$_2$), −3.4, −6.0, −8.4, −12.7, −13.8, −15.9, −17.8, −18.7, −23.2	27.7
4	23.1 (B−OEt$_2$), 4.8 (B−C$_6$H$_4$), −6.4, −9.2 (2B), −11.9, −15.4, −17.3, −18.3, −23.9	60.3
5a	9.6 (B−imine), −2.6, −5.5, −6.6, −11.4, −13.9 (2B), −15.2, −17.6, −20.1	30.2
5b	ca. −1.1 (br, B−NCMe), −2.0, −4.2, −6.8, −11.1, −14.3 (2B), ca. −14.5 (sh), −18.2, −19.9	29.8
5c/5d[d]	9.6 (B−imine), 6.9 (B−imine*), −1.5, −4.8, −6.5, −8.3, −9.4, −10.3, −13.3, −15.0, −16.7, −17.5, −20.0	37.7

[a] Measurements were taken at ambient temperature in CD$_2$Cl$_2$. [b] ^{1}H-decoupled chemical shifts (δ) are positive to high frequency of BF$_3$·OEt$_2$ (external). Signals are of unit integral except where indicated; where peaks are ascribed to more than one boron nucleus, this may result from overlapping peaks and does not necessarily indicate symmetry equivalence. [c] ^{1}H-decoupled chemical shifts (δ) are positive to high frequency of 85% H$_3$PO$_4$ (external). [d] Occurs as a mixture of isomers in the approximate ratio 2:1 (**5c**/**5d** − see text). Where discernible, peaks due to the isomer **5d** are marked with an asterisk; no attempt has been made to quantify peak integrals.

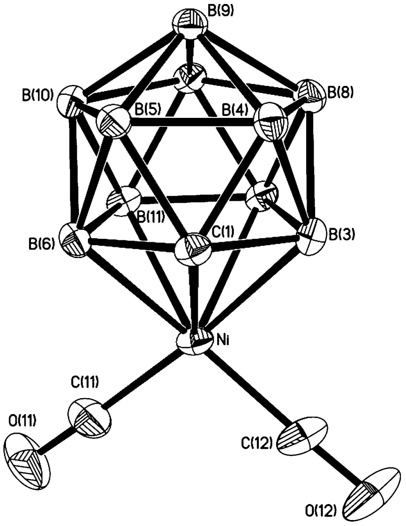

Figure 1. Structure of the anion of compound **1a** showing the crystallographic labeling scheme. In this and subsequent figures, thermal ellipsoids are drawn with 40% probability and, for clarity, only chemically significant hydrogen atoms are shown. Selected distances (Å) and angles (deg) are as follows: Ni−C(1) 2.2010(17), Ni−B(3) 2.077(2), Ni−B(6) 2.1128(19), Ni−B(7) 2.176(2), Ni−B(11) 2.1365(19), Ni−C(11) 1.793(2), Ni−C(12) 1.784(2), C(11)−O(11) 1.132(2), C(12)−O(12) 1.133(2); C(12)−Ni−C(11) 99.64(9), O(11)−C(11)−Ni 175.9(2), O(12)−C(12)−Ni 178.1(2).

All four compounds **1a**−**d** show characteristic peaks in the appropriate ratios in their ^{1}H and ^{13}C{^{1}H} NMR spectra corresponding to their respective nickel-bound ligands, to the carborane CH unit, and, of course, to the cation. Thus, the cage CH moieties all resonate with small typical ranges, δ 2.01−2.75 (^{1}H) and δ 42.4−47.5 (^{13}C).[22] Their ^{11}B{^{1}H} NMR spectra confirm the cluster to be mirror symmetric on the NMR time scale, with each compound showing six peaks in the ratio 1:2:1:2:2:2.

A single-crystal X-ray diffraction study on compound **1a** revealed the structure shown in Figure 1. As expected, the anion consists of a nickel center that is bonded on one side by the η^5-$\overline{\text{CBBBB}}$ face of a {*nido*-7-CB$_{10}$H$_{11}$} ligand and on the other by two essentially linear CO groups (Ni−C(11) 1.793(2) Å and Ni−C(12) 1.784(2) Å). The metal vertex is approximately symmetrically bonded to the five coordinating atoms of the carborane face, being closest to B(3) and B(6) (Ni−B(3) 2.077(2) Å and Ni−B(6) 2.1128(19) Å) as a result of a slight folding of the CB$_4$ face along the B(3)···B(6) vector, which sends C(1), B(7), and B(11) away from the metal (Ni−C(1) 2.2010(17) Å, Ni−B(7) 2.176(2) Å, and Ni−B(11) 2.1365(19) Å). In addition, it is noted that the {Ni(CO)$_2$} plane is essentially orthogonal to the notional mirror plane of the carborane moiety (i.e., through C(1), B(9), and B(12)). These findings are consistent with the results of molecular orbital calculations that predict this conformation to provide the most efficient overlap of the metal fragment frontier orbitals with those of the *nido*-carborane ligand.[23]

During the synthesis of compound **1b**, it was observed that a second nickelacarborane was always isolated in low variable yields (ca. 3−5%) following chromatographic workup. This species, [2,2,7-(CNBu^t)$_3$-*closo*-2,1-NiCB$_{10}$H$_{10}$] (**2a**, see Chart 2 for the structure), was apparently formed on the chromatography column, as prior IR spectroscopic analysis of the reaction mixture showed no evidence of it. Formation of this complex is readily understood in terms of protonation of **1b** by the silica, thereby removing a boron-bound hydride, and then attachment of a CNBu^t molecule at the resulting vacant site. It was noted that compound **1b** was somewhat unstable on silica, and thus, any slight decomposition would liberate isocyanide for formation of **2a**. Attempts to prepare **2a** rationally by deliberate protonation of **1b** in the presence of CNBu^t met with only modest success and afforded only low yields of the desired product. Intractable mixtures of other species, along with uncomplexed carboranes, were also obtained. It is well known that metal-bound isocyanide ligands are themselves susceptible to protonation,[24] and presumably, such reactions complicate matters here.

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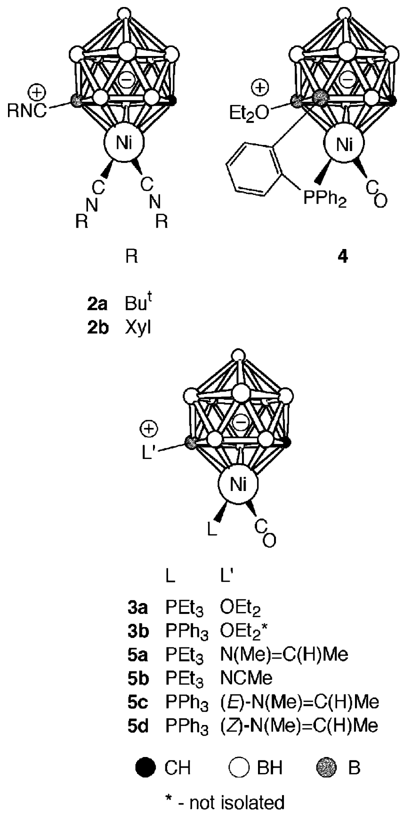
(22) Brew, S. A.; Stone, F. G. A. *Adv. Organomet. Chem.* **1993**, *35*, 135.

(23) Mingos, D. M. P.; Forsyth, M. I.; Welch, A. J. *J. Chem. Soc., Dalton Trans.* **1978**, 1363.

Chart 2



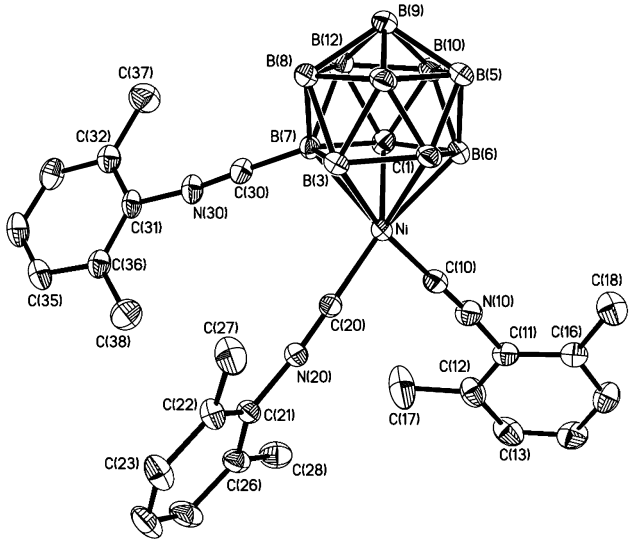


Figure 2. Structure of compound **2b** showing the crystallographic labeling scheme. Selected distances (Å) and angles (deg) are as follows: Ni−C(1) 2.201(3), Ni−B(3) 2.086(3), Ni−B(6) 2.089(3), Ni−B(7) 2.123(3), Ni−B(11) 2.137(3), Ni−C(10) 1.819(3), C(10)−N(10) 1.159(4), Ni−C(20) 1.830(3), C(20)−N(20) 1.168(3), B(7)−C(30) 1.532(4), C(30)−N(30) 1.139(3); C(10)−Ni−C(20) 95.20(12), C(30)−B(7)−Ni 113.6(2), N(10)−C(10)−Ni 178.6(3), N(20)−C(20)−Ni 179.0(3), N(30)−C(30)−B(7) 178.7(3).

In contrast with **1b**, compound **1c** was never accompanied by a tris(isocyanide) species during its synthesis and isolation. This is reasonable, as **1c** was clearly more stable on silica than **1b**, and the relatively poorly electron-donating CNXyl groups render the anion of **1c** much less nucleophilic. However, protonation of **1c** using $H[BF_4]\cdot OEt_2$ in the presence of CNXyl did afford [2,2,7-$(CNXyl)_3$-*closo*-2,1-$NiCB_{10}H_{10}$] (**2b**) in reasonably good yields (42%). The best yield of compound **2a** (11%) was in fact obtained by preparing a CH_2Cl_2 solution of **1b** containing an excess of the appropriate isocyanide and stirring this mixture with silica overnight.

Each of the IR spectra of compounds **2a** and **2b** (Table 1) shows a characteristic band for the boron-bound C≡NR group that is some 70 cm^{-1} higher in frequency than those for the nickel-bound isocyanides. Likewise, ^1H and $^{13}C\{^1H\}$ NMR spectra (Table 2) confirm the presence of two different isocyanide moieties in a 2:1 ratio in each of compounds **2a** and **2b**. The boron-bound C≡N groups appear as broad resonances at δ 128.1 (**2a**) and 141.0 (**2b**) in their $^{13}C\{^1H\}$ NMR spectra, deshielded by around 16 ppm as compared to the peaks for the nickel-bound C≡N units at δ 144.1 (**2a**) and 157.2 (**2b**), respectively. Cage substitution is also evident in the $^{11}B\{^1H\}$ NMR spectra (Table 3), with cluster asymmetry shown by the presence of 10 separate signals (some are coincident), of which one resonance in each case remains a singlet in fully ^1H-coupled ^{11}B NMR spectra. These singlets, at δ −19.1 (**2a**) and −18.2 (**2b**) correspond to the B−CNR nucleus and are in positions typical for similarly substituted compounds.[10]

Although the IR and NMR spectra for compounds **2a** and **2b** indicated the presence of a boron-bound isocyanide and, specifically, the ^{11}B NMR data indicated that this substitution had occurred at a boron atom lying off the notional mirror plane through the {*closo*-2,1-$NiCB_{10}$} core, the exact site of B−CNR attachment was only confirmed following an X-ray diffraction study on compound **2b**. This afforded the structure shown in Figure 2, which clearly shows a {$Ni(CNXyl)_2$} moiety (Ni−C(10) 1.819(3) Å and Ni−C(20) 1.830(3) Å) that is η^5 coordinated by the open face of a *nido*-carborane ligand. The carborane itself has been modified by substitution at B(7). This vertex, in a β position with respect to the carbon atom in the Ni-bound $\overline{\text{CB}BB\text{B}}$ face, bears the third CNXyl ligand (B(7)−C(30) 1.532(4) Å). This two-electron donor has replaced a formerly boron-bound hydride ligand, reducing the overall molecular anionic charge by one unit, so that **2b** and, likewise, **2a** are neutral and zwitterionic. This site of substitution is typical of such systems,[4] with this β-B−H being the most hydridic and, therefore, the most susceptible to abstraction by a proton. Dimensions within the two types of C≡N groups correlate well with the IR spectroscopic parameters: the Ni-bound isocyanides have longer C≡N bonds (C(10)−N(10) 1.159(4) Å and C(20)−N(20) 1.168(3) Å) than the boron-bound isocyanides (C(30)−N(30) 1.139(3) Å), a feature readily rationalized by Ni → C≡N(π^*) back-bonding, which is not available to the boron vertex.

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(24) Recent examples include: Seino, H.; Nokonawa, D.; Nakamura, G.; Mizobe, Y.; Hidai, M. *Organometallics* **2000**, *19*, 2002. Pombeiro, A. J. L. *Inorg. Chem. Commun.* **2001**, *4*, 585. Kang, D.-H.; Trenary, M. *J. Am. Chem. Soc.* **2001**, *123*, 8432. Adams, C. J.; Anderson, K. M.; Bartlett, I. M.; Connelly, N. G.; Orpen, A. G.; Paget, T. J. *Organometallics* **2002**, *21*, 3454. Knorr, M.; Jourdain, I.; Lentz, D.; Willemsen, S.; Strohmann, C. *J. Organomet. Chem.* **2003**, *684*, 216. Hou, H.; Gantzel, P. K.; Kubiak, C. P. *Organometallics* **2003**, *22*, 2817.

As in **1a**, the {Ni(CN)$_2$} plane is approximately orthogonal to the plane through C(1), B(9), and B(12), with some slight twisting away from the ideal orientation, presumably to relieve steric crowding between the three bulky isocyanide ligands.

It was of interest to further investigate the protonation reactions of compound **1a** and its analogues beyond those preliminary studies that gave rise to compounds **2a** and **2b**. It has previously been observed that whereas most {*closo*-$MCB_{10}H_{11}$} anions (M = Mo,[8,10] W,[10] Fe,[8,13] and Co[15]) undergo cage boron hydride abstraction upon protonation, for M = Pt protonation typically occurs at the metal center, forming Pt−H species.[6,25] Although compound **1a** is quite stable, in contrast with the above reactions of **1b** and **1c**, attempted protonation of compound **1a** led to decomposition via rapid CO evolution and formation of an intractable mixture in which the only identifiable species was the [*closo*-2-$CB_{10}H_{11}$]$^-$ anion, detected by $^{11}B\{^1H\}$ NMR spectroscopy. It is thought that in any initially formed products, which would presumably be neutral, the CO ligands are extremely labile and, thus, rapidly lost.

Seeking derivatives of **1a** that would be amenable to further reactivity studies, the species [N(PPh$_3$)$_2$][2-CO-2-L-*closo*-$NiCB_{10}H_{11}$] (L = PEt$_3$ (**1e**), PPh$_3$ (**1f**), CNBu^t (**1g**), and CNXyl (**1h**)) were prepared by treatment of **1a** in CH_2Cl_2 with donor ligands L in the presence of Me$_3$NO. Characterizing data for compounds **1e**−**h** are presented in Tables 1−3. The significant lowering of the CO stretching frequency for complexes **1e**−**h** confirms their stronger Ni → CO(π^*) back-bonding upon introduction of the more powerful donors L. Like compounds **1a**−**d**, all four of the species **1e**−**h** show typical resonances in their ^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectra corresponding to the various groups present. In addition, they again show a 1:2:1:2:2:2 intensity ratio pattern in their $^{11}B\{^1H\}$ NMR spectra, consistent with a time-averaged mirror symmetry due to free rotation of the {Ni(CO)L} fragment with respect to the ligating $\overline{\mathrm{CBBBB}}$ face of the carborane cage. Perhaps surprisingly, complex **1g** was the least tractable of **1e**−**h**, and considerable difficulty was encountered in isolating it in pure form. This was apparently due to its facile conversion to **1b** along with considerable decomposition. We note that a Pt analogue of **1f** was reported some years ago from the reaction of [*nido*-7-$CB_{10}H_{11}$]$^{3-}$ with [PtCl$_2$(CO)(PPh$_3$)]. This platinacarborane has spectroscopic properties very similar to those of **1f**.[6]

In view of the observed formation of compounds **2a** and **2b** from **1b** and **1c**, it was expected that protonation of **1e** and **1f** in the presence of Et$_2$O would simply result in hydride abstraction, leading to the B−OEt$_2$ complexes [2-CO-2-PR$_3$-7-OEt$_2$-*closo*-2,1-$NiCB_{10}H_{10}$] (R = Et (**3a**) and Ph (**3b**)), respectively.[8,10,13,15] Perusal of the spectroscopic data for the products (Tables 1−3) showed that **3a** was indeed formed, but it was immediately clear that **3b** was not produced and that another compound, complex **4**, was instead produced. Thus, ^1H and $^{13}C\{^1H\}$ NMR spectra showed that both **3a** and **4** incorporated an ether molecule: the ^1H NMR spectra contain multiplets at δ 4.50 and 4.62 (**3a**) and 4.41 (**4**) and at δ 1.46 (**3a**) and 1.27 (**4**), in positions quite typical for B−OCH$_2$ and B−OCH$_2$CH_3 protons, respectively. Likewise, the $^{13}C\{^1H\}$ spectra showed resonances for these moieties at δ 78.8 (**3a**) and 77.7 (**4**) and at δ 13.3 (**3a**) and 13.1 (**4**), respectively. Their $^{11}B\{^1H\}$ NMR data also confirmed B−OEt$_2$ substitution by the loss of cluster symmetry (10 inequivalent boron atoms, with one coincidence for **4**) and the appearance of a strongly deshielded resonance, at δ 22.9 (**3a**) and 23.1 (**4**), which remains a singlet upon retention of proton coupling and which has a chemical shift characteristic for a B−OEt$_2$ unit in such systems.[8,10,13,15] However, there is also a second singlet, at δ 4.8, in the fully ^1H-coupled ^{11}B NMR spectrum of **4**, indicating the presence of a second boron-bound substituent. Also notable is the $^{31}P\{^1H\}$ NMR spectrum of **4**, which shows a resonance at δ 60.3, significantly shifted from that (δ 37.3) for the parent **1f**. This contrasts with the hardly different values of δ 26.6 and 27.7, respectively, when compound **1e** is converted to **3a**. This observation was suggestive of the possibility that compound **4** perhaps possesses a different structure than that which would be expected.

As the ^1H and ^{13}C NMR data for **4** lacked any peaks attributable to the second substituent, it was not readily identified. Initially, it was thought that it might be a boron-bound chloride moiety, as there is good precedent for a boron vertex to acquire a halide substituent upon hydride abstraction in halogenated solvents.[26] However, the ^{11}B chemical shift for this boron atom is a little lower than would be expected for a boron atom bearing such a substituent[26] and, moreover, the microanalytical data were not consistent with the presence of a chloride.

Seeking to positively identify this boron-bound group, an X-ray diffraction study was undertaken. The structure of **4** determined thereby is shown in Figure 3, in which the diethyl ether group is clearly bonded to B(7) (B(7)−O(1) 1.552(3) Å), as expected. An *ortho*-cycloboronation, involving one of the phosphine phenyl rings, has also taken place adjacent to the point of OEt$_2$ attachment, and this is revealed as the second boron vertex substituent. Thus, compound **4** is formulated as [2-CO-2,11-{μ-PPh$_2$(C$_6$H$_4$-*o*)}-7-OEt$_2$-*closo*-2,1-$NiCB_{10}H_9$]. The terminal H atom at B(11) has been replaced (B(11)−C(22) 1.593(4) Å), and significantly, this boron atom is the second of the two β-B−H vertexes with respect to the carbon atom in the nickel-bound $\overline{\mathrm{CBB}B\mathrm{B}}$ belt.

Although such cycloboronation of phenyl rings has multiple precedents in boron cluster chemistry,[27] these processes very often occur during thermal processes, with H$_2$ elimination between cage B−H and phenyl C−H and concomitant B−C bond formation. In the present case, the reaction might be viewed as a "protonation-induced" electrophilic aromatic substitution. If the first step of the reaction is the initial protonation of the anion of **1f** at a BH vertex,

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[25] Blandford, I.; Jeffrey, J. C.; Redfearn, H.; Rees, L. H.; Rudd, M. D.; Stone, F. G. A. *J. Chem. Soc., Dalton Trans.* **1998**, 1669.

[26] For example: Hata, M.; Kautz, J. A.; Lu, X. L.; McGrath, T. D.; Stone, F. G. A. *Organometallics* **2004**, *23*, 3590.

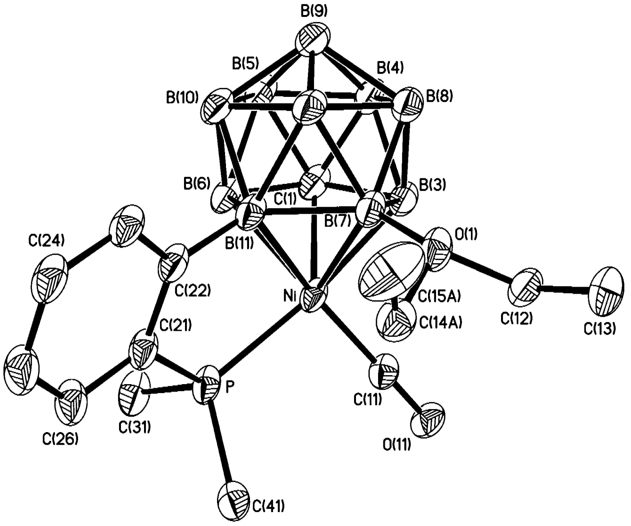

Figure 3. Structure of compound **4** showing the crystallographic labeling scheme. Only the major component of the disordered ethyl group is shown, and for clarity, all but the ipso carbons of the two C_6H_5 rings are omitted. Selected distances (Å) and angles (deg) are as follows: Ni−C(1) 2.180(3), Ni−B(3) 2.072(3), Ni−B(6) 2.123(2), Ni−B(7) 2.136(2), Ni−B(11) 2.116(2), Ni−P 2.1812(9), Ni−C(11) 1.774(2), C(11)−O(11) 1.143(2), B(7)−O(1) 1.552(3), B(11)−C(22) 1.593(4); P−Ni−C(11) 96.01(8), O(1)−B(7)−Ni 119.16(15), C(22)−B(11)−Ni 113.56(15), O(11)−C(11)−Ni 178.0(2), C(21)−P−Ni 106.45(8), C(31)−P−Ni 117.06(11), C(41)−P−Ni 117.22(8), C(22)−C(21)−P 113.60(18).

eliminating H_2 and forming a naked, "electrophilic" $B^{\delta+}$ center, the latter might then be envisaged as attacking the adjacent phenyl ring to ultimately form the B−C bond and eliminate H^+. Formation of the five-membered $\overline{\text{NiPCCB}}$ ring would act as a driving force. The nickelacarborane so formed retains an anionic charge and, hence, would be susceptible to further boron hydride abstraction and, thence, substitution by OEt_2 to give **4**. Such mechanistic details are, of course, somewhat speculative, but in any event, this scenario requires that it is more than likely that OEt_2 attachment occurs *after* the cycloboronation. Otherwise, the intermediate would be *neutral* **3b**, which would be rather more resistant to further hydride abstraction. Moreover, it is notable that **3b** is not observed in the product mixture and that reducing the amount of added acid only serves to reduce the yield of **4**. Conversely, the reaction might proceed via initial formation of **3b**, which then spontaneously eliminates H_2: the latter might be a simple consequence of C−H and B−H proximity, but if so, it is surprising that it is not observed in other systems described herein. Notwithstanding these observations, it is clearly a complex system and it may be that as yet undetected side products will shed further light on the processes at play here.

In contrast with our attempts to append OEt_2 substituents, we have found in earlier studies that hydride abstraction reactions similar to those above in the presence of MeCN can behave somewhat differently. Although straightforward B−NCMe substitution is known,[15] a more common outcome was B−imine formation.[10,13,15] The latter typically occurred when an anionic metallacarborane was treated with CF_3SO_3-Me in CH_2Cl_2−NCMe: the Me^+ cation initially and preferentially methylates NCMe to form a nitrilium cation $[MeN{\equiv}CMe]^+$, and this then acts as a hydride abstractor to ultimately yield a B−{N(Me)═C(H)Me} product.[13] In the present system, treatment of **1e** and **1f** with CF_3SO_3Me in CH_2Cl_2−NCMe (5:1) also afforded B−imine species.

However, in both cases, the reaction is complicated by the presence of multiple products. From **1e** is obtained the expected imine compound [2-CO-2-PEt_3-7-{N(Me)═C(H)-Me}-*closo*-2,1-$NiCB_{10}H_{10}$] (**5a**) along with the simpler acetonitrile-substituted complex [2-CO-2-PEt_3-7-NCMe-*closo*-2,1-$NiCB_{10}H_{10}$] (**5b**). In contrast, with **1f**, a mixture of the isomers [2-CO-2-PPh_3-7-{(*X*)-N(Me)═C(H)Me}-*closo*-2,1-$NiCB_{10}H_{10}$] ($X \equiv E$ (**5c**) and *Z* (**5d**)) is formed. All of these compounds were readily identified by their NMR characteristics, save that it is impossible to determine the stereochemistry of the imine moiety in **5a**. Although the two isomers **5c** and **5d** resisted chromatographic separation, the ^1H and ^{13}C NMR parameters could be differentiated and assigned with the aid of ^1H−^1H and $^{13}C\{^1H\}$−^1H correlation spectroscopy. The two isomers are also formed in the approximate ratio 2:1, and this assisted in making NMR assignments.

An X-ray diffraction study on a crystal of **5c** determined the structure shown in Figure 4. NMR analysis (^1H) of the same crystal confirmed it to be the major isomer in the **5c**/**d** mixture, and thus, the imine stereochemistry in the two isomers was established. The two methyl groups of the {N-(Me)═C(H)Me} moiety are clearly transoid (the torsion of C(5)−N−C(3)−C(4) is −179.8(5)°), and thus, **5c** contains an (*E*)-imine. This two-electron donor substituent is bonded to B(7), as seen in compounds **2b** and **4**, and the B(7)−N distance is 1.578(9) Å, comparable to the same parameter in other metallacarborane−imine species.[10,13,26]

All three compounds **5a**, **5c**, and **5d** show a broad resonance to relatively low field (δ 7.82 (**5a**), 7.76 (**5c**), and 7.94 (**5d**)) in their ^1H NMR spectra; this is assigned to the ═CH proton of the imine group. The NMe protons of the same group resonate at δ 3.70 (**5a** and **5c**) and 3.43 (**5d**), while those of the ═CMe unit are seen at δ 2.54 (**5a**), 2.39 (**5c**), and 2.48 (**5d**). Several of the imine moiety resonances show additional structure due to coupling with other protons in the ligand, but broadening due to nearby quadrupolar ^{11}B and ^{14}N nuclei obscures much of this information. Unfortunately, therefore, insufficient data is available in terms of chemical shift and coupling constant values to definitively assign the imine stereochemistry in **5a**. In their $^{11}B\{^1H\}$ NMR spectra, all three of these compounds display one peak that is relatively deshielded and which remains a singlet upon

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(27) Examples include: Crook, J. E.; Greenwood, N. N.; Kennedy, J. D.; McDonald, W. S. *Chem. Commun.* **1983**, 383. Kukina, G. A.; Sergienko, V. S.; Porai-Koshits, M. A. *Koord. Khim.* **1985**, *11*, 400. Elrington, M. J.; Greenwood, N. N.; Kennedy, J. D.; Thornton-Pett, M. *J. Chem. Soc., Dalton Trans.* **1986**, 2277. Ferguson, G.; Faridoon; Spalding, T. R. *Acta Crystallogr.* **1988**, *C44*, 1371. Bould, J.; Greenwood, N. N.; Kennedy, J. D. *J. Chem. Soc., Dalton Trans.* **1990**, 1451. Ferguson, G.; Jennings, M. C.; Lough, A. J.; Coughlan, S.; Spalding, T. R.; Kennedy, J. D.; Fontaine, X. L. R. *J. Chem. Soc., Chem. Commun.* **1990**, 891. Dou, J.-M.; Hu, C.-H.; Li, W.; Yao, H.-J.; Jin, R.-S.; Zheng, P.-J. *Polyhedron* **1997**, *16*, 2323. Bould, J.; Clegg, W.; Teat, S. J.; Barton, L.; Rath, N. P.; Thornton-Pett, M.; Kennedy, J. D. *Inorg. Chim. Acta* **1999**, *289*, 95.

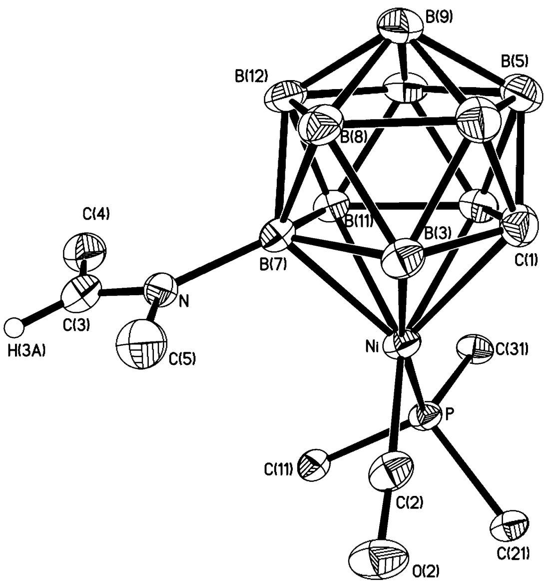

Figure 4. Structure of compound **5c** showing the crystallographic labeling scheme. For clarity, only the major component of the disordered imine group and only the ipso carbons of phenyl rings are shown. Selected distances (Å) and angles (deg) are as follows: Ni−C(1) 2.196(3), Ni−B(3) 2.090(3), Ni−B(6) 2.101(3), Ni−B(7) 2.154(3), Ni−B(11) 2.125(3), Ni−P 2.2142(8), Ni−C(2) 1.757(3), C(2)−O(2) 1.149(3), B(7)−N 1.578(9), N−C(3) 1.256(12), N−C(5) 1.486(9), C(3)−C(4) 1.477(7); N−B(7)−Ni 116.1(3), C(3)−N−C(5) 116.3(6), C(3)−N−B(7) 127.6(6), C(5)−N−B(7) 116.1(7), N−C(3)−C(4) 125.5(5).

retention of proton coupling. These signals are at δ 9.6 (**5a** and **5c**) and 6.9 (**5d**); on this basis, it is tempting to assign an *E* geometry to the imine in **5a**, but as other factors are also involved in determining the chemical shift, we are reluctant to make such an assignment.

For compound **5b**, the NMR spectra are essentially straightforward. The protons of the NCMe ligand resonate as a singlet at δ 2.63, with the carbon atoms of this unit seen at δ 110.2 (C≡N) and 4.6 (Me). The ^{1}H and ^{13}C{^{1}H} NMR spectra for this compound merit little further comment. Similarly, the ^{11}B{^{1}H} NMR spectrum of **5b** shows 10 signals of unit integral (two are coincident), consistent with the absence of mirror symmetry. As with compounds **5a**, **5c**, and **5d**, the signal at highest frequency in this spectrum (δ −1.1) is a singlet in the fully coupled ^{11}B spectrum and is assigned to the B−NCMe nucleus.

Conclusion

We have prepared the anion [2,2-(CO)$_2$-*closo*-2,1-NiCB$_{10}$H$_{11}$]$^-$, which represents for the nickel triad the parent compound of half-sandwich, carbonyl−metal−monocarbollide clusters. This anion is an analogue of the presumed [Ni(CO)$_2$(η-C$_5$H$_5$)]$^+$ cation, but it is notable as a very stable, anionic Ni(II)−carbonyl complex. Similarly, the anion of **1d** is an example of a stable and anionic Ni(II)−olefin species. Several related species and derivatives have been prepared, and some further derivative chemistry has been explored. The reactivity demonstrated for compounds **1a**−**h** showed that a range of substituents can be introduced onto the boron vertexes of the metallacarborane cluster. With these boron-bound groups in place, there is scope for extensive further functionalization of the cluster, a feature that is the subject of much current interest.[13,26]

Experimental Section

General Considerations. All reactions were carried out under an atmosphere of dry, oxygen-free dinitrogen using standard Schlenk line techniques. Solvents were distilled from appropriate drying agents under nitrogen prior to use. Petroleum ether refers to that fraction of boiling point between 40 and 60 °C. Chromatography columns (typically ca. 15 cm in length and ca. 2 cm in diameter) were packed with silica gel (Acros, 60−200 mesh). Preparative thin-layer chromatography (TLC) was performed on 20 cm × 20 cm glass plates (250 μm thickness silica gel GF$_{254}$, Merck). Filtration through Celite typically employed a plug ca. 5 cm in length and ca. 2 cm in diameter. NMR spectra were recorded at the following frequencies (MHz): ^{1}H, 360.1; ^{13}C, 90.6; ^{11}B, 115.5; ^{31}P, 145.8. The reagent [NMe$_4$][*closo*-2-CB$_{10}$H$_{11}$][28] was prepared according to the literature method; all other materials were used as received.

Synthesis of [N(PPh$_3$)$_2$][2,2-L$_2$-*closo*-2,1-NiCB$_{10}$H$_{11}$] (L = CO, CNXyl, and CNBu^t; L$_2$ = cod). (i) A THF (50 mL) solution of [Ni(CO)$_4$] was prepared in situ by bubbling CO through a suspension of [Ni(cod)$_2$] (0.500 g, 1.81 mmol) at −50 °C with vigorous stirring. To this was added [NMe$_4$][*closo*-2-CB$_{10}$H$_{11}$] (0.370 g, 1.80 mmol), and stirring continued at the same temperature for 16 h. (During this period, the reaction mixture appeared to be exceptionally sensitive and often significant amounts of metallic nickel could be deposited at this stage, drastically reducing the ultimate yield.) After being warmed to ambient temperature, solid [N(PPh$_3$)$_2$]Cl (1.050 g, 1.83 mmol) was added and the mixture stirred for an additional 2 h. Removal of volatiles in vacuo gave a dark residue that was extracted with CH$_2$Cl$_2$ (ca. 50 mL). The extract was filtered (Celite), concentrated to ca. 10 mL, and applied to the top of a chromatography column. Elution with CH$_2$Cl$_2$−petroleum ether (4:1) removed an orange fraction, which was collected and evaporated in vacuo to give orange microcrystals of [N(PPh$_3$)$_2$][2,2-(CO)$_2$-*closo*-2,1-NiCB$_{10}$H$_{11}$] (**1a**) (up to ca. 0.976 g). Further elution, using neat CH$_2$Cl$_2$, on occasion gave small quantities of impure **1d**, but this species was far more conveniently prepared as described later.

(ii) Solid [Ni(cod)$_2$] (0.670 g, 2.44 mmol) was suspended in THF (30 mL), and the mixture was cooled to −80 °C. To this was added CNBu^t (555 μL, 0.408 g, 4.91 mmol), followed by solid [NMe$_4$][*closo*-2-CB$_{10}$H$_{11}$] (0.500 g, 2.43 mmol). After being warmed to room temperature, the mixture was stirred for 16 h. To the resulting dark red-orange suspension was added a solution of [N(PPh$_3$)$_2$]Cl (1.40 g, 2.44 mmol) in CH$_2$Cl$_2$ (5 mL), and stirring continued for an additional 1 h. After evaporation in vacuo, the dark orange residue was extracted with CH$_2$Cl$_2$ (50 mL), the extract was filtered (Celite), and all volatiles were removed in vacuo. The resultant mixture was redissolved in CH$_2$Cl$_2$ (5 mL) and subjected to column chromatography. (Some darkening that indicated decomposition was evident upon initial application to the silica.) Elution with CH$_2$Cl$_2$−petroleum ether (3:2) gave an orange band from which was obtained [2,2,7-(CNBu^t)$_3$-*closo*-2,1-NiCB$_{10}$H$_{10}$] (**2a**) (variable, ca. 0.005−0.010 g) as orange-red microcrystals, following removal of the solvent in vacuo. Further elution with neat CH$_2$Cl$_2$ gave an orange band from which was obtained crude [N(PPh$_3$)$_2$][2,2-

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(28) Hyatt, D. E.; Scholer, F. R.; Todd, L. J.; Warner, J. L. *Inorg. Chem.* **1967**, *6*, 2229.

$(CNBu^t)_2$-*closo*-2,1-$NiCB_{10}H_{11}$] (**1b**). The latter was purified by further column chromatography, again eluting with CH_2Cl_2, to give pure **1b** (0.870 g) as an orange microcrystalline powder. Such a purification step always also afforded a few more milligrams of **2a** each time.

(iii) Similarly, from [Ni(cod)$_2$] (1.00 g, 3.64 mmol), CNXyl (0.955 g, 7.28 mmol), and [NMe_4][*closo*-2-$CB_{10}H_{11}$] (0.750 g, 3.65 mmol) in THF (100 mL), stirred for 40 h, with subsequent addition of [N(PPh_3)$_2$]Cl (2.15 g, 3.75 mmol) in CH_2Cl_2 (10 mL), was obtained [N(PPh_3)$_2$][2,2-(CNXyl)$_2$-*closo*-2,1-$NiCB_{10}H_{11}$] (**1c**) (2.94 g) as orange microcrystals. (No **2b** was observed by this route, and the product workup needed only a single chromatographic step, eluting with neat CH_2Cl_2.)

(iv) The solids [Ni(cod)$_2$] (0.500 g, 1.82 mmol) and [NMe_4]-[*closo*-2-$CB_{10}H_{11}$] (0.375 g, 1.82 mmol) were suspended in THF (50 mL) at −80 °C, and the mixture was allowed to warm to room temperature before it was stirred for 16 h. Solid [N(PPh_3)$_2$]Cl (1.2 g, 2.1 mmol) was added and stirring continued for an additional 1 h. Evaporation in vacuo gave a dark brick red oily residue that was extracted with CH_2Cl_2 (50 mL), and the extract was filtered (Celite) and concentrated by evaporation to ca. 5 mL. The latter was transferred to a chromatography column, from which elution with CH_2Cl_2−petroleum ether (4:1) gave a dark red band that yielded brick red microcrystals of [N(PPh_3)$_2$][2,2-(cod)-*closo*-2,1-$NiCB_{10}H_{11}$] (**1d**) (0.777 g) after removal of the solvent in vacuo.

All of compounds **1a**−**d** isolated as described above were sufficiently pure for further reactions. Analytically pure samples were obtained by recrystallization from CH_2Cl_2−petroleum ether at −30 °C.

Synthesis of [N(PPh_3)$_2$][2-CO-2-L-*closo*-2,1-$NiCB_{10}H_{11}$] (L = PEt_3, PPh_3, $CNBu^t$, and CNXyl). (i) Compound **1a** (0.500 g, 0.64 mmol) was dissolved in CH_2Cl_2 (50 mL), and PEt_3 (125 μL, 0.10 g, 0.85 mmol) was added. The mixture was stirred for 16 h, evaporated to dryness in vacuo, and then redissolved in CH_2Cl_2 (ca. 5 mL) and applied to a chromatography column. Elution with CH_2Cl_2 gave a bright yellow-orange band from which was obtained [N(PPh_3)$_2$][2-CO-2-PEt_3-*closo*-2,1-$NiCB_{10}H_{11}$] (**1e**) (0.353 g) as a yellow-orange microcrystalline solid by evaporation in vacuo.

(ii) Compound **1a** (0.600 g, 0.76 mmol) was dissolved in CH_2Cl_2 (25 mL), and to this was added PPh_3 (0.200 g, 0.76 mmol), followed by Me_3NO (0.060 g, 0.80 mmol). The mixture was stirred overnight and then concentrated to ca. 5 mL by evaporation in vacuo. The resulting solution was transferred to the top of a chromatography column. Elution with CH_2Cl_2−petroleum ether (4:1) removed a dark green band that was shown (^{11}B NMR) to contain [*closo*-2-$CB_{10}H_{11}$]$^-$ as the only carborane-containing species, and so it was discarded. Further elution with CH_2Cl_2−THF (100:1) removed a red fraction, from which removal of the solvent afforded [N(PPh_3)$_2$][2-CO-2-PPh_3-*closo*-2,1-$NiCB_{10}H_{11}$] (**1f**) (0.610 g) as orange-red microcrystals.

(iii) To a cooled (−30 °C) solution of **1a** (0.200 g, 0.25 mmol) in CH_2Cl_2 (10 mL) was added $CNBu^t$ (29 μL, 0.021 g, 0.25 mmol), followed by Me_3NO (0.020 g, 0.27 mmol). The mixture was allowed to warm to room temperature and was stirred for 16 h. After removal of all volatiles in vacuo, the crude product was redissolved in CH_2Cl_2 (2 mL) and chromatographed. (As with **1b**, some decomposition was evident upon application to silica.) Elution with CH_2Cl_2 gave two orange bands, of which the first was identified (IR and ^{11}B NMR) as **1b**. From the second band was obtained [N(PPh_3)$_2$][2-CO-2-$CNBu^t$-*closo*-2,1-$NiCB_{10}H_{11}$] (**1g**) (0.091 g, 43%) as an oily orange solid after removal of the solvent in vacuo. IR (CH_2Cl_2): ν_{max}/cm^{-1} 2174 m (CN), 2031 m (CO). Compound **1g** proved to be rather unstable over time, and hence, good microanalytical results could not be obtained. Its identity is, nevertheless, reasonably confirmed by its spectroscopic data (Tables 1−3).

(iv) Similar to the formation of **1f**, compound **1a** (0.200 g, 0.25 mmol) with CNXyl (0.034 g, 0.26 mmol) and Me_3NO (0.020 g, 0.27 mmol) gave orange microcrystals of [N(PPh_3)$_2$][2-CO-2-CNXyl-*closo*-2,1-$NiCB_{10}H_{11}$] (**1h**) (0.081 g) after column chromatography using neat CH_2Cl_2. On occasion, a small quantity (ca. 10−15%) of **1c** was also isolated from this reaction.

Synthesis of [2,2,7-L_3-*closo*-2,1-$NiCB_{10}H_{10}$] (L = $CNBu^t$ and CNXyl). (i) To a solution of compound **1b** (0.150 g, 0.17 mmol) in CH_2Cl_2 (15 mL) was added $CNBu^t$ (30 μL, 0.022 g, 0.26 mmol) and silica gel (ca. 2 g), and the mixture was stirred for 16 h. After removal of the solvent in vacuo, the silica mixture was transferred to the top of a chromatography column. Elution with CH_2Cl_2−petroleum ether (3:2) afforded an orange band from which was obtained [2,2,7-($CNBu^t$)$_3$-*closo*-2,1-$NiCB_{10}H_{10}$] (**2a**) (0.008 g) as orange-red microcrystals. Compound **2a**, as noted earlier, is often also observed as a side product in the synthesis or reactions of **1b**.

(ii) A solution of **1c** (0.500 g, 0.50 mmol) and CNXyl (0.066 g, 0.50 mmol) in CH_2Cl_2 (50 mL) was treated with H[BF_4]·OEt_2 (54 wt % in Et_2O, 0.1 mL), and the mixture was stirred overnight. The resulting dark orange solution was evaporated to dryness, the residue was extracted with CH_2Cl_2−petroleum ether (1:1, 10 mL), and the filtered extract was transferred to the top of a chromatography column. Elution with the same solvent mixture gave a single orange-red band that was collected and evaporated to dryness, yielding orange-red crystals of [2,2,7-(CNXyl)$_3$-*closo*-2,1-$NiCB_{10}H_{10}$] (**2b**) (0.123 g).

Synthesis of [2-CO-2-PEt_3-7-L-*closo*-2,1-$NiCB_{10}H_{10}$] (L = OEt_2, N(Me)=C(H)Me, and NCMe). (i) A solution of compound **1e** (0.200 g, 0.23 mmol) in CH_2Cl_2−OEt_2 (4:1, 25 mL) was cooled to 0 °C, and $CF_3SO_3CH_3$ (0.1 mL) was added. The resulting mixture was stirred for 6 h at room temperature and then evaporated in vacuo. The resulting dark yellow residue was extracted with CH_2Cl_2−petroleum ether (1:1, 5 mL), and the extract was applied to a chromatography column. Elution with CH_2Cl_2−petroleum ether (7:3) gave a pale yellow band that was collected and after removal of the solvent gave pale yellow microcrystals of [2-CO-2-PEt_3-7-OEt_2-*closo*-2,1-$NiCB_{10}H_{10}$] (**3a**) (0.034 g).

(ii) To a solution of **1e** (0.090 g, 0.10 mmol) in CH_2Cl_2−NCMe (5:1, 25 mL) was added $CF_3SO_3CH_3$ (0.1 mL), and the mixture was stirred for 0.5 h at ambient temperature. After the solvent was removed from the reaction mixture, the resultant was applied to a chromatographic column. Elution with CH_2Cl_2−petroleum ether (4:1) gave a yellow-orange band that was shown (^{11}B NMR) to contain two species. Preparative TLC of this mixture using CH_2Cl_2−petroleum ether (2:1) gave yellow and orange bands that were collected and identified as [2-CO-2-PEt_3-7-{N(Me)=C(H)Me}-*closo*-2,1-$NiCB_{10}H_{10}$] (**5a**) (R_f 0.65, ca. 0.010 g, 25%) and [2-CO-2-PEt_3-7-NCMe-*closo*-2,1-$NiCB_{10}H_{10}$] (**5b**) (R_f 0.40, ca. 0.005 g, 13%), respectively.

Compounds **3a**, **5a**, and **5b** were all somewhat unstable in the solid state (especially the latter two) and even more so in solution. This prevented us from obtaining good microanalytical data for **5a** and **5b**.

Synthesis of [2-CO-2,11-{μ-PPh_2(C_6H_4-*o*)}-7-OEt_2-*closo*-2,1-$NiCB_{10}H_9$]. To a solution of compound **1f** (0.100 g, 0.10 mmol) in CH_2Cl_2−OEt_2 (5:1, 25 mL) was added $CF_3SO_3CH_3$ (0.5 mL), and the mixture was stirred for 12 h. After this time, removal of the solvent in vacuo afforded a dark orange residue that was transferred to the top of a chromatography column. Elution with CH_2Cl_2−petroleum ether (2:1) gave a dark red-orange band that

Table 4. Crystallographic Data for **1a**, **2b**·CH_2Cl_2, **4**, and **5c**·$0.5CH_2Cl_2$

	1a	**2b**·CH_2Cl_2	**4**[a]	**5c**·$0.5CH_2Cl_2$
formula	$C_{39}H_{41}B_{10}NNiO_2P_2$	$C_{29}H_{39}B_{10}Cl_2N_3Ni$	$C_{24}H_{33}B_{10}NiO_2P$	$C_{23.5}H_{33}B_{10}ClNNiOP$
fw	784.48	667.34	551.28	578.74
space group	$P2_1/c$	$P2_1/c$	$C2/c$	$P\bar{1}$
a, Å	14.542(2)	12.558(3)	32.049(6)	9.7282(15)
b, Å	18.249(4)	18.357(4)	11.7723(17)	12.0324(16)
c, Å	15.482(3)	16.282(4)	18.731(4)	13.360(3)
α, deg	90	90	90	100.440(9)
β, deg	101.796(8)	111.944(4)	124.065(19)	97.678(18)
γ, deg	90	90	90	107.274(10)
V, Å^3	4021.9(13)	3481.5(14)	5854.3(19)	1439.0(4)
Z	4	4	8	2
ρ_{calc}, g cm^{-3}	1.296	1.273	1.251	1.336
T, K	110(2)	173(2)	110(2)	173(2)
reflns measured	95236	21177	53532	14377
indept reflns	13022	7962	8905	6514
R_{int}	0.0620	0.0359	0.0603	0.0369
μ(Mo Kα), cm^{-1}	0.598	0.736	0.739	0.843
wR2 (all data), R1[b]	0.1092, 0.0421	0.1676, 0.0547	0.1299, 0.0481	0.1062, 0.0424

[a] Cocrystallizes with an unidentified solvate (see text). The formula and values for fw, ρ_{calc}, and μ given here ignore the presence of this solvate. [b] wR2 $= [\Sigma\{w(F_o^2 - F_c^2)^2\}/\Sigma w(F_o^2)^2]^{1/2}$; R1 $= \Sigma||F_o| - |F_c||/\Sigma|F_o|$ with $F_o > 4\sigma(F_o)$.

was collected and purified by preparative TLC. Elution of the latter using CH_2Cl_2−petroleum ether (5:2) gave an orange-red band (R_f = 0.72) that was collected and identified as [2-CO-2,11-{μ-PPh_2-(C_6H_4-*o*)}-7-OEt_2-*closo*-2,1-$NiCB_{10}H_9$] (**4**) (0.027 g).

Synthesis of [2-CO-2-PPh$_3$-7-{N(Me)═C(H)Me}-*closo*-2,1-NiCB$_{10}$H$_{10}$]. A solution of **1f** (0.250 g, 0.25 mmol) in CH_2Cl_2−NCMe (5:1, 20 mL) was treated with $CF_3SO_3CH_3$ (0.25 mL), and the mixture was stirred overnight. Volatiles were removed in vacuo, and the resulting dark red residue was subjected to column chromatography. Elution with CH_2Cl_2−petroleum ether (3:2) gave an orange band from which removal of the solvent in vacuo gave red-orange microcrystals of a mixture of [2-CO-2-PPh_3-7-{(*X*)-N(Me)═C(H)Me}-*closo*-2,1-$NiCB_{10}H_{10}$] ($X \equiv E$ (**5c**), Z (**5d**)) (0.051 g total).

Structure Determinations. Experimental data for compounds **1a**, **2b**, **4**, and **5a** are recorded in Table 4. Diffracted intensities for **1** and **4** were collected at 110(2) K on a Bruker-Nonius X8 APEX CCD area-detector diffractometer, while those for **2b** and **5a** were acquired at 173(2) K on a Siemens SMART CCD area-detector diffractometer. Both machines employed graphite-monochromated Mo Kα X-radiation (λ = 0.71073 Å). In the former two cases, several sets of narrow data "frames" were collected at different values of θ, for various initial values of ϕ and ω, using 0.5° increments of ϕ or ω; in the latter two, frame sets were collected for 0.3° increments of ω at four settings of ϕ. Frames were integrated using SAINT;[29] the substantial redundancy in data allowed an empirical absorption correction (SADABS)[29] to be applied, based on multiple measurements of equivalent reflections.

All structures were solved by direct methods and refined by full-matrix least-squares analysis on all F^2 data using SHELXTL versions 5.03 and 6.12.[30] All non-hydrogen atoms were successfully refined with anisotropic thermal parameters. The locations of the cage carbon atoms were verified by examination of their isotropic thermal parameters, in conjunction with comparisons of B−B and C−B internuclear distances. All hydrogen atoms were set riding on their parent atoms with fixed isotropic thermal parameters calculated as $U_{iso}(H) = 1.2U_{iso}$(parent) or $U_{iso}(H) = 1.5U_{iso}$(parent) for methyl hydrogens.

Compound **2b** cocrystallized with one molecule of CH_2Cl_2 as solvate, located in general space. The molecule was disordered over two distinct positions, and the two were fully refined as above with complementary occupancies, with their respective ratios being ca. 59:41 at convergence. The C−Cl distances were restrained toward sensible values (1.76(2) Å) using the DFIX card in SHELXL-97.[30]

The lattice of **4** also contained solvent molecules, but in this case, they could not definitively be identified. It is thought that the solvate consisted of a mixture of highly disordered fractional pentane and CH_2Cl_2 molecules, lying close to a crystallographic C_2 axis (Wyckoff position *e*). In practice, these ultimately were successfully modeled as seven fractional carbon atoms with refining occupancies and anisotropic temperature factors; no attempt was made to include hydrogen atoms. Additionally, one of the ethyl groups of the cage-bound OEt_2 molecule was disordered over two positions. The two components were included with refining complementary occupancies, in the approximate ratio of 67:33 at convergence, and otherwise were treated as described above.

One-half molecule of CH_2Cl_2 cocrystallizes with one formula unit of **5a**, lying close to a crystallographic inversion center (Wyckoff position *d*) such that there are two alternative positions for the CH_2 moiety. This solvate was otherwise ordered and treated normally, as above. The imine group was also disordered over two alternative locations, the two being approximately related by a notional reflection in the plane through Ni, B(7), and B(9). Positional and displacement parameters for all C, N, and H atoms in the two components were refined as described above, and the parts had refining complementary occupancies that converged at the approximate ratio of 74:26.

Acknowledgment. We thank the Robert A. Welch Foundation for support and Dr. John C. Jeffery, Bristol University, U.K., for assistance with the structure determinations of **2b** and **5c**. The Bruker X8 APEX diffractometer was purchased with funds received from the National Science Foundation Major Research Instrumentation Program (Grant CHE-0321214).

Supporting Information Available: Full details of the crystal structure analyses in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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(29) *APEX 2*, version 1.0; Bruker AXS: Madison, WI, 2003−2004.
(30) *SHELXTL*, versions 5.03 and 6.12; Bruker AXS: Madison, WI, 1995 and 2001.