for generous financial support. P.C.K. thanks the Deutsche Forschungsgemeinschaft for a fellowship.

Supplementary Material Available: Tables of bond distances, bond angles, atomic coordinates, and thermal parameters (11 pages); a listing of structure factor amplitudes (22 pages). Ordering information is given on any current masthead page.

Pyrrolyl–Transition Metal–Carboranyl Double-Decker and Triple-Decker Sandwich Complexes[1]

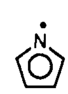
Kevin J. Chase and Russell N. Grimes*

Department of Chemistry, University of Virginia
Charlottesville, Virginia 22901

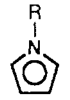
Received May 30, 1989

Summary: A series of pyrrolyl–transition metal sandwich complexes stabilized by cyclic $Et_2C_2B_3H_n^{n-7}$ (n = 3, 5) carborane ligands, including the first pyrrolyl triple-decker compounds, has been prepared. Reaction of the *nido*-$Et_2C_2B_4H_5^-$ ion with $CoCl_2$ and dimethyl- or tetramethylpyrrolide ions in THF followed by TMEDA (tetramethylethylenediamine) generated (η^5-$NC_4Me_2R_2$)Co($Et_2C_2B_3H_5$) (R = Me, H) sandwich complexes, which in turn were converted into a bis(pyrrolyl) triple decker (η^5-NC_4Me_4)$_2$$Co_2$($\mu,\eta^5$-$Et_2C_2B_3H_3$), dicobalt triple deckers (η^5-$NC_4Me_2R_2$)Co(μ,η^5-$Et_2C_2B_3H_3$)Co(η^5-C_5Me_5), and cobalt-ruthenium triple deckers (η^5-$NC_4Me_2R_2$)Co(μ,η^5-$Et_2C_2B_3H_3$)Ru(η^6-1,4-$MeC_6H_4CHMe_2$), all obtained as air-stable crystalline solids.

The transition-metal chemistry of nitrogen heterocycles is dominated by σ-interactions between the metal and the electron lone pair on nitrogen.[2] Accordingly, there are relatively few well-characterized examples of metal sandwich complexes incorporating η^5-bonded pyrrolyl (1) or pyrrole (2) ligands; most of those reported are "half-sandwich" species such as (η^5-pyrrole)$Cr(CO)_3$.[3] Thus, diazaferrocene [$(C_4H_4N)_2Fe$] is unknown, although its octa-*C*-methyl derivative has recently been prepared[4] as a bis(tetramethylpyrrolyl) adduct.



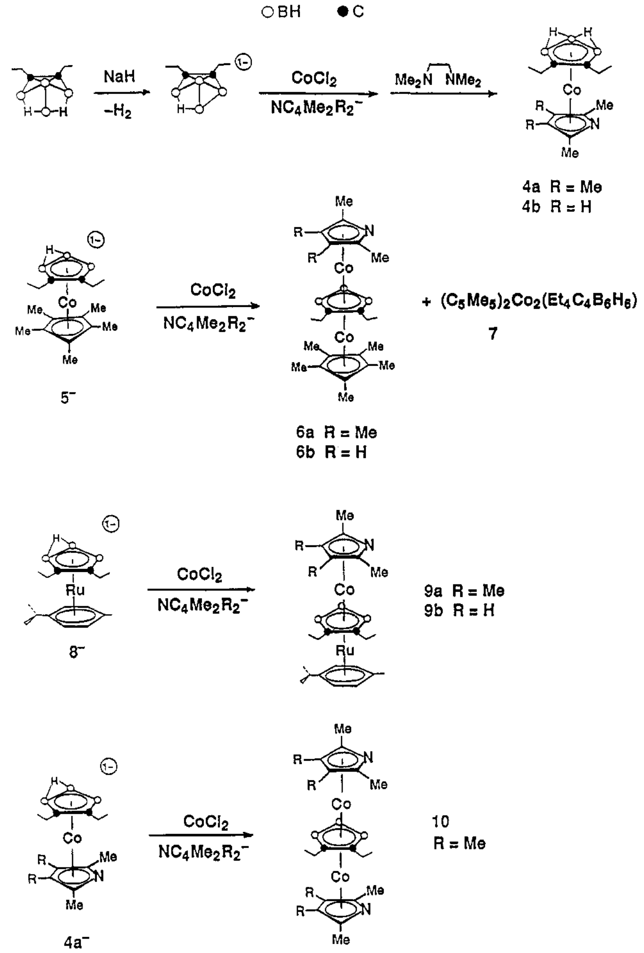
1



2

We report here the designed synthesis and characterization of novel carboranyl–metal–pyrrolyl complexes and their conversion to triple-decker sandwiches containing pyrrolyl ligands, the first reported examples of this genre. This chemistry exploits the remarkable ability of the small carborane ligands *nido*-$R_2C_2B_4H_4^{2-}$ and *cyclo*-$R_2C_2B_3H_3^{4-}$ to stabilize transition metal–organometallic systems that are otherwise unstable or nonexistent,[1b,5] e.g., the first neutral triple-decker complexes,[6] (η^5-C_5H_5)$_2$$Co_2$($\mu,\eta^5$-$R_2C_2B_3H_3$). The reaction of the $Et_2C_2B_4H_5^-$ ion with $CoCl_2$ and the 2,3,4,5-tetramethylpyrrolide or 2,5-dimethylpyrrolide ion in THF gave a mixture of *closo*-(η^5-$NC_4Me_2R_2$)Co($Et_2C_2B_4H_4$) (3) and *nido*-(η^5-$NC_4Me_2R_2$)Co($Et_2C_2B_3H_5$) (4) as shown by NMR and mass spectra. The addition of wet tetramethylethylenediamine (TMEDA) to the mixture converted all of the **3** to **4** via "decapitation" (apex BH removal), affording the desired **4a** or **4b** in 35–45% yields (Scheme I).[7]

Scheme I



Deprotonation of the known *nido*-cobaltacarborane[1b] (C_5Me_5)Co($Et_2C_2B_3H_5$) (5) and the subsequent reaction of

---

[1] (a) Organotransition-Metal Metallacarboranes. 14. (b) Parts 12 and 13: Davis, J. H., Jr.; Sinn, E.; Grimes, R. N. *J. Am. Chem. Soc.* **1989**, *111*, 4776, 4784.

[2] Pannell, K. H.; Kalsotra, B. L.; Parkanyi, C. *J. Heterocycl. Chem.* **1978**, *15*, 1057.

[3] Öfele, K.; Dotzauer, E. *J. Organomet. Chem.* **1971**, *30*, 211.

[4] Kuhn, N.; Horn, E.; Boese, R.; Augart, N. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 1368.

[5] (a) Grimes, R. N. *Pure Appl. Chem.* **1987**, *59*, 847 and references therein. (b) Merkert, J. M.; Geiger, W. E., Jr.; Davis, J. H., Jr.; Attwood, M. D.; Grimes, R. N. *Organometallics* **1989**, *8*, 1580.

[6] (a) Beer, D. C.; Miller, V. R.; Sneddon, L. G.; Grimes, R. N.; Mathew, M.; Palenik, G. J. *J. Am. Chem. Soc.* **1973**, *95*, 3046. (b) Pipal, J. R.; Grimes, R. N. *Inorg. Chem.* **1978**, *17*, 10. (c) Grimes, R. N.; Beer, D. C.; Sneddon, L. G.; Miller, V. R.; Weiss, R. *Inorg. Chem.* **1974**, *13*, 1138.

[7] **4a**: anhydrous $CoCl_2$ (0.170 g, 1.32 mmol) in 50 mL of THF was combined with $LiNC_4Me_4$ (prepared from HNC_4Me_4 (1.80 g, 1.46 mmol) and n-C_4H_9Li in 30 mL of THF) and stirred for 1 h. $Na^+(Et_2C_2B_4H_5)^-$ (1.16 mmol, prepared from 0.153 g of $Et_2C_2B_4H_6$) and NaH in 50 mL of THF, was added, the mixture was stirred for 1 h and opened to the atmosphere, and the THF was removed by rotary evaporation. The residue was extracted with diethyl ether, the extract was filtered through 2 cm of silica gel and concentration by rotary evaporation, and 10 mL of TMEDA and 0.5 mL of water were added and the solution stirred for 15 min. Following the removal of volatiles by evaporation, the residue was extracted in n-hexane and filtered through silica gel, after which the silica was washed with diethyl ether and the filtrate rotary-evaporated to give **4a** as a yellow oil (0.123 g, 35%): ^1H NMR (δ, ppm, $CDCl_3$) –5.95 (s, 2 H, bridge H), 1.13 (t, 6 H, ethyl CH_3), 1.88 (s, 6 H, 2,5-CH_3), 2.02 (s, 6 H, 3,4-CH_3), 2.07 (m, 2 H, ethyl CH_2), 2.18 (m, 2 H, ethyl CH_2); ^{11}B NMR (^1H-decoupled, δ, ppm relative to BF_3 etherate, CH_2Cl_2) 6.12 (1 B, B[5]), 3.44 (2 B, B[4,6]); IR (neat, cm^{-1}[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; MS (70 eV) m/z 301 (base peak), parent, 181, loss of pyrrolyl; exact mass calcd for $^{59}Co^{14}N^{12}C_{14}{}^{11}B_3{}^1H_{27}{}^+$ 301.1755, found 301.1753. A procedure analogous to that employed for **4a** but employing the 2,5-dimethylpyrrolide ion gave **4b** as a yellow oil (0.209 g, 44%).

0276-7333/89/2308-2492$01.50/0

its anion 5^- with $CoCl_2$ and di- or tetramethylpyrrolide ion in THF yielded the triple-decker complexes $(\eta^5\text{-}NC_4Me_2R_2)Co(\mu,\eta^5\text{-}Et_2C_2B_3H_3)Co(\eta^5\text{-}C_5Me_5)$ (**6**) as red-brown crystals,[8] accompanied by the tetracarbon metallacarborane[9] side product $(C_5Me_5)_2Co_2Et_4C_4B_6H_6$ (**7**) which evidently forms via metal-promoted oxidative fusion[10] of 5^-. The corresponding reaction of the cymene–ruthenium–carborane complex anion[1b] 8^- with $CoCl_2$ and di- or tetramethylpyrrolide ion afforded the mixed-metal triple-decker complexes $(\eta^5\text{-}NC_4Me_2R_2)Co(\mu,\eta^5\text{-}Et_2C_2B_3H_3)Ru(\eta^6\text{-}1,4\text{-}MeC_6H_4CHMe_2)$ (**9**) as Kelly green solids.[11] A bis(pyrrolyl) triple decker **10**, was prepared via treatment of $4a^-$ with $CoCl_2$ and the tetramethylpyrrolide ion.[12]

The new complexes, all air-stable species, were characterized from unit- and high-resolution mass spectra, ^{11}B and ^1H NMR spectra, and infrared spectra, which in all cases are consistent with the assigned structures. In particular, the ^{11}B NMR patterns are similar to those observed for analogous arene- and cyclopentadienyl–metal–carboranyl double- and triple-decker complexes whose structures have been established crystallographically.[1b,6a–c] Thus, **6**, **9**, and **10** all exhibit low-field ^{11}B NMR signals (ca. 44–60 ppm to low field of BF_3 etherate) which are characteristic[1b,6a,c] of triple-decker complexes containing *cyclo*-$R_2C_2B_3H_3^{4-}$ bridging ligands.

These findings further document the extraordinary versatility of the small C_2B_3 and C_2B_4 carborane ligands as building-block units for the construction of highly stable multidecker sandwich compounds of first-, second-, and third-row transition metals.[1b,5,13] In the pyrrolyl species, functionalization at the nitrogen site(s) is anticipated to extend still further the versatility of this chemistry, e.g., via controlled N–X–N intermolecular linkage.

Acknowledgment. We thank Dr. Mike Kinter and Dr. James Davis, Jr., for the mass spectra and Dr. Martin Attwood for the boron NMR spectra. The support of the National Science Foundation (Grant No. CHE 87-21657) is gratefully acknowledged.

---

[8] **6a**: a filtered solution of KNC_4Me_4, prepared from 66 mg (0.54 mmol) of HNC_4Me_4 and excess KH in THF, was combined with a THF solution of 5^-, prepared from 0.168 g (0.54 mmol) of $(C_5Me_5)Co(Et_2C_2B_3H_5)$ (**5**) and excess KH in THF, and added to anhydrous $CoCl_2$ (0.070 g, 0.54 mmol) at −196 °C. After the solution was stirred at room temperature for 2 h, the flask was opened in air, the THF removed by evaporation, the residue extracted with diethyl ether and filtered through silica gel, and the volume of the filtrate reduced by evaporation. Purification was achieved via column chromatography on silica, initially with 1:1 dichloromethane/*n*-hexane, which afforded 23 mg (14%) of brown crystalline **7**, identified spectroscopically (closely resembling its known C_5H_5 counterpart[9]), followed by 1:1 CH_2Cl_2/acetone, which gave 67 mg (25%) of red-brown crystalline **6a**: mp 165 °C; ^1H NMR (δ, ppm, $CDCl_3$) 1.55 (s, 15 H, Cp^*CH_3), 1.59 (t, 6 H, ethyl CH_3), 1.80 (s, 6 H, 3,4-CH_3), 1.81 (s, 6 H, 2,5-CH_3), 2.55 (m, 2 H, ethyl CH_2), 2.74 (m, 2 H, ethyl CH_2); ^{11}B NMR (δ, ^1H decoupled) 8.39 (2 B, B[4,6]), 56.53 (1 B, B[5]); IR (neat, cm^{-1}) 2960 s, 2906 s, 2870 s, 2488 s, 1728 m, 1469 s, 1446 s, 1376 s, 1316 m, 1285 m, 1026 s, 906 w, 819 s; MS (70 eV) *m/z* 493 (base), parent; exact mass calcd for $^{59}Co_2{}^{14}N^{12}C_{24}{}^{11}B_3{}^1H_{40}{}^+$ 493.2104, found 493.2113. An analogous procedure using dimethylpyrrolide gave 19 mg (15%) of brown **7** and 34 mg (18%) of red-brown crystalline **6b**, mp 90 °C.

[9] (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.

[10] Grimes, R. N. *Adv. Inorg. Chem. Radiochem.* **1983**, *26*, 55 and references therein.

[11] **9a**: filtered solutions of KNC_4Me_4, prepared from 0.85 g (0.70 mmol) of HNC_4Me_4 and excess KH in THF, and 0.245 g (0.70 mmol) of $K^+(p\text{-}MeC_6H_4CHMe_2)Ru(Et_2C_2B_4H_5)^-$ (ref 1b) were combined with anhydrous $CoCl_2$ (90 mg, 0.70 mmol) at liquid N_2 temperature, then warmed to room temperature, and stirred for 2 h. The reactor was opened in air, and the products were worked up as described for **6a** above to give 50 mg (14%) of **9a**: ^1H NMR (δ, ppm, $CDCl_3$) 1.18 (d, 6 H, isopropyl CH_3), 1.48 (t, 6 H, ethyl CH_3), 1.83 (s, 6 H, 3,4-CH_3), 1.87 (s, 6 H, 2,5-CH_3), 1.97 (s, 3 H, cymene CH_3), 2.46 (m, 3 H, ethyl CH_2 and isopropyl H), 2.88 (m, 2 H, ethyl CH_2), 4.86 (dd, 4 H, cymene H); ^{11}B NMR (δ, ^1H decoupled) 5.94 (2 B, B[4,6]), 45.53 (1 B, B[5]); IR (neat, cm^{-1}) 2960 s, 2925 s, 2870 s, 2474 s, 1731 m, 1465 s, 1447 s, 1379 s, 1276 m, 1032 m, 823 s; MS (70 eV) *m/z* 534 (base), parent; exact mass calcd for $^{104}Ru^{59}Co^{14}N^{12}C_{24}{}^{11}B_3{}^1H_{39}{}^+$ 537.1748, found 537.1758. The procedure employed for **9a**, with the same molar quantities of reagents but with $HNC_4Me_2H_2$ in place of tetramethylpyrrole afforded 67 mg (19%) of **9b**.

[12] **10**: filtered solutions of KNC_4Me_4, prepared from 0.55 g (0.45 mmol) of HNC_4Me_4 and excess KH in THF, and 0.125 g (0.42 mmol) of $K^+(\eta^5\text{-}NC_4Me_4)Co(Et_2C_2B_3H_4{}^-)$ ($4b^-$, prepared from 0.45 mmol of **4b** and excess KH in THF) were combined with anhydrous $CoCl_2$ (57 mg, 0.44 mmol) at liquid N_2 temperature, then warmed to room temperature, and stirred for 2 h. The reactor was opened in air, and the products were worked up as described for **6a** to give 27 mg (14%) of red-brown solid **10** accompanied by the fusion products $(NC_4Me_4)_2Co_2Et_4C_4B_6H_6$ and $(NC_4Me_4)CoEt_4C_4B_7H_7$. **10**: ^1H NMR (δ, ppm $CDCl_3$): 1.65 (t, 6 H, ethyl CH_3), 1.77 (s, 12 H, 3,4-CH_3), 1.80 (s, 12 H, 2,5-CH_3), 2.77 (q, 4 H, ethyl CH_2); ^{11}B NMR (δ, ^1H decoupled) 8.90 (2 B, B[4,6]), 59.10 (1 B, B[5]); IR (neat, cm^{-1}) 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; MS (70 eV) *m/z* 480 (base), parent; exact mass calcd for $^{59}Co_2{}^{14}N_2{}^{12}C_{22}{}^{11}B_3{}^1H_{37}{}^+$ 480.1900, found 480.1879.

[13] Attwood, M. A.; Fonda, K. K.; Grimes, R. N.; Brodt, G.; Hu, D.; Zenneck, U.; Siebert, W. *Organometallics* **1989**, *8*, 1300.

Clusters Containing Carbene Ligands. A New Route to Alkyl(dialkylamino)carbene Ligands by a Novel 1,1-Hydrogenation of Ynamine Ligands

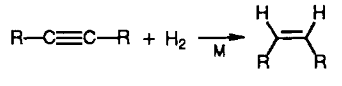
Richard D. Adams,* Gong Chen, James T. Tanner, and Jianguo Yin

Department of Chemistry, University of South Carolina
Columbia, South Carolina 29208

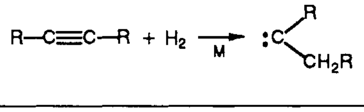
Received June 26, 1989

Summary: The cluster complex $Os_3(CO)_9(\mu_3\text{-}MeC_2NMe_2)(\mu_3\text{-}S)$ (**1**) was synthesized in 87% yield from the reaction of $Os_3(CO)_{10}(\mu_3\text{-}S)$ with MeC_2NMe_2 at 68 °C. The ynamine ligand in **1** was found to resemble an (α,α-dimetallioethyl)(dimethylamino)carbene ligand. When treated with H_2 (10 atm/125 °C), compound **1** was converted to $Os_3(CO)_8[C(Et)NMe_2](\mu_3\text{-}S)(\mu\text{-}H)_2$ (**2**) in 33% yield by a novel 1,1 hydrogenation of the ynamine ligand to yield an ethyl(dimethylamino)carbene ligand. Compounds **1** and **2** were characterized by IR, ^1H NMR, and single-crystal X-ray diffraction analyses. For **1**: space group $P\bar{1}$, $a = 9.397$ (1) Å, $b = 13.406$ (7) Å, $c = 8.914$ (3) Å, $\alpha = 92.84$ (4)°, $\beta = 115.20$ (3)°, $\gamma = 97.54$ (4)°. For 2814 reflections, $R = 0.030$ and $R_w = 0.035$. For **2**: space group $P\bar{1}$, $a = 9.955$ (1) Å, $b = 13.971$ (2) Å, $c = 8.227$ (1) Å, $\alpha = 102.91$ (1)°, $\beta = 113.134$ (9)°, $\gamma = 92.06$ (1)°. For 2606 reflections, $R = 0.027$ and $R_w = 0.031$.

The hydrogenation of alkynes by metal complexes invariably proceeds to yield olefins, usually with cis stereochemistry, by the 1,2 addition of hydrogen to the alkynyl group (eq 1).[1,2] An alternative, 1,1 dihydrogenation to form carbenes has not yet been reported (eq 2).[3]



(1)



(2)

---

[1] James, B. R. *Homogeneous Hydrogenation*; Wiley: New York, 1973; pp 240–242.

[2] (a) Muetterties, E. L.; Krause, M. J. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 135. (b) Muetterties, E. L. *Pure Appl. Chem.* **1978**, *50*, 941. (c) Burch, R. R.; Muetterties, E. L.; Teller, R. G.; Williams, J. M. *J. Am. Chem. Soc.* **1982**, *104*, 4257.