5164 *Inorg. Chem.* **1990**, *29*, 5164-5168

Contribution from the Department of Chemistry, University of Virginia, Charlottesville, Virginia 22901,
and Anorganisch-Chemisches Institut der Universität, D-6900 Heidelberg, Federal Republic of Germany

Tetradecker $LM(C_3B_2)Co(C_2B_3)CoCp$ Sandwich Complexes [LM = Cp*Co, Cp*Rh, or (cymene)Ru]. Designed Synthesis and Electronic Properties

Achim Fessenbecker,[1a,b] Martin D. Attwood,[1a] Russell N. Grimes,*[,1a] Martin Stephan,[1b] Hans Pritzkow,[1b]
Ulrich Zenneck,[1b] and Walter Siebert*[,1b]

Received June 5, 1990

A family of novel tetradecker transition-metal sandwich complexes, each incorporating four different ring ligands, was prepared via the addition of metal–ligand units to the open face of the $(Et_2C_2B_3H_4)Co(Et_2MeC_3B_2Et_2)CoCp^-$ anion. The "hybrid" complexes (containing both carborane and dihydrodiborole bridging rings) $(C_5Me_5)Co(Et_2C_2B_3H_2R)Co(Et_2MeC_3B_2Et_2)CoCp$ (**2a**, R = H; **2b**, R = Cl), $(C_5Me_5)Rh(Et_2C_2B_3H_2R)Co(Et_2MeC_3B_2Et_2)CoCp$ (**3a**, R = H; **3b**, R = Cl), and $(MeC_6H_4CHMe_2)Ru(Et_2C_2B_3H_3)Co(Et_2MeC_3B_2Et_2)CoCp$ (**4**) were isolated as air-stable solids and characterized from their ^{11}B and ^1H FT NMR, IR, and mass spectra and cyclic voltammetry measurements. The tetradecker geometry postulated from NMR data was confirmed by an X-ray crystallographic analysis of the Rh–Co–Co complex **3a**, which showed the four rings to be not quite parallel with a 10.6° tilt between the end rings and no significant slip-distortions in the stack. Each of the 42-electron neutral complexes exhibits a reversible oxidation and two reversible reductions, affording the respective monocation, monoanion, and dianion, respectively. crystal data for **3a**: mol wt 727.6; space group $P2_1/c$; $Z = 4$; $a = 11.831$ (6), $b = 17.967$ (8), $c = 17.352$ (8) Å; $\beta = 107.22$ (4)°; $V = 3523$ (9) Å^3; $R = 0.042$ for 4294 reflections having $F_o^2 > 2.0\sigma(F_o^2)$.

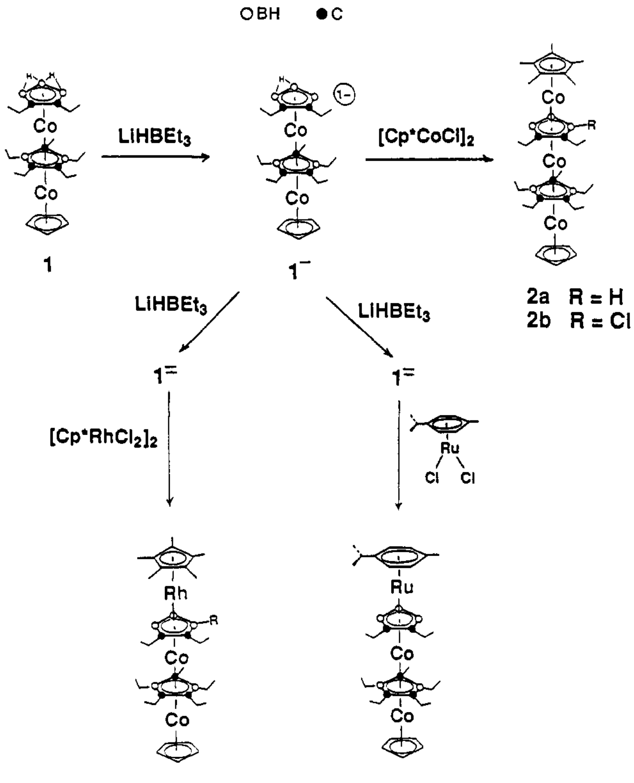
Introduction

Multidecker sandwich complexes larger than triple-deckers are of intrinsic interest in at least two respects. As synthetic agents, they are possible precursors to electronically active networks or polymers; as molecular systems containing several metals in a stable matrix, they are ideal candidates for investigating electronic communication and intramolecular electron transfer between metal centers. All of the structurally characterized examples of tetra- or higher-decker metal sandwiches[2] have utilized 1,3-diborole (C_3B_2) or thiadiborole (C_2B_2S) bridging rings; these include a series of tetradeckers[2,3] and one pentadecker.[4] In addition, while not structurally established by diffraction methods, a hexadecker sandwich[5] and a polymer[6] of composition $[Ni(R_5C_3B_2)]_n$ have also been synthesized.

In contrast, fully characterized sandwiches of more than three decks that incorporate C_2B_3 (carborane) rings have not been reported,[7] notwithstanding the extensive family of known C_2B_3-containing triple-decker sandwiches.[8,9] (The phenylene- and fulvalene-linked triple-decker species[9c] $[(MeC_6H_4CHMe_2)Ru(Et_2C_2B_3H_3)Co(Me_4C_5)]_2(C_6H_4)_n$ (n = 1, 2) and $[(MeC_6H_4CHMe_2)Ru(Et_2C_2B_3H_3)Co(C_5H_4)]_2$ could, however, be described as tetrametallic "pentalevel" complexes).

Recently, our groups prepared the first "hybrid" metal sandwich complexes that utilize both carborane (C_2B_3, C_2B_4) and 1,3-diborole (C_3B_2) ligands,[10] thereby joining two previously separate families of boron–metal complexes; this chemistry is further developed in the accompanying paper.[11] Here we extend this approach to tetradeckers and report the first such species to incorporate both carborane and diborole ring ligands.

Scheme I



Results and Discussion

Synthesis of $(C_5Me_5)Co(Et_2C_2B_3H_2R)Co(Et_2MeC_3B_2Et_2)CoCp$ (2a, R = H; 2b, R = Cl). These and all other tetradecker complexes reported herein were prepared from the known[11] dicobalt triple-decker compound **1** (compound **4a** in the accompanying article), via bridge deprotonation followed by addition of a metal–ligand unit to the open C_2B_3 face. From earlier work,[9b] we were aware that sandwich bonding of the C_2B_3 ring to cobalt works best with monodeprotonated (monoanion) substrates, while other transition metals, including rhodium and ruthenium, require the doubly deprotonated dianionic species. This approach was followed in the current study, as shown in Scheme I. Our initial attempts to bridge-deprotonate **1** with reagents that have proved useful for this purpose in earlier studies (e.g., NaH, KH, and BuLi)

---

(1) (a) University of Virginia. (b) University of Heidelberg.
(2) (a) Siebert, W. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 943. (b) Siebert, W. *Pure Appl. Chem.* **1987**, *59*, 947.
(3) For a recent listing, see: Jemmis, E. D.; Reddy, A. C. *J. Am. Chem. Soc.* **1990**, *112*, 722 and references therein.
(4) Whiteley, M. W.; Pritzkow, H.; Zenneck, U.; Siebert, W. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 453.
(5) Kuhlmann, T.; Siebert, W. *Z. Naturforsch.* **1985**, *40B*, 167.
(6) Siebert, W. *Pure Appl. Chem.* **1988**, *60*, 1345.
(7) The complex $[CpCo(Me_2C_2B_3H_3)]_2CoH$ having a proposed tetradecker structure was characterized from ^{11}B and mass spectra only: Grimes, R. N. *Coord. Chem. Rev.* **1979**, *28*, 47, ref 95a; Finster, D. A.; Grimes, R. N. Unpublished results. Very recently, an analogous Ni^{IV} sandwich, $[Cp^*Co(Et_2C_2B_3H_2\text{-}C(O)Me)]_2Ni$, has been prepared and crystallographically confirmed as a tetradecker: Piepgrass, K. W.; Davis, J. H., Jr.; Sabat, M.; Grimes, R. N. *J. Am. Chem. Soc.*, in press.
(8) Grimes, R. N. *Coord. Chem. Rev.* **1979**, *28*, 47.
(9) (a) Grimes, R. N.; Beer, D. C.; Sneddon, L. G.; Miller, V. R.; Weiss, R. *Inorg. Chem.* **1974**, *13*, 1138. (b) Davis, J. H., Jr.; Sinn, E.; Grimes, R. N. *J. Am. Chem. Soc.* **1989**, *111*, 4776. (c) Davis, J. H., Jr.; Sinn, E.; Grimes, R. N. *Ibid.* **1989**, *111*, 4784.
(10) Attwood, M. A.; Fonda, K. K.; Grimes, R. N.; Brodt, G.; Hu, D.; Zenneck, U.; Siebert, W. *Organometallics* **1989**, *8*, 1300.
(11) Fessenbecker, A.; Attwood, M. D.; Bryan, R. F.; Grimes, R. N.; Woode, M. K.; Stephan, M.; Zenneck, U.; Siebert, W. *Inorg. Chem.*, preceding paper in this journal and references therein.

0020-1669/90/1329-5164$02.50/0

Table I. 115.8-MHz ^{11}B and 300-MHz ^1H FT NMR Data

^{11}B NMR Data

compd[a-c]	δ (J_{BH}, Hz)	rel areas
$(C_5Me_5)Co(Et_2C_2B_3H_3)Co(Et_2MeC_3B_2Et_2)CoCp$ (**2a**)	67.7 (123), 14.3,[d] 6.0 (80)	1:2:2
$(C_5Me_5)Rh(Et_2C_2B_3H_3)Co(Et_2MeC_3B_2Et_2)CoCp$ (**3a**)	60.3 (124), 15.0,[d] 2.9 (80)	1:2:2
$(C_5Me_5)Rh(Et_2C_2B_3H_2Cl)Co(Et_2MeC_3B_2Et_2)CoCp$ (**3b**)	61.1,[e] 14.5,[d] 11.9,[f] 4.4[e]	1:2:1:1
$(MeC_6H_4CHMe_2)Ru(Et_2C_2B_3H_3)Co(Et_2MeC_3B_2Et_2)CoCp$ (**4**)	54.6 (90), 14.9,[d] 3.5[e]	1:2:2

^1H NMR Data

compd	δ[g-i]
2a	4.42 s (C_5H_5), 2.91 m (CH_2), 2.70 m (CH_2), 2.25 m (CH_2), 2.07 m (CH_2), 1.94 q (CH_2), 1.81 s (diborolyl C–CH_3), 1.5 t (ethyl CH_3),[j] 1.37 s (C_5Me_5), 1.18 t (ethyl CH_3)
3a	4.48 s (C_5H_5), 3.02 m (CH_2), 2.74 m (CH_2), 2.32 m (CH_2), 2.02 q (CH_2), 1.96 m (CH_2), 1.86 s (diborolyl C–CH_3), 1.53 t (ethyl CH_3), 1.43 s (C_5Me_5), 1.29 t (ethyl CH_3), 1.23 t (ethyl CH_3)
3b	4.54 s (C_5H_5), 3.04 m (CH_2), 2.77 m (CH_2), 2.31 m (CH_2), 2.09 m (CH_2), 1.98 m (CH_2), 1.88 s (diborolyl C–CH_3), 1.45 s (C_5Me_5), 1.6–1.0[k]
4	4.71 d (cymene ring protons), 4.61 d (cymene ring protons), 4.51 s (C_5H_5), 3.12 m (CH_2), 2.91 m (CH_2), 2.49 m (cymene isopropyl CH), 2.32 m (CH_2), 2.12 m (CH_2), 2.04 q (CH_2), 1.87 (CH_3), 1.84 (CH_3), 1.52 t (ethyl CH_3), 1.33 t (C_5Me_3), 1.22 t (ethyl CH_3), 1.1 d (cymene isopropyl CH_3)

[a] Shifts relative to $BF_3{\cdot}OEt_2$, positive values downfield. [b] *n*-Hexane solution. [c] H–B coupling constant in Hz is given in parentheses, when resolved. [d] Diborolyl ring B–alkyl singlet resonance. [e] Doublet, *J* not measurable. [f] B–Cl singlet resonance. [g] $CDCl_3$ solution. [h] 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. [i] B–$H_{terminal}$ resonances are broad quartets and mostly obscured by other signals. [j] Superimposed triplets. [k] Overlapping multiplets, not assignable.

Table II. Infrared Absorptions (cm^{-1}, Neat Films on KBr Plates)[a]

compd	abs
2a	2956 s, 2924 s, 2869 s, 2854 s, 2482 m, 1456 s, 1375 m, 1026 m, 814 s
3a	2958 s, 2926 s, 2866 s, 2854 s, 2472 m, 2363 m, 2316 m, 1289 w, 1174 w, 1020 m, 825 m, 816 m
3b	2956 s, 2925 s, 2869 s, 2477 s, 1376 m, 1296 m, 1177 w, 1011 m, 960 w, 907 w, 815 s
4	2957 s, 2925 s, 2868 s, 2853 s, 2479 m, 1635 m, 1445 m, 822 m

[a] Legend: vs = very strong, s = strong, m = medium, and w = weak.

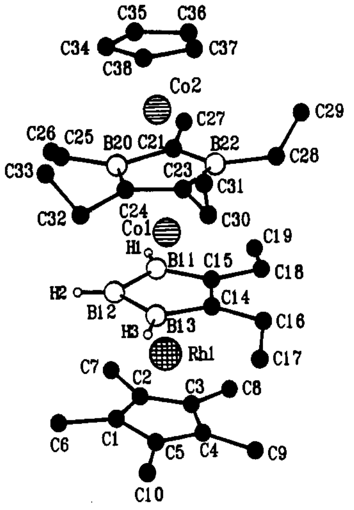


Figure 1. Molecular structure of **3a**.

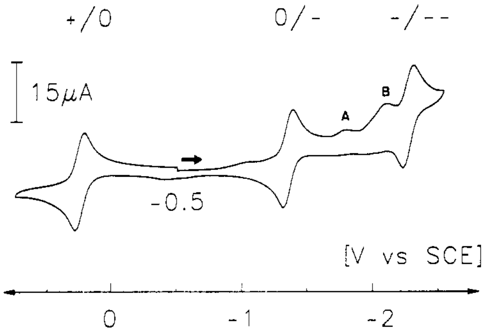


Figure 2. Cyclic voltammogram for **3a** at GC electrodes vs SCE at 20 °C in 0.1 M Bu_4NPF_6/DME (scan rate 0.1 V s^{-1}). Peaks A and B are due to impurities in the sample.

gave unsatisfactory results, failing to produce the desired anion cleanly. However, treatment of **1** with $LiHBEt_3$ in a cold THF/DME solution formed the monoanion $\mathbf{1}^-$, which was then combined with $[(C_5Me_5)CoCl]_2$ at −78 °C. The brown parent complex **2a** was isolated via column and plate chromatography in air and characterized from its ^{11}B and ^1H FT NMR, infrared, and unit- and high-resolution mass spectra (Tables I and II and Experimental Section). A small quantity of the B-chloro derivative **2b**, a side product[12] of the reaction with $[(C_5Me_5)CoCl]_2$, was isolated and identified via mass spectroscopy. Previous work[9b,c] in which chlorination occurred exclusively at B(4) [or equivalent B(6)], rather than at the middle boron [B(5)] suggests a similar pattern in the present study, but this was not further explored. The proton-decoupled boron NMR spectrum of **2a** exhibits a 1:2:2 pattern in which the unique resonance has a pronounced downfield shift at ca. 68 ppm relative to $BF_3{\cdot}OEt_2$, strongly supporting the structure indicated in Scheme I, which has three distinguishable boron environments (assuming mirror symmetry on the NMR time scale). Moreover, the area 1 low-field peak, assigned to the central boron in the carborane ring, is diagnostic for cyclic planar C_2B_3 ligands sandwiched between two transition-metal atoms.[9] The proton NMR spectrum is complex but has been completely assigned (Table I) and is consistent with the proposed structure.

Synthesis and Structure of $(C_5Me_5)Rh(Et_2C_2B_3H_2R)Co(Et_2MeC_3B_2Et_2)CoCp$ (3a, R = H; 3b, R = Cl). The reaction of the dianion $\mathbf{1}^{2-}$ with $[(C_5Me_5)RhCl_2]_2$ at −78 °C gave, on workup in air, two brown compounds, which were isolated as **3a** (the major product) and **3b**. From the close similarity of the NMR spectra, it is apparent that **3a** is structurally analogous to **2a**, and the tetradecker structure shown in Scheme I was assigned. This geometry was subsequently confirmed by an X-ray diffraction analysis, which revealed the detailed structure shown in Figure 1 with atomic parameters, bond distances, and selected angles listed in Tables III and IV. In addition to establishing that these compounds are indeed tetradeckers, one can make some useful comparisons with previously published tetradecker structures. The stacking in **3a** is nearly linear, as measured by the Rh–Co1–Co2 angle of 175°. Each of the three metal atoms is approximately centered over the faces of its η^5-coordinated C_5, C_3B_2, and/or C_2B_3 ligands. The rings are planar but not quite parallel, with a tilt of 10.6° between the two end rings. The metal–metal and

---

(12) Halogenation at boron in the presence of metal halide reagents is frequently observed in reactions of **1** and related metallacarboranes: e.g., see ref 9b,c.

Table III. Atomic Coordinates and Equivalent Isotropic Thermal Parameters for **3a**

atom	x	y	z	$\bar{U}$,[a] Å^2
Rh	0.08412 (3)	0.23702 (2)	0.06952 (3)	0.047
Co1	0.32433 (5)	0.14870 (4)	0.17966 (4)	0.048
Co2	0.56769 (6)	0.07683 (4)	0.29276 (4)	0.055
C1	−0.0084 (5)	0.3413 (3)	0.0546 (5)	0.054
C2	0.0223 (6)	0.3280 (5)	−0.0159 (5)	0.074
C3	−0.0348 (7)	0.2648 (5)	−0.0516 (4)	0.097
C4	−0.1047 (5)	0.2360 (4)	−0.0041 (5)	0.059
C5	−0.0886 (5)	0.2843 (4)	0.0626 (4)	0.056
C6	0.0260 (9)	0.4075 (5)	0.1117 (7)	0.127
C7	0.1039 (8)	0.3793 (7)	−0.0456 (9)	0.123
C8	−0.0307 (12)	0.2322 (8)	−0.1313 (5)	0.211
C9	−0.1835 (7)	0.1690 (5)	−0.0241 (7)	0.094
C10	−0.1485 (8)	0.2793 (7)	0.1278 (6)	0.106
B11	0.2698 (5)	0.2185 (4)	0.0794 (4)	0.051
B12	0.2473 (5)	0.2548 (3)	0.1653 (4)	0.055
B13	0.1620 (5)	0.1877 (4)	0.1898 (4)	0.057
C14	0.1406 (4)	0.1274 (3)	0.1244 (3)	0.050
C15	0.2015 (4)	0.1436 (3)	0.0636 (3)	0.050
C16	0.0685 (5)	0.0572 (3)	0.1181 (4)	0.061
C17	−0.0080 (6)	0.0531 (5)	0.1744 (5)	0.091
C18	0.1883 (5)	0.0914 (4)	−0.0072 (3)	0.076
C19	0.2449 (7)	0.1185 (6)	−0.0707 (5)	0.101
B20	0.4988 (5)	0.1782 (4)	0.2387 (4)	0.049
C21	0.4932 (5)	0.1131 (3)	0.1769 (3)	0.055
B22	0.4215 (5)	0.0460 (3)	0.1968 (4)	0.051
C23	0.3872 (5)	0.0715 (3)	0.2736 (3)	0.059
C24	0.4315 (4)	0.1481 (3)	0.2966 (3)	0.053
C25	0.5633 (8)	0.2544 (4)	0.2485 (6)	0.080
C26	0.5983 (18)	0.2912 (8)	0.2020 (11)	0.558
C27	0.5520 (6)	0.1144 (4)	0.1075 (4)	0.086
C28	0.3905 (6)	−0.0322 (3)	0.1564 (4)	0.086
C29	0.4652 (11)	−0.0683 (7)	0.1148 (9)	0.182
C30	0.3089 (6)	0.0258 (4)	0.3135 (4)	0.098
C31	0.3650 (10)	−0.0085 (8)	0.3900 (6)	0.155
C32	0.4077 (6)	0.1938 (4)	0.3646 (3)	0.086
C33	0.5074 (7)	0.1985 (6)	0.4421 (4)	0.105
C34	0.7250 (6)	0.0952 (5)	0.3824 (6)	0.063
C35	0.7459 (6)	0.0788 (6)	0.3094 (6)	0.057
C36	0.7004 (8)	0.0080 (6)	0.2855 (5)	0.090
C37	0.6506 (8)	−0.0185 (5)	0.3440 (7)	0.096
C38	0.6650 (7)	0.0358 (6)	0.4032 (5)	0.091
H1	0.315 (4)	0.240 (2)	0.051 (3)	0.060
H2	0.279 (3)	0.3045 (14)	0.2095 (18)	0.039
H3	0.127 (4)	0.187 (3)	0.236 (3)	0.065

[a] $\bar{U}$ is defined as one-third of the trace of the orthogonalized **U** tensor.

Table IV. Interatomic Distances (Å) and Angles (deg) for **3a**

Rh–Co1	3.321 (1)	C3–C4	1.425 (12)
Rh–C1	2.147 (6)	C3–C8	1.516 (13)
Rh–C2	2.182 (8)	C4–C5	1.412 (10)
Rh–C3	2.212 (6)	C4–C9	1.500 (10)
Rh–C4	2.221 (6)	C5–C10	1.506 (13)
Rh–C5	2.184 (6)	B11–B12	1.718 (10)
Rh–B11	2.177 (7)	B11–C15	1.551 (8)
Rh–B12	2.166 (5)	B11–H1	0.917 (53)
Rh–B13	2.203 (6)	B12–B13	1.704 (9)
Rh–C14	2.203 (5)	B12–H2	1.164 (27)
Rh–C15	2.199 (5)	B13–C14	1.535 (8)
Co1–Co2	3.235 (1)	B13–H3	1.004 (56)
Co1–B11	2.086 (6)	C14–C15	1.472 (8)
Co1–B12	2.095 (6)	C14–C16	1.508 (7)
Co1–B13	2.100 (7)	C15–C18	1.517 (8)
Co1–C14	2.134 (4)	C16–C17	1.519 (11)
Co1–C15	2.107 (4)	C18–C19	1.529 (11)
Co1–B20	2.083 (6)	B20–C21	1.576 (9)
Co1–C21	2.112 (6)	B20–C24	1.552 (9)
Co1–B22	2.148 (6)	B20–C25	1.552 (10)
Co1–C23	2.101 (5)	C21–B22	1.570 (8)
Co1–C24	2.051 (5)	C21–C27	1.559 (10)
Co2–B20	2.100 (6)	B22–C23	1.571 (9)
Co2–C21	2.047 (5)	B22–C28	1.564 (8)
Co2–B22	2.089 (5)	C23–C24	1.485 (8)
Co2–C23	2.063 (6)	C23–C30	1.547 (10)
Co2–C24	2.075 (6)	C24–C32	1.530 (9)
Co2–C34	2.069 (7)	C25–C26	1.208 (23)
Co2–C35	2.043 (7)	C28–C29	1.449 (17)
Co2–C36	2.032 (10)	C30–C31	1.435 (12)
Co2–C37	2.043 (8)	C32–C33	1.505 (8)
Co2–C38	2.058 (8)	C34–C35	1.394 (15)
C1–C2	1.396 (12)	C34–C38	1.388 (14)
C1–C5	1.431 (9)	C35–C36	1.396 (15)
C1–C6	1.524 (12)	C36–C37	1.400 (16)
C2–C3	1.373 (11)	C37–C38	1.389 (14)
C2–C7	1.530 (16)		
Co2–Co1–Rh	175.0 (0)	C18–C15–B11	127.0 (5)
C5–C1–C2	108.3 (6)	C18–C15–C14	120.2 (4)
C6–C1–C2	127.9 (7)	C17–C16–C14	115.2 (5)
C6–C1–C5	123.6 (7)	C19–C18–C15	115.2 (5)
C3–C2–C1	108.4 (7)	C24–B20–C21	104.8 (4)
C7–C2–C1	123.1 (8)	C25–B20–C21	130.5 (6)
C7–C2–C3	128.4 (9)	C25–B20–C24	124.5 (6)
C4–C3–C2	109.3 (7)	B22–C21–B20	109.7 (5)
C8–C3–C2	125.9 (9)	C27–C21–B20	125.2 (5)
C8–C3–C4	124.6 (8)	C27–C21–B22	125.1 (5)
C5–C4–C3	106.9 (5)	C23–B22–C21	104.7 (4)
C9–C4–C3	125.8 (7)	C28–B22–C21	131.3 (5)
C9–C4–C5	127.3 (8)	C28–B22–C23	123.9 (5)
C4–C5–C1	107.0 (6)	C24–C23–B22	109.9 (4)
C10–C5–C1	126.0 (7)	C30–C23–B22	124.3 (4)
C10–C5–C4	126.9 (6)	C30–C23–C24	125.6 (5)
C15–B11–B12	106.0 (5)	C23–C24–B20	110.9 (4)
H1–B11–B12	125.1 (28)	C32–C24–B20	124.0 (5)
H1–B11–C15	128.9 (28)	C32–C24–C23	125.1 (5)
B13–B12–B11	101.8 (4)	C26–C25–B20	131.7 (10)
H2–B12–B11	139.7 (19)	C29–C28–B22	122.0 (7)
H2–B12–B13	118.2 (18)	C31–C30–C23	117.9 (6)
C14–B13–B12	107.1 (5)	C33–C32–C24	116.4 (6)
H3–B13–B12	128.2 (26)	C38–C34–C35	108.3 (8)
H3–B13–C14	124.6 (26)	C36–C35–C34	107.8 (8)
C15–C14–B13	112.4 (4)	C37–C36–C35	107.6 (8)
C16–C14–B13	127.6 (5)	C38–C37–C36	108.1 (8)
C16–C14–C15	119.9 (4)	C37–C38–C34	108.1 (8)
C14–C15–B11	112.7 (4)		

metal–ring distances are within normal ranges for multidecker boron-containing sandwich complexes; for example, the Co1–Co2 and Co1–Rh vectors (3.235 and 3.321 Å, respectively) are comparable to corresponding values in other diborole and carborane multidecker sandwich complexes.[2,9] The orientation of the C_2B_3 and C_3B_2 rings is decidedly asymmetric, as is evident in Figure 1; this is ascribed to relief of interligand alkyl–alkyl repulsions in the solid state. In solution, it can be assumed that the ligands rotate with respect to the metal–metal axes, although probably with some steric hindrance arising from the alkyl groups (the NMR spectra of **3a**, as well as those of **2a** and **4**, imply time-averaged mirror symmetry). The alkyl substitutents on the ring ligands are well ordered and exhibit no unusual orientations. There are no particularly short intermolecular contacts.

Synthesis of $(MeC_6H_4CHMe_2)Ru(Et_2C_2B_3H_3)Co(Et_2MeC_3B_2Et_2)CoCp$ (4). In a reaction similar to those described above, (cymene)ruthenium(II) chloride (cymene = *p*-isopropyltoluene) and $\mathbf{1}^{2-}$ combined to form brown solid **4** accompanied by several minor products, which were observed on TLC but were not characterized. The spectroscopic data on **4**, an air-stable solid, are closely similar to those of **2** and **3** and support a tetradecker structure as shown in Scheme I.

Electronic Structure and Redox Chemistry. The FT NMR spectra of the neutral complexes **2a**, **3a**, **3b**, and **4** are consistent with their formulation as diamagnetic 42-electron tetradecker sandwich systems in which the C_3B_2 and C_2B_3 (neutral) ligands contribute 3 and 2 electrons, respectively. On this basis, "slipped" or otherwise distorted geometry was not expected, as confirmed by the structural analysis of **3a** described above. One can also apply the polyhedral skeletal electron counting theory[13] to these species, which consist of seven-vertex pentagonal-pyramidal MC_2B_3Co and CoC_3B_2Co clusters joined at a common Co vertex.

---

(13) (a) Wade, K. *Adv. Inorg. Chem. Radiochem.* **1976**, *18*, 1. (b) Mingos, D. M. P. *Acc. Chem. Res.* **1984**, *17*, 311.

Table V. Cyclic Voltammetry Data[a]

compd	couple	$E^{\circ\,b}$	$\Delta E_p{}^c$	current ratio[d]	v^e	solvent
2a	+/0	+0.27	100	1	0.05–0.50	DME
	0/−	−1.32	100	1	0.05–0.50	DME
	−/2−	−2.23	100	1	0.05–0.50	DME
3a	2+/+	+1.20	*f*		0.1	DME
	+/0	+0.23	70	1	0.10–1.00	DME
	0/−	−1.34	65	1	0.10–1.00	DME
	−/2−	−2.25	70	~1	0.10–1.00	DME
3a	+/0	+0.27	65	1	0.1	CH_2Cl_2
4	2+/+	+1.19	*f*		0.1	DME
	+/0	+0.20	100	1	0.10–0.50	DME
	0/−	−1.39	100	1	0.10–0.50	DME
	−/2−	−2.28	115	~1	0.10–0.50	DME

[a] Data reported for glassy-carbon (GC) working electrodes at room temperature; electrolyte (Bu_4NPF_6) concentration = 0.1 M. [b] Volts vs aqueous SCE; E° reported for reversible systems and peak potentials ($E_p{}^{ox}$, $E_p{}^{red}$ for irreversible systems. [c] Separation in mV of anodic and cathodic peaks; values for reversible systems in DME exceeded 60–70 mV due to uncompensated *iR* drop. ΔEp for $Cp_2Fe^{0/+}$ is 100–110 mV under the same conditions. [d] Ratio is given as i_a/i_c for reductions and i_c/i_a for oxidations. [e] Scan rate in V s^{-1}. [f] Irreversible.

The total of skeletal electrons in each complex[14] is 32, corresponding to 16 electrons or $n + 1$ pairs per cluster, consistent with the observed closo geometry.

The formal oxidation state of cobalt and rhodium in each of these neutral, diamagnetic complexes is +3 while that of ruthenium is +2. Cyclic voltammetry measurements on **2a**, **3a**, and **4**, summarized in Table V, reveal in each case a reversible one-electron oxidation and two one-electron reductions in dimethoxyethane (DME), affording respectively the monocation, monoanion, and dianion. As expected, the 41-electron monocation and 43-electron monoanion are paramagnetic. The rhodium and ruthenium cations $\mathbf{3a}^+$ and $\mathbf{4}^+$ also exhibited irreversible oxidations to the respective dications.

Conclusions

The tetradecker complexes reported herein are the first such compounds to incorporate both C_2B_3 and C_3B_2 bridges and moreover are novel in having four different ring ligands. The stability of the diamagnetic 42-electron parent species, which makes it possible to handle them in air without degradation, is also reflected in their facile, reversible electrochemical oxidation and reduction to give paramagnetic monoanions and monocations. These properties, together with their syntheses by rational methods, augur well for further systematic extension of the stacking concept to even larger multimetal stacked sandwiches. In general, we anticipate that multidecker systems of this type will exhibit substantial electron delocalization, since closely related paramagnetic M^{II}–M^{III} cationic C_2B_3-bridged triple-deckers of the class $LM(R_2C_2B_3H_3)M'L'^+$ (L, L′ = arenes or cyclopentadienes) have been shown to be class III mixed-valence systems, i.e., exhibiting complete delocalization between metal centers.[15]

Experimental Section

Except where otherwise indicated, materials, instrumentation, and general procedures, including electrochemical methods, were identical with those described in the accompanying paper.[11] 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. The starting material $(Et_2C_2B_3H_5)Co(Et_2MeC_3B_2Et_2)CoCp$ (**1**) was obtained as described elsewhere.[11]

Synthesis of $(C_5Me_5)Co(Et_2C_2B_3H_2R)Co(Et_2MeC_3B_2Et_2)CoCp$ (2a, R = H; 2b, R = Cl). A solution of $[(C_5Me_5)CoCl]_2$ was obtained in vacuo by addition of $Li^+C_5Me_5^-$ (prepared from 0.3 mmol of *n*-butyllithium and 0.3 mmol of C_5Me_5H) to a dispersion of $CoCl_2$ in 50:50 DME/THF over a 30-min period, followed by stirring for 1 h at room temperature. In a separate vessel on the vacuum line, a solution of $\mathbf{1}^-$ was prepared from 140 mg (0.28 mmol) of **1** and an equimolar quantity of $LiHBEt_3$ in DME/THF at 0 °C. After 30 min of stirring, the dark olive green $\mathbf{1}^-$ solution was filtered in vacuo into the $[(C_5Me_5)CoCl]_2$ solution at −78 °C. The mixture was stirred at −78 °C for 1 h, after which it was stirred at 0 °C overnight. The solution was opened to the air and stirred for 10 min, the solvent was removed by rotary-evaporation, and the solid residue was taken up in hexane, giving a brown-green solution. The solution was filtered through silica, and the filtrate was eluted in 3:1 hexane/dichloromethane on a silica TLC plate, giving two brown bands, of which the first was **2a** (20 mg, 21% based on starting material consumed) and the second was the chlorine-substituted derivative **2b** (5 mg, 5%). A 70-mg quantity of **1** was recovered. Exact mass for **2a**: calcd for $^{59}Co_3{}^{12}C_{33}{}^{11}B_5{}^1H_{56}{}^+$, 684.2843; found, 684.2855. Exact mass for **2b**: calcd for $^{59}Co_3{}^{37}Cl^{12}C_{33}{}^{11}B_5{}^1H_{55}{}^+$, 720.2424; found, 720.2420.

Synthesis of $(C_5Me_5)Rh(Et_2C_2B_3H_2R)Co(Et_2MeC_3B_2Et_2)CoCp$ (3a, R = H; 3b, R = Cl). With use of the procedure used in the synthesis of **2a**, 1 equiv (0.30 mmol) of $LiHBEt_3$ was added to 150 mg (0.30 mmol) of **1** in 50:50 DME/THF at 0 °C, and the mixture was stirred for 1 h. A color change from green to brownish green was observed. The solution was cooled to −40 °C, and a second equiv of $LiHBEt_3$ was added. The solution was warmed with stirring over a 15-min period as the solution was warmed to 0 °C. The solution was cooled to −78 °C, and 35 mg (0.3 mmol) of $[(C_5Me_5)RhCl_2]_2$ was added in vacuo from a side-arm flask. The solution was stirred overnight, the solvent removed by evaporation, and the residue dissolved in hexane and filtered through a silica column, affording a green band, which was identified as recovered **1** (50 mg). Elution with dichloromethane gave a brown band, which was collected and chromatographed on silica TLC plates in 3:1 hexane/dichloromethane. Two brown bands were obtained, of which the first was **3a** (40 mg, 28% yield based on **1** consumed) and the second was **3b** (10 mg, 7%). Exact mass for **3a**: calcd for $^{103}Rh^{59}Co_2{}^{12}C_{33}{}^{11}B_5{}^1H_{56}{}^+$, 728.2566; found, 728.2564. Exact mass for **3b**: calcd for $^{103}Rh^{59}Co_2{}^{37}Cl^{12}C_{33}{}^{11}B_5{}^1H_{55}{}^+$, 764.2147; found, 764.2148.

Synthesis of $(MeC_6H_4CHMe_2)Ru(Et_2C_2B_3H_3)Co(Et_2MeC_3B_2Et_2)$-CoCp (4). To a green solution of **1** (120 mg, 0.25 mmol) in 50:50 DME/THF was added, via syringe, 1 equiv of $LiHBEt_3$ at 0 °C, followed by stirring for 30 min. The solution was cooled to −40 °C, and a second equivalent of $LiHBEt_3$ was added. The solution was warmed to 0 °C with stirring, following which the olive-colored solution was cooled to −78 °C and 75 mg (0.25 mmol) of $(MeC_6H_4CHMe_2)RuCl_2$ was added in vacuo from a sidearm tube. After being stirred at −78 °C for 1 h, the mixture was warmed to 0 °C and stirred overnight. The solvent was removed and the residue worked up as described in the preceding synthesis, affording two major bands, the first of which was recovered green **1** (50 mg) while the second was brown **4** (18 mg, 17% yield). Several minor bands were also observed but were not characterized. Exact mass for **4**: calcd for $^{104}Ru^{59}Co_2{}^{12}C_{33}{}^{11}B_5{}^1H_{55}{}^+$, 728.2487; found, 728.2483.

X-ray Structure Determination on 3a. The compound crystallizes in the space group $P2_1/c$, with a = 11.831 (6) Å, b = 17.967 (8) Å, c = 17.352 (8) Å, β = 107.22 (4)°, V = 3523 Å^3, Z = 4, and D(calcd) = 1.37 g cm^{-3}. Intensities were collected on a Siemens-Stoe four-circle diffractometer (Mo Kα, graphite monochromator, λ = 0.7107 Å) using the ω-scan technique. Of the 6441 measured unique reflections (2θ range 3–50°, *hkl* range −14,0,0 to 14,19,19), 4294 were considered observed ($I > 2\sigma(I)$). An empirical absorption correction was applied (crystal size 0.3 × 0.4 × 0.4 mm, μ(Mo Kα) = 13.3 cm^{-1}). The structure was solved by the heavy-atom method and refined via least-squares calculations with anisotropic thermal parameters for all non-hydrogen atoms. The three hydrogen atoms attached to boron were located and refined isotropically. The methyl units were refined as rigid groups. All other hydrogen atoms were included in calculated positions (C-H 0.95 Å), but only common isotropic temperature factors for each type were refined. The refinement (424 parameters) converged at R = 0.042 and R_w = 0.055 (w = 1.2)/ $(\sigma(F)^2 + 6 \times 10^{-4}F^2)$. The highest electron density in the final difference Fourier map was 0.7 e Å^{-3}. Scattering factors were taken from Cromer and Mann.[16] All calculations were carried out by using the programs

---

(14) In the two seven-vertex clusters present in each complex, the five CR units, five BH (BR) units, and two metal-ligand (cymene-Ru, CpCo, or Cp*Co) groups each contribute 3, 2, and 2 electrons, while the cobalt atom common to both clusters contributes a total of 3 electrons (assigning the other 6 electrons to its nonbonding orbitals[13]). It should be noted that this result is unaffected by the arbitrary assignment of zero metal oxidation states for electron-counting purposes.

(15) Merkert, J.; Davis, J. H., Jr.; Grimes, R. N.; Geiger, W. *Abstracts of Papers*, 199th National Meeting of the American Chemical Society, Boston, MA, April 1990; American Chemical Society: Washington, DC, 1990; INOR 92.

(16) Cromer, D. T.; Mann, J. B. *Acta Crystallogr.* **1968**, *A24*, 321.

SHELX76 and SHELXS86.[17]

Acknowledgment. This work was supported by NATO International Collaborative Research Grant No. 0196/85, by the Deutsche Forschungsgemeinschaft, Grant SFB247, and by National Science Foundation Grant No. CHE 8721657 (to R.N.G.). We thank Dr. James Davis for the unit resolution mass spectra.

Supplementary Material Available: Tables of thermal parameters and mean planes (2 pages); a table of calculated and observed structure factors (12 pages). Ordering information is given on any current masthead page.

---

(17) Sheldrick, G. M., SHELX76 program for crystal structure determination. Cambridge, England, 1976; SHELXS86. Göttingen, FRG, 1986.

Contribution from the Departament de Química, Universitat de les Illes Balears, Carretera de Valldemossa, km 7.5, 07071 Palma de Mallorca, Spain, Departament de Química Inorgânica, Universitat de Barcelona, Plaça Imperial Tarraco 1, 43005 Tarragona, Spain, and Departament de Cristal.lografia, Universitat de Barcelona, Martí i Franquès s/n, 08028 Barcelona, Spain

Synthesis and Characterization of Nickel(II) Complexes of Purine and Pyrimidine Bases. Crystal and Molecular Structure of *trans*-Bis(cytosine-O^2)bis(ethylenediamine)nickel(II) Bis(tetraphenylborate). An Unusual Metal Binding Mode of Cytosine

Gemma Cervantes,† Juan J. Fiol,† Angel Terrón,† Virtudes Moreno,*,‡ Juan R. Alabart,‡ Magdalena Aguiló,‡ Montserrat Gómez,§ and Xavier Solans§

Received March 8, 1990

Three nucleobase complexes $[Ni(en)_2(Ade)]Cl_2$ (**1**), $[Ni(en)_2(Hyp)]Cl\cdot 0.5CH_3OH\cdot H_2O$ (**2**) and $[Ni(en)_2(Cyt)_2][B(C_6H_5)_4]_2$ (**3**) (en = ethylenediamine; Ade = adenine; Hyp = hypoxanthine; Cyt = cytosine) have been prepared by reaction of $Ni(en)_2Cl_2$ and the corresponding purine or pyrimidine base in a methanol (**1**, **2**) or an ethanol–water (**3**) medium. The cytosine complex was obtained in the form of suitable crystals for X-ray crystallography. The complex crystallizes in the monoclinic space group $P2_1/a$ with a = 18.985 (4) Å, b = 9.685 (2) Å, c = 16.010 (4) Å, β = 113.23 (3)°, V = 2705 (2), and Z = 2. The structure was refined by a full-matrix least-squares technique on the basis of 2090 observed reflections ($I \geq 2.5\sigma(I)$) to a final R value of 0.061. Contrary to what could be expected, both unsubstituted cytosine bases are bound in the trans position exclusively via O(2) to the nickel atom. The octahedral coordination of Ni(II) is completed by four nitrogen atoms of two ethylenediamine molecules. Metal binding sites of the nucleobases in the three complexes are discussed in terms of their IR and electronic spectra and magnetic properties. Thermogravimetric data are in agreement with the stoichiometry and formulas proposed.

Introduction

The participation of transition-metal ions in the replication and transcription processes of DNA is well documented.[1] The influences of several divalent metal ions including Ni(II) on DNA structure unwinding and rewinding the double helix under appropiate conditions indicate that these metal ions can bind to both the bases and the phosphate groups.[2] Interest in the specific interactions between Ni(II) and nucleic acid constituents arises in part due to its high carcinogenity and accumulation indices (the ratio of the amount of atoms endogenously bound with calf thymus-DNA to their concentration in mammalian serum) as compared to other essential elements.[3] A considerable number of X-ray crystallographic studies on model compounds have provided information about nucleobase–metal interactions and have identified the ring nitrogen atoms as the preferred coordination sites.[4] However, very little structural information is available regarding the binding site of Ni(II) in unsubstituted purine and pyrimidine bases[5] and fewer studies have definitively shown direct involvement in metal binding of the exocyclic groups of these heterocycles.[6-8] Marzilli and co-workers have evaluated the role that exocyclic groups on nucleic acid bases play in determining both the structure and stability of metal complexes.[9] We have recently described structures of two octahedral Ni(II) ternary complexes with guanosine 5′-monophosphate and inosine 5′-monophosphate nucleotides. In both complexes, Ni(II) is surrounded by two water molecules, one ethylenediamine molecule, and two nucleotide molecules bound through N(7).[10] We report here the synthesis and characterization by spectroscopic methods of three nickel(II) nucleobase ternary complexes and the structural properties of the unusual cytosine complex. This is the first crystallographic evidence of monodentate O(2) binding in neutral unsubstituted cytosine.

Experimental Section

Analyses and Physical Measurements. Analytical results were carried out in a Carlo Erba model 1106 microanalyzer (Centro de Investigación y Desarrollo-CSIC, Depto. Q.O.B., Barcelona, Spain). Nickel content was determined by atomic absorption in a Perkin-Elmer 703 spectrophotometer. The infrared spectra were registered in the solid state (KBr pellets) on a PE 683 instrument with a PE 1600 infrared data station,

---

† Universitat Illes Balears.
‡ Department de Química, Universitat de Barcelona.
§ Departament de Cristal.lografia, Universitat de Barcelona.

(1) (a) Martin, R. B.; Mariam, Y. H. *Met. Ions Biol. Syst.* **1979**, *8*, 57–124. (b) Spiro, T. G., Ed. *Nucleic Acid-Metal Ion Interactions*; Wiley: New york, 1980; Vol. 1. (c) Marzilli, L. G. *Prog. Inorg. Chem.* **1977**, *23*, 255–378. (d) Hodgson, D. J. *Prog. Inorg. Chem.* **1977**, *23*, 211–254. (e) Eichhorn, G. L. In *Inorganic Biochemistry*; Eichhorn, G. L., Ed.; Elsevier: Amsterdam, 1973; Vol. 2, Chapters 33 and 34.

(2) Eichhorn, G. L. *J. Am. Chem. Soc.* **1968**, *90*, 7323.

(3) Andronikashvili, E. L.; Bregadze, V. G.; Monaselidze, J. R. *Met. Ions Biol. Syst.* **1988**, *23*, 331–357.

(4) (a) Swaminathan, V.; Sundaralingam, M. *CRC Crit. Rev. Biochem.* **1979**, *6*, 245–336. (b) Aoki, K. *Nippon Kessho Gakkarischi* **1981**, *23*, 309–327. (c) Pezzano, H.; Podo, F. *Chem. Rev.* **1980**, *80*, 365–401.

(5) Dubler, E.; Hanggi, G.; Bensch, W. J. *J. Inorg. Biochem.* **1987**, *29*, 269.

(6) (a) Marzilli, L. G.; Kistenmacher, T. J.; Rossi, M. *J. Am. Chem. Soc.* **1977**, *99*, 2797. (b) Beyerle-Pfnur, R.; Shollhorn, H.; Thewalt, U.; Lippert, B. *J. Chem. Soc., Chem. Commun.* **1985**, 1510–1511. (c) Aoki, K. *J. Chem. Soc., Chem. Commun.* **1976**, 748–749.

(7) (a) Charland, J. P.; Beauchamp, A. L. *Inorg. Chem.* **1986**, *25*, 4870. (b) Prizant, L.; Olivier, M. J.; Rivest, R.; Beauchamp, A. L. *J. Am. Chem. Soc.* **1979**, *101*, 2765. (c) Charland, J. P. *Inorg. Chim. Acta* **1987**, *135*, 191.

(8) (a) Guay, F.; Beauchamp, A. L. *J. Am. Chem. Soc.* **1979**, *101*, 6260. (b) Cartwright, B. A.; Goodgame, M.; Johns, K. W.; Skapski, A. C. *Biochem. J.* **1978**, *175*, 337. (c) Schollhorn, H.; Eisenmann, P.; Thewalt, U.; Lippert, B. *Inorg. Chem.* **1986**, *25*, 3384.

(9) (a) Marzilli, L. G.; Kistenmacher, T. J. *Acc. Chem. Res.* **1977**, *10*, 146. (b) Marzilli, L. G.; Steward, R. C.; Van Vuuren, C. P.; Castro, B.; Caradona, J. R. *J. Am. Chem. Soc.* **1978**, *100*, 3967. (c) Kistenmacher, T. J.; Rossi, M.; Marzilli, L. G. *Inorg. Chem.* **1979**, *18*, 240. (d) Szalda, D. J.; Kistenmacher, T. J.; Marzilli, L. G. *J. Am. Chem. Soc.* **1976**, *98*, 8371.

(10) Fiol, J. J.; Terrón, A.; Calafat, A. M.; Moreno, V.; Aguiló, M.; Solans, X. *J. Inorg. Biochem.* **1989**, *35*, 191.

0020-1669/90/1329-5168$02.50/0