Transition-Metal Sandwich Complexes of Heterocyclic Ligands. Carborane-Stabilized η^5-Pyrrolyl and η^5-Phospholyl Double-Decker and Triple-Decker Compounds: Synthesis, Structure, and Electrochemistry[1,2]

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This paper reports the controlled synthesis, characterization, and study of a series of pyrrolyl- and phospholyl-containing transition-metal sandwich complexes stabilized by cyclic $Et_2C_2B_3H_n^{n-7}$ (n = 3, 5) carborane units, including the first triple-decker complexes of N- or P-containing heterocyclic ligands. The reaction of the *nido*-$Et_2C_2B_4H_5^-$ ion with $CoCl_2$ and a dimethyl- or tetramethylpyrrolide ion in THF generated the sandwich complexes (η^5-$NC_4Me_2R_2$)Co($Et_2C_2B_4H_4$) (**1a/1b**, R = Me, H) together with the corresponding "decapitated" species (η^5-$NC_4Me_2R_2$)Co($Et_2C_2B_3H_5$) (**2a/2b**, R = Me, H); in each case, subsequent treatment of the mixture with TMEDA (tetramethylethylenediamine) generated pure **2a** or **2b**. The reaction of the cobaltacarborane anion Cp*Co($Et_2C_2B_3H_6$)$^-$ with $CoCl_2$ and a di- or tetramethylpyrrolide ion in THF yielded the dicobalt triple-deckers (η^5-$NC_4Me_2R_2$)Co($Et_2C_2B_3H_3$)CoCp* (**5a/5b**, R = Me, H). Reaction of the cymene–ruthenium–carborane complex anion ($MeC_6H_4CHMe_2$)Ru($Et_2C_2B_3H_4$)$^-$ with $CoCl_2$ and a di- or tetramethylpyrrolide ion afforded the cobalt–ruthenium triple-decker complexes (η^5-$NC_4Me_2R_2$)Co($Et_2C_2B_3H_3$)Ru(η^6-1,4-$MeC_6H_4CHMe_2$) (**8a/8b**, R = Me, H). Treatment of the deprotonated anion of **2a** with $CoCl_2$ and $NC_4Me_4^-$ gave the bis(pyrrolyl) triple-decker complex (η^5-NC_4Me_4)$_2$Co$_2$($Et_2C_2B_3H_3$) (**9**). Although **5a** reacted with CH_3I to give the *N*-methyl cationic derivative **12**, similar treatment of the dimethylpyrrolyl species **5b** resulted only in iodo substitution at the central boron atom, B(5). Attempts at nucleophilic substitution at the ring nitrogen on the triple-decker pyrrolyl complexes, via reactions with alkyl halides, gave only *B*-halo derivatives. However, treatment of the monopyrrolyl and bis(pyrrolyl) triple-decker complexes **5a** and **9** with BH_3·THF formed *N*-BH_3 and *N,N'*-$(BH_3)_2$ adducts. The phospholyl analogue of **1a** was prepared via the reaction of the tetramethylphospholide anion with *nido*-$Et_2C_2B_4H_5^-$ and $CoCl_2$, forming the desired species (η^5-PC_4Me_4)Co($Et_2C_2B_4H_4$) (**25**), which was readily converted to (η^5-PC_4Me_4)Co($Et_2C_2B_3H_5$) (**26**) via treatment with wet TMEDA. The cobaltacarborane anion Cp*Co($Et_2C_2B_3H_6$)$^-$ underwent a similar reaction to give the phospholyl-containing triple-decker (η^5–PC_4Me_4)Co($Et_2C_2B_3H_3$)CoCp* (**27**); a cobalt–ruthenium analogue, (PC_4Me_4)Co($Et_2C_2B_3H_3$)Ru($MeC_6H_4CHMe_2$) (**28**), was synthesized from the ($MeC_6H_4CHMe_2$)Ru($Et_2C_2B_3H_4$)$^-$ anion, $CoCl_2$, and the $PC_4Me_4^-$ ion. Reactions of the (η^5-PC_4Me_4)Co($Et_2C_2B_3H_4$)$^-$ anion (**26**$^-$) with $CoCl_2$ and with $PC_4Me_4^-$ or $NC_4Me_4^-$ ions gave, respectively, a bis(phospholyl) triple-decker, (PC_4Me_4)$_2$Co$_2$($Et_2C_2B_3H_3$) (**29**), and a phospholyl–pyrrolyl triple-decker, (PC_4Me_4)Co($Et_2C_2B_3H_3$)Co(NC_4Me_4) (**30**). All of the new double- and triple-decker sandwich species were isolated via column and/or plate chromatography as crystalline solids or oils and were characterized via multinuclear NMR, IR, UV–visible, and mass spectra, supported by X-ray diffraction data on **9** (to be reported elsewhere) and **30**. Except for **22**, **23**, **27**, and **28**, all new complexes are air-stable. Cyclic voltammetry on **5a/5b**, **8a/8b**, **9**, and **27–30** in dichloromethane and dimethoxyethane (DME) solutions gave reversible oxidations in both solvents and reversible 1-electron reductions in DME only; in several cases a second, irreversible oxidation was observed. The pyrrolyl and phospholyl triple-deckers exhibited higher oxidation and reduction potentials than are seen in analogous C_2B_3-bridged triple-decker complexes having Cp or Cp* end ligands, with the highest values observed in the case of the bis(pyrrolyl) species **9**. These data are interpreted in terms of known electron-donor properties of pyrrolyl and phospholyl π-bonded ligands. Crystal data for **30**: mol wt 496.8; space group $P\bar{1}$; Z = 2; a = 9.017 (5) Å, b = 9.966 (7) Å, c = 15.115 (9) Å, α = 109.95 (5)°, β = 93.97 (4)°, γ = 71.55 (5)°; V = 1210 Å^3; R = 0.069 for 3390 reflections having $I > 2.5\sigma(I)$.

Introduction

Transition-metal sandwich complexes that combine aromatic hydrocarbon and small carborane ($R_2C_2B_3H_3^{4-}$, $R_2C_2B_3H_5^{2-}$, $R_2C_2B_4H_4^{2-}$) ligands have opened the way to a rich and diverse chemistry that has been extensively developed over the past decade.[3] Perhaps the most striking feature of this chemistry is the ability of these carborane ligands to stabilize unusual or novel organometallic molecular systems, including multidecker sandwiches,[3a,4] η^8-C_8H_8 complexes of first-row transition metals,[5] and Fe(III)–arene compounds.[6] As a consequence of the generally high stability and robustness of these compounds, they are well suited, as a class, for use as building block reagents in the systematic construction of electron-delocalized oligomers[4b,d] and polymers.[7]

(1) Organotransition-Metal Metallacarboranes. 21. Part 20: Benvenuto, M.; Grimes, R. N. *Inorg. Chem.* **1991**, *30*, 2836. Part 19: Fessenbecker, A.; Stephan, M.; Grimes, R. N.; Pritzkow, H.; Zenneck, U.; Siebert, W. *J. Am. Chem. Soc.* **1991**, *113*, 3061. Part 18: Davis, J. H., Jr.; Benvenuto, M. A.; Grimes, R. N. *Inorg. Chem.* **1991**, *30*, 1765.

(2) Based in part on the Ph.D. Thesis of Kevin Chase, University of Virginia, 1990.

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Table I. 115.8-MHz ^{11}B FT NMR Data

compd	δ (J_{BH}, Hz)[a,b,c]	rel areas
$(NC_4Me_4)Co(Et_2C_2B_3H_5)$ (**2a**)	6.1 (148), 3.4 (138)	1:2
$(NC_4Me_2H_2)Co(Et_2C_2B_3H_5)$ (**2b**)	2.6 (156), 4.1 (155)	1:2
$(NC_4Me_4)Co(Et_2C_2B_3H_3)CoCp^*$ (**5a**)	56.5 (124), 8.4 (92)	1:2
$(NC_4Me_2H_2)Co(Et_2C_2B_3H_3)CoCp^*$ (**5b**)	54.7 (79), 8.0 (79)	1:2
$Cp^*_2Co_2Et_4C_4B_6H_6$ (**6**)	49.5 (117), 29.4	1:2
$(NC_4Me_4)Co(Et_2C_2B_3H_3)Ru(1,4\text{-}MeC_6H_4CHMe_2)$ (**8a**)	45.5 (107), 5.9 (104)	1:2
$(NC_4Me_2H_2)Co(Et_2C_2B_3H_3)Ru(1,4\text{-}MeC_6H_4CHMe_2)$ (**8b**)	43.4 (114), 4.9 (113)	1:2
$(NC_4Me_4)_2Co_2(Et_2C_2B_3H_3)$ (**9**)	59.1 (136), 8.9 (104)	1:2
$(NC_4Me_4)CoEt_4C_4B_7H_7$ (**10**)	19.0 (139), 0.22 (91), −0.4,[d] −5.0,[d] −6.2,[d] −15.2 (125), −20.0 (141)	1:1:1:1:1:1:1
$[(MeNC_4Me_4)Co(Et_2C_2B_3H_3)CoCp^*]^+I^-$ (**12**)	71.8 (70), 10.9 (34)	1:2
$(NC_4Me_4)Co(Et_2C_2B_3H_2I)CoCp^*$ (**13**)	43.1, 10.7 (98)	1:2
$(NC_4Me_4)Co(Et_2C_2B_3H_2Cl)CoCp^*$ (**17**)	61.8, 5.6 (49)	1:2
$(NC_4Me_4)Co(Et_2C_2B_3H_2Br)CoCp^*$ (**19**)	56.3, 7.7 (107)	1:2
$(NC_4Me_4)_2Co_2(Et_2C_2B_3H_2I)$ (**21**)	41.4, 10.6 (66)	1:2
$(H_3B\text{-}NC_4Me_4)Co(Et_2C_2B_3H_3)CoCp^*$ (**22**)	62.1 (131), 9.2 (87), −23.6 (86)[e]	1:2:1
$(H_3B\text{-}NC_4Me_4)_2Co_2(Et_2C_2B_3H_3)$ (**23**)	70.5 (131), 10.3 (103), −23.1 (95)[e]	1:2:2
$(PC_4Me_4)Co(Et_2C_2B_4H_4)$ (**25**)	11.8 (136), 6.8 (164), 3.8 (142)	1:1:2
$(PC_4Me_4)Co(Et_2C_2B_3H_5)$ (**26**)	4.9,[d] 3.1[d]	1:2
$(PC_4Me_4)Co(Et_2C_2B_3H_3)CoCp^*$ (**27**)	57.2 (118), 8.7 (106)	1:2
$(PC_4Me_4)Co(Et_2C_2B_3H_3)Ru(MeC_6H_4CHMe_2)$ (**28**)	46.7 (107), 6.4 (98)	1:2
$(PC_4Me_4)_2Co_2(Et_2C_2B_3H_3)$ (**29**)	60.5 (124), 9.4 (113)	1:2
$(PC_4Me_4)Co(Et_2C_2B_3H_3)Co(NC_4Me_4)$ (**30**)	59.5 (117), 9.1 (107)	1:2

[a] Shifts relative to $BF_3{\cdot}OEt_2$, positive values downfield. [b] Dichloromethane solution. [c] H–B coupling constant is given when resolved. [d] Overlapping doublets. [e] Quartet.

The known (arene)metal(carborane) species incorporate a wide variety of arenes including linked and polyaromatic systems.[3a,b] This versatility led us to explore the possible extension of this family of complexes to aromatic heterocycles, partly in order to examine the changes in structure and properties that occur upon replacement of arene ligands with heterocycles. Moreover, the proposed carborane–metal–heterocycle systems were of interest for two additional reasons. First, most known transition-metal complexes of nitrogen-containing rings such as pyrrole and pyrrolyl involve σ-bonded rather than π (sandwich) M–N

interactions, owing to the dominant electron-donor base character of the ring nitrogen atom;[8] consequently, metal–pyrrole and –pyrrolyl sandwich species are relatively rare.[9] Hence, the prospect that carborane ligands might promote metal–heterocycle π-interaction was intriguing. Further, we considered that the ring heteroatom(s) in carborane-stabilized complexes could serve as sites for attaching reactive functional groups and for linking monomeric units together in chains. In this paper we describe the rational synthesis, structural characterization, chemistry, and electrochemical behavior of a family of pyrrolyl- and phospholyl-containing sandwich compounds, including the first known examples of triple-decker complexes incorporating these ligands.[10]

(8) Pannell, K. H.; Kalsotra, B. L.; Parkanyi, C. *J. Heterocycl. Chem.* **1978**, *15*, 1057.

(9) See, for example: (a) Öfele, K.; Dotzauer, E. *J. Organomet. Chem.* **1971**, *30*, 211 [(η^5-pyrrole)Cr(CO)$_3$]. (b) Kuhn, N.; Horn, E.,; Boese, R.; Augart, N. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 1368 (octa-*C*-methyl–diazaferrocene adduct).

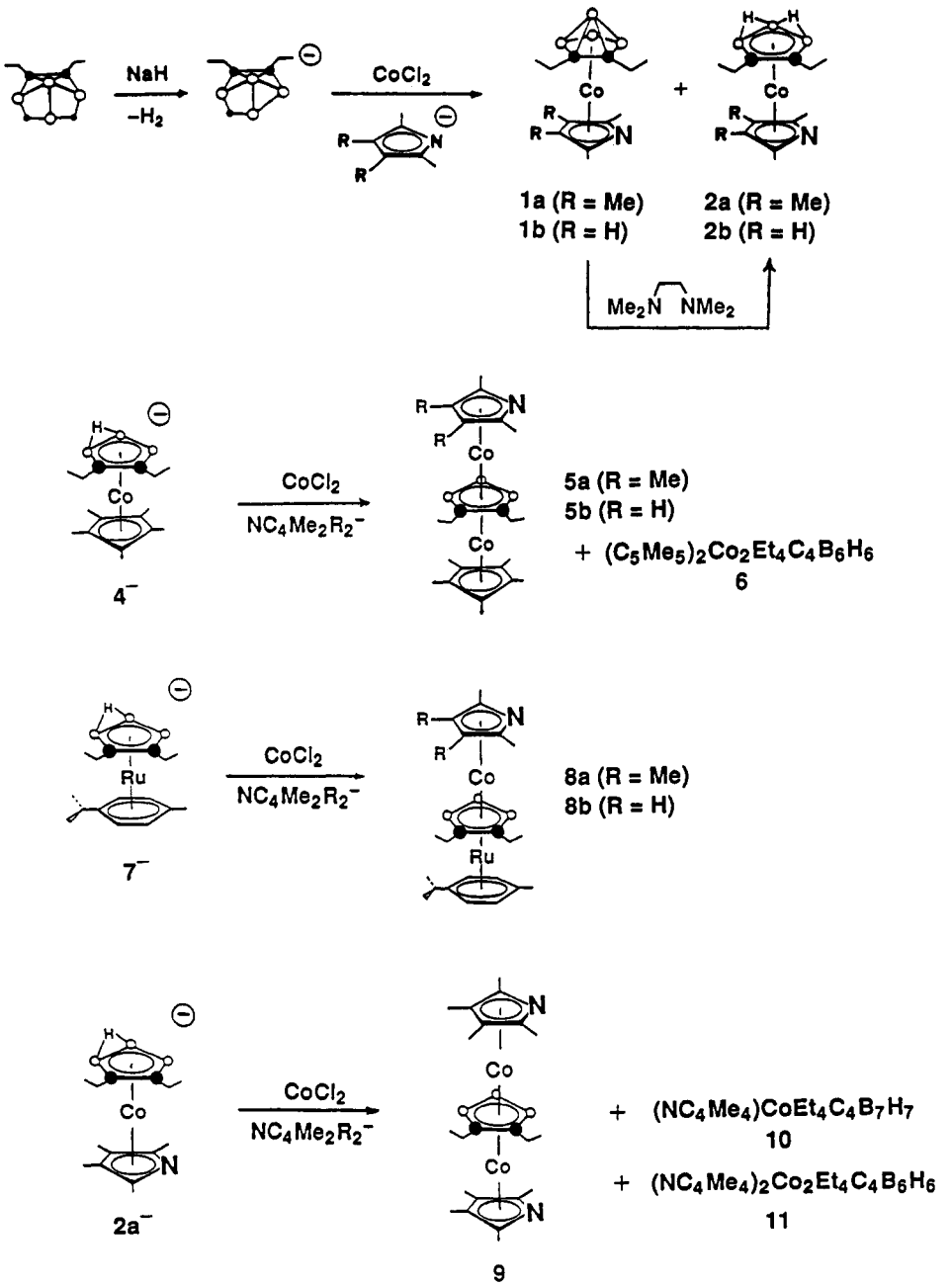
(10) (a) A preliminary report on a portion of this work has appeared: Chase, K. J.; Grimes, R. N. *Organometallics* **1989**, *8*, 2492. See also: (b) Bryan, R. F.; Grimes, R. N.; Chase, K. J.; Fessenbecker, A.; Woode, M. K. *Abstracts of Papers*; National Meeting of the American Crystallographic Association, New Orleans, LA, April 1990; Abstract PL-11. (c) Bryan, R. F.; Grimes, R. N.; Chase, K. J.; Fessenbecker, A. *Abstracts of Papers*; 15th International Union of Crystallography Congress, Bordeaux, France, July 1990; Abstract PS-06.03.24.

Results and Discussion

Pyrrolyl Double-Decker Complexes. Reactions of the sodium salt of *nido*-$Et_2C_2B_4H_5^-$ with $CoCl_2$ and the 4,5-dimethyl- or 2,3,4,5-tetramethylpyrrolide anion in THF generated mixtures of the anticipated complexes $(NC_4Me_2R_2)Co(Et_2C_2B_4H_4)$ (**1a**, R = Me; **1b**, R = H) and the corresponding "decapitated" species $(NC_4Me_2R_2)Co(Et_2C_2B_3H_5)$ (**2a**, R = Me; **2b**, R = H) (Scheme I). The **1a**:**1b** and **2a**:**2b** ratios were approximately 3:1, as measured by proton NMR spectroscopy. Attempts to separate these mixtures by thin-layer chromatography on silica or via high-performance liquid chromatography (HPLC) yielded, in each case, two well-separated yellow bands, of which one was pure **2a** (or **2b**) while the other was a **1a**/**1b** (**2a**/**2b**) mixture, again in a 3:1 ratio. These findings indicated that the capped complexes **1a** and **1b** are susceptible to decapitation (loss of the apex BH and replacement by two B–H–B bridging hydrogens) to form **2a** and **2b**, a process which is well-known to occur in $LM(R_2C_2B_4H_4)$ complexes via attack by Lewis bases.[3] In this case it appeared that the decapitation was occurring via intermolecular reaction of the pyrrolyl nitrogens on **1a** or **1b** at the apex boron atoms on neighboring molecules, but this hypothesis was not pursued and the species **1a**/**1b** were not further characterized. Since in any event the nido complexes **2a** and **2b** were the desired species for our purposes (vide infra), each mixture was treated with wet tetramethylethylenediamine (TMEDA)[3a] to afford pure **2a** or **2b** (Scheme I). Improved yields of these complexes (ca. 35–45%) were obtained by a modified procedure in which $CoCl_2$ and the pyrrolide anion were first combined to generate in situ a species presumed to be $[(NC_4Me_2R_2)CoCl_2]_2$ (**3**), which was subsequently reacted with the $Et_2C_2B_4H_5^-$ ion followed by addition of TMEDA to generate **2a** or **2b**.

Complexes **2a** and **2b** are air-stable yellow oils that were characterized from their ^{1}H and ^{11}B NMR, IR, UV–visible, and mass spectra (Tables I–III and Experimental Section). In general, these compounds spectroscopically resemble those of the analogous and readily accessible[4a] species $Cp^*Co(Et_2C_2B_3H_5)$ (Cp^* = C_5Me_5) and, like the latter compounds, are readily soluble in moderately polar as well as nonpolar solvents. However, an unusual characteristic of **2a** and **2b**, and indeed of all the pyrrolyl complexes

Scheme I[a]



[a] Key: (○) BH; (●) C.

reported herein, is their low mobility on silica gel in polar solvents, relative to the analogous Cp* complexes.

Pyrrolyl Triple-Decker Complexes. An approach similar to that employed previously in the synthesis of $CpCo(R_2C_2B_3H_3)CoCp$ sandwiches[11] (and their Cp* counterparts[12]) was used to prepare the pyrrolyl-containing species. Reaction of the $Cp^*Co(Et_2C_2B_3H_4)^-$ anion[4a] (4^-) with $CoCl_2$ and $NC_4Me_2R_2^-$ in THF produced the compounds $(NC_4Me_2R_2)Co(Et_2C_2B_3H_3)CoCp^*$ (**5a**, R = Me; **5b**, R = H), which were isolated as red-brown air-stable crystalline solids in 18–25% yield (Scheme I). Also obtained in both reactions was a minor product, $Cp^*_2Co_2Et_4C_4B_6H_6$ (**6**),[13] which evidently forms via metal-promoted oxidative fusion[14] of 4^-. Similar reactions of the cymene–ruthenacarborane anion[4a] 7^- with $CoCl_2$ and the di- or tetramethylpyrrolide ion gave the mixed-metal triple-decker complexes $(NC_4Me_2R_2)Co(Et_2C_2B_3H_3)Ru(1,4\text{-}MeC_6H_4CHMe_2)$ (**8a**, **8b**) as Kelly green solids. Treatment of the $2a^-$ ion (obtained by bridge-deprotonation of **2a**) with $CoCl_2$ and tetramethylpyrrolide ion gave a bis(pyrrolyl) sandwich (**9**), a red-brown solid, accompanied by minor amounts of the fusion products $(NC_4Me_4)CoEt_4C_4B_7H_7$ (**10**) and $(NC_4Me_4)_2Co_2Et_4C_4B_6H_6$ (**11**).

The diamagnetic 30-electron triple-decker complexes **5a,b**, **8a,b**, and **9** were characterized spectroscopically

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(12) Finster, D. C.; Sinn, E.; Grimes, R. N. *J. Am. Chem. Soc.* **1981**, *103*, 1399.

(13) The $(\eta^5\text{-}C_5H_5)_2Co_2$ analogue of **6** has been reported: (a) Wong, K.-S.; Bowser, J. R.; Pipal, J. R.; Grimes, R. N. *J. Am. Chem. Soc.* **1978**, *100*, 5045. (b) Pipal, J. R.; Grimes, R. N. *Inorg. Chem.* **1979**, *18*, 1936.

(14) Grimes, R. N. *Adv. Inorg. Chem. Radiochem.* **1983**, *26*, 55 and references therein.

Table II. 300-MHz ^{1}H FT NMR Data

compd	$\delta^{a,b,c}$
2a	2.18 (m, CH_2), 2.07 (m, CH_2), 2.02 (s, 3,4-CH_3), 1.88 (s, 2,5-CH_3), 1.13 (t, ethyl CH_3), −5.95 (s, B–H–B)
2b	5.03 (s, 3,4-H), 2.09 (m, CH_2), 2.04 (s, 2,5-CH_3), 1.09 (t, ethyl CH_3), −6.00 (s, B–H–B)
5a	2.74 (m, CH_2), 2.55 (m, CH_2), 1.81 (s, 2,5-CH_3), 1.80 (s, 3,4-CH_3), 1.59 (t, ethyl CH_3), 1.55 (s, Cp*)
5b	4.89 (s, 3,4-H), 2.75 (m, CH_2), 2.59 (m, CH_2), 1.91 (s, 2,5-CH_3), 1.62 (t, ethyl CH_3), 1.56 (s, Cp*)
6	2.06 (m, CH_2), 1.59 (s, Cp*), 0.98 (t, ethyl CH_3)
8a	4.92 (d, C_6H_4), 4.81 (d, C_6H_4), 2.88 (m, CH_2), 2.46 (m, cymene CH_2 and $CHMe_2$), 1.97 (s, cymene CH_3), 1.87 (s, 2,5-CH_3), 1.83 (s, 3,4-CH_3), 1.48 (t, ethyl CH_3), 1.18 (d, $(CH_3)_2CH$)
8b	4.98 (s, 3,4-H), 4.96 (d, C_6H_4), 4.84 (d, C_6H_4), 2.89 (m, CH_2), 2.50 (m, cymene CH_2 and $CHMe_2$), 1.97 (s, 2,5-CH_3), 1.50 (t, ethyl CH_3), 1.18 (d, $(CH_3)_2CH$)
9	2.77 (q, CH_2), 1.80 (s, 2,5-CH_3), 1.77 (s, 3,4-CH_3), 1.65 (t, ethyl CH_3)
10	3.12 (m, CH_2), 2.89 (m, CH_2), 2.30 (m, CH_2), 2.11 (s, CH_3), 1.95 (s, CH_3), 1.90 (s, CH_3), 1.74 (s, CH_3), 1.24 (t, ethyl CH_3), 0.79 (t, ethyl CH_3)
11	3.09 (m, CH_2), 2.70 (m, CH_2), 2.40 (m, CH_2), 2.21 (m, CH_3), 2.08 (s, CH_3), 1.91 (s, CH_3), 1.67 (s, CH_3), 1.58 (s, CH_3), 1.39 (t, ethyl CH_3), 1.25 (t, ethyl CH_3)
12	2.82 (s, N–CH_3), 2.55 (q, CH_2), 1.93 (s, 2,5-CH_3), 1.88 (s, 3,4-CH_3), 1.50 (t, s,[d] Cp*, ethyl CH_3)
13	2.82 (m, CH_2), 2.66 (m, CH_2), 1.85 (s, 2,5-CH_3), 1.72 (s, 3,4-CH_3), 1.67 (t, ethyl CH_3), 1.54 (s, Cp*)
17	2.77 (m, CH_2), 2.60 (m, CH_2), 1.85 (s, 2,5-CH_3), 1.77 (s, 3,4-CH_3), 1.64 (t, ethyl CH_3), 1.57 (s, Cp*)
19	2.79 (m, CH_2), 2.62 (m, CH_2), 1.85 (s, 2,5-CH_3), 1.76 (s, 3,4-CH_3), 1.65 (t, ethyl CH_3), 1.56 (s, Cp*)
20	4.86 (s, 3,4-H), 2.77 (m, CH_2), 2.64 (m, CH_2), 1.93 (s, 2,5-CH_3), 1.66 (t, ethyl CH_3), 1.54 (s, Cp*)
21	2.86 (q, CH_2), 1.84 (s, 2,5-CH_3), 1.74 (t, ethyl CH_3), 1.54 (s, 3,4-CH_3)
22	2.95 (m, CH_2), 2.39 (m, CH_2), 1.95 (s, 2,5-CH_3), 1.91 (s, 3,4-CH_3), 1.57 (t, ethyl CH_3), 1.54 (s, Cp*)
23	2.83 (q, CH_2), 1.98 (s, 2,5-CH_3), 1.86 (s, 3,4-CH_3), 1.63 (t, ethyl CH_3)
25	2.55 (m, CH_2), 2.36 (m, CH_2), 1.98 (s, 3,4-CH_3), 1.72 (d, 2,5-CH_3), 1.23 (t, ethyl CH_3)
26	2.08 (m, CH_2), 1.95 (s, 3,4-CH_3), 1.91 (m, CH_2), 1.67 (d, 2,5-CH_3), 1.12 (t, ethyl CH_3), −5.76 (s, B–H–B)
27	2.50 (m, CH_2), 1.57 (s,[d] 2,5-CH_3, Cp*, 3,4-CH_3), 1.51 (t, ethyl CH_3)
28	4.95 (d, C_6H_4), 4.83 (d, C_6H_4), 2.74 (m, CH_2), 2.50 (m, ethyl CH_2 and $CHMe_2$), 1.98 (s, cymene CH_3), 1.82 (s, 3,4-CH_3), 1.62 (d, 2,5-CH_3), 1.44 (t, ethyl CH_3), 1.19 (d, $(CH_3)_2CH$)
29	2.63 (q, CH_2), 1.77 (s, 3,4-CH_3), 1.57 (t, ethyl CH_3), 1.56 (d, 2,5-CH_3)
30	2.78 (m, CH_2), 2.58 (m, CH_2), 1.81 (s, CH_3),[e] 1.72 (s, CH_3),[e] 1.60 (t, ethyl CH_3), 1.54 (d, 2,5-CH_3 on PC_4Me_4)

[a] $CDCl_3$ solution. [b] Shifts relative to $(CH_3)_4Si$. Integrated peak areas in all cases are consistent with the assignments given. Legend: m = multiplet, s = singlet, d = doublet, t = triplet, q = quartet. [c] B–$H_{terminal}$ resonances are broad quartets and mostly obscured by other signals. [d] Overlapping signals. [e] 2,3,4,5-Methyls on pyrrolyl group and/or 3,4-methyls on phospholyl group.

(Tables I–III and Experimental) with further support from X-ray crystallographic data[15] on **9**, which established the triple-decker geometry. Their proposed structures, depicted with arbitrary ring orientations in Scheme I, follow from their ^{1}H and ^{11}B NMR spectra, which are similar to those of other triple-decker complexes bridged by formal $R_2C_2B_3H_3^{4-}$ ligands.[4a,b,11a,c] In particular, the low-field area-1 resonance (δ 44–60 ppm) in the ^{11}B spectrum of each compound is characteristic of C_2B_3 rings sandwiched between two metals. The effects of replacing a Cp* ligand with a pyrrolyl group are, in general, small and consist of slight downfield shifts in the boron-11 signals and in the ethyl resonances in the proton spectra, as seen by comparing the data for **5a,b**, **8a,b**, and **9** with those of triple-deckers characterized earlier.[4a,11a,c] In the UV–visible spectra of these complexes, some metal d–d transitions are observed but the most prominent feature in most cases is a metal-to-ligand charge-transfer peak.

The crystallographically determined[15] geometry of **9** is fully consistent with the spectroscopic data and closely resembles those of other structurally characterized C_2B_3-bridged triple-decker complexes.[4a,b,11a,b] The pyrrolyl ligands are planar and nearly parallel with the central ring, with dihedral angles of 0.9 and 2.6°, respectively. The solid-state rotational conformation of the pyrrolyl rings places the nitrogens close to the C_2B_3 carbon atoms, an arrangement that reduces steric interaction between the *C*-ethyl groups and the *B*-methyl substituents on the pyrrolyls. In solution, the NMR data indicate time-averaged mirror symmetry for **9** and the other triple-decker species, implying relatively unrestricted rotation of the outer rings.

Compound **9** and its phospholyl–pyrrolyl counterpart **30**, described below, are thus far the only structurally characterized examples of pyrrolyl-containing triple-decker species. Two examples of double-decker cobalt–pyrrolyl sandwiches have been reported,[16] but no crystallographic data are available. Moreover, of the few metal–(η^5-pyrrolyl) sandwiches on which X-ray structure determinations have been carried out,[17–20] all but one of these, $[(3,4\text{-}NC_4Me_2H_2)Mn(CO)_3]$[19] have σ-coordinated substituents on the ring nitrogen. Consequently, only indirect comparison is possible between **9** and earlier structures. Those closest to **9** are a bis(tetramethylpyrrole)diazaferrocene adduct $[(NC_4Me_4)_2Fe{\cdot}2(HNC_4Me_4)]$, in which the "extra" pyrrole molecules are linked to the complex via N–hydrogen bonds,[9b,20] and the dimethylpyrrolyl manganese species mentioned above. In the latter complex,[19] the Mn–N distance of 2.11 (1) Å is comparable to the Co–N bonds in **9**, whose lengths are 2.07 (2) Å; the corresponding Fe–N distance in the diazaferrocene adduct[9b,20] is 2.015 Å. In contrast to the structure of $(3,4\text{-}NC_4Me_2H_2)Mn(CO)_3$ in which the Mn–N bonds are slightly (ca. 0.04 Å) shorter than the average Mn–C length,[19] no such pattern of ring slippage is discernible in the structure of **9**, where the average Co–C distance is 2.05 (2) Å, not significantly shorter than the Co–N values of 2.07 (2) Å.

Reactions of Pyrrolyl Sandwich Complexes. The chemistry of the new triple-decker compounds **5a**, **5b**, and

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Table III. Infrared Absorptions (Neat Films on KBr Plates)[a,b]

compd	absorption, cm^{-1}
2a	2962 (s), 2918 (s), 2862 (s), 2525 (s), 2360 (w), 2329 (w), 1862 (m), 1725 (w), 1612 (m), 1547 (m), 1450 (s), 1374 (s), 1330 (m), 1275 (m), 1110 (m), 1022 (m), 921 (m)
2b	2964 (s), 2929 (s), 2870 (m), 2540 (s), 1872 (m), 1631 (w), 1559 (m), 1457 (s), 1374 (m), 1340 (w), 1303 (w), 1290 (w), 1261 (m), 1126 (w), 1094 (w), 1038 (m), 1024 (m), 949 (m), 929 (m), 909 (w), 837 (w), 782 (m), 739 (w), 699 (w)
5a	2960 (s), 2906 (s), 2870 (s), 2488 (s), 1819 (s), 1728 (m), 1469 (s), 1446 (s), 1376 (s), 1316 (m), 1285 (m), 1026 (s), 906 (w)
5b	2962 (s), 2926 (s), 2855 (m), 2485 (s), 1732 (w), 1452 (s), 1377 (s), 1338 (m), 1260 (s), 813 (s)
6	2958 (m), 2925 (m), 2856 (m), 2468 (m), 2418 (m), 2400 (m), 1732 (w), 1430 (w), 1261 (m), 1093 (s), 1066 (s), 1026 (s), 901 (w), 799 (m), 731 (m), 699 (m)
8a	2960 (s), 2925 (s), 2870 (s), 2474 (s), 1732 (w), 1465 (s), 1447 (s), 1379 (s), 1276 (m), 1032 (m), 823 (s)
8b	2960 9s), 2926 (s), 2869 (s), 2483 (s), 1728 (w), 1449 (s), 1374 (s), 1338 (m), 1261 (m), 1034 (m), 949 (w), 818 (s)
9	2962 (s), 2925 (s), 2871 (s), 2854 (m), 2507 (s), 1468 (m), 1446 (m), 1434 (m), 1376 (s), 1334 (m), 1285 (m), 1032 (m), 962 (w), 904 (w), 815 (s)
10	2926 (s), 2854 (m), 2554 (m), 2525 (m), 1712 (w), 1463 (m), 1378 (m), 1289 (w), 1121 (w), 1102 (s), 931 (w)
12	2965 (s), 2917 (s), 2860 (s), 2496 (s), 1523 (w), 1450 (s), 1381 (m), 1338 (m), 1266 (m), 1027 (s), 815 (s), 733 (m)
13	2960 (s), 2970 (s), 1874 (s), 2851 (s), 2488 (s), 1734 (w), 1700 (w), 1685 (w), 1653 (w), 1559 (w), 1476 (m), 1473 (m), 1469 (m), 1465 (m), 1457 (m), 1451 (m), 1448 (m), 1437 (m), 1430 (m), 1420 (w), 1378 (s), 1363 (m), 1261 (m), 1126 (m), 1094 (m), 1074 (m), 1025 (s), 921 (m), 821 (m), 798 (s), 698 (w)
17	2915 (s), 2874 (s), 2854 (s), 2485 (s), 1734 (w), 1700 (w), 1696 (w), 1685 (w), 1653 (w), 1636 (w), 1576 (w), 1559 (w), 1539 (w), 1507 (w), 1476 (w), 1473 (w), 1465 (w), 1457 (m), 1452 (w), 1448 (m), 1442 (m), 1440 (w), 1437 (m), 1430 (w), 1420 (w), 1378 (s), 1363 (w), 1026 (s), 957 (m), 843 (w), 799 (s)
19	2960 (s), 2920 (s), 2679 (s), 2872 (s), 2854 (s), 2487 (s), 1734 (m), 1718 (w), 1700 (m), 1696 (w), 1685 (m), 1675 (w), 1653 (s), 1646 (w), 1636 (w), 1617 (w), 1576 (w), 1559 (m), 1542 (w), 1539 (m), 1521 (w), 1507 (m), 1496 (w), 1476 (w), 1473 (s), 1468 (w), 1465 (m), 1462 (w), 1457 (s), 1452 (s), 1448 (m), 1440 (m), 1437 (s), 1430 (m), 1424 (w), 1419 (m), 1395 (w), 1378 (m), 1363 (m), 1336 (m), 1026 (s), 936 (m), 797 (s)
20	2961 (s), 2921 (s), 2872 (s), 2850 (s), 2498 (s), 2486 (s), 1734 (w), 1717 (w), 1700 (m), 1696 (w), 1685 (w), 1653 (m), 1559 (w), 1539 (w), 1507 (w), 1476 (w), 1473 (m), 1465 (m), 1457 (s), 1448 (m), 1437 (m), 1430 (w), 1419 (w), 1377 (m), 1023 (m), 921 (m), 801 (s)
21	2957 (s), 2924 (s), 2669 (s), 2854 (s), 2500 (m), 1700 (m), 1696 (m), 1685 (m), 1675 (w), 1669 (w), 1653 (m), 1646 (w), 1636 (w), 1617 (w), 1576 (w), 1559 (m), 1554 (w), 1542 (w), 1539 (w), 1472 (m), 1465 (m), 1462 (m), 1457 (s), 1453 (m), 1448 (m), 1442 (m), 1440 (m), 1437 (m), 1425 (w), 1419 (m), 1405 (w), 1399 (w), 1394 (w), 1378 (m), 1364 (w), 1345 (w), 1336 (w), 1287 (w), 1119 (w), 1103 (w), 1100 (w), 1077 (w), 1029 (w), 799 (m)
22	2958 (s), 2924 (s), 2854 (s), 2495 (m), 2387 (m), 2368 (m), 2363 (m), 2356 (m), 2353 (m), 2348 (m), 2338 (m), 2326 (m), 2266 (m), 1497 (w), 1456 (m), 1457 (m), 1379 (m), 1342 (w), 1320 (w), 1262 (w), 1177 (w), 1154 (m), 1094 (m), 1074 (m), 1027 (m), 816 (m)
23	2964 (s), 2926 (s), 2892 (s), 2852 (m), 2504 (s), 2397 (s), 2348 (m), 2338 (m), 2328 (m), 2301 (m), 2268 (m), 1653 (w), 1457 (w), 1437 (w), 1430 (w), 1420 (w), 1384 (s), 1369 (m), 1316 (w), 1155 (s), 1025 (m), 814 (s)
25	2963 (s), 2925 (s), 2871 (s), 2855 (s), 2545 (s), 2539 (s), 1457 (m), 1451 (m), 1449 (m), 1377 (m), 1124 (w), 1115 (w), 1098 (w), 1063 (w), 1021 (w), 871 (w)
26	2962 (s), 2926 (s), 2869 (s), 2537 (s), 1869 (m), 1628 (w), 1559 (s), 1449 (s), 1404 (w), 1376 (s), 1368 (m), 1307 (w), 1123 (w), 1113 (w), 1095 (w), 1074 (w), 1065 (w), 1046 (m), 1022 (m), 981 (w), 929 (m), 908 (w), 785 (m), 748 (w)
27	2954 (s), 2922 (s), 2853 (s), 2462 (m), 1456 (m), 1376 (m), 1261 (w), 1158 (w), 1098 (w), 1093 (w), 1024 (w), 1023 (m), 821 (m)
28	2960 (s), 2925 (s), 2869 (s), 2477 (s), 1476 (m), 1447 (s), 1420 (m), 1411 (m), 1375 (s), 1321 (m), 1297 (w), 1276 (w), 1262 (w), 1235 (w), 1198 (w), 1172 (m), 1151 (m), 1139 (m), 1110 (m), 1085 (m), 1053 (m), 1022 (s), 957 (w), 926 (w), 916 (w), 906 (w), 889 (w), 824 (s), 802 (m)
29	2953 (s), 2924 (s), 2854 (s), 2491 (m), 1456 (m), 1377 (m), 1316 (w), 1259 (w), 1252 (w), 1245 (w), 1235 (w), 1170 (w), 1166 (w), 1157 (w), 1151 (w), 1121 (w), 1095 (w), 1074 (w), 1071 (w), 1021 (m), 821 (m)
30	2962 (s), 2925 (s), 2870 (s), 2855 (s), 2506 (s), 2487 (s), 1734 (m), 1730 (m), 1464 (m), 1457 (m), 1447 (m), 1437 (m), 1431 m), 1375 (s), 1361 (m), 1332 (w), 1319 (w), 1285 (m), 1264 (w), 1239 (w), 1118 (w), 1094 (w), 1092 (w), 1074 (w), 1024 (m), 816 (s)

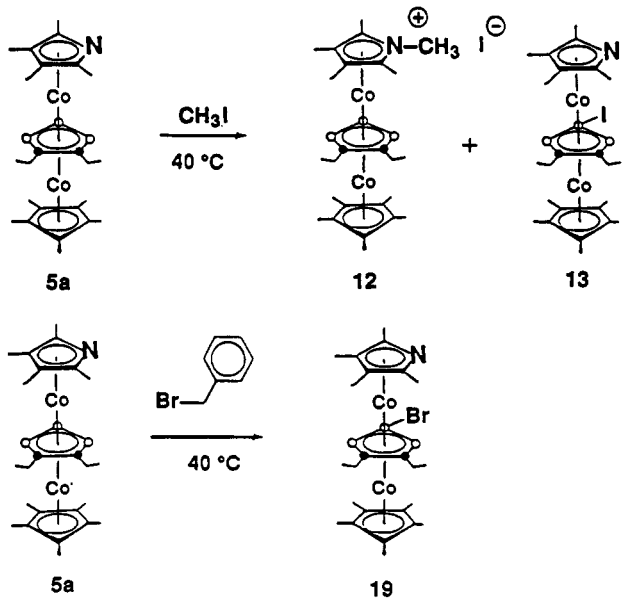
[a] Microcrystalline films obtained by evaporation of solutions. [b] Legend: vs = very strong, s = strong, m = medium, w = weak, sh = shoulder, br = broad.

9 was investigated selectively, with attention directed primarily to the presumed electron-donor properties of the pyrrolyl nitrogen atoms. Accordingly, these species were treated with a variety of electrophiles, some of which produced the anticipated base adducts while others gave quite unexpected results. The reaction of **5a** with excess iodomethane gave an apparent, partially characterized *N*-methyl cation salt $[(MeNC_4Me_4)Co(Et_2C_2B_3H_3)CoCp^*]^+I^-$ (**12**), an air-stable red-brown solid, in 71% yield, accompanied by a small amount of a B-iodinated product, $(NC_4Me_4)Co(Et_2C_2B_3H_2I)CoCp^*$ (**13**), as shown in Scheme II. Complex **12** is insoluble in hexane but dissolves in polar organic solvents such as CH_2Cl_2. Its ^1H and ^{11}B NMR spectra are clearly consistent with the proposed structure, as are the IR and UV–visible spectra. In **13**, the iodide substituent is located at B(5), the middle boron atom, as shown by the singlet B(5) resonance in the undecoupled ^{11}B spectrum.

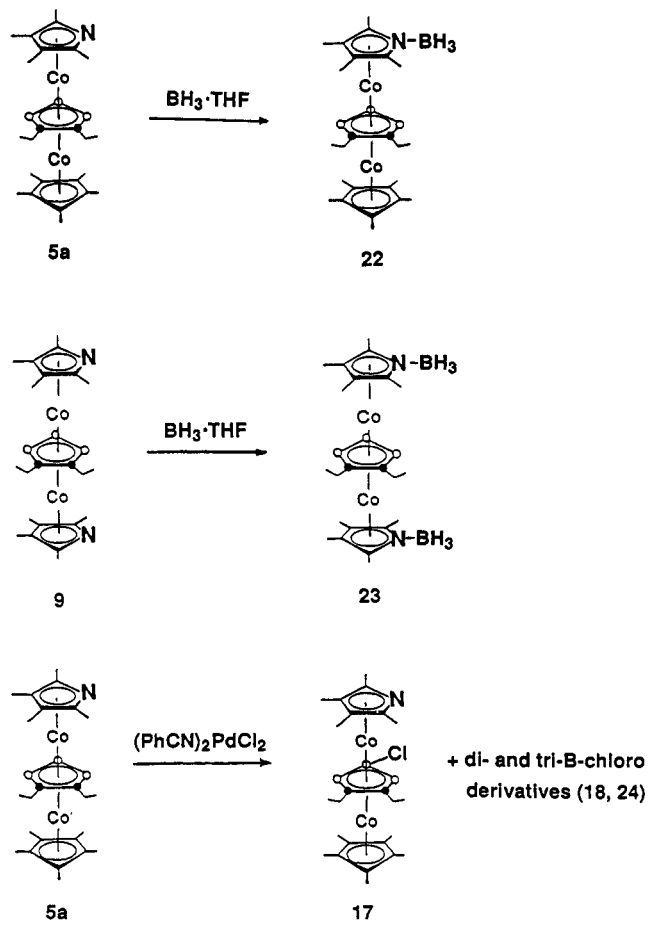
The reaction generating **12** did not prove to be general. Thus, when **5a** was treated with 1,3-diiodopropane at 40 °C in an attempt to form an *N,N'*-trimethylene-linked bis(triple-decker) cation $(CH_2)_3[NC_4Me_4)Co(Et_2C_2B_3H_3)CoCp^*]_2^{2+}$ (**14**), only the *B*-iodo species **13** was obtained. An effort was made to prepare the xylyl-substituted species $(CH_2C_6H_5CH_2)[N(C_4Me_4)Co(Et_2C_2B_3H_3)CoCp^*]_2Br_2$ (**15**) and/or $[(BrCH_2C_6H_5CH_2)(NC_4Me_4)Co(Et_2C_2B_3H_3)CoCp^*]Br$ (**16**) via reactions of α,α'-dibromo-*p*-xylene with **5a**. However, neither of these target compounds was produced, the only identifiable products after workup in dichloromethane being the B-chlorinated derivatives $(NC_4Me_4)Co(Et_2C_2B_3H_2Cl)CoCp^*$ (**17**) and $(NC_4Me_4)Co(Et_2C_2B_3HCl_2)CoCp^*$ (**18**). Similarly, the treatment of **5a** with benzyl bromide and workup in diethyl ether instead of CH_2Cl_2 gave the B-brominated product $(NC_4Me_4)Co(Et_2C_2B_3H_2Br)CoCp^*$ (**19**) (Scheme II). As in the case of **13**, ^{11}B NMR spectroscopy on **17** and **19** demonstrated that the halogen is located on B(5) in each case. The reactivity of B(5)–H toward halogenation by alkyl halides at moderately elevated temperatures suggested attack by free radicals, which are generated by homolytic cleavage of the R–X bond. As a test of this postulate, **5a** was reacted with excess I_2 at 25 °C, which as expected yielded **13** exclusively.

Replacement of **5a** by **5b** or **9** in reactions with alkyl halides did not result in alkyl substitution at nitrogen.

Scheme II



Scheme III



Even the treatment of these complexes with excess iodomethane at 40 °C afforded only the *B*-iodo derivatives $(NC_4Me_2H_2)Co(Et_2C_2B_3H_2I)CoCp^*$ (**20**) and $(NC_4Me_4)_2Co_2(Et_2C_2B_3H_2I)$ (**21**), respectively.

These seemingly incongruous findings can be rationalized in terms of the electronic properties of the pyrrolyl ligands relative to cyclopentadienyl. It is known that pyrrolyl groups are poorer σ-donors and better π-acceptors than C_5R_5, suggesting that replacement of one or both Cp groups in $CpCo(R_2C_2B_3H_3)CoCp$ with pyrrolyl rings should decrease the electron density in the C_2B_3 ring and thereby increase its susceptibility to attack by $X^\bullet$ or X_2. The fact that **5a**, but not **5b**, undergoes methylation on treatment with MeI may be a consequence of electron donation by the additional pyrrolyl methyl groups in **5a**, which would render that species more basic than the dimethylpyrrolyl complex **5b**. The observation that alkyl halides other than MeI do not alkylate the pyrrolyl rings can be explained in terms of the higher stability of other alkyl radicals relative to $^\bullet CH_3$; this would tend to favor a radical mechanism for the interaction of most alkyl halides with the substrates, leading to halogenation rather than alkyl substitution at nitrogen.

The mono- and bis(pyrrolyl) complexes **5a** and **9** reacted readily with BH_3·THF to give the respective *N*-BH_3 and *N,N'*-$(BH_3)_2$ complexes **22** and **23** in high yield (Scheme III). Analogous borane adducts have been produced via treatment of pyrrolyl–iron complexes with BH_3·SMe_2.[20b] Both compounds are slightly air-sensitive and poorly soluble in hexane but very soluble in diethyl ether and dichloromethane; in the electron-impact mass spectra, the dominant feature is facile loss of BH_3, giving weak (ca. 10% of base) parent peaks. An attempt to link two **5a** units via a geminal diborylpentyl unit was made via the reaction of **5a** with 1,1'-diborapentane prepared in situ, but only starting material was recovered. In an effort to effect linkage via metalation, **5a** was treated with 0.5 mol equiv of $PdCl_2(PhCN)_2$ in the expectation of preparing Pd-$[(NC_4Me_4)Co(Et_2C_2B_3H_3)CoCp^*]_2$, which would be analogous to known[21] Pd- and Pt-linked bis(pyrrolyl) complexes. No such compound was obtained; instead, the isolated products were the mono- and di-*B*-chloro derivatives **17** and **18** and a small amount of the tri-*B*-chloro species $(NC_4Me_4)Co(Et_2C_2B_3Cl_3)CoCp^*$ (**24**), identified by mass spectroscopy only. The propensity of these pyrrolyl triple-deckers to undergo halogenation at boron could no doubt be curtailed by employing *B*-alkyl derivatives of species such as **5a** and **9**, but this idea was not pursued in the current study.

Phospholyl Double- and Triple-Decker Complexes. Extension of this investigation to sandwich complexes containing phosphorus heterocycles was undertaken in order to compare the structures and properties of phospholyl–metal–carborane complexes with their pyrrolyl analogues. Of particular interest to us was the opportunity to probe well-known differences between the two ligand types, e.g., the greater π-complexing ability of phospholyl rings[22] and the electrophilicity of phospholyl–metal sandwiches,[23] which contrasts with the nucleophilic character of the nitrogen atom in azametallocenes.[18] In order to prepare phospholyl species directly analogous to the pyrrolyl compounds **5a** and **9**, we employed the recently reported reagent[24] (2,3,4,5-tetramethylphospholyl)lithium, prepared in situ from the 1-phenylphosphole. Reaction of this reagent with $CoCl_2$ and $Et_2C_2B_4H_5^-$ generated the desired complex $(PC_4Me_4)Co(Et_2C_2B_4H_4)$ (**25**), an air-stable yellow solid, in 23% isolated yield (Scheme IV). In sharp contrast to the preparation

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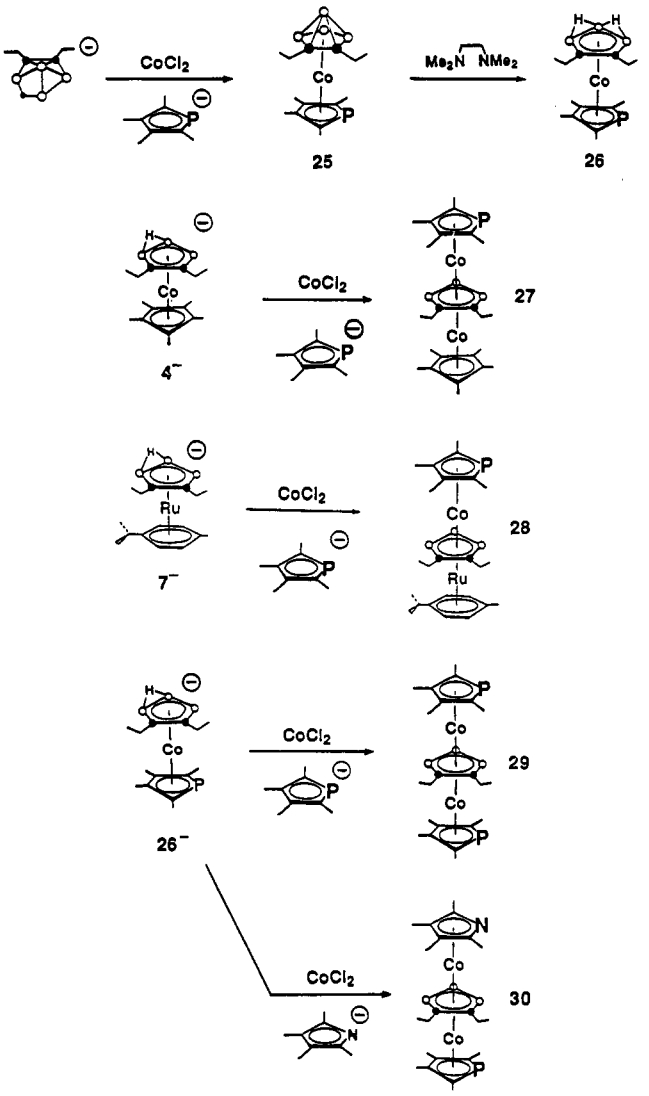
Scheme IV



of the pyrrolyl–cobaltacarborane complexes **1a** and **1b**, which was accompanied by extensive decapitation to give **2a** and **2b** as described above, no such degradation was observed here; undoubtedly, the difference is due to the inability of the much less nucleophilic phosphorus atom (compared to the pyrrolyl nitrogen) to attack the apex BH group. However, the decapitated species $(PC_4Me_4)Co(Et_2C_2B_3H_5)$ (**26**), an air-stable yellow oil, was readily obtained via treatment of **25** with wet TMEDA.

Several phospholyl-containing triple-decker complexes were synthesized via straightforward application of the approaches used to prepare pyrrolyl and other triple-decker compounds. As shown in Scheme IV, the (tetramethylphospholyl)lithium reagent reacted with $CoCl_2$ and the cobaltacarborane or ruthenacarborane anion 4^- and 7^- to form the respective 30-electron complexes $(PC_4Me_4)Co(Et_2C_2B_3H_3)CoCp^*$ (**27**) and $(PC_4Me_4)Co(Et_2C_2B_3H_3)Ru(MeC_6H_4CHMe_2)$ (**28**) in low to moderate yields. A similar reaction employing the phospholylcobaltacarborane anion 26^- gave the bis(phospholyl) sandwich $(PC_4Me_4)_2Co_2(Et_2C_2B_3H_3)$ (**29**). As in the case of the corresponding pyrrolyl and cyclopentadienyl[4a] triple-deckers, the CoCo species **27** and **29** are red-brown while the CoRu compound **28** is green. Unlike the earlier complexes, however, the phospholyl compounds are not air-stable (they do survive short periods of exposure); this can be attributed to the oxidation of phosphorus leading to decomposition. A mixed phospholyl–pyrrolyl complex (the first example of this genre), $(PC_4Me_4)Co(Et_2C_2B_3H_3)Co(NC_4Me_4)$ (**30**), was prepared via treatment of 26^- with $CoCl_2$ and the tetramethylpyrrolide anion (Scheme IV).

Table IV. Experimental X-ray Diffraction Parameters and Crystal Data for 30

M_r	496.8	D(calcd), g cm^{-3}	1.364
space group	$P\bar{1}$	$2\theta_{max}$, deg	50.1
a, Å	9.017 (5)	no. of reflns collcd	4270
b, Å	9.966 (7)	no. of reflns obsd	3390
c, Å	15.115 (9)	R	0.069
α, deg	109.95 (5)	R_w	0.068
β, deg	93.97 (4)	F(000)	520
γ, deg	71.55 (5)	Z	2
V, Å^3	1210	S	1.33
μ, mm^{-1} (Mo Kα)	1.44		

Table V. Positional Parameters Defining the Crystal Structure of 30 with Equivalent Isotropic Displacement Parameters[a] and Associaited Esd's[b]

atom	x/a	y/b	z/c	B_{eq}, Å^2
Co(1)	0.23746 (15)	0.12726 (14)	0.30865 (9)	2.2
Co(7)	0.15666 (14)	0.29420 (14)	0.15960 (8)	2.0
P	0.1585 (4)	0.1252 (4)	0.4507 (2)	4.6
C(11)	0.1839 (12)	−0.0329 (12)	0.3496 (8)	3.6
C(12)	0.3413 (12)	−0.0910 (11)	0.3057 (7)	3.3
C(13)	0.4347 (12)	0.0006 (11)	0.3547 (7)	3.1
C(14)	0.3498 (13)	0.1226 (11)	0.4351 (7)	3.3
C(11M)	0.0548 (16)	−0.1030 (17)	0.3130 (11)	6.4
C(12M)	0.4014 (16)	−0.2294 (14)	0.2258 (9)	5.3
C(13M)	0.6004 (13)	−0.0313 (15)	0.3281 (9)	4.8
C(14M)	0.4169 (18)	0.2380 (15)	0.5003 (9)	6.2
C(2)	0.0525 (10)	0.2904 (10)	0.2805 (6)	2.1
C(3)	0.1884 (11)	0.3439 (11)	0.3039 (6)	2.3
B(4)	0.3436 (14)	0.2277 (15)	0.2413 (9)	3.2
B(5)	0.2851 (13)	0.0902 (14)	0.1686 (14)	3.1
B(6)	0.0839 (15)	0.1429 (14)	0.2004 (8)	2.9
C(2M)	−0.0999 (12)	0.3842 (13)	0.3321 (8)	3.6
C(2E)	−0.2273 (15)	0.3146 (19)	0.3048 (14)	9.8
C(3M)	0.1723 (13)	0.4953 (12)	0.3786 (7)	3.6
C(3E)	0.3098 (19)	0.5529 (16)	0.3863 (10)	6.7
N	0.1507 (9)	0.4850 (9)	0.1279 (5)	2.8
C(21)	0.2583 (12)	0.3498 (11)	0.0687 (6)	2.9
C(22)	0.1833 (11)	0.2438 (11)	0.0162 (6)	2.6
C(23)	0.0206 (12)	0.3125 (11)	0.0447 (7)	3.0
C(24)	0.0049 (13)	0.4600 (11)	0.1139 (7)	3.4
C(21M)	0.4245 (13)	0.3414 (14)	0.0609 (9)	4.4
C(22M)	0.2565 (13)	0.0919 (12)	−0.0567 (7)	3.7
C(23M)	−0.1139 (14)	0.2520 (15)	0.0086 (8)	4.6
C(24M)	−0.1418 (14)	0.5774 (14)	0.1602 (9)	4.8

[a] $B_{eq} = (4/3)(\beta_{11}a^2 + \beta_{22}b^2 + \beta_{33}c^2 + 2\beta_{12}ab\cos\gamma + 2\beta_{13}ac\cos\beta + 2\beta_{23}bc\cos\alpha)$. [b] Estimated standard deviations, given in parentheses, are applicable to the least significant digits quoted.

The molecular structure of the triple-dedkers **27–30** was deduced from their ^1H, ^{11}B, and ^{31}P NMR spectra, supported by an X-ray diffraction study of **30**. The ^1H and ^{11}B NMR spectra are similar to those of other 2,3-C_2B_3-bridged triple-deckers, each compound exhibiting a low-field ^{11}B resonance (δ 47–60 ppm) that is characteristic of this class.[4a,b,11a,c] In comparison to the corresponding pyrrolyl complexes, there are no large differences in the proton or boron spectra of **25–30** although a slight upfield tendency is evident in the phospholyl species. The most obvious difference is the splitting of the phospholyl 2,5-methyl resonances in the proton spectrum with observed coupling constants of 7–9 Hz at 360 MHz, a range consistent with those seen in phosphametallocenes.[24] The ^{31}P shifts in all of the phospholyl species **25–30** are in the high-field range of −20 to −40 ppm (relative to H_3PO_4), which is characteristic of η^5-phospholyl–metal complexes.[24] Only singlet resonances are seen, with no observable coupling arising from interaction with the adjacent methyl protons; this is a consequence of large peak width relative to the small P–H coupling constant.

Table VI. Bond Distances (Å) for 30

Co(1)–P	2.318 (3)	C(13)–C(14)	1.440 (14)
Co(1)–C(11)	2.090 (11)	C(13)–C(13M)	1.480 (14)
Co(1)–C(12)	2.065 (10)	C(14)–C(14M)	1.498 (17)
Co(1)–C(13)	2.062 (10)	C(2)–C(3)	1.462 (12)
Co(1)–C(14)	2.108 (10)	C(2)–C(2M)	1.486 (13)
Co(1)–C(2)	2.064 (8)	C(2)–B(6)	1.508 (14)
Co(1)–C(3)	2.087 (9)	C(3)–C(3M)	1.514 (13)
Co(1)–B(4)	2.095 (12)	C(3)–B(4)	1.614 (15)
Co(1)–B(5)	2.072 (11)	C(2M)–C(2E)	1.489 (17)
Co(1)–B(6)	2.083 (12)	C(3M)–C(3E)	1.505 (19)
Co(7)–C(2)	2.129 (8)	B(4)–B(5)	1.647 (17)
Co(7)–C(3)	2.086 (8)	B(5)–B(6)	1.773 (16)
Co(7)–B(4)	2.090 (12)	N–C(21)	1.424 (12)
Co(7)–B(5)	2.042 (12)	N–C(24)	1.403 (13)
Co(7)–B(6)	2.097 (12)	C(21)–C(22)	1.417 (13)
Co(7)–N	2.098 (8)	C(21)–C(21M)	1.485 (15)
Co(7)–C(21)	2.011 (9)	C(22)–C(23)	1.434 (13)
Co(7)–C(22)	2.064 (9)	C(22)–C(22M)	1.507 (14)
Co(7)–C(23)	2.081 (9)	C(23)–C(24)	1.454 (14)
Co(7)–C(24)	2.073 (10)	C(23)–C(23M)	1.510 (15)
P–C(11)	1.746 (11)	C(24)–C(24M)	1.482 (15)
P–C(14)	1.748 (11)	Co(1)–cent(1)[a]	1.709 (9)
C(11)–C(12)	1.462 (15)	Co(1)–cent(2)	1.613 (11)
C(11)–C(11M)	1.520 (17)	Co(2)–cent(2)	1.617 (11)
C(12)–C(13)	1.425 (14)	Co(2)–cent(3)	1.704 (9)
C(12)–C(12M)	1.461 (16)		

[a] cent(1) = PC_4 ring centroid, cent(2) = C_2B_3 ring centroid, cent(3) = NC_4 ring centroid.

Table VII. Selected Bond Angles (deg) for 30

Co(1)–C(2)–Co(7)	97.5 (3)	P–C(11)–C(12)	113.1 (7)
Co(1)–C(3)–Co(7)	98.1 (3)	P–C(11)–C(11M)	112.7 (8)
Co(1)–B(4)–Co(7)	97.7 (4)	P–C(14)–C(13)	113.8 (7)
Co(1)–B(5)–Co(7)	100.0 (5)	P–C(14)–C(14M)	112.3 (8)
Co(1)–B(6)–Co(7)	97.9 (5)	C(11)–P–C(14)	90.4 (5)
C(13)–C(14)–C(14M)	123.9 (10)	C(11)–C(12)–C(13)	111.1 (8)
C(14)–C(13)–C(13M)	124.8 (9)	C(11)–C(12)–C(12M)	125.6 (9)
C(2)–C(3)–C(3M)	120.0 (8)	C(12)–C(11)–C(11M)	124.2 (10)
C(2)–C(3)–B(4)	112.6 (8)	C(12)–C(13)–C(14)	111.5 (8)
C(2)–C(2M)–C(2E)	114.3 (10)	C(12)–C(13)–C(13M)	123.7 (9)
C(2)–B(6)–B(5)	104.8 (8)	C(13)–C(12)–C(12M)	123.2 (9)
C(3)–C(2)–C(2M)	119.4 (8)	C(21)–N–C(24)	104.6 (7)
C(3)–C(2)–B(6)	113.9 (8)	C(21)–C(22)–C(23)	105.7 (8)
C(3)–C(2M)–C(3E)	116.2 (9)	C(21)–C(22)–C(22M)	127.8 (8)
C(3)–B(4)–B(5)	104.6 (8)	C(22)–C(21)–C(21M)	128.2 (9)
C(2M)–C(2)–B(6)	126.7 (8)	C(22)–C(23)–C(24)	106.8 (8)
C(3M)–C(3)–B(4)	127.3 (8)	C(22)–C(23)–C(23M)	128.4 (9)
B(4)–B(5)–B(6)	104.0 (8)	C(23)–C(22)–C(22M)	126.5 (8)
N–C(21)–C(22)	112.3 (8)	C(23)–C(24)–C(24M)	127.3 (9)
N–C(21)–C(21M)	119.1 (8)	C(24)–C(23)–C(23M)	124.8 (9)
N–C(24)–C(23)	110.5 (8)	Co(1)–cent(2)[a]–Co(7)	173.7 (8)
N–C(24)–C(24M)	122.1 (8)	cent(1)–Co(2)–cent(2)	178.0 (5)
		cent(2)–Co(7)–cent(3)	178.9 (5)

[a] cent(1) = PC_4 ring centroid, cent(2) = C_2B_3 ring centroid, cent(3) = NC_4 ring centroid.

The crystallographically determined geometry of **30**, shown in Figure 1 with relevant data in Tables IV–VII, is that of a triple-decker sandwich closely analogous to the bis(pyrrolyl) species **9**[15] except for deviations arising from the presence of phosphorus (covalent radius 1.10 Å) in place of nitrogen (0.74 Å) in one ring. These are evident in the small C–P–C bond angle (90.4°), which compares with the C–N–C angle of 104.7°, the longer P–C vs N–C bond lengths, and a slight puckering of the PC_4 ring, with the phosphorus pushed out of the C_4 plane away from the cobalt atom. These features are similar to those observed in earlier structure determinations on phosphametallocenes.[22,24] The relatively large displacement ellipsoid of the ethyl carbon atom C(2E) suggests possible disorder of that atom; however, the fact that two of the three hydrogens on C(2E) were located argues against this interpretation.

The conformation of the pyrrolyl and phospholyl ligands relative to the central C_2B_3 ring is close to that found in

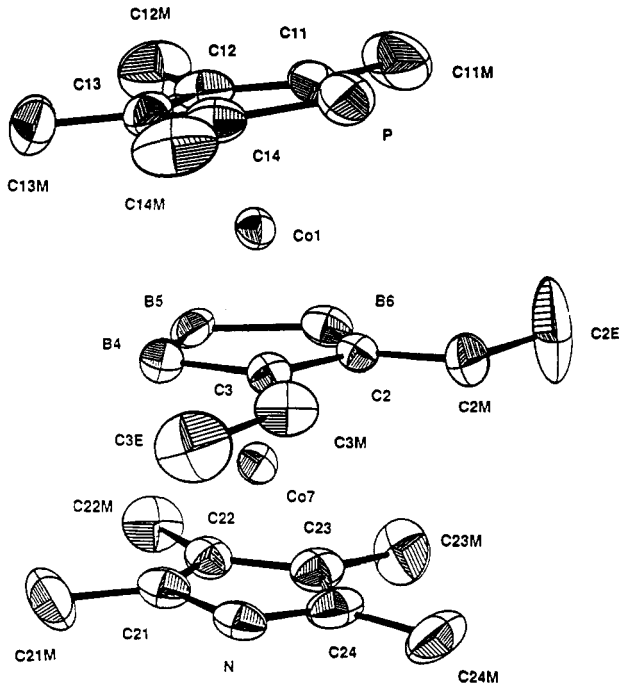


Figure 1. ORTEP drawing of the molecular structure of **30** with 50% thermal ellipsoids. Hydrogen atoms are omitted.

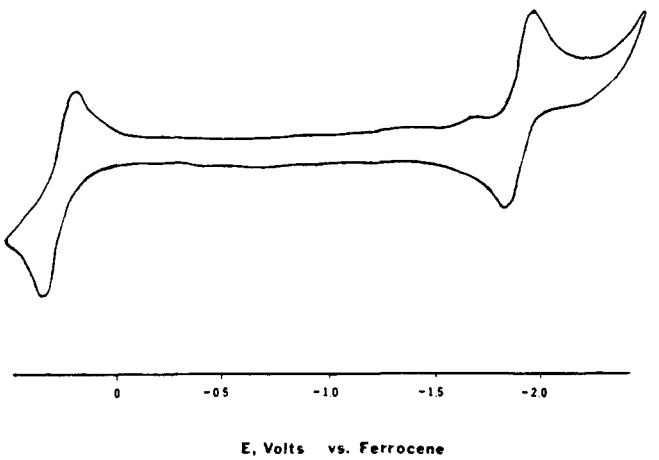


Figure 2. Cyclic voltammogram of **9** in dimethoxyethane with Bu_4NPF_6 as supporting electrolyte.

9, with the N and P heteroatoms located near the carborane carbon atoms. As in **9**, this is attributed in part to minimization of steric crowding between the alkyl substituents on the end and central ligands. The remaining features of the structure, including bond distances and angles in the $Co_2C_2B_3$ cluster, are closely comparable to those in **9**.

Not surprisingly, the phospholyl complexes exhibited no observable nucleophilic behavior. Thus, attempted reactions with BH_3·THF, CH_3I, and $PdCl_2(PHCN)_2$ in all cases resulted only in the recovery of starting material.

Electrochemistry. Cyclic voltammetry was conducted on the pyrrolyl- and phospholyl-containing triple-decker complexes in dichloromethane and dimethoxyethane solvents, using Bu_4NPF_6 as supporting electrolyte. All of the compounds exhibited a reversible oxidation in both solvents and a reversible reduction in DME only; the voltammogram of **9**, shown in Figure 2, is typical. Reversibility was confirmed by (1) ΔE values no larger than 70 mV at very slow scan rates (30 mV/s), (2) i_a/i_c ratios of ca. 1 for all couples observed, and (3) close similarity, at all scan rates, of the ΔE values to those of the Cp_2Fe/Cp_2Fe^+

Table VIII. Cyclic Voltammetry Data[a]

compd	$E_{1/2}^{0/+}$, V (DCM)	$E_{1/2}^{0/+}$, V (DME)	$E_{1/2}^{0/-}$, V (DME)
5a	−0.18	0.01	−2.17
5b	−0.11	0.07	−2.07
8a	−0.16	−0.03	−2.31
8b	−0.12	0.04	−2.16
9	0.02	0.22	−1.94
27	0.40	−0.22	−2.48
28	−0.22	*b*	−2.42
29	−0.08	0.03	−2.22
30	−0.02	0.12	−1.98
$Cp^*_2Co_2(Et_2C_2B_3H_3)$	−0.38	−0.18	−2.46

[a] $E_{1/2}$ values vs Cp_2Fe for oxidations in CH_2Cl_2 (DCM), oxidations in dimethoxyethane (DME), and reductions in DME. Scan rate was 0.1 V s^{-1}. Electrolyte was 0.1 M Bu_4NPF_6. [b] Oxidation potential not measured.

couple used as an internal standard.

In several cases a second, irreversible, oxidation was observed at ca. 1.2 V. Although a number of other 2,3-C_2B_3-bridged triple-decker complexes have shown one reversible oxidation and *two* reversible reductions,[25] the failure to observe more than one reduction in the present species may (for some compounds at least) be due to the relatively small electrochemical window with a lower limit of −2.5 V vs Ag/AgCl; the possibility that a second reduction could be observed in a different (e.g., "superdry") solvent cannot be excluded.

The redox potentials of these compounds (Table VIII) show several interesting trends that reflect the relative electron-donor and -acceptor properties of the heterocyclic end ligands; i.e., the more donating ligand increases the electron density on the metal, and hence, both oxidation and reduction potentials are lowered. Previous studies of substituted ferrocenes,[26] phosphaferrocenes,[27] and arsaferrocene[28] quite clearly demonstrate a relationship between the oxidation potential and the Hammett constant, σ_p.[26] Formal replacement of CH by P or As produces an increase in the oxidation potential (e.g., 0.38 and 0.24 V for diphosphaferrocene and diarsaferrocene, respectively, compared to ferrocene itself). That pyrrolyl ligands are superior π-acceptors and inferior σ-donors compared to cyclopentadienyl is also supported by infrared data on corresponding cymantrenes[29] [$(CO)_3MnL$), in which the C–O stretching frequency increases in the order L = C_5H_5 < $PC_4Me_2H_2$ ~ $AsC_4Me_2H_2$ < NC_4H_4 ~ $NC_4Me_2H_2$. These findings are consistent with reduced metal-to-CO back-bonding and hence increased donation of electron density from the metal to the ring, when the cyclopentadienyl is replaced by a heterocyclic ligand.

This picture is reinforced by the trends found in our study, in that our phospholyl-containing complexes show small increases in both oxidation and reduction potential, while the pyrrolyl compounds exhibit larger increases. These effects are additive, as the bis(pyrrolyl) (**9**) and bis(phospholyl) (**29**) compounds show correspondingly greater increases in potentials; as expected, the mixed-ligand pyrrolyl–phospholyl species **30** gives an intermediate value. The consequence of electron donation from the methyl substituents is also evident, as comparison of the redox potentials of the dimethylpyrrolyl species with those of the corresponding tetramethylpyrrolyl compounds shows that the latter values are lower, as expected, in agreement with earlier observations on substituted ferrocenes.[26]

Conclusions

This work combines metal–heterocycle sandwich chemistry and metallacarborane chemistry via the designed synthesis, characterization, and study of several families of mixed-ligand complexes, thereby enlarging the scope of both fields. The stabilization provided by the presence of a formal $Et_2C_2B_4H_4^{2-}$ or $Et_2C_2B_3H_3^{4-}$ unit has allowed the isolation of the first examples of triple-decker sandwiches containing η^5-bound pyrrolyl or phospholyl rings and opens still other, largely unexplored possibilities in synthesis. Among the new avenues to be pursued are the use of polycyclic heteroaromatic ligands and chalocogen-containing rings in concert with carborane ligands. We have investigated these areas to a limited extent, via the synthesis of indole- and thiophene-containing sandwich species,[34] and will report on these findings separately.

Experimental Section

Instrumentation. ^{11}B (115.8 MHz), ^1H (300 MHz), and ^{31}P (146 MHz) NMR spectra were acquired on a Nicolet NT-360 or GE QE300 spectrometer, and visible–ultraviolet spectra were recorded on a Hewlett-Packard 8452A diode array spectrophotometer with an HP Vectra computer interface. Unit-resolution mass spectra were obtained on a Finnegan MAT 4600 GC/MS spectrometer with perfluorotributylamine (FC43) as a calibration standard. High-resolution mass measurements were obtained on a Finnegan MAT 8230 instrument with an SSX 300 data system and perfluorokerosene as a reference standard. Infrared spectra were recorded on a Mattson Cygnus FTIR spectrometer. All new products gave unit-resolution mass spectra in good agreement with calculated spectra, supported by high-resolution mass measurements. In addition, the fragmentations exhibited in the unit-resolution spectra are consistent with the proposed structures, e.g., loss of ligand or M(ligand) units from the parent ions. Normal-phase high-performance liquid chromatography was conducted on a Waters Delta Prep 3000 chromatograph on silica gel columns with hexane/dichloromethane mixtures as the mobile phase.

Electrochemistry. Cyclic voltammetry was conducted in quiet solutions on a Bioanalytical Systems CV-27 instrument equipped with a Kipp and Zonen x-y recorder. A three-electrode arrangement was used, employing a platinum-disk working electrode, a saturated Ag/AgCl reference electrode (stored in concentrated aqueous KCl when not in use), and a platinum wire as the auxiliary electrode. The scan rate was 0.1 V s^{-1}, and the supporting electrolyte was 0.1 M Bu_4NPF_6, used as received and stored in a drybox. The solvents utilized were dichloromethane (DCM) or dimethoxyethane (DME), which were stored over molecular sieves for several days before use. For the reductions, the cell was purged with dry N_2 for 20 min prior to each run. All voltages given are relative to the Cp_2Fe/Cp_2Fe^+ couple, which was employed as an internal standard.

Materials. The starting materials $Cp^*Co(Et_2C_2B_3H_5)$ (**4**),[4a] $(Et_2C_2B_3H_3)Ru(1,4\text{-}MeC_6H_4CHMe_2)$ (**7**),[4a] *nido*-2,3-$Et_2C_2B_4H_6$,[30]

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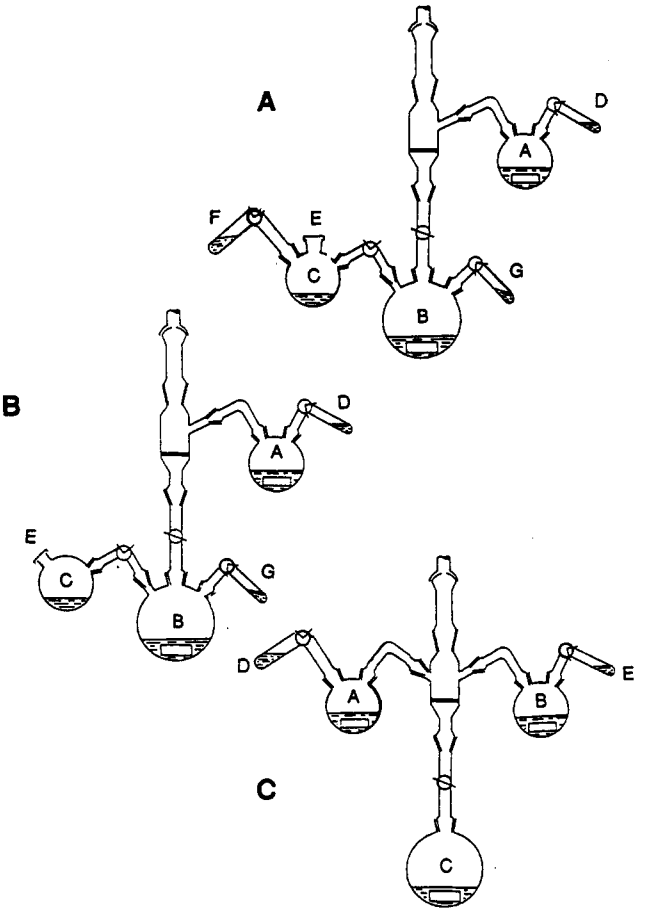

Figure 3. Apparatus for syntheses of pyrrolyl- and phospholyl-metal-carborane complexes in vacuo. Apparatus A and B each contain a rubber septum (E).

and 1-phenyl-2,3,4,5-tetramethylphosphole[24] were prepared by literature methods. NaH (60% in mineral oil) and KH (35% in mineral oil) were washed repeatedly with *n*-hexane to remove the oil before use. 2,5-Dimethylpyrrole, 1.0 M BH_3·THF in THF, 2,3,4,5-tetramethylpyrrole, and $PdCl_2(PhCN)_2$ were purchased commercially and used as received. Reagent grade dichloromethane and *n*-hexane were stored over molecular sieves, and THF was stored over benzophenone/Na and distilled immediately prior to use.

Synthesis of $(NC_4Me_4)Co(Et_2C_2B_3H_5)$ (2a). The apparatus in Figure 3A was charged with 180 mg (1.46 mmol) of tetramethylpyrrole in sidearm F, 170 mg (1.32 mmol) of anhydrous $CoCl_2$ in sidearm G, and 153 mg (1.16 mmol) of $Et_2C_2B_4H_6$ in sidearm D, and an excess of dry, oil-free NaH in flask A, and the entire apparatus was evacuated on the vacuum line. THF (50 mL) was distilled into flask C and 75 mL into flask B, while both flasks were cooled in liquid nitrogen. Flasks B and C were warmed slightly and the tetramethylpyrrole was added to flask C and stirred. Flask C was cooled until the solvent had frozen, at which point the liquid nitrogen was removed and 0.47 mL of 2.5 M *n*-butyllithium solution (1.18 mmol) was added to flask C through the rubber septum. Flask C was warmed to room temperature with stirring, and the $CoCl_2$ was added to flask B. Flasks B and C were stirred separately in vacuo for 1 h, during which most of the $CoCl_2$ had dissolved and a white precipitate formed in flask C. The contents of flask C were slowly added to flask B over a 15-min period, causing a color change from blue to red-brown, and stirred for 1 h. A solution of $Na^+Et_2C_2B_4H_5^-$, prepared by adding the contents of sidearm D to the NaH in flask A, was slowly filtered in vacuo through a frit into flask B. The contents of flask B were stirred for 1 h and opened to the air, and the solvent was removed by rotary evaporation to leave a brown residue, which was extracted with two 100-mL portions of anhydrous ether and suction-filtered through 2 cm of silica gel. The silica was washed with ether until the effluent was colorless and the orange filtrate was rotary evaporated, yielding an orange oil. A stirring bar and 10 mL to TMEDA were added to the oil, and the mixture was stirred for 15 min, after which the remaining TMEDA was removed by evaporation and the residue was dissolved in *n*-hexane and filtered through silica gel. The silica was washed with hexane, the washings were discarded, and the silica was then washed with anhydrous ether. The ether filtrate was rotary-evaporated to leave 0.123 g (0.41 mmol, 35%) of **2a** as a yellow oil. UV-visible absorptions (nm, in CH_2Cl_2): 390, 284, 234. Exact mass for $^{59}Co^{14}N^{12}C_{14}{}^{11}B_3{}^1H^+$: calcd 301.1755; found 301.1753.

Synthesis of $(NC_4Me_2H_2)Co(Et_2C_2B_3H_5)$ (2b). A procedure identical with that employed in the synthesis of **2a** was followed except that apparatus B in Figure 3 was used, and the 2,5-dimethylpyrrole was introduced to flask C via syringe instead of a sidearm. From 229 mg (1.69 mmol) of $Et_2C_2B_4H_6$, 165 mmol (1.73 mmol) of 2,5-dimethylpyrrole, 224 mg (1.76 mmol) of $CoCl_2$, and 0.69 mL (1.73 mmol) of 2.5 M *n*-butyllithium, 209 mg (0.77 mmol, 44%) of **2b** was isolated as a yellow oil. UV-visible absorptions (nm, in CH_2Cl_2): 382, 280, 234. Exact mass for $^{59}Co^{14}N^{12}C_{12}{}^{11}B_3{}^1H_{23}^+$: calcd 273.1442; found 273.1455.

Synthesis of $(NC_4Me_2R_2)Co(Et_2C_2B_3H_3)CoCp^*$ (5a, R = Me; 5b, R = H), $(NC_4Me_2R_2)Co(Et_2C_2B_3H_3)Ru(1,4\text{-}MeC_6H_4CHMe_2)$ (8a, R = Me; 8b, R = H), and $(NC_4Me_4)_2Co_2(Et_2C_2B_3H_3)$ (9). General Procedure. In apparatus C (Figure 3), a 2–3-fold molar excess of KH in oil was placed in flasks A and B and washed with *n*-hexane to remove the oil. Flask A was fitted with a stirring bar and a sidearm containing dimethyl- or tetramethylpyrrole. Flask B was fitted with a stirring bar and a sidearm containing the appropriate cobalt- or ruthenium-carborane reagent **4**, **7**, or **2a**. Flask C was charged with a stirring bar and anhydrous $CoCl_2$. The entire apparatus was evacuated, and 50 mL of anhydrous THF was distilled into flasks A and B, which were immersed in liquid nitrogen. After slight warming, the contents of the sidearms were added to flasks A and B, and the solutions were stirred for 30 min, during which H_2 evolution was observed. Flask C was immersed in liquid nitrogen and the contents of flasks A and B were filtered into it in vacuo, after which it was immersed in a dry ice/2-propanol bath and stirred for 2 h. The reactor was opened to the air, the THF was removed by rotary evaporation, and the residue was extracted in anhydrous ether and suction-filtered through 2 cm of silica gel. The silica was washed with ether until the eluent was colorless, following which the filtrate was rotary-evaporated, dissolved in 5 mL of 1:1 CH_2Cl_2/*n*-hexane, and placed on a 5 × 25 cm silica gel column charged with 1:1 CH_2Cl_2/hexane (DCH). Elution with this mixed solvent afforded recovered starting materials and side products. Subsequent elution with 1:1 CH_2Cl_2/acetone (DCA) gave the desired triple-decker complexes. Quantities of reagents and product yields for specific syntheses were as follows.

$(NC_4Me_4)Co(Et_2C_2B_3H_3)CoCp^*$ (5a). $Cp^*Co(Et_2C_2B_3H_5)$ (**4**, 168 mg, 0.54 mmol), 2,3,4,5-tetramethylpyrrole (66 mg, 0.54 mmol), and $CoCl_2$ (70 mg, 0.54 mmol) gave 20 mg (0.06 mmol) of recovered **4**, 10 mg (0.08 mmol) of recovered tetramethylpyrrole, and 23 mg (0.04 mmol) of a brown solid identified as $Cp^*_2Co_2Et_4C_4B_6H_6$ (**6**), all eluted with DCH. Elution with DCA afforded 67 mg (0.14 mmol, 29% based on **4** consumed) of red-brown crystalline **5a**. UV-visible absorptions (nm, in CH_2Cl_2): for **5a**, 350, 292, 236; for **6**, 434, 308, 250. Exact mass for **5a** ($^{59}Co_2{}^{14}N^{12}C_{24}{}^{11}B_3{}^1H_{40}^+$): calcd 493.2104; found 493.2113. Exact mass for **6** ($^{59}Co_2{}^{12}C_{32}{}^{11}B_6{}^1H_{56}^+$): calcd 624.3604; found 624.3618.

$(NC_4Me_2H_2)Co(Et_2C_2B_3H_3)CoCp^*$ (5b). Compound **4** (125 mg, 0.40 mmol), 2,5-dimethylpyrrole (38 mg, 0.40 mmol), and $CoCl_2$ (70 mg, 0.54 mmol) gave 25 mg (0.07 mmol) of recovered **4** and 19 mg (0.03 mmol) of **6** upon elution with DCH. Elution with DCA afforded 34 mg (0.07 mmol, 21% based on **4** consumed) of red-brown crystalline **5b**. UV-visible absorptions (nm, in CH_2Cl_2): 346, 290, 236. Exact mass for $^{59}Co_2{}^{14}N^{12}C_{22}{}^{11}B_3{}^1H_{36}^+$: calcd 465.1791; found 465.1801.

$(NC_4Me_4)Co(Et_2C_2B_3H_3)Ru(1,4\text{-}MeC_6H_4CHMe_2)$ (8a). $(MeC_6H_4CHMe_2)Ru(Et_2C_2B_3H_5)$ (**7**, 245 mg, 0.69 mmol), 2,3,4,5-tetramethylpyrrole (85 mg, 0.69 mmol), and $CoCl_2$ (90 mg, 0.70 mmol) gave 47 mg (0.13 mmol) of recovered **7** and 16 mg (0.13 mmol) of tetramethylpyrrole upon elution with DCH. Elution with DCA afforded 50 mg (0.090 mmol, 16% based on **7** consumed) of green crystalline **8a**. UV-visible absorptions (nm, in CH_2Cl_2): 608, 310, 236. Exact mass for $^{104}Ru^{59}Co^{14}N^{12}C_{24}{}^{11}B_3{}^1H_{39}^+$: calcd 537.1748; found 537.1758.

$(NC_4Me_2H_2)Co(Et_2C_2B_3H_3)Ru(1,4\text{-}MeC_6H_4CHMe_2)$ (8b). $(MeC_6H_4CHMe_2)Ru(Et_2C_2B_3H_5)$ (7, 246 mg, 0.69 mmol), 2,5-dimethylpyrrole (66 mg, 0.69 mmol), and $CoCl_2$ (90 mg, 0.70 mmol) gave 66 mg (0.18 mmol) of recovered 7 on elution with DCH. Elution with DCA afforded 67 mg (0.13 mmol, 25% based on 7 consumed) of green crystalline **8b**. UV-visible absorptions (nm, in CH_2Cl_2): 620, 304, 236. Exact mass for $^{104}Ru^{59}Co^{14}N^{12}C_{22}{}^{11}B_3{}^1H_{35}{}^+$: calcd 509.1435; found 509.1438.

$(NC_4Me_4)_2Co_2(Et_2C_2B_3H_3)$ (9). $(NC_4Me_4)Co(Et_2C_2B_3H_5)$ (**2a**, 125 mg, 0.42 mmol), 2,3,4,5-tetramethylpyrrole (85 mg, 0.69 mmol), and $CoCl_2$ (57 mg, 0.44 mmol) gave 9 mg (0.02 mmol) of red, crystalline $(NC_4Me_4)CoEt_4C_4B_7H_7$ (**10**), 19 mg (0.06 mmol) of **2a**, and 21 mg (0.04 mmol) of brown crystalline $(NC_4Me_4)_2Co_2Et_4C_4B_6H_6$ (**11**) on elution with DCH. Elution with DCA gave 27 mg (0.06 mmol, 17%) of red-brown crystalline **9**. UV-visible absorption (nm, in CH_2Cl_2): for **9**, 344, 280, 234; for **10**, 536, 428, 276, 236. Exact mass for **9** ($^{59}Co_2{}^{14}N_2{}^{12}C_{22}{}^{11}B_3{}^1H_{37}{}^+$): calcd 480.1900; found 480.1879. Exact mass for **10** ($^{59}Co^{14}N^{12}C_{20}{}^{11}B_7{}^1H_{39}{}^+$): calcd 429.3066; found 429.3080. Exact mass for **11** ($^{59}Co_2{}^{14}N_2{}^{12}C_{28}{}^{11}B_6{}^1H_{50}{}^+$): calcd 598.3196; found 598.3196.

Reaction of 5a with Iodomethane. A 25-mL round-bottom flask was charged with 69 mg (0.14 mmol) of **5a**, 10 mL of iodomethane, and a stirring bar. The flask was fitted with a reflux condenser, placed in a hot oil bath, and refluxed with stirring for 35 min, after which the solution was cooled and rotary-evaporated to dryness. The flask was washed with hexane repeatedly and the washings were filtered to remove a dark insoluble material. The filtrate was reduced in volume and placed on 20 × 20 cm silica gel TLC plates and eluted with 3:1 hexane/CH_2Cl_2, affording three bands. Band 1 (R_f 0.74) was yellow **4** (3 mg); band 2 (R_f 0.48) was red-brown $(NC_4Me_4)Co(Et_2C_2B_3H_2I)CoCp^*$ (**13**, 10 mg, 0.01 mmol); band 3 (R_f 0.08) was red-brown **5a**. The hexane-insoluble material was washed with CH_2Cl_2, filtered, and the filtrate was evaporated to give a red-brown residue, which was pure $[(MeNC_4Me_4)Co(Et_2C_2B_3H_3)CoCp^*]^+I^-$ (**12**, 45 mg, 0.07 mmol, 71%). UV-visible absorptions (nm, in CH_2Cl_2): for **12** 356, 298, 248; for **13** 424, 368, 314, 238. Exact mass for **13** ($^{127}I^{59}Co_2{}^{14}N^{12}C_{24}{}^{11}B_3{}^1H_{39}{}^+$): calcd 619.1070; found 619.1079.

Reaction of 5a with Excess 1,3-Diiodopropane. Following a procedure similar to that used in the preceding experiment, 40 mg of **5a** and 5 mL of diiodopropane were refluxed with stirring for 1 h. After the solvent was removed, the brown residue was dissolved in CH_2Cl_2 and placed on silica plates. Elution with CH_2Cl_2 gave only **13** (15 mg) and **5a** (20 mg).

Reaction of 5a with α,α'-Dibromo-*p*-xylene. In a procedure similar to the preceding synthesis, 41 mg of **5a**, 100 mg of dibromoxylene, and 15 mL of dry cyclohexane were refluxed with stirring for 5 h. The solvent was removed, the residue was dissolved in CH_2Cl_2, and the solution was suction-filtered through 2 cm of silica gel on a sintered glass disk using hexane followed by CH_2Cl_2 until the filtrate was colorless; only the colored portion was collected. The colored portion was evaporated and the residue dissolved in a minimum of CH_2Cl_2. Elution on a silica plate with CH_2Cl_2 gave three bands: 5 mg (0.01 mmol) of red-brown $(NC_4Me_4)Co(Et_2C_2B_3HCl_2)CoCp^*$ (**18**); 16 mg (0.03 mmol) of red-brown $(NC_4Me_4)Co(Et_2C_2B_3H_2Cl)CoCp^*$ (**17**); and **5a**, 15 mg (0.03 mmol). UV-visible absorptions for **17** (nm, in CH_2Cl_2): 414, 358, 238. Exact mass for **17** ($^{59}Co_2{}^{37}Cl^{14}N^{12}C_{24}{}^{11}B_3{}^1H_{39}{}^+$): calcd 529.1685; found 529.1679.

Reaction of 5a with Excess Benzyl Bromide. In a 50-mL round-bottom flask, 30 mg (0.06 mmol) of **5a**, 1 mL of benzyl bromide, and 30 mL of dry pentane were refluxed with stirring for 50 min. The volatiles were removed, the residue was extracted with *n*-hexane and placed on a silica TLC plate, and the plate was eluted with diethyl ether, which afforded a single band, identified as $(NC_4Me_4)Co(Et_2C_2B_3H_2Br)CoCp^*$ (**19**, 10 mg, 0.02 mmol). The hexane-insoluble residue was extracted with ether and found via ^{11}B NMR to contain no boron. UV-visible absorptions for **19** (nm, in CH_2Cl_2): 424, 362, 238. Exact mass for **19** ($^{81}Br^{59}Co_2{}^{14}N^{12}C_{24}{}^{11}B_3{}^1H_{39}{}^+$): calcd 573.1189; found 573.1181.

Reaction of 5a with I_2. In a 50-mL flask, 39 mg (0.080 mmol) of **5a** was dissolved in 15 mL of *n*-hexane, and a solution containing a molar excess of iodine in hexane was added dropwise in vacuo, forming a dark precipitate. The mixture was filtered, washed with hexane, and the filtrate was rotary-evaporated. No isolable products were found in the filtrate. The residue from the filtrate was dissolved in CH_2Cl_2, placed on a TLC plate, and eluted with CH_2Cl_2 to give two bands, of which the first was **13**, 34 mg (0.054 mmol, 69%), and the second was **5a**, 8 mg (0.01 mmol).

Synthesis of $(H_3B\text{-}NC_4Me_4)Co(Et_2C_2B_3H_3)CoCp^*$ (22). A two-neck 50-mL round-bottom flask equipped with a stopcock, rubber septum, and stirring bar was charged with 23 mg (0.05 mmol) of **5a** and evcuated on the vacuum line. THF (30 mL) was distilled into the flask, which was immersed in a dry ice bath, and the mixture was stirred until all solid had dissolved. A 0.14-mL aliquot of 1.0 M BH_3·THF (0.14 mmol) was added via syringe, producing an immediate darkening of the solution. The flask was warmed to room temperature and the volatiles were distilled away, leaving a dark residue. In a drybox, the residue was extracted with a large volume of hexane and filtered. The red filtrate was transferred to a vacuum line and the solvent removed, leaving pure red-brown solid **22**, 20 mg (0.040 mmol, 85%). Compound **22** is slightly air-sensitive, slightly soluble in hexane, and very soluble in CH_2Cl_2 and ether. UV-visible absorptions (nm, in CH_2Cl_2): 352, 298, 238. Exact mass for $^{59}Co_2{}^{14}N^{12}C_{24}{}^{11}B_4{}^1H_{43}{}^+$: calcd 507.2432; found 507.2451.

Synthesis of $(H_3B\text{-}NC_4Me_4)_2Co(Et_2C_2B_3H_3)$ (23). Following a procedure similar to that used in the preparation of **22**, 56 mg (0.12 mmol) of **9** was treated with 1.0 mmol of BH_3·THF. Workup was different from that used for **22**, in that the residue was dissolved in dry diethyl ether and filtered to give a red solution, which was reduced to red-brown solid **23**, 54 mg (0.11 mmol, 91%). Compound **23** is sparingly soluble in hexane but very soluble in CH_2Cl_2 and ether. UV-visible absorption (nm, in CH_2Cl_2): 348, 240. Exact mass for $^{59}Co_2{}^{14}N_2{}^{12}C_{22}{}^{11}B_5{}^1H_{43}{}^+$: calcd 508.2556; found 508.2550.

Reaction of 5a with $PdCl_2(PhCN)_2$. Into a 25-mL two-neck round-bottom flask equipped with a nitrogen inlet and an oil bubbler were placed 15 mg (0.04 mmol) of $PdCl_2(PhCN)_2$ and a stirring bar. Dry benzene was added, and was stirred to give a yellow solution. The flask was purged with N_2 for 10 min, after which a previously purged benzene solution of 39 mg (0.08 mmol) of **5a** was added dropwise under a stream of N_2. The color immediately changed to dark brown. After stirring for 3 h, the flask was opened to the air, the volatiles were removed by evaporation, and the residue, was dissolved in a small amount of CH_2Cl_2. Elution on a silica gel TLC plate gave 4 bands: yellow-brown $(NC_4Me_4)Co(Et_2C_2B_3Cl_3)CoCp^*$ (**24**), 2 mg, R_f 0.46; 18, 8 mg (0.014 mmol, 23%), R_f 0.35; **17**, 26 mg (0.05 mmol, 83%), R_f 0.30; and **5a**, 12 mg (0.02 mmol). UV-visible absorptions for **24** (nm, in CH_2Cl_2): 348, 240.

Synthesis of $Li(PC_4Me_4)$. A variation of the method of Nief et al.[24] was employed. Apparatus C in Figure 3 was charged with a 5–10-fold molar excess of Li foil in flask A, 1-phenyl-2,3,4,5-tetramethylphosphole in sidearm D, and 0.33 equiv of dry $AlCl_3$ in sidearm F (attached to flask C). The apparatus was evacuated, and 50 mL of dry THF was distilled into flask A, which was immersed in liquid nitrogen. After partial warming, the phosphole was added to flask A with stirring, and flask A was warmed to room temperature. The solution was stirred for 1 h, during which it became dark red. The solution was decanted in vacuo onto the frit and filtered into flask C, which in turn was cooled to 0 °C, and the $AlCl_3$ was added with stirring. The stirring was continued at 0 °C for 40 min, during which the color lightened considerably. Flask C was cooled in liquid nitrogen, and the solution was ready for use.

Synthesis of $(PC_4Me_4)Co(Et_2C_2B_4H_4)$ (25). Apparatus C (Figure 3) was modified to include a sidearm F and tiptube G, both attached to flask C. Sidearm D was charged with 1.010 g (4.68 mmol) of 1-phenyl-2,3,4,5-tetramethylphosphole, sidearm E was charged with 617 mg (4.67 mmol) of $Et_2C_2B_4H_6$, 208 mg (1.56 mmol) of $AlCl_3$ was placed in sidearm F, and 608 mg (4.71 mmol) of $CoCl_2$ was added to tiptube G. Excess lithium foil and excess NaH were placed in flasks A and B, respectively. The entire apparatus was evacuated, and the phospholyllithium solution was prepared in flask C as described above. A solution of Na^+-$Et_2C_2B_4H_5^-$ (vide supra) was prepared and filtered into flask C, which was cooled in liquid nitrogen. The $CoCl_2$ was added to flask C; the mixture was warmed to room temperature with stirring and stirred for an additional 90 min. The dark brown solution

in flask C was opened to the air and stirred for 10 min, after which the volatiles were removed by rotary evaporation, leaving a brown residue. The residue was extracted with 50 mL of dry ether, suction-filtered through 2 cm of silica gel on a sintered glass disk, and the silica was washed with ether until the effluent was colorless. The orange filtrate was evaporated to give a residue that was placed on a 5 × 20 cm silica column and eluted with *n*-hexane. Subsequent elution with 1:1 CH_2Cl_2/hexane gave a single orange band, which was pure **25**, 349 mg (1.06 mmol, 23%). ^{31}P NMR ($CDCl_3$, 146 MHz): δ-29.51. UV-visible absorption (nm, in CH_2Cl_2): 268, 236, 234. Exact mass for $^{59}Co^{31}P^{12}C_{14}{}^{11}B_4{}^1H_{26}{}^+$: calcd 328.1476; found 328.1470.

Synthesis of $(PC_4Me_4)Co(Et_2C_2B_3H_5)$ (26). In a 50-mL round-bottom flask, 349 mg (1.06 mmol) of **25**, 10 mL of TMEDA, and three drops of water were stirred at room temperature for 1 h. The solution was evaporated, leaving a yellow residue, which was extracted in *n*-hexane and eluted in hexane on a 5 × 20 cm silica column. The single yellow band obtained was pure **26**, 116 mg (0.37 mmol, 34%). Subsequent elution with 1:1 CH_2Cl_2/hexane gave 30 mg of **25**. ^{31}P NMR for **26** ($CDCl_3$, 146 MHz): δ -21.94. UV-visible absorptions for **26** (nm, in CH_2Cl_2): 386, 288, 238. Exact mass for **26** ($^{59}Co^{31}P^{12}C_{14}{}^{11}B_3{}^1H_{27}{}^+$): calcd 318.1462; found 318.1470.

Synthesis of $(PC_4Me_4)Co(Et_2C_2B_3H_3)CoCp^*$ (27), $(PC_4Me_4)Co(Et_2C_2B_3H_3)Ru(MeC_6H_4CHMe_2)$ (28), and $(PC_4Me_4)_2Co_2(Et_2C_2B_3H_3)$ (29). General Procedure. In the apparatus used in the preparation of **25**, flask B was charged with a 2–3-fold excess of KH in oil and washed with hexane to remove the oil. Sidearm E was charged with the starting material **4**, **7**, or **26**, while sidearm D was charged with 1-phenyl-2,3,4,5-tetramethylphosphole and excess lithium metal. Flask C was fitted with a tiptube containing $CoCl_2$ and a sidearm charged with $AlCl_3$. The apparatus was evacuated, and the phospholyllithium and metallacarborane were prepared as described above. The metallacarborane anion was prepared by distillation of ca. 50 mL of dry THF into flask B, addition of the metallacarborane, and stirring 30 min at room temperature. This solution was filtered into flask C, which was cooled in liquid nitrogen, and after the contents were completely frozen, the $CoCl_2$ was added. Flask C was warmed to room temperature with stirring and was stirred for 2–4 h, during which the solution became dark brown. The residue was dissolved in ether, the solution was suction-filtered through 2 cm of silica on a glas disk, and the silica was washed with ether until the effluent was colorless. The filtrate was evaporated to dryness, and the residue was dissolved in hexane and eluted in hexane on a 5 × 10 cm silica column, which afforded only the unreacted metallacarborane. Subsequent elutions with 1:1 CH_2Cl_2/hexane gave the desired triple-decker complex **27**, **28**, or **29**.

Reagent quantities and yields were as follows. For **27**, 177 mg (0.56 mmol) of **4**, 122 mg (0.56 mmol) of 1-phenyl-2,3,4,5-tetramethylphosphole, 25 mg (0.19 mmol) of $AlCl_3$, and 73 mg (0.57 mmol) of $CoCl_2$ gave 10 mg (0.03 mmol) of recovered **4** and 36 mg (0.07 mmol, 13%) of **27**. ^{31}P NMR for **27** ($CDCl_3$, 146 MHz): δ -36.00. UV-visible absorptions for **27** (nm, in CH_2Cl_2): 354, 236. Exact mass for **27** ($^{59}Co_2{}^{31}P^{12}C_{24}{}^{11}B_3{}^1H_{40}{}^+$): calcd 510.1811; found 510.1820. For **28**, 217 mg (0.61 mmol) of **7**, 132 mg (0.61 mmol) of 1-phenyl-2,3,4,5-tetramethylphosphole, 27 mg (0.20 mmol) of $AlCl_3$, and 78 mg (0.60 mmol) of $CoCl_2$ gave 20 mg (0.06 mmol) of recovered **7** and 75 mg (0.14 mmol, 25%) of **28**. ^{31}P NMR for **28** ($CDCl_3$, 146 MHz): δ -31.94. UV-visible absorptions for **28** (nm, in CH_2Cl_2): 314, 238. Exact mass for **28** ($^{104}Ru^{59}Co^{31}P^{12}C_{24}{}^{11}B_3{}^1H_{39}{}^+$): calcd 554.1455; found 554.1458. For **29**, 88 mg (0.28 mmol) of **26**, 60 mg (0.28 mmol) of 1-phenyl-2,3,4,5-tetramethylphosphole, 13 mg (0.10 mmol) of $AlCl_3$, and 36 mg (0.28 mmol) of $CoCl_2$ gave a trace of **26** and 30 mg (0.06 mmol, 21%) of **29**. ^{31}P NMR for **29** ($CDCl_3$, 146 MHz): δ -35.03. UV-visible absorptions for **29** (nm, in CH_2Cl_2): 356, 236. Exact mass for **29** ($^{59}Co_2{}^{31}P_2{}^{12}C_{22}{}^{11}B_3{}^1H_{37}{}^+$): calcd 514.1314; found 514.1322.

Synthesis of $(PC_4Me_4)Co(Et_2C_2B_3H_3)Co(NC_4Me_4)$ (30). In apparatus C (Figure 3), flasks A and B were each charged with a 2–3-fold excess of KH in oil and washed with hexane to remove the oil. Sidearm D was charged with 82 mg (0.26 mmol) of the starting material **27**, and sidearm E was charged with 32 mg (0.26 mmol) of 1-phenyl-2,3,4,5-tetramethylphosphole. Flask C contained 33 mg (0.26 mmol) of $CoCl_2$. The apparatus was evacuated, and 50 mL of dry THF was distilled into flasks A and B while immersed in liquid nitrogen. After slight warming, the sidearm contents were added to flasks A and B, and both were stirred until hydrogen evolution ceased. After 10 min, the contents of flask B were filtered into flask C while the latter was frozen in liquid nitrogen. After 30 min of stirring, the contents of flask A were added to flask C, and flask C was warmed to room temperature and stirred for 2.5 h. Flask C was opened to the air and the red-brown solution was stirred for 2 min, after which the solvent was removed, the residue was extracted with ether, the solution was suction-filtered through 2 cm of silica on a glass disk, and the silica was washed with acetone until the effluent was colorless. The filtrate was evaporated to dryness and the residue was dissolved in hexane and eluted in hexane on a short (5 × 3 cm) silica column, which afforded only the starting material **27**, 21 mg (0.07 mmol). Subsequent elution with CH_2Cl_2 afforded red-brown air-stable **30**, 30 mg (0.06 mmol, 32%). ^{31}P NMR for **30** ($CDCl_3$, 146 MHz): δ -36.17. UV-visible absorptions (nm, in CH_2Cl_2): 348, 234. Exact mass for $^{59}Co_2{}^{31}P^{14}N^{12}C_{22}{}^{11}B_3{}^1H_{37}{}^+$: calcd 497.1607; found 497.1618.

X-ray Structure Determination on 30. Relevant crystal data and experimental parameters are listed in Table IV. Intensities were collected on a Nicolet P3m diffractometer (Mo Kα, graphite monochromator, λ = 0.7107 Å) using the θ–2θ scan technique and employing a crystal of dimensions 0.5 × 0.5 × 0.6 mm. Scan rates ranged from 2 to 30° min^{-1}, with background measurements taken at either end of the scan range for at total time equal to that of the scan. Scintillation counting was used in conjunction with pulse-height analysis. Structure amplitudes were derived in the usual way. No correction was applied for absorption. Only those reflections for which $I > 2.5\ \sigma(I)$ were used in the final refinement of the structural parameters. Application of SHELXS86[31] using the Patterson option yielded the positions of the two cobalt atoms; the remaining non-hydrogen atoms and 33 of the 37 hydrogens were located by difference Fourier analysis. Refinement was carried out via the block-diagonal least-squares method (3 × 3, 6 × 6 blocks), employing anisotropic thermal parameters for the non-hydrogen atoms. Scattering factors for the heavier atoms were taken from Cromer and Waber[32] and used without correction for anomalous dispersion effects. For the hydrogen atoms, the values of Stewart et al.[33] were employed.

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Supplementary Material Available: Tables of atomic coordinates for hydrogen atoms, thermal parameters, intermolecular contacts, and mean planes (3 pages); a table of calculated and observed structure factors (14 pages). Ordering information is given on any current masthead page.