Synthesis, structural characterization, and reactivity of late transition-metal complexes bearing linked cyclopentadienyl–carboranyl ligands

Dongmei Liu, Zaozao Qiu, Hoi-Shan Chan, and Zuowei Xie

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Abstract: Late transition-metal complexes bearing linked cyclopentadienyl/indenyl–carboranyl ligands were synthesized and their reactivities were examined. Reaction of $Li_2[Me_2C(L)(C_2B_{10}H_{10})]$ (L = C_5H_4, C_9H_6, $Me_2NCH_2CH_2C_5H_3$) with $MCl_2(PPh_3)_2$ in Et_2O afforded $[\eta^5{:}\sigma\text{-}Me_2C(C_5H_4)(C_2B_{10}H_{10})]M(PPh_3)$ (M = Co (**4**), Ni (**5**)), $[\eta^5{:}\sigma\text{-}Me_2C(C_9H_6)(C_2B_{10}H_{10})]M(PPh_3)$ (M = Co (**6**), Ni (**7**)), and $[\eta^5{:}\sigma\text{-}Me_2C(Me_2NCH_2CH_2C_5H_3)(C_2B_{10}H_{10})]Ni(PPh_3)$ (**8**). Treatment of **4** or **5** with 2,6-dimethylphenylisocyanide, N-heterocyclic carbene (NHC), PCy_3, or 1,2-bis(diphenylphosphino)ethane (dppe) gave the corresponding PPh_3 displacement complexes $[\eta^5{:}\sigma\text{-}Me_2C(C_5H_4)(C_2B_{10}H_{10})]M(2,6\text{-}Me_2C_6H_3NC)$ (M = Co (**9**), Ni (**10**)), $[\eta^5{:}\sigma\text{-}Me_2C(C_5H_4)(C_2B_{10}H_{10})]M[1,3\text{-}(2,6\text{-}i\text{-}Pr_2C_6H_3)_2C_3N_2H_2]$ (M = Co (**11**), Ni (**12**)), $[\eta^5{:}\sigma\text{-}Me_2C(C_5H_4)(C_2B_{10}H_{10})]Ni(PCy_3)$ (**13**), or $\{[\eta^5{:}\sigma\text{-}Me_2C(C_5H_4)(C_2B_{10}H_{10})]Co\}_2(dppe)$ (**14**), respectively. These complexes were characterized by various spectroscopic techniques and elemental analyses. The molecular structures of **4**–**14** were further confirmed by single-crystal X-ray analyses.

Key words: carborane, cyclopentadienyl, cobalt complexes, nickel complexes, substitution reaction.

Résumé : On a effectué la synthèse de complexes de métaux de transition portant des ligands liés cyclopentadiényl/indényl-carboranyles et on en a examiné les réactivités. La réaction du $Li_2[Me_2C(L)(C_2B_{10}H_{10})]$ (L = C_5H_4, C_9H_6, $Me_2NCH_2CH_2C_5H_3$) avec le $MCl_2(PPh_3)_2$, dans l'éther, conduit à la formation des $[\eta^5{:}\sigma\text{-}Me_2C(C_5H_4)(C_2B_{10}H_{10})]M(PPh_3)$ (M = Co (**4**); Ni (**5**)), $[\eta^5{:}\sigma\text{-}Me_2C(C_9H_6)(C_2B_{10}H_{10})]M(PPh_3)$ (M = Co (**6**); Ni (**7**)) et $[\eta^5{:}\sigma\text{-}Me_2C(Me_2NCH_2CH_2CH_2C_5H_3)(C_2B_{10}H_{10})]Ni(PPh_3)$ (**8**). Le traitement des composés 4 et 5 avec de l'isocyanure de 2,6-diméthylphényle, des carbènes N-hétérocycliques (NHC), du PCy_3 ou du 1,2-bis(diphénylphosphino)éthane (dppe), conduit aux complexes correspondants avec remplacement du PPh_3, soit respectivement les $[\eta^5{:}\sigma\text{-}Me_2C(C_5H_4)(C_2B_{10}H_{10})]M(2,6\text{-}Me_2\text{-}C_6H_3NC)$ (M = Co (**9**); Ni (**10**)), $[\eta^5{:}\sigma\text{-}Me_2C(C_9H_6)(C_2B_{10}H_{10})]M[1,3\text{-}(2,6\text{-}i\text{-}Pr_2C_6H_3NC)_2(C_3N_2H_2)]$ (M = Co (**11**); Ni (**12**)) $[\eta^5{:}\sigma\text{-}Me_2C(C_5H_4)(C_2B_{10}H_{10})]Ni(PCy_3)$ (**13**) ou $\{[\eta^5{:}\sigma\text{-}Me_2C(Me_2C_5H_4)(C_2B_{10}H_{10})]Co\}_2(dppe)$ (**14**). Ces complexes ont été caractérisés par diverses techniques spectroscopiques et par des analyses élémentaires. Les structures moléculaires des composés **4**–**14** ont de plus été confirmées par des diffractions de rayons-X sur des cristaux uniques.

Mots-clés : carborane, cyclopentadiényle, complexes du cobalt, complexes du nickel, réaction de substitution.

[Traduit par la Rédaction]

Introduction

Linked cyclopentadienyl/indenyl/fluorenyl–carboranyl ligands have been widely used for the synthesis of constrained-geometry transition-metal complexes,[1–3] in which the nontraditional metal–carbon(cage) (M–C_{cage}) bonds are generally inert toward electrophiles because of steric reasons.[1e,1f] On the other hand, they can offer transition-metal complexes unique features.[4] For example, the constrained-geometry ruthenium complexes, $[\eta^5{:}\sigma\text{-}Me_2C(C_5H_4)(C_2B_{10}H_{10})]Ru(L_2)$ (L = NHR_2, CH_3CN) can react with alkynes to produce Ru–carbene, –diene, and –bisvinylidene complexes bearing the $[Me_2C(C_5H_4)(C_2B_{10}H_{10})]^{2-}$ ligand.[4] In addition, $[\eta^5{:}\sigma\text{-}Me_2C(C_5H_4)(C_2B_{10}H_{10})]Ru(CH_3CN)_2$ can also react with 3 equiv of terminal alkynes ArC≡CH to form the unexpected tricyclic compounds with the activation of the incorporated C_5H_4 ring.[4f]

It has been documented that the Co and Ni complexes show some common features with the Ru ones in [2+2+2] cyclotrimerization of alkynes and C–C coupling reactions.[5] Connected to this and to understand the similarities and differences among late transition-metal complexes with linked cyclopentadienyl–carboranyl ligands, we extended our research to include cobalt and nickel metals. We report herein the synthesis, structure, and reactivity of Co and Ni complexes

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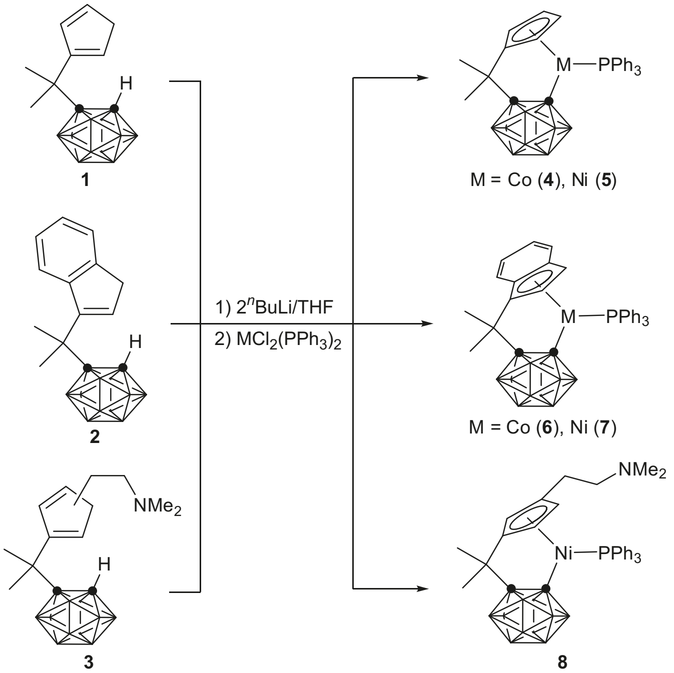
Scheme 1. Synthesis of cobalt and nickel complexes.



bearing carbon-linked cyclopentadienyl/indenyl–carboranyl ligands.

Results and discussion

Synthesis and structure

Treatment of $Li_2[Me_2C(C_5H_4)(C_2B_{10}H_{10})]^{2d}$ with 1 equiv of $MCl_2(PPh_3)_2$ (M = Co, Ni) in THF at room temperature afforded, after recrystallization from Et_2O, constrained-geometry transition-metal complexes $[\eta^5{:}\sigma\text{-}Me_2C(C_5H_4)(C_2B_{10}H_{10})]M(PPh_3)$ (M = Co (**4**) or Ni (**5**)) in ~90% isolated yields (Scheme 1). In a similar manner, complexes $[\eta^5{:}\sigma\text{-}Me_2C(C_9H_6)(C_2B_{10}H_{10})]M(PPh_3)$ (M = Co (**6**) or Ni (**7**)) and $[\eta^5{:}\sigma\text{-}Me_2C(Me_2NCH_2CH_2C_5H_3)(C_2B_{10}H_{10})]Ni(PPh_3)$ (**8**) were also synthesized from the interaction of $Li_2[Me_2C(C_9H_6)(C_2B_{10}H_{10})]^{2e}$ or $Li_2[Me_2C(Me_2NCH_2CH_2C_5H_3)(C_2B_{10}H_{10})]$ with 1 equiv of $MCl_2(PPh_3)_2$ in 63%–79% isolated yields, respectively (Scheme 1).

Complexes **4** and **6** were paramagnetic species, which did not provide useful NMR information. For complexes **5**, **7**, and **8**, the ^1H and ^{13}C NMR spectra showed the presence of the ligand and coordinated PPh_3 with an 1:1 molar ratio. Their ^{11}B NMR spectra exhibited the same 2:3:5 pattern. The ^{31}P NMR spectra displayed a singlet at 47.3 ppm for **5**, 33.8 ppm for **7**, and 36.5 ppm for **8**, respectively. The compositions of complexes **4**–**8** were confirmed by elemental analyses.

Fig. 1. Molecular structure of $[\eta^5{:}\sigma\text{-}Me_2C(C_5H_4)(C_2B_{10}H_{10})]NiPPh_3$ (**5**).

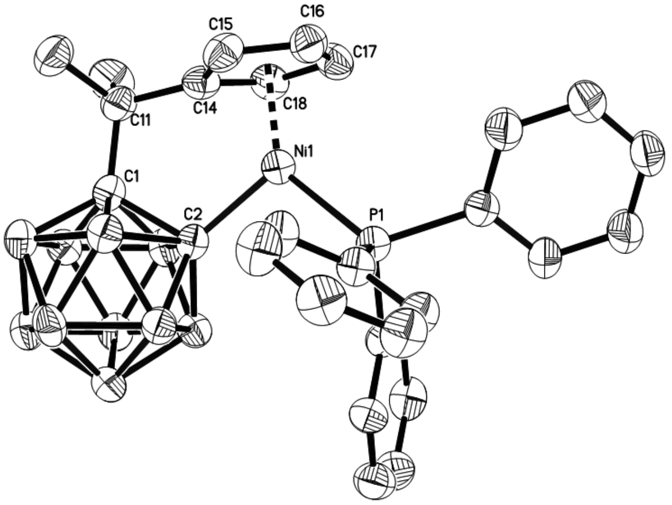
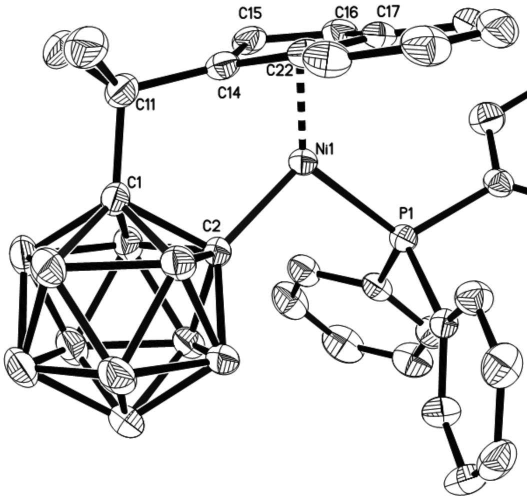


Fig. 2. Molecular structure of $[\eta^5{:}\sigma\text{-}Me_2C(C_9H_6)(C_2B_{10}H_{10})]NiPPh_3$ (**7**).



The solid-state structures of **4**–**8** as revealed by single-crystal X-ray analyses show that the metal atoms are η^5-bound to the cyclopentadienyl ligand (in **4**, **5**, and **8**) or indenyl ligand (in **6** and **7**), σ-bound to one cage carbon atom, and coordinated to a triphenylphosphine in a trigonal planar geometry, leading to the formation of 17 e^- cobalt and 18 e^- nickel complexes. The representative structures of **5**, **7**, and **8** are shown in Figs. 1–3, respectively. The selected bond distances and angles around the metal atoms are listed in Table 1 for comparison. It is noted that the appended N atom in **8** does not substitute the P atom to form the intramolecular coordination to the Ni atom as the N atom is a harder base than the P atom.

The distances between the Co atom and the five-membered ring atoms ($Co–C_{ring}$) range from 2.028(3) to 2.126(3) Å in **4** and from 2.044(4) to 2.259(4) Å in **6**. These values are comparable to the 2.102(2) Å in $(\eta^5\text{-}C_5H_5)Co(PPh_3)[\eta^1(N)\text{-}N(O)Me]$,[6] to the 2.06(5) Å in $(\eta^5\text{-}C_5H_5)Co(S_2C_2B_{10}H_{10})$,[7] and to the 2.154(9) Å in $(\eta^5\text{-}C_9H_6)(C_3H_7)(PMe_3)_2CoI$.[8] The average $Ni–C_{ring}$ distances of 2.145(6) Å in **5**, 2.17 ± 0.01 Å in **7**, and 2.131(3) Å in **8** are very close to each other. They are also similar to the 2.102(6) Å in $[Ni(\eta^5\text{-}C_5H_5)(PPh_3)C{\equiv}CCHO]$,[9] to the 2.182(3) Å in $[(\eta^5\text{-}1\text{-}TMS\text{-}C_9H_5)NiCl(PPh_3)$,[10] to the 2.114(7) Å in $(\eta^5{:}\eta^1\text{-}C_5H_4CH_2CH_2NMe_2)Ni(C_{12}H_8N)$,[11] and to the 2.098(9) Å in $[(\eta^5\text{-}C_5H_4CH_2CH_2NMe_2)Ni(dmpe)][PF_6]$.[12]

The metal – cage carbon distances ($M–C_{cage}$) between 1.95 and 2.01 Å for **4**–**8** are comparable to the 1.998(9)–2.013(9) Å in $[Ni\{(C_2B_{10}H_{10})_2\}_2]^{2-}$,[13] to the 2.051(12)–2.070(12) Å

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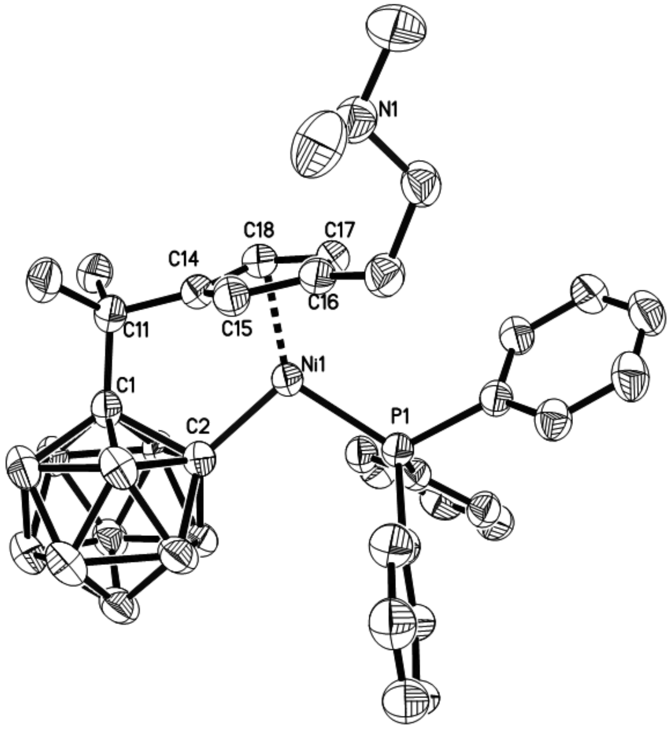
Fig. 3. Molecular structure of $[\eta^5{:}\sigma\text{-}Me_2C(Me_2NCH_2CH_2C_5H_3)(C_2B_{10}H_{10})]NiPPh_3$ (**8**).



in $[Co\{(C_2B_{10}H_{10})_2\}_2]^{2-}$,[13] and to the 1.972(5) Å in $[\eta{:}\sigma\text{-}(2\text{-}C_5H_4NCH_2C_2B_{10}H_{10})]_2Ni$.[14]

The metal–phosphorus distances (M–P) in **4**–**8** fall in the range 2.19–2.25 Å. They are comparable to the 2.184(1) Å in $(\eta^5\text{-}C_5H_5)Co(PPh_3)[\eta^1(N)\text{-}N(O)Me]$,[6] to the 2.146(1) Å in $(\eta^5\text{-}C_9H_6)Co(CO)(PPh_3)$,[15] to the 2.29(1)/2.20(1) Å in $(PPh_3)_2Ni(C_2B_{10}H_{10})$,[16] to the 2.211(2)/2.214(2) Å in $\{(PPh_3)_2Ni[\mu\text{-}(\eta^5\text{-}C_5H_4)CMe_2(\eta^5\text{-}C_5H_4)]Ni(PPh_3)_2\}\{PF_6\}_2$,[17] and to the 2.134(1) Å in $Cp^*Ni(PPh_3)(CH_2COt\text{-}Bu)$.[18]

Reactivity

The substitution reactions of **4** and **5** with various Lewis bases were examined to gain information on the lability of the PPh_3 ligand. The results showed that the PPh_3 in **4** and **5** were easily replaced by isocyanide, N-heterocyclic carbene (NHC), and other phosphines.

Treatment of **4** or **5** with 1 equiv of 2,6-dimethylphenylisocyanide at room temperature in toluene afforded, after recrystallization from Et_2O, the PPh_3 displacement products, $[\eta^5{:}\sigma\text{-}Me_2C(C_5H_4)(C_2B_{10}H_{10})]M(CNC_6H_3Me_2\text{-}2,6)$ (M = Co (**9**) or Ni (**10**)) in 77% and 59% isolated yield, respectively (Scheme 2). The reactions were monitored by ^{31}P NMR spectra. Complex **10** showed a distinct NMR spectrum from its parent complex **5**. Except for the resonances corresponding to the protons of the bridging ligand, signals in the range 6.66–6.51 ppm assignable to the aromatic protons and one singlet at 2.11 ppm attributable to the methyl protons on the phenyl ring were observed in the ^1H NMR spectrum. The characteristic resonance of the N=*C* at 162.8 ppm was observed in the ^{13}C NMR spectrum. The ^{11}B NMR spectrum showed a 1:2:3:4 pattern.

The structures of both **9** and **10** were confirmed by single-crystal X-ray analyses. They are isomorphous and isostructural with a trigonal planar geometry. The representative structure of **9** is shown in Fig. 4. The average M–C_{ring} bond distances of 2.074(3)/2.099(4) Å in Co (**9**)/Ni (**10**) are comparable to those of 2.085(3)/2.145(6) Å observed in **4**/**5**, and the M–C_{cage} bond distances of 1.922(3)/1.898(3) Å in **9**/**10** are slightly shorter than those of 1.989(3)/1.975(5) Å found in **4**/**5**. The M–C bond distances of 1.838(3)/1.790(3) Å in **9**/**10** compare to those of 1.87(1)/1.89(1) Å in $[Co(L_{C=O}{:}N_2(SO)_2)(CNt\text{-}Bu)_2]^-$,[19] to 1.772(18)/1.963(18) Å in $CoBr(PhCOCH)(CNC_6H_3Me_2\text{-}2,6)_6$,[20] to 1.787(3) Å in $Ni(triphos)(CNC_6H_3Me_2\text{-}2,6)$,[21] to 1.820(4) Å in $Ni\{S_2P(O)(OEt)\}(CNC_6H_3Me_2\text{-}2,6)(PCy_3)$,[22] and to 1.789(9)/1.789(8) Å in $[Ni(\mu\text{-}t\text{-}Bu_2As)(p\text{-}tol\text{-}NC)_2]_2$.[23]

Reaction of **4** or **5** with 1 equiv of NHC (1,3-bis(2,6-diisopropylphenyl)-1,3-dihydro-2*H*-imidazol-2-ylidene) in toluene at room temperature afforded $[\eta^5{:}\sigma\text{-}Me_2C(C_5H_4)(C_2B_{10}H_{10})]M[C(2,6\text{-}i\text{-}Pr_2C_6H_3\text{–}NCH)_2]$ (M = Co (**11**) or Ni (**12**)) in 51% and 60% isolated yield, respectively (Scheme 2). The characteristic ^{13}C resonance at 163.1 ppm corresponding to the NHC carbene carbon was observed in the ^{13}C NMR spectrum of **12**. Its ^{11}B NMR spectrum showed a 2:3:5 pattern.

The structures of complexes **11** and **12** were confirmed by single-crystal X-ray analyses. They are isomorphous and isostructural. The metal atom is η^5-bound to the Cp ring, σ-bound to the cage carbon atom, and coordinated to the carbene atom in a trigonal planar geometry. The representative structure of **11** is shown in Fig. 5. The average M–C_{ring}/M–C_{cage} bond distances of 2.143(3)/2.152(4) Å in **11** and 2.003(3)/1.945(3) Å in **12** are comparable to the corresponding values observed in **4** and **5**, respectively. The Co–C_{NHC} bond distance of 2.011(2) Å in **11** is similar to that of 2.043(2)/2.019(2) Å in $[(TIMEN^{xyl})Co][BPh_4]_2$ (TIMEN = tris[2-(3-arylimidazol-2-ylidene)ethyl]amine; xyl = 2,6-dimethylphenyl))[24] and to 1.914(2) Å in $(\eta^5\text{-}C_5H_4)Co[C(2,6\text{-}i\text{-}Pr_2C_6H_3\text{–}NCH)_2]Me_2$.[25] The Ni–$C_{NHC}$ bond distance of 1.934(2) Å in **12** is somewhat longer than the 1.882(4) Å in $Cp[(\eta^2{:}\eta^2\text{-}CH_2{=}CHCH_2NCHCHNMe)]C]Ni$,[26] than the 1.886(3) Å in $(C_9H_7)[(i\text{-}PrNCH)_2C]NiCl$,[27] than the 1.888(4) Å in $(C_9H_7)[(i\text{-}PrNCH)_2C]NiBr$,[27] and than the 1.901(3) Å in $[(m\text{-}MeOC_6H_4CH_2NCHCHNCH_2CH_2PPh_2)C]_2NiCl_2$.[28]

Interaction of **5** with 1 equiv of PCy_3 (Cy = cyclohexyl) in refluxing toluene afforded $[\eta^5{:}\sigma\text{-}Me_2C(C_5H_4)(C_2B_{10}H_{10})]Ni(PCy_3)$ (**13**) in 57% isolated yield. The room-temperature reaction was very slow. An equimolar reaction of **4** with 0.5 equiv of dppe (1,2-bis(diphenylphosphino)ethane) gave $\{[\eta^5{:}\sigma\text{-}Me_2C(C_5H_4)(C_2B_{10}H_{10})]Co\}_2(dppe)$ (**14**) in 62% isolated yield (Scheme 2). The substitution of PPh_3 in **5** by PCy_3 was confirmed by ^1H and ^{31}P NMR spectra. In addition to the resonances assignable to the protons of the bridging ligand, multiplets in the region 2.11–1.07 ppm corresponding to the cyclohexyl protons were observed in the ^1H NMR spectrum. Its ^{31}P NMR spectrum showed a singlet at 44.4 ppm compared with the 47.3 ppm in **5**.

The molecular structure of **13** is shown in Fig. 6. The Ni atom is η^5-bound to the cyclopentadienyl ring, σ-bound to one cage carbon atom, and coordinated to the P atom of the tricyclohexylphosphine in a trigonal planar geometry. The average Ni–C_{ring}/Ni–C_{cage}/Ni–P bond distances of 2.140(5)/1.949(5)/2.226(1) Å are very close to those of 2.145(6)/1.975(5)/2.210(1) Å in **5**. On the other hand, as revealed by

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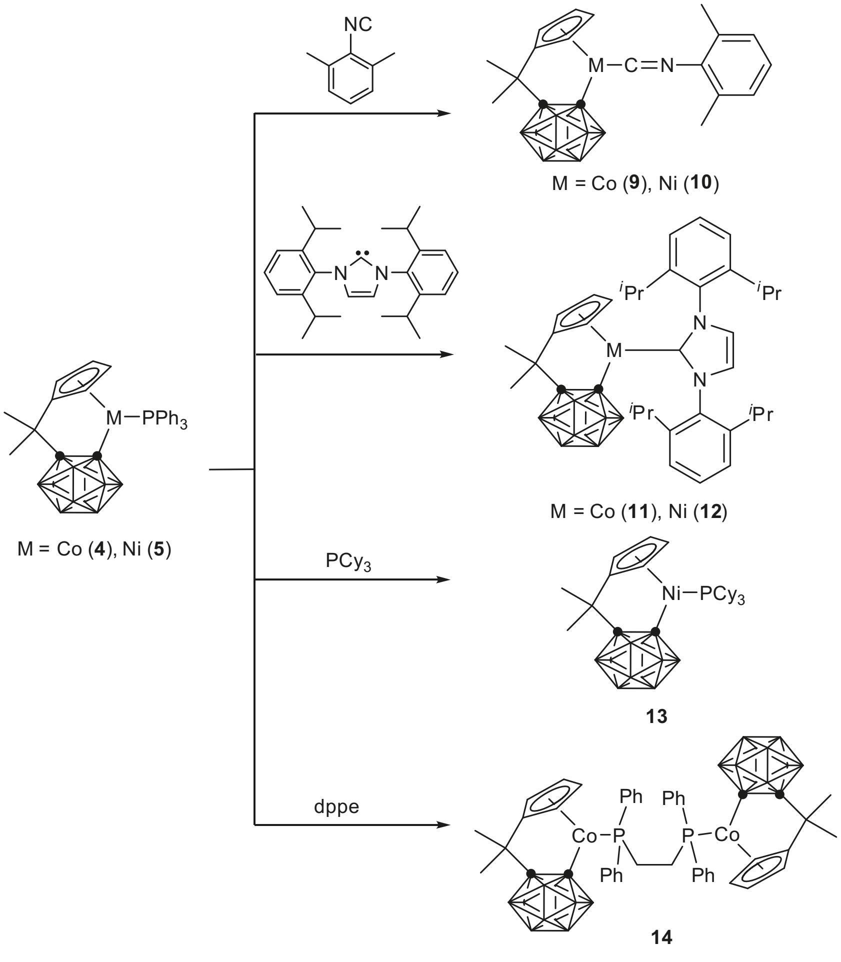
Table 1. Selected bond lengths (Å) and angles (°) in compounds **4–14**.

	Bond length (Å)				Bond angle (°)	
Compd.	M–C_{cage}	Av. M–C_{ring}	M–Cent[a]	M–X	Cent–M–C_{cage}[a]	C_{ring}–C_{bridge}–C_{cage}
4	1.989(3)	2.085(3)	1.706	2.209(1) (X = P)	122.6	113.9(2)
5	1.975(5)	2.145(6)	1.765	2.210(1) (X = P)	122.0	114.1(4)
6	2.008(5)	2.15±0.01	1.763	2.247(1) (X = P)	123.3	114.7(3)
7	1.950(3)	2.17±0.01	1.800	2.194(1) (X = P)	122.4	114.3(2)
8	1.960(2)	2.131(3)	1.752	2.188(1) (X = P)	122.0	114.4(2)
9	1.922(3)	2.074(3)	1.689	1.838(3) (X = C)	124.0	114.1(2)
10	1.898(3)	2.099(4)	1.722	1.790(3) (X = C)	123.4	114.0(2)
11	2.003(3)	2.143(3)	1.762	2.011(2) (X = C)	121.0	114.3(2)
12	1.945(3)	2.152(4)	1.786	1.934(2) (X = C)	120.5	114.2(2)
13	1.949(5)	2.140(5)	1.770	2.226(1) (X = P)	121.4	114.1(4)
14	1.951(3)	2.084(4)	1.697	2.216(1) (X = P)	123.4	114.3(2)

[a]Cent: the centroid of the five-membered ring.

Scheme 2. Reactivity of cobalt and nickel complexes.



single-crystal X-ray analyses, **14** is a dinuclear complex (shown in Fig. 7), in which two trigonal planar $[\eta^5{:}\sigma\text{-}Me_2C(C_5H_4)(C_2B_{10}H_{10})]Co$ moieties are connected by a $Ph_2PCH_2CH_2PPh_2$ linkage resulting in the formation of a 17 e$^-$ complex for each Co atom. The average Co–C_{ring}/Co–C_{cage}/Co–P bond distances of 2.084(4)/1.951(3)/2.216(1) Å are very similar to the 2.085(3)/1.989(3)/2.207(1) Å observed in **4**.

The aforementioned results show that the coordinated PPh_3 in complexes **4** and **5** is labile and can be replaced by Lewis bases. However, they are inert toward alkynes, nitriles, and H_2. Complexes **9** and **10** are also very thermally stable. The inertness of the M–C_{cage} σ bonds in these late transition-metal complexes can be ascribed to the steric hindrance of the icosahedral carborane cage.[1e,1f]

Conclusion

A series of cobalt and nickel complexes bearing carbon-bridged cyclopentadienyl/indenyl/$C_5H_3CH_2CH_2NMe_2$–carboranyl

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Fig. 4. Molecular structure of [η^5:σ-$Me_2C(C_5H_4)(C_2B_{10}H_{10})$]Co ($CNC_6H_3Me_2$-2,6) (**9**).

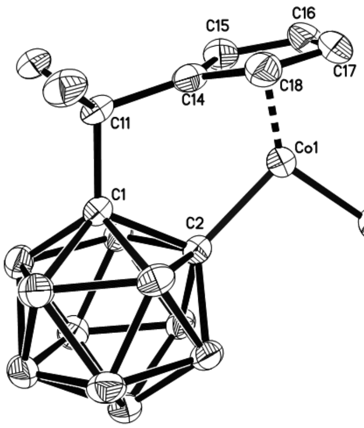


Fig. 5. Molecular structure of [η^5:σ-$Me_2C(C_5H_4)(C_2B_{10}H_{10})$]Co[1,3-(2,6-*i*-$Pr_2C_6H_3)_2C_3N_2H_2$] (**11**).

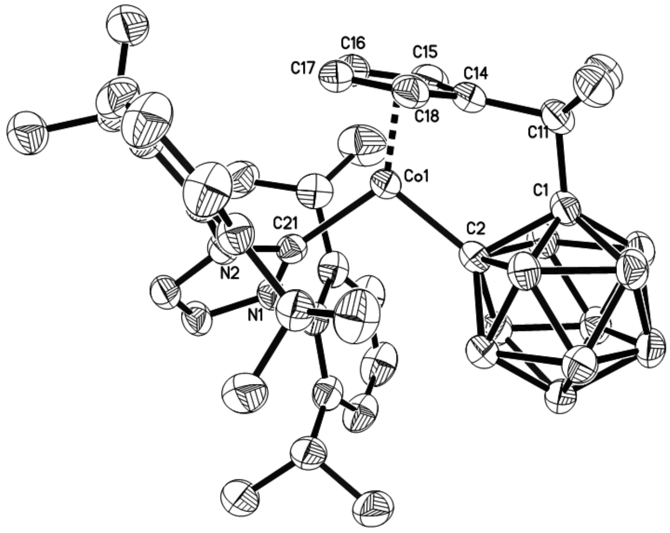


Fig. 6. Molecular structure of [η^5:σ-$Me_2C(C_5H_4)(C_2B_{10}H_{10})$]NiPCy$_3$ (**13**).

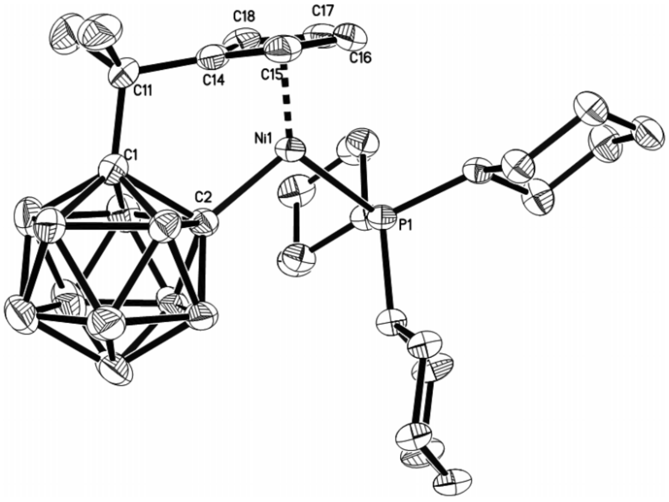
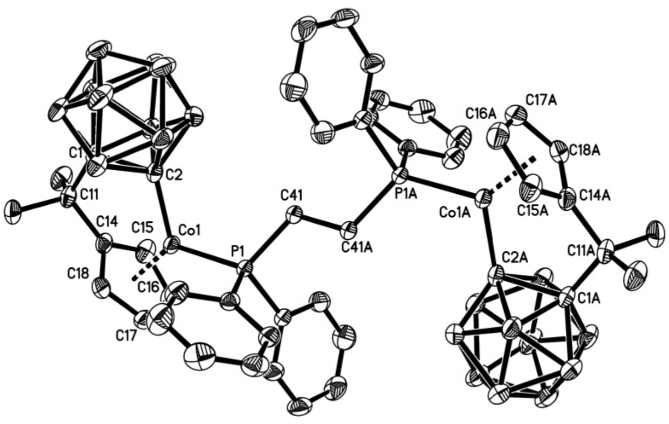


Fig. 7. Molecular structure of {[η^5:σ-$Me_2C(C_5H_4)(C_2B_{10}H_{10})$]Co}$_2$ (dppe) (**14**).



ligands were synthesized via salt metathesis reactions between the dilithium salts of these ligands and metal halides. They adopt a trigonal planar geometry, leading to a 17 e$^-$ cobalt and a 18 e$^-$ nickel complex, respectively. The phosphines in [η^5:σ-$Me_2C(C_5H_4)(C_2B_{10}H_{10})$]M($PPh_3$) are labile and can be displaced by other Lewis bases. However, the M–C$_{cage}$ bonds in these complexes are inert toward electrophiles such as alkynes, nitriles, isonitriles, and H_2 because of the steric hindrance of the carboranyl ligand.

Experimental section

General procedures

All experiments were performed under an atmosphere of dry dinitrogen with the rigid exclusion of air and moisture using standard Schlenk or cannula techniques or in a glovebox. All organic solvents were refluxed over sodium benzophenone ketyl for several days and freshly distilled prior to use. All chemicals were purchased from either Sigma-Aldrich or Acros Chemical Co. and used as received unless otherwise noted. $Me_2NCH_2CH_2Cl$,[29] $Me_2NCH_2CH_2C_5H_3CMe_2$,[30] $Me_2C(C_5H_5)(C_2B_{10}H_{11})$,[2d] $Me_2C(C_9H_7)(C_2B_{10}H_{11})$,[2e] $NiCl_2(PPh_3)_2$,[31] and $CoCl_2(PPh_3)_2$[32] were prepared according to literature methods. Infrared spectra were obtained from KBr pellets prepared in the glovebox on a PerkinElmer 1600 Fourier transform spectrometer. ^1H and ^{13}C NMR spectra were recorded on a Bruker DPX 300 spectrometer at 300 and 75.5 MHz, respectively. ^{11}B and ^{31}P NMR spectra were recorded on a Varian Inova 400 spectrometer at 128 and 162 MHz, respectively. All chemical shifts were reported in δ units with references to the residual protons of the deuterated solvents for proton and carbon chemical shifts, to external $BF_3 \cdot OEt_2$ (0.00 ppm) for boron chemical shifts, and to external 85% H_3PO_4 (0.00 ppm) for phosphorus chemical shifts. Elemental analyses were performed by the Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, China.

Preparation of $Me_2C(Me_2NCH_2CH_2C_5H_4)(C_2B_{10}H_{11})$ (3)

To a toluene/Et_2O (2:1) solution (15 mL) of *o*-$C_2B_{10}H_{12}$ (1.44 g, 10.0 mmol) was added a 1.60 mol/L solution of *n*-BuLi in hexane (12.6 mL, 20.2 mmol) at 0 °C, and the reaction mixture was warmed to room temperature and stirred for 2 h. The resulting $Li_2C_2B_{10}H_{10}$ solution was then cooled to 0 °C, to which was slowly added a solution

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of dimethyl(dimethylaminoethyl)fulvene (2.12 g, 12.0 mmol) in a toluene/Et_2O (2:1) mixture (9 mL). The reaction mixture was maintained at 0 °C for 1 h, slowly warmed to room temperature, and then refluxed overnight. After removal of the solvent, Et_2O was added. The solution was quenched with a saturated NH_4Cl solution. The organic layer was separated and washed with water and then dried with anhydrous $MgSO_4$. After removal of the solvent by rotary evaporation, the residue was subjected to column chromatography on silica gel to give **3** as a yellow oil (2.66 g, 83%). IR (KBr, cm^{-1}) ν_{BH}: 2521 (vs). ^1H NMR ($CDCl_3$) δ: 6.25–5.70 (m, 3H) (vinylic *H*), 3.32 + 3.15 (s, 1H) (cage C*H*), 2.97 + 2.93 (s, 1H) (methylene *H* on Cp), 2.53 (m, 2H) ($CH_2CH_2N(CH_3)_2$), 2.43 (m, 2H) ($CH_2CH_2N(CH_3)_2$), 2.28 + 2.25 (s, 6H) ($CH_2CH_2N(CH_3)_2$), 1.58 + 1.50 (s, 6H) ($C(CH_3)_2$). $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ: 150.1, 149.2, 133.2, 130.9, 127.1, 126.9, 126.3, 126.1 (vinylic *C*), 84.8 (cage *C*), 63.9, 63.4 ($N(CH_3)_2$), 59.5, 58.8 ($CH_2CH_2N(CH_3)_2$), 45.5, 42.9 ($CH_2CH_2N(CH_3)_2$), 44.3, 42.1 (methylene *C* on Cp), 42.1, 40.4 ($C(CH_3)_2$), 31.5, 30.8, 29.0, 28.3 ($C(CH_3)_2$). $^{11}B\{^1H\}$ NMR ($CDCl_3$): δ –3.9 (2B), –8.9 (2B), –11.3 (2B), –13.5 (4B). The ^1H and ^{13}C NMR data suggested that **3** was a mixture of isomers with the $Me_2NCH_2CH_2$ group bound to either the sp^2 or sp^3 carbon of the Cp ring.[2d]

Preparation of [η^5:σ-$Me_2C(C_5H_4)(C_2B_{10}H_{10})$]Co($PPh_3$) (4)

An *n*-BuLi solution in *n*-hexane (1.60 mol/L, 1.25 mL, 2.0 mmol) was slowly added to a THF (10 mL) solution of $Me_2C(C_5H_5)(C_2B_{10}H_{11})$ (0.25 g, 1.0 mmol) at –78 °C and the mixture was warmed up to room temperature and then stirred for 3 h. The resulting solution was slowly added to a THF suspension (10 mL) of $CoCl_2(PPh_3)_2$ (0.65 g, 1.0 mmol) at room temperature, and the reaction mixture was stirred overnight. After removal of the solvent, the residue was extracted with Et_2O (2 × 25 mL). The Et_2O solution was concentrated to ~10 mL. Complex **4** was isolated as brown crystals after this solution stood at room temperature for 2 days (0.50 g, 87%). IR (KBr, cm^{-1}) ν_{BH}: 2579 (vs). Anal. calcd for $C_{28}H_{35}B_{10}CoP$ (**4**): C 59.04, H 6.19; found: C 59.08, H 6.61.

Preparation of [η^5:σ-$Me_2C(C_5H_4)(C_2B_{10}H_{10})$]Ni($PPh_3$) (5)

This complex was prepared as green crystals from $Me_2C(C_5H_5)(C_2B_{10}H_{11})$ (0.25 g, 1.0 mmol), *n*-BuLi (1.60 mol/L, 1.25 mL, 2.0 mmol), and $NiCl_2(PPh_3)_2$ (0.65 g, 1.0 mmol) in THF (20 mL) using the same procedure as reported for **4**; yield: 0.53 g (93%). IR (KBr, cm^{-1}) ν_{BH}: 2581 (vs). ^1H NMR (C_6D_6) δ: 7.62 (m, 6H), 7.01 (m, 9H) (C_6H_5), 5.96 (br, 2H), 3.70 (br, 2H) (C_5H_4), 1.39 (s, 6H) ($(CH_3)_2C$). $^{13}C\{^1H\}$ NMR (C_6D_6) δ: 134.8, 134.7, 131.0, 128.9 (C_6H_5), 99.6, 88.2 (C_5H_4), 66.3 (cage *C*), 41.3 ($(CH_3)_2C$), 32.3 ($(CH_3)_2C$). $^{11}B\{^1H\}$ NMR (C_6D_6) δ: –3.5 (2B), –7.0 (3B), –9.8 (5B). $^{31}P\{^1H\}$ NMR (C_6D_6) δ: 47.3. Anal. calcd for $C_{28}H_{35}B_{10}NiP$ (**5**): C 59.07, H 6.20; found: C 58.51, H 6.25.

Preparation of [η^5:σ-$Me_2C(C_9H_6)(C_2B_{10}H_{10})$]Co($PPh_3$) (6)

This complex was prepared as brown crystals from $Me_2C(C_9H_7)(C_2B_{10}H_{11})$ (0.30 g, 1.0 mmol), *n*-BuLi (1.60 mol/L, 1.25 mL, 2.0 mmol), and $CoCl_2(PPh_3)_2$ (0.65 g, 1.0 mmol) in THF (20 mL) using the same procedure as reported for **4**; yield: 0.49 g (79%). IR (KBr, cm^{-1}) ν_{BH}: 2593 (vs). Anal. calcd for $C_{32}H_{37}B_{10}CoP$ (**6**): C 62.03, H 6.02; found: C 62.30, H 6.17.

Preparation of [η^5:σ-$Me_2C(C_9H_6)(C_2B_{10}H_{10})$]Ni($PPh_3$) (7)

This complex was prepared as green crystals from $Me_2C(C_9H_7)(C_2B_{10}H_{11})$ (0.30 g, 1.0 mmol), *n*-BuLi (1.60 mol/L, 1.25 mL, 2.0 mmol), and $NiCl_2(PPh_3)_2$ (0.65 g, 1.0 mmol) in THF (20 mL) using the same procedure as reported for **4**; yield: 0.43 g (69%). IR (KBr, cm^{-1}) ν_{BH}: 2581 (vs). ^1H NMR (C_6D_6) δ: 7.75 (d, *J* = 8.0 Hz, 1H), 6.78 (t, *J* = 8.0 Hz, 2H), 6.45 (d, *J* = 3.6 Hz, 1H), 5.13 (d, *J* = 8.0 Hz, 1H), 3.88 (t, *J* = 3.6 Hz, 1H) (C_9H_6), 7.32 (m, 6H), 6.99 (m, 9H) (C_6H_5), 1.60 (s, 3H), 1.54 (s, 3H) ($(CH_3)_2C$). $^{13}C\{^1H\}$ NMR (C_6D_6) δ: 135.0, 135.8, 134.4, 132.8, 132.7, 131.9, 130.9, 129.6, 126.6, 125.3, 123.8, 121.9, 117.3, 106.5 (C_9H_6 + C_6H_5), 64.5 (cage *C*), 44.1 ($(CH_3)_2C$), 32.3, 31.3 ($(CH_3)_2C$). $^{11}B\{^1H\}$ NMR (C_6D_6) δ: –3.2 (2B), –6.4 (3B), –9.3 (5B). $^{31}P\{^1H\}$ NMR (C_6D_6) δ: 33.8. Anal. calcd for $C_{32}H_{37}B_{10}NiP$ (**7**): C 62.05, H 6.02; found: C 62.07, H 5.80.

Preparation of [η^5:σ-$Me_2C(C_5H_3CH_2CH_2NMe_2)$ $(C_2B_{10}H_{10})$]Ni(PPh_3) (8)

This complex was prepared as green crystals from $Me_2C(C_5H_4CH_2CH_2NMe_2)(C_2B_{10}H_{11})$ (0.32 g, 1.0 mmol), *n*-BuLi (1.60 mol/L, 1.25 mL, 2.0 mmol), and $NiCl_2(PPh_3)_2$ (0.65 g, 1.0 mmol) in THF (20 mL) using the same procedure as reported for **4**; yield: 0.40 g (63%). IR (KBr, cm^{-1}) ν_{BH}: 2587 (vs). ^1H NMR (C_6D_6) δ: 7.69 (m, 6H), 7.02 (m, 9H) (C_6H_5), 6.07 (d, *J* = 1.5 Hz, 1H), 5.87 (s, 1H), 3.76 (d, *J* = 2.4 Hz, 1H) (C_5H_3), 2.11 (m, 2H) ($CH_2CH_2NMe_2$), 1.90 (m, 2H) ($CH_2CH_2NMe_2$), 1.86 (s, 6H) ($N(CH_3)_2$), 1.45 (s, 3H), 1.40 (s, 3H) ($(CH_3)_2C$). $^{13}C\{^1H\}$ NMR (C_6D_6) δ: 135.5, 135.4, 134.8, 132.5, 132.1, 131.1, 109.8, 99.4, 97.7 (C_6H_5 + C_5H_3), 88.0 (cage *C*), 66.5 ($CH_2CH_2NMe_2$), 45.9 ($N(CH_3)_2$), 41.5 ($CH_2CH_2NMe_2$), 32.5 ($C(CH_3)_2$), 31.3, 30.7 ($C(CH_3)_2$). $^{11}B\{^1H\}$ NMR (C_6D_6) δ: –3.6 (2B), –6.8 (3B), –9.5 (5B). $^{31}P\{^1H\}$ NMR (C_6D_6) δ: 36.5. Anal. calcd for $C_{32}H_{44}B_{10}NNiP$ (**8**): C 60.01, H 6.92, N 2.19; found: C 60.35, H 6.83, N 2.06.

Preparation of [η^5:σ-$Me_2C(C_5H_4)(C_2B_{10}H_{10})$]Co(2,6-$Me_2C_6H_3NC$) (9)

To a toluene (5 mL) solution of [η^5:σ-$Me_2C(C_5H_4)$ $(C_2B_{10}H_{10})$]Co(PPh_3) (**4**; 0.29 g, 0.50 mmol) was added 2,6-$Me_2C_6H_3NC$ (0.07 g, 0.50 mmol) at room temperature. The reaction mixture was stirred at room temperature overnight. After removal of the solvent, the residue was extracted with Et_2O (10 mL × 2). The combined Et_2O solutions were concentrated to ~5 mL. Complex **9** was isolated as brown crystals after this solution stood at room temperature for 1 day (0.17 g, 77%). IR (KBr, cm^{-1}) ν_{BH}: 2575 (vs). Anal. calcd for $C_{19}H_{29}B_{10}CoN$ (**9**): C 52.05, H 6.67, N 3.19; found: C 52.26, H 6.70, N 3.42.

Preparation of [η^5:σ-$Me_2C(C_5H_4)(C_2B_{10}H_{10})$]Ni(2,6-$Me_2C_6H_3NC$) (10)

This complex was prepared as green crystals from [η^5:σ-$Me_2C(C_5H_4)(C_2B_{10}H_{10})$]Ni($PPh_3$) (**5**; 0.29 g, 0.50 mmol) and 2,6-$Me_2C_6H_3NC$ (0.07 g, 0.50 mmol) in toluene (5 mL)

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Table 2. Crystal data and summary of data collection and refinement details for compounds **4**–**9**.

	Compound					
Parameter	**4**	**5**	**6**	**7**	**8**	**9**
Empirical formula	$C_{28}H_{35}B_{10}CoP$	$C_{28}H_{35}B_{10}NiP$	$C_{32}H_{37}B_{10}CoP$	$C_{32}H_{37}B_{10}NiP$	$C_{32}H_{44}B_{10}NNiP$	$C_{19}H_{29}B_{10}CoN$
Formula weight	569.6	569.3	619.6	619.4	640.5	438.5
Crystal size (mm)	0.50×0.40×0.10	0.50×0.30×0.20	0.50×0.40×0.10	0.50×0.40×0.40	0.40×0.30×0.20	0.40×0.30×0.30
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Triclinic	Orthorhombic
Space group	$P2_1/c$	$P2_1/n$	$P2_1/c$	$P2_1/c$	$P(-1)$	$P2_12_12_1$
a (Å)	11.562(2)	11.720(2)	12.490(3)	12.322(2)	10.510(2)	12.585(5)
b (Å)	20.123(4)	20.529(4)	13.598(3)	13.403(2)	13.019(3)	12.826(5)
c (Å)	13.887(3)	13.938(3)	19.877(4)	19.755(3)	13.996(3)	14.284(6)
α (°)	90	90	90	90	101.90(3)	90
β (°)	114.60(3)	114.86(3)	90.00(3)	91.25(1)	106.00(3)	90
γ (°)	90	90	90	90	98.73(3)	90
V (Å^3)	2937.8(10)	3042.7(10)	3375.9(12)	3261.8(7)	1756.4(6)	2305.6(16)
Z	4	4	4	4	2	4
D_c (Mg m^{-3})	1.288	1.243	1.219	1.261	1.211	1.263
μ (mm^{-1})	0.658	0.709	0.578	0.667	0.622	0.752
Radiation (λ, Å)	Mo K (0.71073)	Mo K (0.71073)	Mo K (0.71073)	Mo K (0.71073)	Mo K (0.71073)	Mo K (0.71073)
F(000)	1180	1184	1284	1288	672	908
θ range (°)	1.9–25.6	1.9–25.4	1.6–25.0	1.6–25.0	1.5–25.5	2.0–28.0
Observed reflections	4864	4651	5388	5744	5630	5763
Parameters	361	361	397	397	406	280
R indices ($I > 2\sigma(I)$)[a]	$R_1 = 0.046$ $wR_2 = 0.119$	$R_1 = 0.075$ $wR_2 = 0.189$	$R_1 = 0.094$ $wR_2 = 0.242$	$R_1 = 0.036$ $wR_2 = 0.085$	$R_1 = 0.038$ $wR_2 = 0.105$	$R_1 = 0.041$ $wR_2 = 0.086$
Goodness-of-fit (S)[b]	1.158	1.148	1.142	1.076	1.086	1.020

[a] $R_1 = \sum||F_0| - |F_c||/\sum|F_0|$; $wR_2 = \{\sum[w(F_0^2 - F_c^2)^2]/\sum[w(F_0^2)^2]\}^{1/2}$.

[b] $S = \{\sum[w(F_0^2 - F_c^2)^2]/\ (n - p)\}^{1/2}$ (n = No. of data; p = No. of parameters varied).

Table 3. Crystal data and summary of data collection and refinement details for compounds **10**–**14**.

	Compound				
Parameter	**10**	**11**	**12**	**13**	**14**
Empirical formula	$C_{19}H_{29}B_{10}NNi$	$C_{37}H_{56}B_{10}CoN_2$	$C_{37}H_{56}B_{10}N_2Ni$	$C_{30}H_{58}B_{10}NiO_{0.5}P$	$C_{54}H_{84}B_{20}Co_2O_2P_2$
Formula weight	438.2	695.9	695.7	624.5	1161.2
Crystal size (mm)	0.50×0.40×0.30	0.50×0.40×0.40	0.50×0.40×0.30	0.30×0.20×0.10	0.40×0.30×0.20
Crystal system	Orthorhombic	Monoclinic	Monoclinic	Triclinic	Monoclinic
Space group	$P2_12_12_1$	$P2_1/n$	$P2_1/n$	$P(-1)$	$P2_1/c$
a (Å)	12.462(3)	10.585(2)	10.447(2)	10.233(2)	10.932(1)
b (Å)	12.866(3)	20.471(4)	20.103(4)	11.973(2)	16.750(2)
c (Å)	14.204(3)	19.337(4)	19.072(4)	15.377(2)	17.431(2)
α (°)	90	90	90	98.02(1)	90
β (°)	90	98.77(3)	90.86(3)	95.42(1)	103.11(1)
γ (°)	90	90	90	110.62(1)	90
V (Å^3)	2277.4(8)	4141.1(14)	3957.5(14)	1724.8(5)	3108.4(5)
Z	4	4	4	2	2
D_c (Mg m^{-3})	1.278	1.116	1.168	1.203	1.241
μ (mm^{-1})	0.859	0.442	0.519	0.631	0.625
Radiation (λ, Å)	Mo K (0.71073)	Mo K (0.71073)	Mo K (0.71073)	Mo K (0.71073)	Mo K (0.71073)
F(000)	912	1476	1480	670	1216
θ range (°)	4.0–51.2	3.0–50.6	3.0–50.0	2.7–50.0	3.4–56.0
Observed reflections	4056	6512	5968	6038	7716
Parameters	280	451	451	394	361
R indices ($I > 2\sigma(I)$)[a]	$R_1 = 0.040$	$R_1 = 0.052$	$R_1 = 0.048$	$R_1 = 0.055$	$R_1 = 0.054$
	$wR_2 = 0.110$	$wR_2 = 0.134$	$wR_2 = 0.124$	$wR_2 = 0.129$	$wR_2 = 0.129$
Goodness-of-fit (S)[b]	1.091	1.131	1.119	1.014	1.034

[a] $R_1 = \sum||F_0| - |F_c||/\sum|F_0|$; $wR_2 = \{\sum[w(F_0^2 - F_c^2)^2]/\sum[w(F_0^2)^2]\}^{1/2}$.

[b] $S = \{\sum[w(F_0^2 - F_c^2)^2]/(n - p)\}^{1/2}$ (n = No. of data; p = No. of parameters varied).

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using the same procedure as reported for **9**; yield: 0.13 g (59%). IR (KBr, cm^{-1}) ν_{BH}: 2573 (vs). ^{1}H NMR (C_6D_6) δ: 6.66 (t, J = 7.8 Hz, 1H), 6.51 (d, J = 7.8 Hz, 2H) (C_6H_3), 5.65 (t, J = 2.4 Hz, 2H), 4.47 (d, J = 2.4 Hz, 2H) (C_5H_4), 2.11 (s, 6H) ($(CH_3)_2C_6H_3$), 1.29 (s, 6H) ($(CH_3)_2C$). ^{13}C{^{1}H} NMR (C_6D_6) δ: 162.7 (N=*C*), 132.8, 132.7, 132.0, 129.2 (C_6H_3), 98.5, 88.4 (C_5H_4), 32.3 ($(CH_3)_2C$), 30.6 ($(CH_3)_2C_6H_3$), 23.4 ($(CH_3)_2C$). ^{11}B{^{1}H} NMR (C_6D_6) δ: –2.03 (1B), –4.11 (2B), –6.79 (3B), –8.70 (4B). Anal. calcd for $C_{19}H_{29}B_{10}NNi$ (**10**): C 52.07, H 6.67, N 3.20; found: C 52.52, H 6.86, N 3.28.

Preparation of [η^5:σ-$Me_2C(C_5H_4)(C_2B_{10}H_{10})$]Co[1,3-(2,6-*i*-$Pr_2C_6H_3)_2C_3N_2H_2$] (11)

To a toluene (5 mL) solution of [η^5:σ-$Me_2C(C_5H_4)(C_2B_{10}H_{10})$]Co($PPh_3$) (**4**; 0.29 g, 0.50 mmol) was added 1,3-(2,6-*i*-$Pr_2C_6H_3)_2C_3N_2H_2$ (0.20 g, 0.50 mmol) at room temperature, and the reaction mixture was stirred overnight. After removal of the solvent, the residue was extracted with Et_2O (10 mL × 2). The combined Et_2O solutions were concentrated to ~5 mL. Complex **11** was isolated as brown crystals after this solution stood at room temperature for 1 day (0.18 g, 51%). IR (KBr, cm^{-1}) ν_{BH}: 2570 (vs). Anal. calcd for $C_{37}H_{56}B_{10}CoN_2$ (**11**): C 63.86, H 8.11, N 4.03; found: C 63.35, H 7.67, N 4.01.

Preparation of [η^5:σ-$Me_2C(C_5H_4)(C_2B_{10}H_{10})$]Ni[1,3-(2,6-*i*-$Pr_2C_6H_3)_2C_3N_2H_2$] (12)

This complex was prepared as green crystals from [η^5:σ-$Me_2C(C_5H_4)(C_2B_{10}H_{10})$]Ni($PPh_3$) (**5**; 0.29 g, 0.50 mmol) and 1,3-(2,6-*i*-$Pr_2C_6H_3)_2C_3N_2H_2$ (0.20 g, 0.50 mmol) in toluene (5 mL) using the same procedure as reported for **11**; yield: 0.21 g (60%). IR (KBr, cm^{-1}) ν_{BH}: 2573 (vs). ^{1}H NMR (C_6D_6) δ: 7.25 (m, 4H), 7.12 (m, 2H) (C_6H_3), 6.47 (s, 2H) ($C_3N_2H_2$), 5.77 (t, J = 2.4 Hz, 2H), 4.98 (d, J = 2.4 Hz, 2H) (C_5H_4), 3.66 (m, 2H), 3.09 (m, 2H) ($(CH_3)_2CH$), 1.62 (d, J = 6.6 Hz, 6H), 1.27 (d, J = 6.6 Hz, 6H), 1.01 (d, J = 6.6 Hz, 6H), 0.80 (d, J = 6.6 Hz, 6H) ($(CH_3)_2CH$), 1.24 (s, 6H) ($(CH_3)_2C$). ^{13}C{^{1}H} NMR (C_6D_6) δ: 163.1 (carbene *C* of NHC), 146.7, 144.8, 138.9, 130.8, 126.8, 125.5, 124.5, 120.6 (C_6H_3 + vinylic *C* of NHC), 98.6, 89.2 (C_5H_4), 40.5 ($(CH_3)_2C$), 30.7 ($(CH_3)_2C$), 29.4, 29.0 ($(CH_3)_2CH$), 26.1, 25.7, 23.5, 22.6 ($(CH_3)_2CH$). ^{11}B{^{1}H} NMR (C_6D_6) δ: –3.2 (2B), –6.3 (3B), –9.2 (5B). Anal. calcd for $C_{37}H_{56}B_{10}N_2Ni$ (**12**): C 63.88, H 8.11, N 4.03; found: C 63.86, H 8.19, N 4.25.

Preparation of [η^5:σ-$Me_2C(C_5H_4)(C_2B_{10}H_{10})$]Ni($PCy_3$) (13)

To a toluene (5 mL) solution of [η^5:σ-$Me_2C(C_5H_4)(C_2B_{10}H_{10})$]Ni($PPh_3$) (**5**; 0.29 g, 0.50 mmol) was added PCy_3 (0.14 g, 0.50 mmol) at room temperature. The reaction mixture was refluxed for 1 day. After removal of the solvent, the residue was extracted with Et_2O (10 mL × 2). The combined Et_2O solutions were concentrated to ~5 mL. Complex **13** was isolated as green crystals after this solution stood at room temperature for 1 day (0.18 g, 57%). IR (KBr, cm^{-1}) ν_{BH}: 2573 (vs). ^{1}H NMR (C_6D_6) δ: 5.94 (m, 2H), 4.23 (m, 2H) (C_5H_4), 2.11–1.07 (m, 33H) (Cy), 1.39 (s, 6H) ($(CH_3)_2C$). ^{13}C{^{1}H} NMR (C_6D_6) δ: 99.7, 90.2 (C_5H_4), 66.3 (cage *C*), 32.3, 31.2, 29.7, 28.1, 27.1, 23.4, 15.9 ($(CH_3)_2C$ + $P(C_6H_{11})_3$).

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$^{11}B\{^1H\}$ NMR (C_6D_6) δ: –2.4 (5B), –6.0 (2B), –8.9 (3B). $^{31}P\{^1H\}$ NMR (C_6D_6) δ: 44.4. Anal. calcd for $C_{30}H_{58}B_{10}NiO_{0.5}P$ (**13** + $0.5Et_2O$): C 57.69, H 9.36; found: C 58.09, H 9.11.

Preparation of {[η^5:σ-$Me_2C(C_5H_4)(C_2B_{10}H_{10})$]Co}$_2$(dppe) (14)

This complex was prepared as brown crystals from [η^5:σ-$Me_2C(C_5H_4)(C_2B_{10}H_{10})$]Co($PPh_3$) (**4**; 0.29 g, 0.50 mmol) and dppe (0.10 g, 0.25 mmol) in toluene (5 mL) using the same procedure as reported for **13**; yield: 0.19 g (62%). IR (KBr, cm^{-1}) ν_{BH}: 2573 (vs). Anal. calcd for $C_{46}H_{64}B_{20}Co_2P_2$ (**14** + $2Et_2O$): C 54.54, H 6.37; found: C 54.24, H 6.25.

X-ray structure determination

All single crystals were immersed in Paraton-N oil and sealed under N_2 in thin-walled glass capillaries. Data were collected at 293 K on a Bruker SMART 1000 CCD diffractometer using Mo Kα radiation. An empirical absorption correction was applied using the SADABS program.[33] All structures were solved by direct methods and subsequent Fourier difference techniques and refined anisotropically for all non-hydrogen atoms by full-matrix least-squares calculations on F^2 using the SHELXTL program package.[34] All hydrogen atoms were geometrically fixed using the riding model. Molecular structures of **13** and **14** showed the solvation of half and two Et_2O molecules, respectively. For the noncentrosymmetric structures **9** and **10**, the appropriate enantiomorph of **9** was chosen by refining Flack's parameter χ toward zero;[35] however, the appropriate enantiomorph of **10** was unable to be chosen as its $\chi \approx 0.5$ after refinement. Crystal data and details of data collection and structure refinements were given in Tables 2 and 3 (X-ray data can be found in the Supplementary data).

Supplementary data

Supplementary data are available for this article through the journal Web site at http://nrcresearchpress.com/doi/suppl/10.1139/v11-115. CCDC 823250–823260 contain the X-ray data in CIF format for this manuscript (compounds **4**–**14**). These data can be obtained, free of charge, via http://www.ccdc.cam.ac.uk/cgi-bin/catreq.cgi (Or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1Ez, UK; fax +44 1223 336033; or e-mail deposit@ccdc.cam.ac.uk).

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