Preparation and Reactions of a Half-Sandwich Dicarbollyl Nickel(II) Complex Containing a Dimethylamino Pendent Group

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The dicarbollylamino nickel complex [$(\eta^5:\eta^1$-C$_2$B$_9$H$_{10}$-CH$_2$NMe$_2$)Ni(PPh$_3$)] (**3**), in which the ligating amino group is connected to the dicarbollyl ligand, was prepared by the treatment of the lithium salt of Dcab^{N}H [*nido*-7-NMe$_2$CH$_2$-7,8-C$_2$B$_9$H$_{11}$]$^{1-}$ (**2**) with NiCl$_2$(PPh$_3$)$_2$ in THF. Ligand substitution at **3** with a variety of mono- or bidentate ligand systems has been studied. The intramolecularly coordinated dicarbollylamino nickel complex **3** reacted with soft donor ligands, such as PEt$_3$ and CNBu^t, at the metal center to provide substituted bis(ligand) nickel complexes with an uncoordinated amino side group [$(\eta^5$-C$_2$B$_9$H$_{10}$CH$_2$NMe$_2$)Ni(PPh$_3$)(L)] (L = PEt$_3$ (**4a**); CNBu^t (**4b**)). However, **3** reacted with bidentate ligands, such as dpe (bis(diphenylphosphino)ethane) and bipy (2,2′-bipyridine), to give nickel complexes with a coordinated amino group [$(\eta^5:\eta^1$-C$_2$B$_9$H$_{10}$-CH$_2$NMe$_2$)Ni(L−L)] (L−L = dpe (**5a**); bipy (**5b**)) after removal of the phosphine ligand. In particular, the *tert*-butylisocyanide complex **4b** reacted with the methyl iodide to provide exclusive formation of a deaminated species [$(\eta^5$-C$_2$B$_9$H$_{10}$CH$_2$PPh$_3$)Ni(CNBu^t)(I)] (**6**). All of these new compounds have been isolated in good yield and characterized by IR and NMR spectroscopies. In addition, the solid state structures of **3**, **5b**, and **6** were characterized by single-crystal X-ray analyses.

Introduction

Recent reports have shown that cyclopentadienyl derivatives with a functionalized side chain, such as [2-(dimethylamino)alkyl]cyclopentadiene containing a hard and a soft donor,[1] form half-sandwich complexes with metals with specific structures and reactivity. In such a ligand system, the amine coordinates only weakly to low-valent transition metals and forms relatively labile complexes due to the lack of a π-acceptor capability. In fact, the functionalized side chain reversibly coordinates to a metal ion, thus stabilizing the reactive intermediates.[2] As a consequence, a heterobifunctional ligand containing two types of nonequivalent donors, one firmly bound to a metal center and another weakly bonded, which can temporarily block and protect a metal coordination site, holds promise as a novel class of ligands for homogeneous catalysts.[3] In this context, we became interested in the combinations of dicarbollide and amine ligands. Therefore, it was of interest to investigate the possibility of synthesizing such an intramolecularly coordinated nickel complex, [$(\eta^5:\eta^1$-C$_2$B$_9$H$_{10}$-CH$_2$NMe$_2$)Ni(PPh$_3$)] (**3**), bearing both *nido* icosahedral and dimethylamino units that might potentially stabilize the metal center. Therefore, the dimethylamino group may be regarded as an "intramolecular protecting group of a vacant coordination site" as illustrated in Chart 1.

Chart 1

(Dcab^N)Ni(PPh$_3$) **3**
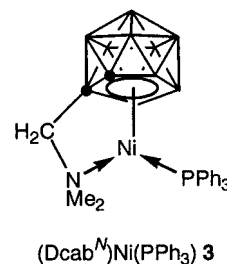
In such an intramolecularly coordinating ligand system, the dimethylamino group will in general be decomplexed more easily than the dicarbollide fragment. Indeed, our results show that the dimethylamino group in **3** can be displaced by soft donor ligands such as triethylphosphine and *tert*-butyl isocyanide. On the other hand, the intramolecular coordination of the side chain is still observed with chelating ligands such as dpe and bipy. Thus, the dimethylamino group seems to be bound strong enough to the nickel(II) center to form stable complexes with chelating ligands but weak enough to be displaced by soft donors. In addition, the first observation of the substitution reactivity of [$(\eta^5$-C$_2$B$_9$H$_{10}$CH$_2$NMe$_2$)Ni(PPh$_3$)(CNBu^t)] (**4b**) is also reported together with X-ray diffraction studies of a new type of zwitterionic methyl phosphonium pendent nickel complex with [$(\eta^5$-C$_2$B$_9$H$_{10}$CH$_2$PPh$_3$)Ni(CNBu^t)(I)] (**6**).

Results and Discussion

Ligand Synthesis. The dicarbollyl ligand, Dcab^{N}H [*nido*-7-NMe$_2$CH$_2$-7,8-C$_2$B$_9$H$_{11}$]$^{1-}$ (**2**), was prepared us-

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ing a standard deborination procedure[4] involving *o*-carboranylamine Cab^{N}H (*closo*-1-NMe$_2$CH$_2$-1,2-C$_2$B$_{10}$H$_{11}$) (**1**) (eq 1). The reaction of **1** with KOH in methanol at 65 °C leads to the formation of the deborinated monoanionic system **2**. Thus, carborane **1** undergoes facile degradation in methanolic KOH to selectively remove the boron atom and generate the anion **2**. Having a pendent dimethylamino group on the dicarbollyl ring, ligand **2** serves as a heterobifunctional ligand for elaboration of the amino group coordinating complexes. Further deprotonation with Bu^{n}Li gives the desired dianionic ligand Dcab^N.

(eq 1)
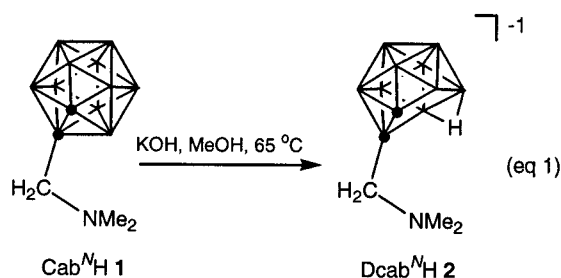
Reaction of the Ligand with Ni Complex. The reaction of the lithium salt of **2** with the NiCl$_2$(PPh$_3$)$_2$ in THF gives a new compound formulated as the mononuclear species [(η^5:η^1-C$_2$B$_9$H$_{10}$-CH$_2$NMe$_2$)Ni(PPh$_3$)] (**3**) (eq 1). Thus, treatment of NiCl$_2$(PPh$_3$)$_2$ with the lithium salt of **2** in THF, followed by stirring for 12 h, afforded the sole product **3** in good yields after chromatographic purification on silica gel. This complex,

obtained as a red powder, was recrystallized in a THF and hexane mixture, affording mostly stable crystals further identified by elemental analysis. The presence of a stable intramolecular coordination, involving the dimethylamino group, is indicated in the ^{1}H NMR spectra by a downfield shift of the methylene protons of the side chain. Furthermore, the multiplicity of the spin system of the NCH_2 moiety changes from a singlet of the free side chain to an AB spin system upon coordination to the metal atom, because they are diastereotopic. This observation is consistent with similar findings for the general intramolecularly coordinated *o*-carboranylmetal complexes of the Cab^{N}H (*closo*-1-NMe$_2$CH$_2$-1,2-C$_2$B$_{10}$H$_{11}$)[5] and Cab^{P}H (*closo*-1-PPh$_2$CH$_2$-1,2-C$_2$B$_{10}$H$_{11}$)[6] ligand systems. The ^{11}B chemical shifts are similar to those observed for other *closo*-bis(phosphine)nickelacarboranes and support the proposed η^5-coordination.[7]

(eq 2)
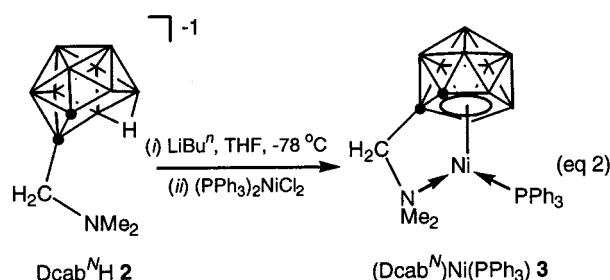
Final proof for the intramolecular coordination of the dimethylamino side chain group to the Ni metal in complex **3** is provided by an X-ray crystal structure analysis. Suitable crystals were grown by the slow diffusion of hexane into a saturated THF solution of **3**. The molecular structure of **3·**THF is shown in Figure 1. The molecule is comprised of a phosphine nickel(II) unit which is bonded to a penta-hapto dicarbollyl ligand. The tertiary amino fragment coordinates to the nickel in the remaining basal site of the overall trigonal pyramid conformation, giving a five-membered ring. The aminoalkyl sidearm is bound in an η^1(N) fashion to the Ni center. The C$_2$B$_3$ bonding face in **3·**THF is essentially planar with no deviation from the least-squares plane by more than 0.026 Å. The nickel is approximately

(1) (a) Ayllon, J. A.; Sayers, S. F.; Sabo-Etienne, S.; Donnadieu, B.; Chaudret, B.; Clot, E. *Organometallics* **1999**, *18*, 3981. (b) Wang, T.-F.; Hwu, C.-C.; Tsai, C.-W.; Wen, Y.-S. *Organometallics* **1999**, *18*, 1553. (c) Hoffmann, H.; Fischer, R. A.; Antelmann, B.; Huttner, G. *J. Organomet. Chem.* **1999**, *584*, 131. (d) Philippopoulos, A. I.; Donnadieu, B.; Poilblanc, R.; Hadjiliadis, N. *J. Organomet. Chem.* **1999**, *582*, 286. (e) Schumann, H.; Rosenthal, E. C. E.; Demtschuk, J.; Molander, G. A. *Organometallics* **1998**, *17*, 5324. (f) Chu, H. S.; Lau, C. P.; Wong, K. Y.; Wong, W. T. *Organometallics* **1998**, *17*, 2768. (g) Wang, T.-F.; Hwu, C.-C.; Tsai, C.-W.; Wen, Y.-S. *Organometallics* **1998**, *17*, 131. (h) Jutzi, P.; Redeker, T. *Eur. J. Inorg. Chem.* **1998**, 663. (i) Wang, T.-F.; Hwu, C.-C.; Tsai, C.-W.; Wen, Y.-S. *J. Chem. Soc., Dalton Trans.* **1998** 2091. (j) Philippopoulos, A. I.; Poilblanc, R.; Hadjiliadis, N. *Inorg. Chim. Acta* **1998**, *283*, 24. (k) Wang, T.-F.; Hwu, C.-C.; Tsai, C.-W.; Lin, K.-J. *Organometallics* **1997**, *16*, 3089. (l) Wang, T.-F.; Lai, C.-Y.; Hwu, C.-C.; Wen, Y.-S. *Organometallics* **1997**, *16*, 1218. (m) Philippopoulos, A. I.; Hadjiliadis, N.; Hart, C. E.; Donnadieu, B.; McGowan, P. C.; Poilblanc, R. *Inorg. Chem.* **1997**, *36*, 1842. (n) McGowan, P. C.; Hart, C. E.; Donnadieu, B.; Poilblanc, R. *J. Organomet. Chem.* **1997**, *528*, 191. (o) Nlate, S.; Herdtweck, E.; Fischer, R. A. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 1861. (p) Fischer, R. A.; Nlate, S.; Hoffmann, H.; Herdtweck, E.; Blümel, J. *Organometallics* **1996**, *15*, 5746. (q) Jutzi, P.; Bangel, M.; Neumann, B.; Stammler, H.-G. *Organometallics* **1996**, *15*, 4559. (r) Molander, G. A.; Schumann, H.; Resenthal, E. C. E.; Demtschuk, J. *Organometallics* **1996**, *15*, 3817. (s) Jutzi, P.; Dahlhaus, J.; Neumann, B.; Stammler, H.-G. *Organometallics* **1996**, *15*, 747. (t) Wang, T.-F.; Lai, C.-Y.; Wen, Y.-S. *J. Organomet. Chem.* **1996**, *523*. 187. (u) Jutzi, P.; Siemeling, U. *J. Organomet. Chem.* **1995**, *500*, 175. (v) Jutzi, P.; Redeker, T.; Neumann, B.; Stammler, H.-G. *J. Organomet. Chem.* **1995**, *498*, 127. (w) Jutzi, P.; Kristen, M. O.; Neumann, B.; Stammler, H.-G. *Organometallics* **1994**, *13*, 3854. (x) Jutzi, P.; Bangel, M. *J. Organomet. Chem.* **1994**, *480*, C18. (y) Dahlhaus, J.; Bangel, M.; Jutzi, P. *J. Organomet. Chem.* **1994**, *474*, 55. (z) Jutzi, P.; Kristen, M. O.; Dahlhaus, J.; Neumann, B.; Stammler, H.-G. *Organometallics* **1993**, *12*, 2980. (a′) Jutzi, P.; Dahlhaus, J.; Bangel, M. *J. Organomet. Chem.* **1993**, *460*, C13. (b′) Jutzi, P.; Dahlhaus, J.; Kristen, M. O. *J. Organomet. Chem.* **1993**, *450*, C1. (c′) Wang, T.-F.; Wen, Y.-S. *J. Organomet. Chem.* **1992**, *439*, 155. (d′) Wang, T.-F.; Lee, T.-Y.; Chou, J.-W.; Ong, C.-W. *J. Organomet. Chem.* **1992**, *423*, 31.

(2) (a) Adams, H.; Bailey, N. A.; Colley, M.; Schofield, P. A.; White, C. *J. Chem. Soc., Dalton Trans.* **1994**, 1445. (b) Lindner, E.; Badger, A. *Coord. Chem. Rev.* **1991**, *108*, 27. (c) Podlahová, J.; Kratochvíl, B.; Langer, V. *Inorg. Chem.* **1981**, 20, 2160.

(3) (a) McKnight, A. L.; Waymouth, R. M. *Chem. Rev.* **1998**, *98*, 2587. (b) Chen, Y.-X.; Metz, M. V.; Li, L.; Stern, C. L.; Marks, T. J. *J. Am. Chem. Soc.* **1998**, *120*, 6287. (c) Koo, K.; Marks, T. J. *J. Am. Chem. Soc.* **1998**, *120*, 4019. (d) Wang, W.; Yan, D.; Charpentier, P. A.; Zhu, S.; Hamielec, A. E.; Sayer, B. G. *Macromol. Chem. Phys.* **1998**, *199*, 2409. (e) Amor, F.; Butt, A.; du Plooy, K. E.; Spaniol, T. P.; Okuda, J. *Organometallics* **1998**, *17*, 5836. (f) Eberle, T.; Spaniol, T. P.; Okuda, J. *J. Eur. J. Inorg. Chem.* **1998**, 237. (g) Amor, F.; du Plooy, K. E.; Spaniol, T. P.; Okuda, J. *J. Organomet. Chem.* **1998**, *558*, 139. (h) Okuda, J.; Eberle, T. *Metallocenes*; Halterman, R. L., Tongi, A., Eds.; Wiley-VCH: Weinheim, 1998; p 415.

(4) (a) Plesek, J.; Hermanek, S.; Stibr, B. *Inorg. Synth.* **1983**, *22*, 231. (b) Wiesboeck, R. A.; Hawthorne, M. F. *J. Am. Chem. Soc.* **1964**, *86*, 1642.

(5) (a) Lee, J.-D.; Kim, S.-J.; Yoo, D.; Ko, J.; Cho, S.; Kang, S. O. *Organometallics* **2000**, *19*, 1695. (b) Bae, J.-Y.; Lee, Y.-J.; Kim, S.-J.; Ko, J.; Cho, S.; Kang, S. O. *Organometallics* **2000**, *19*, 1514. (c) Lee, H.-S.; Bae, J.-Y.; Ko, J.; Kang, Y. S.; Kim, H. S.; Kim, S.-J.; Chung, J.-H.; Kang, S. O. *J. Organomet. Chem.* **2000**, *614−615*, 83. (d) Lee, J.-D.; Baek, C.-K.; Ko, J.; Park, K.; Cho, S.; Min, S.-K.; Kang, S. O. *Organometallics* **1999**, *18*, 2189.

(6) Lee, T.; Lee, S. W.; Jang, H. G.; Ko, J.; Kang, S. O. *Organometallics* **2001**, *20*, 741.

(7) (a) King, R. E., III; Miller, S. B.; Knobler, C. B.; Hawthorne, M. F. *Inorg. Chem.* **1983**, *22*, 3548. (b) Miller, S. B.; Hawthorne, M. F. *J. Chem. Soc., Chem. Commun.* **1976**, 786. (c) Green, M.; Spencer, J. L.; Stone, F. G. A.; Welch, A. *J. J. Chem. Soc., Dalton Trans.* **1975**, 179.
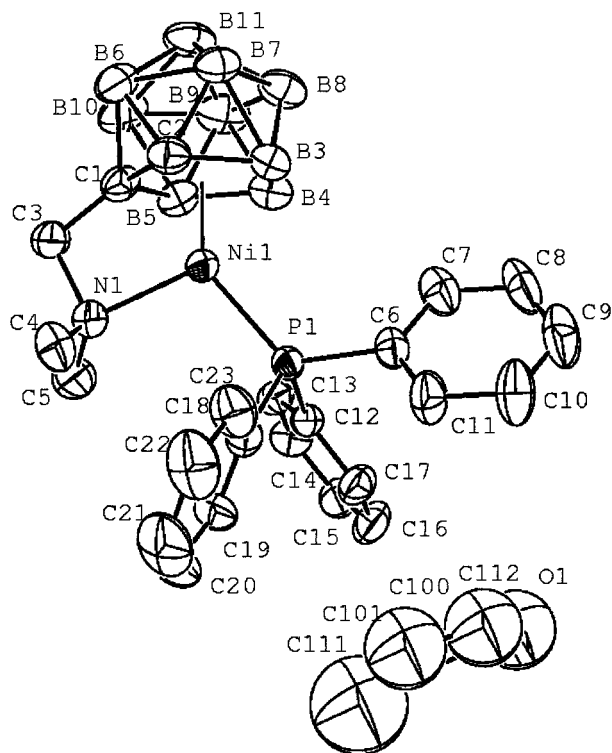
Figure 1. Molecular structure of **3**·THF with atom label-ing; ellipsoids show 30% probability levels, and hydrogen atoms have been omitted for clarity.

centered over the ring, giving rise to an Fe$-$C$_2$B$_3$ face (centroid) distance of 1.50 Å. The selected bond lengths and angles for **3**·THF are listed in Tables 3 and 4. The Ni$-$N bond length of 2.061(6) Å resembles that found in [(η^5:η^1-C$_5$H$_4$-(CH$_2$)$_2$NMe$_2$)NiI] (1.960(5) Å).[8] This value lies within the usual range for the dative bond between nickel and a nitrogen atom, which typically ranges from 2 to 2.20 Å, depending on the coordination number of the Ni atom.[9] The nickel$-$phosphorus bond length of 2.166(1) Å is in reasonable agreement with other values: 2.155 (av) Å for (C$_2$H$_4$)Ni(PPh$_3$)$_2$[10] and 2.138(2) Å for CpNi(PPh$_3$)Ph.[11] Each of these distances repre-sents a considerable decrease from the value of 2.49 Å, which might be predicted on the basis of available covalent radii (octahedral Ni(II) = 1.39 Å, tetrahedral phosphorus = 1.10 Å)[12] and is indicative of a strong metal to phosphorus (d$\pi$$-d\pi$) back-donation.[13] As found in other nickelacarboranes,[7a,14] the Ni$-$B distances (2.12 (av) Å) are longer than the Ni$-$carboranyl carbon distances (2.05 (av) Å). The planes formed by the atoms

N(1), Ni(1), and P(1), on one hand, and C(1), C(2), B(3), B(4), and B(5), on the other, are nearly perpendicular to each other (ca. 88.6(1)°); this feature is also present in the structures of CpNi(PPh$_3$)Ph,[11] MeCpNi(PPh$_3$)I,[15] Cp*Ni(acac),[16] and Cp*Ni(PEt$_3$)X (X = Br, CH$_2$Ph, Me, OMe, N(H)Ar, SAr).[17]

Nature of Ni$-$N Interactions. The reactivities of the late-transition-metal amino compounds are linked to the general lability of the M$-$N bond, a characteristic that has been attributed to the presumed mismatch between the "soft" late metals and the "hard" amino ligands.[1f,h,t,v,y,b'] Therefore, it was of interest to deter-mine whether the nickel-coordinated dimethylamino group in **3** could be cleaved by treatment of the complex with other soft donor molecules. New dicarbollylamino complexes **4** were prepared from the requisite complex **3** and a slight excess of soft donors such as PEt$_3$ and CNBu^t, as shown in Scheme 1.

The treatment of **3** with triethylphosphine and *tert*-butyl isocyanide leads to decomplexation of the side chain and formation of **4a** and **4b**, respectively. In the ^{1}H NMR spectra (Table 1), both complexes show a single peak for the methyl groups of the dimethylamino group, caused by noncoordination of the dimethylamino group. Triethyl phosphines add to **3** to give the corresponding bis(phosphine) complex **4a**. The incorporation of the phosphine ligands was further verified by the ^{31}P chemical shifts, which appeared at δ 31.61 for the triethyl phosphine of **4a**. The addition of *tert*-butyl isocyanide to a solution of **3** resulted in immediate coordination of the isocyanide to the nickel, providing **4b**. The strong band in the IR spectrum appearing at 2532 cm^{-1} for **4b** is characteristic of an isocyanide stretch. In contrast, the displacement of the dimethyl-amino group in **3** with carbon monoxide under normal pressure was not successful. When CO is bubbled through a CDCl$_3$ solutions of **3**, no changes can be detected in the ^{1}H NMR spectra recorded immediately after the exposure to CO.

The irreversible displacement of the dimethylamino group from the metal in **4** is successful with soft ligands such as phosphine and *tert*-butyl isocyanide. The coor-dinating abilities of soft ligands are strong enough to compete with the dimethylamino group coordination at the nickel(II) center, although the intramolecular coor-dination is entropically favored.

Ligand Substitutions at 3. In contrast to the above observation, simple bidentate ligands such as dpe and bipy smoothly displace the phosphine ligand of **4** in THF with complete preservation of the intamolecularly amine coordinated structure to afford the corresponding com-plexes **5a** and **5b** of the type [(η^5:η^1-C$_2$B$_9$H$_{10}$-CH$_2$NMe$_2$)-Ni(L$-$L)] (Scheme 2). Indeed, in complex **3** described here, the bidentate ligand coordination can compete with the coordination of the phosphine ligand, as shown in Scheme 2. **3** reacts with dpe in THF at 25 °C. If 1 equiv of dpe is used, complete conversion of **3** into a new product **5a** occurs after about 1 h. In the ^{1}H NMR

(8) (a) Nlate, S.; Herdtweck, E.; Fischer, R. A. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 1861. (b) Fischer, R. A.; Nlate, S.; Hoffmann, H.; Herdtweck, E.; Blümel, J. *Organometallics* **1996**, *15*, 5746.

(9) (a) Leung, W.-P.; Lee, H.-K.; Zhou, Z.-Y.; Mak, T. C. W. *J. Organomet. Chem.* **1993**, *462*, 7. (b) Bell, N. A.; Glockling, F.; McGregor, A.; Schneider, M. L.; Shearer, H. M. M. *Acta Crystallogr., Sect. C* **1984**, *40*, 623.

(10) Cook, C. D.; Koo, C. H.; Nyburg, S. C.; Shiomi, M. T. *J. Chem. Soc., Chem. Commun.* **1967**, 426.

(11) Churchill, M. R.; O'Brien, T. A. *J. Chem. Soc. (A)* **1970**, 161.

(12) Pauling, L. *The Nature of the Chemical Bond*, 3rd ed.; Cornell University Press: Ithaca, New York, 1973; pp 246$-$249.

(13) (a) Groux, L. F.; Bélanger-Gariépy, F.; Zargarian, D.; Vollm-erhaus, R. *Organometallics* **2000**, *19*, 1507. (b) Dubuc, I.; Dubois, M.-A.; Bélanger-Gariépy, F.; Zargarian, D. *Organometallics* **1999**, *18*, 30. (c) Vollmerhaus, R.; Bélanger-Gariépy, F.; Zargarian, D. *Organome-tallics* **1997**, *16*, 4762. (d) Huber, T. A.; Bélanger-Gariépy, F.; Zarga-rian, D. *Organometallics* **1995**, *14*, 4997.

(14) St. Clair, D.; Zalkin, A.; Templeton, D. H. *J. Am. Chem. Soc.* **1970**, *92*, 1173.

(15) Ballester, L.; Perez, S.; Gutierrez, A.; Perpinan, M. F.; Guti-errez-Puebla, E.; Monge, A.; Ruiz, C. *J. Organomet. Chem.* **1991**, *414*, 411.

(16) Smith, M. E.; Anderson, R. A. *J. Am. Chem. Soc.* **1996**, *118*, 11119.

(17) Holland, P. L.; Smith, M. E.; Anderson, R. A.; Bergman, R. G. *J. Am. Chem. Soc.* **1997**, *119*, 12815.

Table 1. NMR Spectroscopic Data for Compounds 1−6

compd	NMR (δ)		
	^{1}H	^{13}C	^{11}B
1[a]	2.31 (s, 6H, NMe)	46.73 (NMe)	−13.4 (d, 4B, J_{BH} = 120 Hz)
	2.99 (s, 2H, NCH_2)	58.77 (CHCB$_{10}$H$_{10}$)	−11.9 (d, 2B, J_{BH} = 110 Hz)
	3.99 (br s, 1H, C$_{cab}H$)	63.23 (NCH$_2$)	−9.3 (d, 2B, J_{BH} = 160 Hz)
		75.75 (CHCB$_{10}$H$_{10}$)	−5.5 (d, 1B, J_{BH} = 150 Hz)
			−3.3 (d, 1B, J_{BH} = 140 Hz)
2[b]	2.11 (s, 6H, NMe_2)	45.74 (NMe_2)	−36.7 (d, 1B, J_{BH} = 95 Hz)
	2.25 (br s, 1H, C$_{cab}H$)	55.79 (NMe_4^+)	−33.1 (d, 1B, J_{BH} = 85 Hz)
	2.23 (d, 1H, NCH_2, J_{HH} = 14 Hz)	69.57 (NCH$_2$)	−22.3 (d, 1B, J_{BH} = 100 Hz)
	2.42 (d, 1H, NCH_2, J_{HH} = 14 Hz)		−19.3 (d, 1B, J_{BH} = 100 Hz)
	3.45 (s, 12H, NMe_4^+)		−17.7 (d, 1B, J_{BH} = 80 Hz)
			−16.7 (d, 1B, J_{BH} = 80 Hz)
			−13.5 (d, 1B, J_{BH} = 100 Hz)
			−10.3 (d, 1B, J_{BH} = 90 Hz)
			−9.7 (d, 1B, J_{BH} = 90 Hz)
3[a]	1.80 (s, 3H, NMe)	42.44 (NMe_2)	−24.7 (d, 1B, J_{BH} = 95 Hz)
	1.99 (s, 3H, NMe)	60.56 (NCH$_2$)	−20.1 (d, 3B, J_{BH} = 120 Hz)
	3.03 (d, 1H, NCH_2, J_{HH} = 14 Hz)	128.83 (PPh)	−16.2 (d, 1B, J_{BH} = 110 Hz)
	3.20 (d, 1H, NCH_2, J_{HH} = 14 Hz)	130.88 (PPh)	−10.2 (d, 3B, J_{BH} = 100 Hz)
	3.75 (br s, 1H, C$_{cab}H$)	134.59 (PPh)	−3.3 (d, 1B, J_{BH} = 110 Hz)
	7.62 (m, PPh)		
	7.91 (m, PPh)		
4a[a]	1.15 (t, 9H, PCH$_2$CH_3)	10.17 (PCH$_2$$CH_3$)	−36.4 (d, 2B, J_{BH} = 115 Hz)
	1.71 (qt, 6H, PCH_2CH$_3$)	20.15 (d, J_{C-P} = 60 Hz, PCH$_2$CH$_3$)	−28.2 (d, 2B, J_{BH} = 95 Hz)
	2.69 (br s, 6H, NMe_2)	42.44 (NMe)	−19.2 (d, 1B, J_{BH} = 140 Hz)
	3.10 (d, 1H, NCH_2, J_{HH} = 14 Hz)	67.99 (NCH$_2$)	−15.5 (d, 1B, J_{BH} = 90 Hz)
	3.25 (d, 1H, NCH_2, J_{HH} = 14 Hz)	128.68 (PPh)	−14.0 (d, 1B, J_{BH} = 100 Hz)
	3.77 (br s, 1H, C$_{cab}H$)	132.08 (PPh)	−10.0 (d, 2B, J_{BH} = 90 Hz)
	7.48 (m, PPh)	134.13 (PPh)	
	7.62 (m, PPh)		
4b[a]	1.56 (s, 9H, CNBu^t)	29.67 (CNBu^t)	−24.7 (d, 1B, J_{BH} = 115 Hz)
	2.31 (s, 6H, NMe_2)	47.42 (NMe)	−19.1 (d, 2B, J_{BH} = 95 Hz)
	2.69 (d, 1H, NCH_2, J_{HH} = 14 Hz)	69.58 (NCH$_2$)	−14.7 (d, 3B, J_{BH} = 140 Hz)
	2.99 (d, 1H, NCH_2, J_{HH} = 14 Hz)	117.43 (CNBu^t)	−8.2 (d, 1B, J_{BH} = 90 Hz)
	3.61 (br s, 1H, C$_{cab}H$)	128.58 (PPh)	−4.8 (d, 1B, J_{BH} = 100 Hz)
	7.46 (m, PPh)	130.91 (PPh)	−0.3 (d, 1B, J_{BH} = 90 Hz)
	7.80 (m, PPh)	134.59 (PPh)	
5a[a]	1.63 (s, 3H, NMe_2)	29.83 (PCH$_2$)	−24.1 (d, 1B, J_{BH} = 120 Hz)
	1.79 (s, 3H, NMe_2)	47.38 (NMe)	−16.3 (d, 2B, J_{BH} = 100 Hz)
	2.36 (d, 4H, P(CH_2)$_2$, J_{PH} = 6 Hz)	66.49 (NCH$_2$)	−11.6 (d, 2B, J_{BH} = 135 Hz)
	2.65 (d, 1H, NCH_2, J_{HH} = 14 Hz)	128.99 (PPh_{dpe})	−6.8 (d, 2B, J_{BH} = 95 Hz)
	2.79 (d, 1H, NCH_2, J_{HH} = 14 Hz)	131.21 (PPh_{dpe})	6.6 (d, 2B, J_{BH} = 100 Hz)
	4.22 (br s, 1H, C$_{cab}H$)	133.89 (PPh_{dpe})	
	7.45 (br s, PPh_{dpe})		
	7.83 (br s, PPh_{dpe})		
5b[a]	2.79 (s, 3H, NMe_2)	57.44 (NMe)	−69.6 (d, 1B, J_{BH} = 155 Hz)
	2.98 (s, 3H, NMe)	60.37 (NMe)	−50.3 (d, 2B, J_{BH} = 135 Hz)
	3.30 (d, 1H, NCH_2, J_{HH} = 14 Hz)	72.66 (NCH$_2$)	3.8 (d, 2B, J_{BH} = 145 Hz)
	3.23 (d, 1H, NCH_2, J_{HH} = 14 Hz)	155.66 ((NC_5H$_4$)$_2$)	29.7 (d, 2B, J_{BH} = 130 Hz)
	3.88 (br s, 1H, C$_{cab}H$)	163.70 ((NC_5H$_4$)$_2$)	42.7 (d, 1B, J_{BH} = 135 Hz)
	7.40 (m, (NC$_5H_4$)$_2$)	165.96 ((NC_5H$_4$)$_2$)	74.2 (d, 1B, J_{BH} = 130 Hz)
	10.14 (m, (NC$_5H_4$)$_2$)	168.86 ((NC_5H$_4$)$_2$)	
	10.45 (m, (NC$_5H_4$)$_2$)		
6[a]	1.43 (s, 9H, CNBu^t)	30.31 (CNBu^t)	−24.4 (d, 1B, J_{BH} = 90 Hz)
	3.61 (br s, 1H, C$_{cab}H$)	77.46 (NCH$_2$)	−18.7 (d, 2B, J_{BH} = 95 Hz)
	5.25 (dd, 1H, NCH_2, J_{HH} = 14 Hz, J_{HP} = 12 Hz)	117.18 (CNBu^t)	−16.7 (d, 2B, J_{BH} = 110 Hz)
	5.31 (dd, 1H, NCH_2, J_{HH} = 14 Hz, J_{HP} = 12 Hz)	128.17 (PPh)	−10.9 (d, 3B, J_{BH} = 140 Hz)
	7.67 (m, PPh_3)	130.48 (PPh)	−5.2 (d, 1B, J_{BH} = 105 Hz)
	7.92 (m, PPh_3)	134.07 (PPh)	
		135.13 (PPh)	

[a] CDCl$_3$ was used as the solvent, and the chemical shifts are reported relative to the residual H of the solvent. [b] CD$_3$(CO)CD$_3$ was used as the solvent, and the chemical shifts are reported relative to the residual H of the solvent.

spectrum, the CH$_2$ protons of the bound dpe appear as a doublet due to coupling with the phosphrous atom (J_{H-P} = 6 Hz). Similar doublet patterns have been observed for the methylene protons of [CpNi(dpe)]X (X = Cl, Br, I, PF$_6$),[18] [(η^3-C$_4$H$_7$)Pd(dpe)]PF$_6$,[19] and (CO)$_3$-Fe(dme) (dme = dimethylphosphinoethane).[20] The NMR

data are consistent with **5a** being the dpe adduct. The reaction of **3** with bipy has also been examined. In the presence of 1 equiv of bipy in THF at room temperature, **3** was converted into **5b**. The ^{1}H NMR spectrum of the ligands possesses features attributable to the bipyridine, aminomethyl, and *o*-carboranyl segments. Upon com-

(18) Kaempfe, L. A.; Barnett, K. W. *Inorg. Chem.* **1973**, *12*, 2578.
(19) Tibbetts, D. L.; Brown, T. L. *J. Am. Chem. Soc.* **1970**, *92*, 3031.

(20) Akhtar, M.; Ellis, P. D.; MacDiarmid, A. G.; Odom, J. D. *Inorg. Chem.* **1972**, *11*, 2917.

Table 2. X-ray Crystallographic Data and Processing Parameters for Compounds 3·THF, 5b·THF, and 6·Toluene

	3·THF	**5b·THF**	**6·toluene**
formula	$B_9C_{27}H_{33}NniOP$	$B_9C_{19}H_{34}N_3NiO$	$B_9C_{33}H_{35}INNiP$
fw	582.59	476.49	759.49
cryst class	orthorhombic	monoclinic	monoclinic
space group	*Iba*2	*P*2$_1$/*n*	*C2/c*
Z	8	4	8
cell constants			
a, Å	20.497(4)	10.507(1)	24.582(1)
b, Å	19.153(4)	12.532(1)	16.854(1)
c, Å	14.612(3)	19.059(2)	21.817(2)
V, Å^3	5736(2)	2509.9(4)	7657.7(9)
β, deg		90.448(8)	122.090(6)
μ, cm^{-1}	7.53	7.91	13.78
cryst size, mm	0.3 × 0.4 × 0.5	0.3 × 0.3 × 0.4	0.3 × 0.4 × 0.45
D$_{calcd}$, g/cm^3	1.298	1.261	1.318
F(000)	2328	1000	3048
radiation		Mo Kα ($\lambda = 7170$ Å)	
θ range, deg	1.46–25.97	1.94–25.96	1.55–25.98
h, *k*, *l* collected	+25, +23, +18	+12, +5, ±23	±30, +20, +26
no. of reflns collected/unique	11 345/2936	5216/4902	15 377/7512
no. of data/restraints/params	2936/1/359	4902/0/318	7512/0/386
goodness-of-fit on *F*^{2}	0.902	1.247	0.884
final *R* Indices [*I* > 2σ(*I*)]^{a,b}	$R_1 = 0.0357$, $wR_2 = 0.1005$	$R_1 = 0.0598$, $wR_2 = 0.1649$	$R_1 = 0.0674$, $wR_2 = 0.1967$
R indices (all data)^{a,b}	$R_1 = 0.0564$, $wR_2 = 0.1158$	$R_1 = 0.0955$, $wR_2 = 0.1830$	$R_1 = 0.1644$, $wR_2 = 0.2697$
absolute structure param	0.00(2)		
largest diff peak and hole, e/Å^3	0.402 and −0.409	1.291 and −0.614	1.190 and −1.005

$^a R_1 = \sum ||F_o| - |F_c|| $ (based on reflections with $F_o^2 > 2\sigma F^2$). $^b wR_2 = [\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]]^{1/2}$; $w = 1/[\sigma^2(F_o^2) + (0.095P)^2]$; $P = [\max(F_o^2, 0) + 2F_c^2]/3$ (also with $F_o^2 > 2\sigma F^2$).

Table 3. Selected Interatomic Distances (Å) in 3·THF, 5b·THF, and 6·Toluene

Compound **3·THF**

Ni(1)−C(1) 1.979(5)	Ni(1)−N(1) 2.061(6)	Ni(1)−B(3) 2.123(6)	
Ni(1)−B(4) 2.122(6)	Ni(1)−C(2) 2.124(4)	Ni(1)−B(5) 2.139(5)	
Ni(1)−P(1) 2.166(1)	C(1)−C(3) 1.498(9)	N(1)−C(3) 1.520(8)	

Compound **5b·THF**

Ni(1)−N(1) 2.257(3)	Ni(1)−N(2) 2.038(3)	Ni(1)−N(3) 2.040(3)	
Ni(1)−C(1) 2.235(4)	Ni(1)−C(2) 2.221(4)	Ni(1)−B(3) 2.224(4)	
Ni(1)−B(4) 2.210(4)	Ni(1)−B(5) 2.193(4)		

Compound **6·Toluene**

Ni(1)−I(1) 2.5574(1)	Ni(1)−C(1) 2.219(8)	Ni(1)−C(2) 2.019(9)	
Ni(1)−B(3) 2.117(1)	Ni(1)−B(4) 2.081(1)	Ni(1)−B(5) 2.141(1)	
C(1)−C(3) 1.516(1)	P(1)−C(3) 1.810(8)	N(1)−C(22) 1.124(1)	
N(1)−C(23) 1.464(1)			

plexation with nickel (Table 1), a clear downfield shift is observed for the bipyridine protons close to the coordination site, consistent with that observed for the formation of **5b**.

Isolation of the pure products, which ranged from orange to red in color, was achieved by recrystallization. Typically, the yields of **5** were on the order of 59−85%. Compounds **5** were characterized by IR and NMR (^{1}H, ^{11}B, and ^{13}C) spectroscopies. The corresponding NMR data for **5** are summarized in Table 1. In contrast to **2**, the ^{1}H NMR spectrum reveals two signals for the methyl groups at the nitrogen atom of the side chain due to coordination of the metal, which prevents inversion at N atom. The methylene protons of the C*H*$_2$ group in **5** are diastereotopic, each giving rise to an AB spin pattern. The spectroscopic data for the complexes **5a**,**b** prove that the dimethyl amino group of the side chain is coordinated to the metal center in all cases. In addition, the ^{11}B NMR spectra (Table 1) show the expected resonances for the dicarbollyl group in the highly asymmetric environments,[21] due to the metal complexation. Compounds **5** represent the first example

of a dicarbollyl nickel(II) complex having a 20-electron metal center with intramolecular coordination of a donor function in the side chain.

A single-crystal X-ray diffraction study was carried out on **5b·THF** in order to obtain more information on the Ni−N interactions and also to determine the influence of the Ni−N bond on the coordination of the bipy ligand. The structural analysis shows that **5b·THF** forms monomeric molecules where the dimethylamino group is intramolecularly coordinated to the nickel atom, as shown in Figure 2. The geometry around Ni may be described as distorted tetrahedral (with the C_2B_3 centroid occupying a single coordination site) or a highly distorted square pyramidal environment. The C_2B_3 bonding face in **5b·THF** is planar (maximum deviation of 0.004 Å) with the nickel approximately centered over the ring at a distance of 1.683 Å. Selected bond lengths and angles for **5b·THF** are listed in Tables 3 and 4. The Ni−N$_{amino}$ distance in **5b·THF** is 2.2573 Å, which is longer than the corresponding distance in **3** (2.06(2) Å). The chelate 2,2′-bipyridine and nickel atom form a heteronuclear five-membered ring. The Ni−N$_{bipy}$ distances of 2.039(3) (av) Å are longer than those found in (cod)Ni(bipy) (1.938(4) (av) Å).[22] The orientation of the bipy ligand is such that the planes bearing the atoms N(1), Ni(1), $C_2B_{3(centroid)}$ and N(3), Ni(1), N(2), C(10), and C(11) are rotated by 86.5(2)° with respect to each other. The dihedral angle between the planes formed by the atoms N(3), Ni(1), N(2), C(10), and C(11), on one hand, and C(1), C(2), B(3), B(4), and B(5), on the other, is ca. 70.8°.
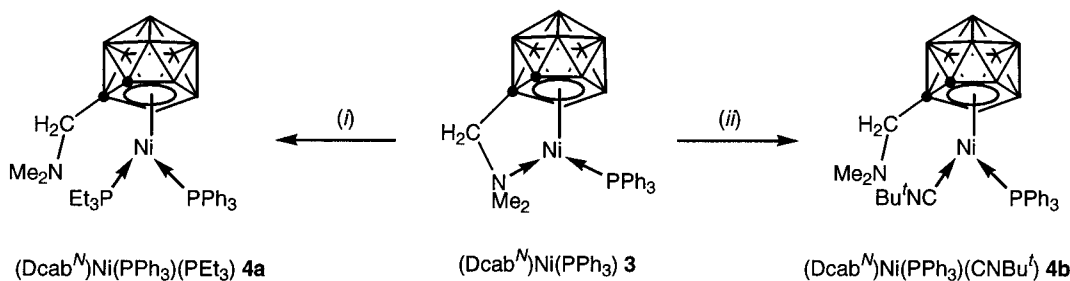
Reaction of the *tert*-Butylisocyanide Complex 4b with Methyl Iodide: Exclusive Deamination. Strong σ donation of the *tert*-butylisocyanide ligand to the low-valent transition metals may make the metal center electron rich, thereby enhancing the ability of the metal

(21) Siedle, A. R.; Bodner, G. M.; Todd, L. J. *J. Organomet. Chem.* **1971**, *33*, 137.

(22) Dinjus, E.; Walther, D.; Kaiser, J.; Sieler, J.; Thanh, N. N. *J. Organomet. Chem.* **1982**, *236*, 123.

Table 4. Selected Interatomic Angles (deg) in 3·THF, 5b·THF, and 6·Toluene

		Compound **3**·THF			
N(1)−Ni(1)−P(1)	105.0(1)	Ni(1)−N(1)−C(3)	90.5(4)	N(1)−C(3)−C(1)	103.4(5)
C(6)−P(1)−C(12)	100.2(2)	C(6)−P(1)−C(18)	103.4(3)	C(12)−P(1)−C(18)	105.1(2)
C(3)−N(1)−C(4)	108.6(6)	C(3)−N(1)−C(5)	109.7(5)	C(4)−N(1)−C(5)	110.0(6)
		Compound **5b**·THF			
N(1)−Ni(1)−N(2)	97.2(1)	N(1)−Ni(1)−N(3)	93.5(1)	N(2)−Ni(1)−N(3)	79.3(5)
N(1)−C(3)−C(1)	106.7(3)	C(3)−N(1)−C(4)	110.8(4)	C(3)−N(1)−C(5)	111.5(4)
C(4)−N(1)−C(5)	109.5(4)				
		Compound **6**·Toluene			
C(22)−Ni(1)−I(1)	89.6(3)	Ni(1)−C(22)−N(1)	178.5(1)	C(22)−N(1)−C(23)	172.4(1)
C(1)−C(3)−P(1)	122.3(6)	C(3)−P(1)−C(4)	112.6(4)	C(3)−P(1)−C(10)	105.9(4)
C(3)−P(1)−C(16)	110.7(4)	C(4)−P(1)−C(10)	106.4(4)	C(4)−P(1)−C(16)	113.6(4)

Scheme 1.   Ligand Substitutions of 3[a]

(Dcab^N)Ni(PPh$_3$)(PEt$_3$) **4a**   (Dcab^N)Ni(PPh$_3$) **3**   (Dcab^N)Ni(PPh$_3$)(CNBu^t) **4b**

[a]Legend: (*i*) PMe$_3$, THF, 25 °C; (*ii*) CNBu^t, THF, 25 °C.

Scheme 2.   Ligand Substitutions of 3[a]

(Dcab^N)Ni(dpe) **5a**   (Dcab^N)Ni(PPh$_3$) **3**   (Dcab^N)Ni(bipy) **5b**
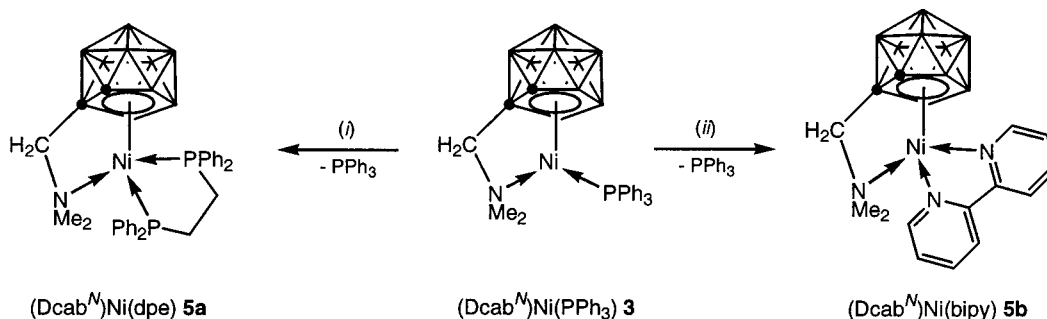
[a]Legend: (*i*) dpe, THF, 25 °C; (*ii*) bipy, THF, 25 °C.

to undergo nucleophilic reaction.[23] Indeed, the neutral isocyanide nickel complex **4b** is reactive enough toward an electrophile such as the methyl iodide as shown in eq 3. Thus, **4b** was treated with methyl iodide to give green needles in quantitative yield. The treatment of **4b** with 2 equiv of methyl iodide in toluene-d_8 at 65 °C while the reaction progress was monitored by ^{1}H NMR spectroscopy resulted in the disappearance of the amino methyl peak and the formation of a new methylene proton signal. The relative intensities of the phenyl group of PPh$_3$ and methyl resonance of CNBu^t are equal to the expected 15:9 ratio within experimental error (Table 1). In particular, the methylene group contains diastereotopic methylene protons and shows a second-order, ABX, multiplet centered at δ 5.28 ($^3J_{PH}$ = 12 Hz). This is explained on the basis of phosphorus-31 coupling, although much smaller values of J_{PH} are generally encountered in alkylphosphine complexes.[24] Moreover, the ^{31}P NMR of the new product exhibited a different single resonance at δ 22.05. The presence of the direct interaction between the methylene unit and phosphine might have been expected to lead to such a low-field shift and a complex coupling pattern of the methylene resonances. The IR spectrum of the complex **6** showed a carbon−nitrogen stretching frequency at

2179 cm^{-1}, attributable to the presence of a coordinated isocyanide group, and the characteristic B−H absorption for a dicarbollyl group near 2532 cm^{-1}.

(Dcab^N)Ni(PPh$_3$)(CNBu^t) **4b**   (Dcab^P)Ni(CNBu^t)I **6**
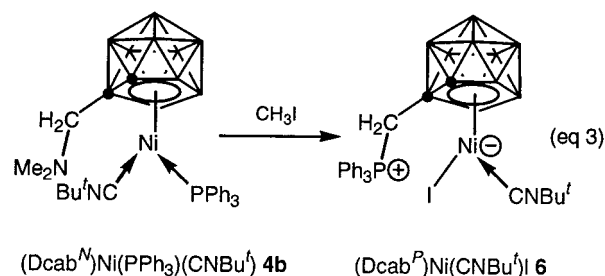
As the structure of the product was not deduced on the basis of the spectroscopic data, a single-crystal X-ray diffraction study was undertaken. The molecular structure of **6**·toluene is shown in Figure 3. Crystallographic data are given in Table 2, and selected bond lengths and angles in Tables 3 and 4. To our surprise, the X-ray study of **6**·toluene showed it to be the zwiterionic

(23) Yamamoto, Y.; Yamazaki, H.; Hagihara, N. *J. Organomet. Chem.* **1969**, *18*, 189.
(24) (a) Jones, C. E.; Coskran, K. J. *Inorg. Chem.* **1971**, *10*, 55. (b) Dewhirst, K. C.; Keim, W.; Reilly, C. A. *Inorg. Chem.* **1968**, *7*, 546.
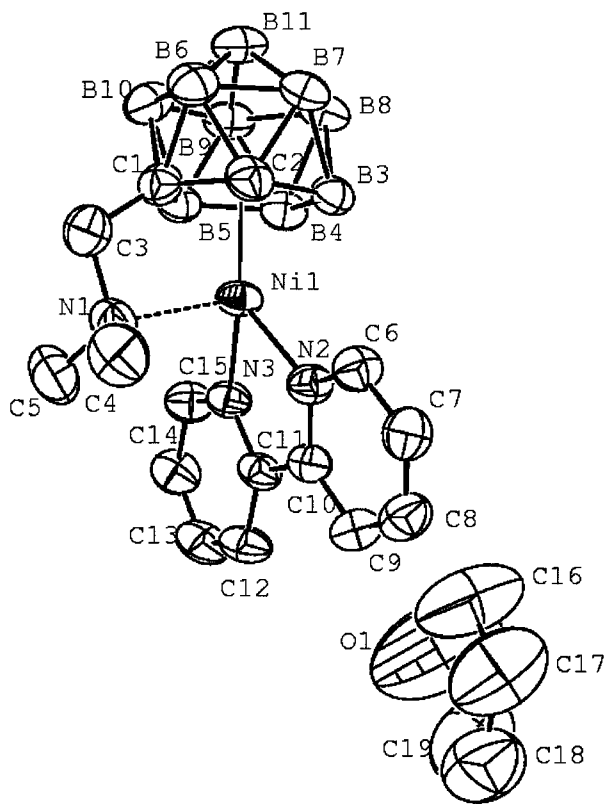
Figure 2. Molecular structure of **5b**·THF with atom labeling; ellipsoids show 30% probability levels, and hydrogen atoms have been omitted for clarity.

compound of the methyl phosphonium tethered dicarbollyl nickel iodide complex. The Ni–I[8] and P–C bond lengths are within the expected range.[25] The coordination of the C_2B_3 ring is distinctly off-center with the Ni closest to B(4) (2.081(1) Å). The molecule contains a noncoordinated methyl phosphonium tether.

The new insertion product **6** is prepared by treatment of **4b** with methyl iodide. To achieve this insertion of MeI into the C–N bond of the aminomethyl group, the presence of strong σ-donor ligand such as *tert*-butyl isocyanide is necessary (Scheme 3). Without this, the complex **3** does not cleanly react with methyl iodide. Interestingly, the related chemistry of **4b** with MeI is very similar to that of the ferrocenylmethyl amino ligands.[26]

Thus, treatment of **4b** with MeI immediately gives orange solutions, which slowly turn yellow-green as the final color. Apparently, the primary step of this reaction involves the substitution of methyl iodide by the dimethylamino tether to give intermediate **A**, which then smoothly reacts with the coordinated triphenylphosphine to yield the corresponding phosphonium salt **B** with the extrusion of trimethylamine. It has been well-established that the trimethylammonium iodide salt serves as an extremely useful intermediate for preparing the corresponding phosphonium salt as shown in Scheme 3.[27] Since the trimethylammonium group is an excellent leaving group,[1j,l,m,v] **A** would undergo a reac-

tion with the free triphenylphosphine to form the corresponding phosphonium salt **B**. The coordination of the iodide ion to the nickel atom in our case then would afford the complex **6**.

Conclusion

We have demonstrated that a stable aminonickel complex could be easily prepared when an amino group was tethered to the dicarbollyl ligand. The amino ligand is an important element for promoting the nickel complex reactivity toward ligand exchanges. Thus, the ligand exchanges of **3** with either the mono- or bidentate ligands provide either noncoordinated or coordinated amine tethered complexes. Such a selectivity is dependent on the nature of the ligands and can be explained by use of either the hard–soft acid–base principle or chelate effect. The resulting ligand exchanged complex with the noncoordinating amino group provides further opportunity for studying the reactivity of the half-sandwich nickel complex such as the nucleophilic reaction with methyl iodide. Alkylation of the neutral aminonickel complex **4b** gives exclusive formation of the zwiterionic phosphonium salt of the nickel iodide complex **6**.

Experimental Section

General Procedures. All manipulations were performed under a dry, oxygen-free, nitrogen or argon atmosphere using standard Schlenk techniques or in a Vacuum Atmospheres HE-493 drybox. THF was freshly distilled over potassium benzophenone. Toluene was dried and distilled from sodium benzophenone. Dichloromethane and hexane were dried and distilled over CaH_2. The ^{11}B, ^{13}C, ^1H, and ^{31}P NMR spectra were recorded on a Varian Gemini 2000 spectrometer operating at 64.2, 50.3, 200.1, and 80.0 MHz, respectively. All the boron-11 chemical shifts were referenced to $BF_3 \cdot O(C_2H_5)_2$ (0.0 ppm) with a negative sign indicating an upfield shift. All the proton and carbon chemical shifts were measured relative to internal residual benzene from the lock solvent (99.5% C_6D_6) and then referenced to Me_4Si (0.00 ppm). The ^{31}P NMR spectra were recorded with 85% H_3PO_4 as the external standard. The IR spectra were recorded on a Biorad FTS-165 spectrophotometer. Elemental analyses were performed with a Carlo Erba Instruments CHNS-O EA1108 analyzer. All melting points were uncorrected. Decaborane and *N,N*-(dimethylamino)-2-propyne were purchased from Katechem and Aldrich, respectively, and used without purification. Cab^NH **1**[28] was prepared by the literature methods. $(PPh_3)_2NiCl_2$ was purchased from Strem Chemical and used as received.

Preparation of [*nido*-7-NMe$_2$CH$_2$-7,8-C$_2$B$_9$H$_{11}$]$^-$ (2). Compound **1** (0.60 g, 3.0 mmol) was dissolved in degassed MeOH (20 mL), KOH (0.22 g, 4.0 mmol) was then added, and the reaction mixture was heated to reflux for 12 h. CO_2 was bubbled through the cooled solution, and the resulting precipitate of K_2CO_3 was filtered off to afford a clear yellow solution. The methanol was removed in vacuo, the residue dissolved in H_2O (40 mL), and an aqueous solution of NMe_4Cl (0.35 g, 3.2 mmol) then added, which resulted in the formation of a white sticky precipitate. The solution was extracted three times with acetone (3 × 30 mL), and the combined extracts were dried over $MgSO_4$ to afford (0.74 g, 2.8 mmol, 93%) **2**. Recrystallization from an acetone/THF mixture gave colorless

(25) (a) Ramakrishna, T. V. V.; Elias, A. J.; Vij, A. *J. Organomet. Chem.* **2000**, *602*, 125. (b) Goodwin, N. J.; Henderson, W.; Nicholson, B. K.; Sarfo, J. K.; Fawcett, J.; Russell, D. R. *J. Chem. Soc., Dalton Trans.* **1997**, 4377.
(26) Togni, A.; Hayashi, T. *Ferrocenes*; VCH Publishers: Weinheim, Germany, 1995.

(27) (a) Glidewell, C.; Royles, B. J. L.; Smith, D. M. *J. Organomet. Chem.* **1997**, *527*, 259. (b) Tanner, D.; Wennerström, O. *Acta Chem. Scand. Ser. B* **1980**, *34*, 529. (c) Sonoda, A.; Moritani, I. *J. Organomet. Chem.* **1971**, *26*, 133.
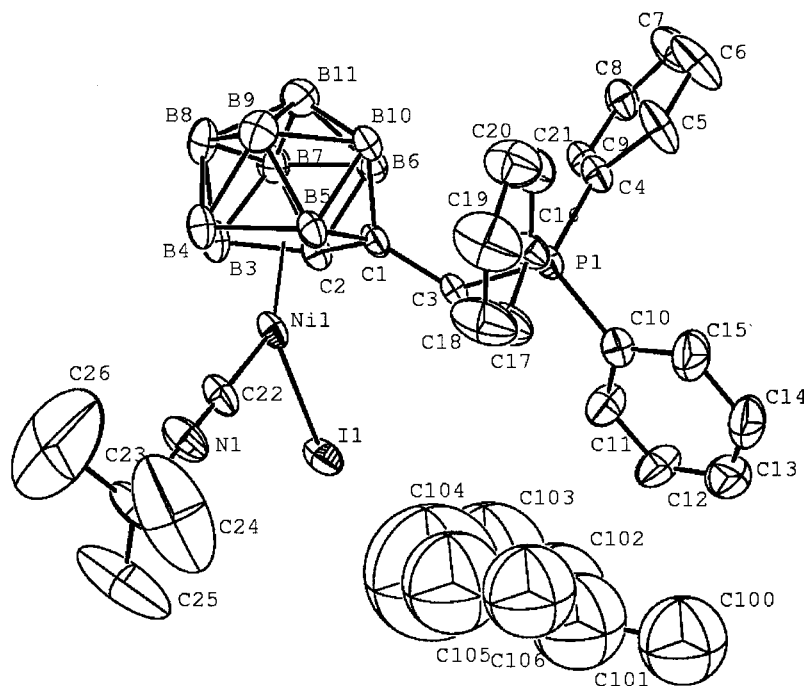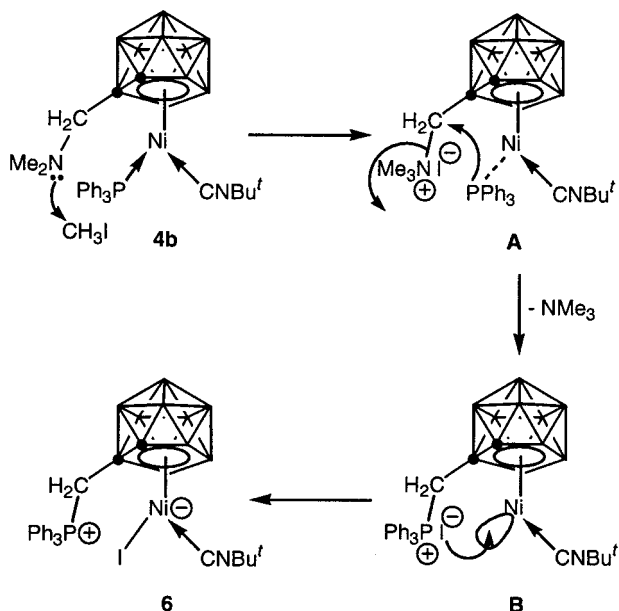
Figure 3. Molecular structure of **6**·toluene with atom labeling; ellipsoids show 30% probability levels, and hydrogen atoms have been omitted for clarity.

Scheme 3. Possible Reaction Sequence for the Formation of 6

crystalline solids. Data for **2**: Anal. Found for $C_9B_9H_{31}N_2$: C 40.89, H 11.92, N 10.54. Calcd: C 40.85, H 11.81, N 10.59. Mp: 130 °C (dec). IR (KBr pellet, cm^{-1}): ν(C–H) 3033, ν(B–H) 2537.

Preparation of (η^5:η^1-C₂B₉H₁₀-CH₂NMe₂)Ni(PPh₃) (3). To a stirred solution of the potassium salt of Cab^{N}HK (0.69 g, 3.0 mmol) in THF (20 mL) was added 2.4 mL of 1.5 M Bu^{n}Li (1.2 equiv). The mixture was stirred for 3 h at room temperature. The resulting clear yellow supernatant was decanted using a syringe. Removal of the solvent in vacuo and washing with light petroleum afforded a yellow tinted powder of the lithium salt of Cab^{N}LiK (0.64 g, 2.7 mmol, 90%). Over a period of 30 min, a 20 mL THF solution of (PPh₃)₂NiCl₂ (1.96 g, 3.0 mmol) was added to a stirred solution of the lithium salt of **2** in THF (20 mL) at −78 °C. After the addition was complete, the cold bath was removed and the solution was stirred at

room temperature for 12 h. The dark residue after removal of the solvents was flash chromatographed on silica gel using 10% EtOAc in hexane to remove some organics, followed by 50% EtOAc in hexane. The red band was collected and concentrated to provide 0.92 g (1.8 mmol, 60%) of **3** as dark red solids. The solids were further purified by recrystallization with a THF/hexane mixture. Anal. Found: C 54.30, H 6.68, N 2.90. Calcd: C 54.12, H 6.52, N 2.74. R_f = 0.38 (TLC silica gel benzene). Mp: 178 °C (dec). ^{31}P{^{1}H} NMR (80.0 MHz, δ, CDCl₃): 37.08 (s, PPh₃). IR (KBr pellet, cm^{-1}): ν(C–H) 3057, 2929, ν(B–H) 2536, ν(C=C) 1436, ν(C–P) 1095.

(η^5-C₂B₉H₁₀CH₂NMe₂)Ni(PPh₃)(PEt₃) (4a). A 0.51 g amount of **3** (1.0 mmol) was dissolved in 15 mL of dry THF and cooled to −10 °C. A 0.15 mL amount of triethylphosphine (1.0 mmol) was added with stirring over 30 min, and the solution was allowed to warm to room temperature. The red solution turned dark red as the solution warmed. The mixture was stirred for an additional 3 h at room temperature. The resulting dark red solution was then concentrated under reduced pressure. The residue was dissolved with CH₂Cl₂ (2 mL) and then chromatographed on silica gel upon elution with 10% EtOAc in hexane. The red band was collected and concentrated to provide the desired product **4a** (0.44 g, 0.70 mmol) with a 70% yield. Anal. Found: C 55.55, H 7.81, N 2.27. Calcd: C 55.41, H 7.7, N 2.23. R_f = 0.05 (TLC silica gel benzene). Mp: 166 °C (dec). ^{31}P{^{1}H} NMR (80.0 MHz, δ, CDCl₃): 31.61 (PEt₃), 56.03 (PPh₃). IR (KBr pellet, cm^{-1}): ν-(C–H) 2963, 2928, ν(B–H) 2534, ν(C=C) 1729, 1410, ν(C–P) 1262.

(η^5-C₂B₉H₁₀CH₂NMe₂)Ni(PPh₃)(CNBu^t) (4b). A procedure analogous to the preparation of **4a** was used, but starting from *tert*-butyl isocyanide (0.12 mL, 1.0 mmol) in THF. Yield: 93% (0.55 g, 0.93 mmol). Anal. Found: C 55.80, H 7.22, N 4.81. Calcd: C 56.65, H 7.13, N 4.72. R_f = 0.09 (TLC silica gel benzene). Mp: 126 °C (dec). ^{31}P{^{1}H} NMR (80.0 MHz, δ, CDCl₃): 30.03 (PPh₃). IR (KBr pellet, cm^{-1}): ν(C–H) 2984, 2822, ν(B–H) 2532, ν(N=C) 2175, ν(C=C) 1435, ν(C–P) 1096.

(η^5:η^1-C₂B₉H₁₀-CH₂NMe₂)Ni(dpe) (5a). A 0.51 g amount of **3** (1.0 mmol) was dissolved in 10 mL of dry THF and cooled to −10 °C. A 0.40 g amount of dpe (1.0 mmol) was added with stirring over 30 min, and the solution was allowed to warm to room temperature. The red solution turned dark red as the

solution warmed. The mixture was stirred for an additional 3 h at room temperature. The resulting red solution was then concentrated under reduced pressure. The residue was dissolved using CH_2Cl_2 (2 mL) and then chromatographed on silica gel upon elution with 50% EtOAc in hexane. The red band was collected and concentrated to provide the desired product **5a** (0.55 g, 0.85 mmol) with an 85% yield. Anal. Found: C 57.71, H 6.70, N 2.21. Calcd: C 57.58, H 6.55, N 2.17. R_f = 0.08 (TLC silica gel methylene chloride). Mp: 164 °C (dec). ^{31}P{^{1}H} NMR (80.0 MHz, δ, CDCl$_3$): 59.97 (*P*Ph$_{dpe}$). IR (KBr pellet, cm^{-1}): ν(C–H) 3057, 2972, 2935, ν(B–H) 2521, ν(C=C) 1434, ν(C–P) 1100.

(η^5:η^1-C$_2$B$_9$H$_{10}$-CH$_2$NMe$_2$)Ni(bipy) (5b). A procedure analogous to the preparation of **5a** was used, but starting from 2,2′-bipyridine (0.16 g, 1.0 mmol) in THF. Yield: 59% (0.24 g, 0.59 mmol). Anal. Found: C 44.60, H 6.55, N 10.46. Calcd: C 44.55, H 6.48, N 10.39. R_f = 0.07 (TLC silica gel methylene chloride). Mp: 126 °C (dec). IR (KBr pellet, cm^{-1}): ν(C–H) 3079, 2957, 2940, ν(B–H) 2538, 2513, ν(C=C) 1471, 1442.

(η^5-C$_2$B$_9$H$_{10}$CH$_2$PPh$_3$)Ni(CNBu^t)(I) (6). Under an inert atmosphere, 0.59 g of **4b** (1.0 mmol) was dissolved in 20 mL of toluene. A 0.14 mL aliquot of MeI (2.2 mmol) in about 5 mL of dry toluene was slowly added to the Ni solution using a cannular for 10 min at room temperature. The mixture was heated at 65 °C, and the reaction was monitored by ^{1}H and ^{31}P NMR spectroscopies. A clean and quantitative conversion to **4b** was observed after about 1 h. The solution was filtered in air, and the solvent was removed under reduced pressure. The remaining solid was passed through a short column of silica gel with CH_2Cl_2 as the eluent. A 0.51 g amount of **6** was obtained after removal of the solvent (0.69 mmol, 69% yield). Anal. Found: C 47.49, H 6.30, N 3.90. Calcd: C 47.36, H 6.17, N 3.81. R_f = 0.15 (TLC silica gel methylene chloride/benzene, 5:5). Mp: 160 °C (dec). ^{31}P{^{1}H} NMR (80.0 MHz, δ, CDCl$_3$): 22.05 (*P*Ph$_3$). IR (KBr pellet, cm^{-1}): ν(C–H) 2984, 2868, ν(B–H) 2532, ν(N=C) 2179, ν(C=C) 1438, ν(C–P) 1208.

X-ray Crystallography. Suitable crystals of **3**·THF, **5b**·THF, and **6**·toluene were obtained by the slow diffusion of toluene into a THF solution of the complexes at room temperature and were mounted on a glass fiber. The crystal data and experimental details are given in Table 2. The data sets of **3**·THF, **5b**·THF, and **6**·toluene were collected on an Enraf CAD4 automated diffractometer. Mo Kα radiation (λ = 0.7107 Å) was used for all the structures. Each structure was solved by the application of direct methods using the SHELXS-96 program[29a] and least-squares refinement using SHELXL-97.[29b] All non-hydrogen atoms in compounds **3**·THF, **5b**·THF, and **6**·toluene were anisotropically refined. All other hydrogen atoms were included in the calculated positions.

Supporting Information Available: Crystallographic data (excluding structure factors) for the structures (**3**·THF, **5b**·THF, and **6**·toluene) reported in this paper. This material is available free of charge via the Internet at http://pubs.acs.org. These data have also been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-163298 (**3**·THF), -163300 (**5b**·THF), and -163301 (**6**·toluene). Copies of the data can be obtained free of charge upon application to CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K. (fax, (+44) 1223-336-033; e-mail, deposit@ccdc.cam. ac.uk).

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(28) Heying, T. L.; Ager, J. W., Jr.; Clark, S. L.; Mangold, D. J.; Goldstein, H. L.; Hillman, M.; Polak, R. J.; Szymanski, J. W. *Inorg. Chem.* **1963**, *2*, 1089.

(29) (a) Sheldrick, G. M. *Acta Crystallogr. A* **1990**, *46*, 467. (b) Sheldrick, G. M. *SHELXL*, Program for Crystal Structure Refinement; University of Göttingen, 1997.