ions, which previously was inferred by comparison with the corresponding rhodium and iridium derivatives, has been confirmed by a single-crystal X-ray diffaction study. The acetyl, which occupies an axial site, is terminally bonded to one cobalt atom unlike many polynuclear acyl complexes containing transition metals from earlier in the periodic table where coordination of the acyl oxygen to adjacent metal centers is often observed.[29] Despite the apparent stability of I toward CO loss and formation of a cluster containing a μ-O-CMe group,[30] reaction with $MeOSO_2CF_3$ in CH_2Cl_2, in an attempt to form a tetranuclear Fischer-type carbene complex, is slow and results in the formation of $Co_4(CO)_{12}$ as the only stable product. Other products could be detected in the solution IR of the reaction mixture but appeared to be thermally unstable and were not characterized.

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Registry No. I, 100682-41-5; $Li[CO_4(CO)_{11}C(O)Me]$, 100837-21-6; $CO_3(*CO)_9*COC(O)Me$, 100682-39-1; $Li[Co_3(CO)_{10}]$, 26248-45-3; MeCOCl, 75-36-5; $Co_3(CO)_9COC(O)Me$, 13682-05-8; $[PPN][Co(CO)_4]$, 53433-12-8; $Co_4(CO)_{12}$, 17786-31-1; Co, 7440-48-4.

Supplementary Material Available: Complete listings of positional parameters, bond lengths, anisotropic thermally parameters, and observed and calculated structure factors for $[PPh_4][Co_4(CO)_{11}C(O)Me]$ and bond angles for $[Co_4(CO)_{11}C(O)Me]^-$ (65 pages). Ordering information is given on any current masthead page.

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Indenylmetallacarboranes. 1. The 18-Valence-Electron Complex $3\text{-}(\eta^5\text{-}C_9H_7)\text{-}3,1,2\text{-}CoC_2B_9H_{11}$ and Comparative Molecular Structures of This Complex and $3\text{-}(\eta^5\text{-}C_5H_5)\text{-}3,1,2\text{-}CoC_2B_9H_{11}$

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The molecular structures of $3\text{-}(\eta^5\text{-}C_9H_7)\text{-}3,1,2\text{-}CoC_2B_9H_{11}$ (1) (two crystalline forms) and $3\text{-}(\eta^5\text{-}C_5H_5)\text{-}3,1,2\text{-}CoC_2B_9H_{11}$ (**2**) have been determined in the solid state. The conformation of the former is cisoid, and the η^5-bonded indenyl ligand is slipped such that the junction carbons are ca. 0.07 Å further from the metal atom. Both the conformation and the direction of slipping have been rationalized by the results of molecular orbital calculations at the extended Hückel level. 1 undergoes two reversible le reductions at $E_{1/2} = -0.8$ and -1.82 V. Crystals of 1α are monoclinic, $C2/c$, with $a = 23.882$ (4) Å, $b = 6.8415$ (24) Å, and $c = 22.824$ (6) Å, $\beta = 130.926$ (16)°, and $Z = 8$. With use of 4111 data collected at 185 K, the structure has been refined to 0.0273. The orthorhombic form 1β crystallizes in $P2_12_12_1$ with $a = 7.1142$ (6) Å, $b = 10.7926$ (15) Å, and $c = 19.1767$ (21) Å and $Z = 4$. A total of 1012 data collected at 291 K have been refined to 0.0393. For **2** the cell is also orthorhombic, $P2_12_12$, with $a = 15.8260$ (24) Å, $b = 10.2226$ (22) Å, and $c = 7.4928$ (19) Å and $Z = 4$. A total of 2948 low-temperature data have afforded a final R index of 0.0475.

Introduction

The slipping distortion in metallacarboranes has been a subject of considerable interest over the last few years. Structural and theoretical studies have identified two classes of metallacarborane that display the distortion, those of the type[1] $L_2M(C_2B_xH_{2+x})$ where L_2M is an angular 14e fragment and those of the type[1d,2] $M(C_2B_xH_{2+x})_2^{n-}$, i.e., symmetrical bis(carborane) complexes in which the electronic configuration of the metal atom is d^8 or greater.

The electronically induced translational slip of a metal fragment across an η-bonded ligand face is not, however, restricted to metallacarboranes. Notably it has also been observed in a number of structural studies of η^5-indenyl complexes,[3,4] and, moreover, facile η^5-η^3 slipping of the indenyl ligand has been suggested[4] to be the process re-

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sponsible for the substantially enhanced ligand substitution rates[5] of indenyl complexes relative to analogous cyclopentadienyl complexes.

Given the above, we reasoned that indenylmetallacarboranes would be potentially interesting molecules to study. The possibility clearly arises of selective slipping distortions (indenylmetal fragment across carborane ligand vs. metallacarborane fragment across indenyl ligand) when the formal number of valence electrons (ve's) associated with the metal atom is in excess of 18. There are, moreover, conformational possibilities in indenylmetallacarboranes that do not arise in analogous cyclopentadienylmetallacarboranes, and since a conformational change occurs in going from (cisoid) d^6 bis(carborane) complexes[6] to (transoid) $d^{>6}$ species,[2a–c,7] such changes are clearly linked to the slipping distortion.

Although cyclopentadienylmetallacarboranes are numerous[8] and have been known for many years (the first reported[9] metallacarborane was 3-(η^5-C_5H_5)-3,1,2-$FeC_2B_9H_{11}$), there are no references to indenylmetallacarboranes in the literature. In the first paper in this series we report the synthesis of the 18ve species 3-(η^5-C_9H_7)-3,1,2-$CoC_2B_9H_{11}$ (1) and its molecular structure as determined in two crystalline phases. This structure is important since it provides the reference against which to measure the slipping distortions in electron-rich indenylmetallacarboranes. We have also determined the structure of 3-(η^5-C_5H_5)-3,1,2-$CoC_2B_9H_{11}$ (2) to assess the consequence of replacement of η^5-C_5H_5 by η^5-C_9H_7. Finally, aspects of these observed molecular structures have been related to the results of extended Hückel molecular orbital (EHMO) calculations on idealized models of 1 and 2. When this work was nearing completion, an assessment of the conformational preferences and slipping distortions in indenyl complexes appeared[3j] which corroborates some of the structural details described herein.

Experimental Section

Synthesis. Standard Schlenk tube techniques were used throughout, and THF, hexane, and CH_2Cl_2 were dried and distilled under nitrogen prior to use. NMR spectra were recorded on Brucker WP80SY and WH360 spectrometers as $CDCl_3$ solutions at room temperature. ^1H chemical shifts were referenced with respect to those of residual solvent protons known relative to $SiMe_4$, and ^{11}B chemical shifts are relative to external $BF_3{\cdot}OEt_2$. For both, positive shifts are to high frequency. The IR spectrum was recorded as a CH_2Cl_2 solution on a Perkin-Elmer 598 spectrophotometer. Microanalyses were performed by the departmental service. The known complex 2 was prepared according to Jones and Hawthorne,[10] and $Tl_2C_2B_9H_{11}$ was synthesised according to Garcia et al.[11] Li[C_9H_7] was prepared from freshly distilled indene (B.D.H.) and BuLi (Aldrich) in THF. Cobalt tris(acetylacetonate) (Koch-Light) was used as supplied.

Synthesis of 3-(η^5-C_9H_7)-3,1,2-$CoC_2B_9H_{11}$ (1). $Co(acac)_3$ (1.17 g, 3.3 mmol) was dissolved in THF (8 mL) to give a dark blue-green solution in which solid $Tl_2C_2B_9H_{11}$ (1.80 g, 3.3 mmol) was suspended. A freshly prepared solution of Li[C_9H_7] (3.3 mmol) in THF was added dropwise and the resulting mixture stirred for 3 h at room temperature. After filtration, volatiles were removed under reduced pressure and the resulting solid was extreacted with CH_2Cl_2 (20 mL). Further filtration was followed by concentration and preparative TLC (silica gel, *n*-hexane:CH_2Cl_2, 1:1, as eluant) to afford yellow (R_f 0.8) and orange (R_f 0.4) bands. The orange band has been identified as 3-(η^5-C_9H_7)-3,1,2-$CoC_2B_9H_{11}$ (1): yield 57 mg, 5%; ν_{max} at 2530 cm^{-1} (B–H); $^1H\{^{11}B\}$ NMR δ 1.35 (1 H, BH), 1.49 (2 H, BH), 1.83 (2 H, BH), 2.5 (br, 2 H, carborane-CH), 2.85 (1 H, BH), 2.93 (2 H, BH), 3.13 (1 H, BH), 5.80 [t, 2.7 Hz, 1 H, H(22)], 6.30 [d, 2.7 Hz, 2 H, H(21), H(23)], 7.3–7.6 [m, 4 H, H(26)–H(29)]; $^{11}B\{^1H\}$ NMR δ –22.42 (1 B), –15.86 (2 B), –4.00 (2 B), –3.62 (2 B), 1.72 (1 B), 7.64 (1 B). Diffraction-quality *crystals* of 1 were obtained as a monoclinic phase (1α) from solvent diffusion of *n*-hexane into CH_2Cl_2 (4:1, room temperature) and as an orthorhombic phase (1β) similarly but in the presence of a small amount of THF.

Crystallographic Studies. Crystals of 2 were grown by diffusion of *n*-hexane into a CH_2Cl_2 solution (4:1) at room temperature. Single crystals of 2 and 1β were sealed in Lindemann capillaries, while a specimen of 1α was mounted on a thin glass fiber. Unit-cell dimensions were determined on an Enraf-Nonius CAD4 diffractometer (fitted with a ULT-1 low-temperature device) by the least-squares refinement of 25 centered diffractometer angles measured by using graphite-monochromated Mo K$\bar{\alpha}$ radiation, λ = 0.71069 Å. Table I lists crystal parameters, details of intensity data collection, and information pertinent to solution and refinement of the structure. Although the space group of 2 $P2_12_12$ is relatively rare, we are confident that there is no additional 2_1 screw axis parallel to *c* since the following *F* were measured: 001, 24.5 (4); 003, 21.0 (8); 005, 15.8 (14); 007, 35.6 (9); 009, 13 (3).

Data were collected by $\omega/2\theta$ scans in 96 steps at variable speeds dependent on an initial prescan. Regular remeasuring of check reflections revealed no significant crystal movement or decay. For 1α and 2 F_o values were empirically[13] corrected for absorption by using isotropically refined molecular models. After merging equivalent reflections only those with $F_o \geq 2.0\sigma(F_o)$ were retained for structure solution and refinement. In the case of 1α the centrosymmetric space group $C2/c$ was suggested by *E* statistics and confirmed by successful refinement.

The structures were solved by Patterson (1β and 2) or direct (1α) methods followed by iterative full-matrix least-squares refinement (on *F*) and ΔF synthesis. Data were weighted according to $w^{-1} = [\sigma^2(F_o) + gF_o^2]$. For 1$\alpha$ and 2 non-H atoms were refined anisotropically, and all H atoms were located and positionally refined. Although (isotropic) H atom thermal parameters were also refined for 1α, a common fixed value of 0.03 Å^2 was used for 2. For 1β, only the Co atom was refined anisotropically, indenyl H atoms were set in idealized positions (C–H = 0.96 Å), and carborane H atoms were positionally refined. Group isotropic thermal parameters were used for these H atoms, refining to 0.081 (9) (indenyl H) and 0.059 (6) Å^2 (cage H).

Refinements were cycled to convergence, and final ΔF syntheses were computed with all data. Programs and packages used were SHELX76[14] and SHELX84[15] for solution and refinement, DIFABS[13] for absorption correction, CALC[16] for molecular geometry calculations, and ORTEPII[17] for plotting. For Co, coefficients for an analytical form of the scattering curve were taken from ref 18, while inlaid[14] scattering factors were used for all other

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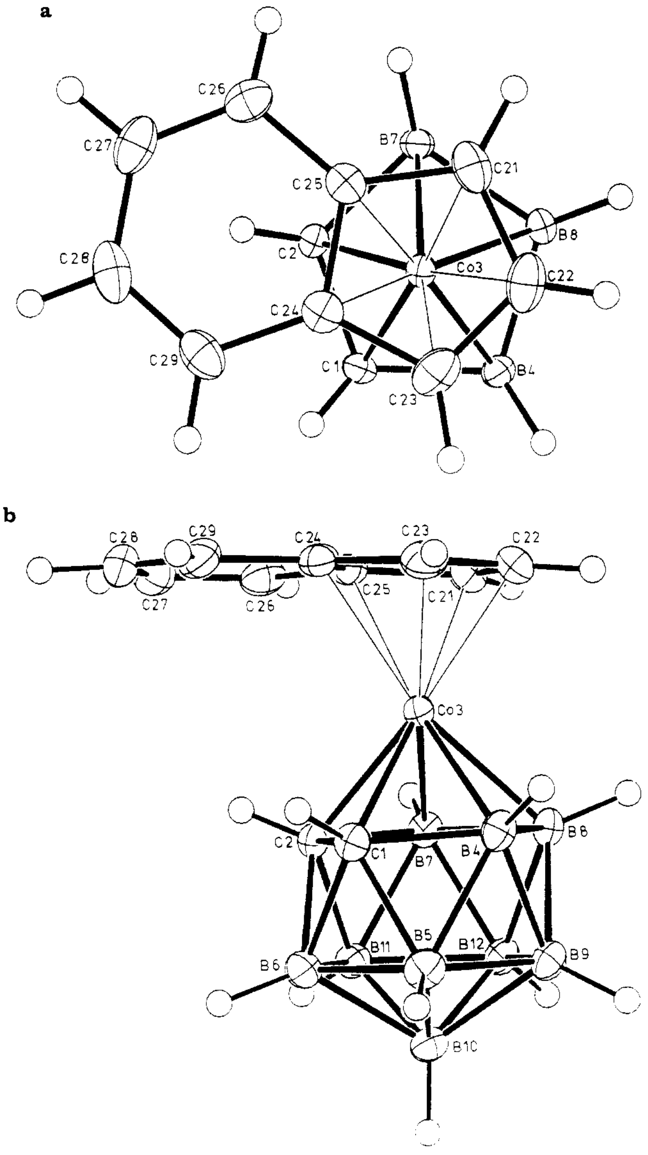

Figure 1. Perspective views of 1α: (a) projection perpendicular to lower B_5 ring, boron atoms in lower half of cage omitted for clarity; (b) projection parallel to B_5 ring. Thermal ellipsoids at 50% probability level except for H atoms, which are given a fixed radius of 0.1 Å for clarity. H atoms carry same number as B or C to which they are bound.

atoms. Refined positional parameters of 1α, 1β, and 2 appear in Tables II–IV, respectively.

Electrochemistry. Electrochemical measurements were made with a Princeton Applied Research 170 electrochemical system. Full compensation for ohmic losses across the cell was achieved by a normal three-electrode system and positive feedback circuitry. The ac measurements employed phase-sensitive detection. Polished Pt wires were used as working and auxilliary electrodes, and E values are quoted against an Ag/AgCl reference electrode. Measurements were made in dry, degassed CH_2Cl_2 by using $TBA{\cdot}BF_4$ as supporting electrolyte.

Theoretical Studies. EHMO calculations were made by using a locally modified version of ICON8[19] and the modified Wolfsberg-Helmholtz formula.[20] H_{ii}'s and orbital exponents are listed in Table V. Idealized models of 1 and 2 were used throughout, with B–B = C–B = C–C(cage) = 1.78 Å, C–C(hydrocarbon) = 1.40 Å, Co–C = Co–B = 2.05 Å, B–H = C–H(cage) = 1.15 Å, and C–H(hydrocarbon) = 1.08 Å.

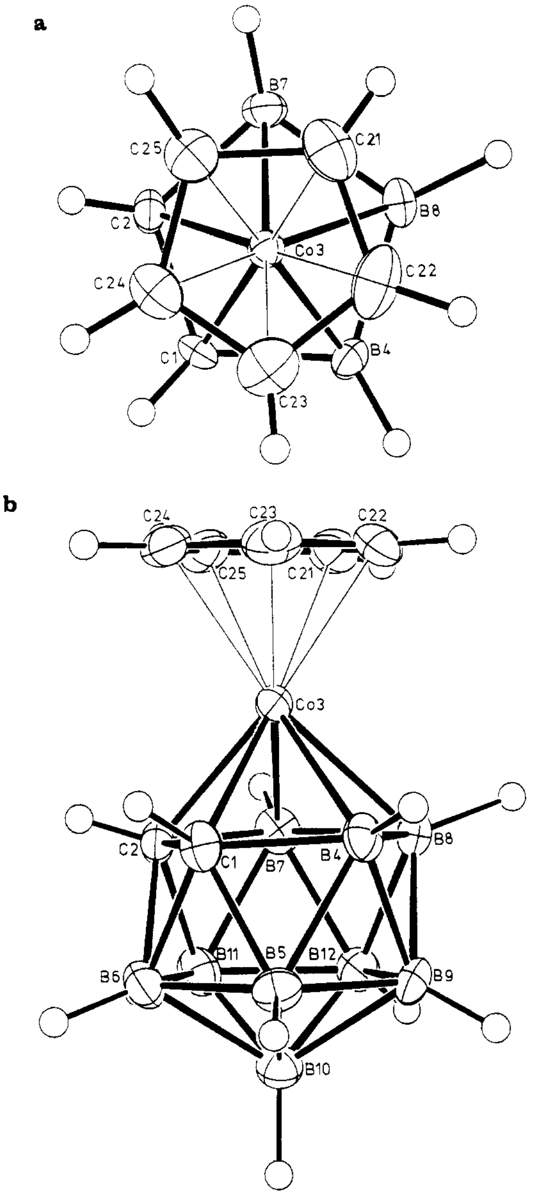

Figure 2. Perspective views of 2: projections as in Figure 1.

Results and Discussion

The first indenyl metallacarborane 3-(η^5-C_9H_7)-3,1,2-$CoC_2B_9H_{11}$ (1) has been synthesised in 5% yield (not optimized) by an analogous reaction to one[21] of several that have previously afforded 3-(η^5-C_5H_5)-3,1,2-$CoC_2B_9H_{11}$ (2). Crystals of 1 have been grown in two forms, α and β, and structural studies of both carried out. The determination for 1α has been performed carefully and at low temperature (we believe that the results are the most accurate yet reported for a metallacarborane), whereas data for 1β were collected less slowly and at ambient temperature since here we were only concerned with establishing if the molecular conformation differed from that in 1α. It turned out that it did not. Molecular volumes of the two forms at room temperature (359 and 368 Å^3, respectively) suggest that the α form is better packed. The indenyl ligands of adjacent molecules in this form are arranged in antiparallel pairs (related by the crystallographic C_2 axis) such that the dihedral angle between them is only 16° with atoms C(21), C(25), C(26), and C(27) in close contact (<3.7 Å). In 1β C(27) lies within 3.7 Å of C(24), C(25), and C(29) of

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Table I. Crystallographic Data for 1α, 1β, and 2

	1α	1β	2
formula	$C_{11}H_{18}B_9Co$	$C_{11}H_{18}B_9Co$	$C_7H_{16}B_9Co$
mol wt	306.5	306.5	256.4
color	orange-red	orange-red	yellow
habit	equant	columnar	lamellar
cryst size, mm	0.35 × 0.4 × 0.45	0.3 × 0.3 × 0.4	0.4 × 0.4 × 0.05
system	monoclinic	orthorhombic	orthorhombic
space group	$C2/c$	$P2_12_12_1$	$P2_12_12$
temperature, K	185 ± 1	291 ± 1	185 ± 1
a, Å	23.882 (4)	7.1142 (6)	15.8260 (24)
b, Å	6.8415 (24)	10.7926 (15)	10.2226 (22)
c, Å	22.824 (6)	19.1767 (21)	7.4928 (19)
β, deg	130.926 (16)	90	90
V, Å^3	2817.6	1472.4	1212.2
Z	8	4	4
D_x, g cm^{-3}	1.445	1.382	1.405
$F(0,0,0)$	1248	624	520
μ(Mo K$\bar{\alpha}$), cm^{-1}	11.9	11.4	13.7
θ range for setting angles, deg	14–15	12–15	14–16
θ range for data, deg	1–30	1–22	1–30
ω scan width, deg	0.8 ± 0.3 tan θ	0.8 ± 0.35 tan θ	0.8 ± 0.35 tan θ
scan speed range, deg min^{-1}	1.3–4.0	1.5–6.7	1.3–4.0
index ranges	$\pm h,\pm k,+l$	$+h,+k,+l$	$+h,\pm k,\pm l$
total data	8173	1078	6313
unique data, no.	4111	1078	3545
R_{merge}	0.0231		0.0273
X-ray exposure, h	185	14	98
data with $F_o \geq 2.0\sigma(F_o)$	3771	1021	2948
absorptn correctns	0.880–1.159		0.858–1.115
g	0.000443	0.014889	0.00092
R^{12}	0.0273	0.0393	0.0475
R_w^{12}	0.0363	0.0633	0.0492
S^{12}	1.131	1.252	1.057
no. variables, nv	262	125	202
max residual peak, e Å^{-3}	0.451	0.418	0.712
min residual trough, e Å^{-3}	−0.588	−0.482	−0.814

the molecule related by the 2_1 screw axis which is parallel to a at $y = {}^1/_4$ and $z = 0$, but here the dihedral angle is 42°.

Complex **2** has been known for many years,[22] but no structural study has previously been performed.[23] For comparison with the structure of **1**, we have determined the crystal structure of **2**, again carefully at low temperature. **2** is not isomorphous with 3-(η^5-C_5H_5)-3,1,2-$FeC_2B_9H_{11}$.[9b]

Figures 1 and 2 show comparative views of single molecules of **1α** and **2** and demonstrate the atomic numbering scheme used. Table VI lists selected interatomic distances for all three structures.

The crystallographic results demonstrate that in both **1** and **2** the metal atom is essentially symmetrically located above the C_2B_3 carborane ligand face and that the C_5 ring of the hydrocarbon ligand is staggered with respect to that face. The CoC_2B_9 icosahedra in all three structures have, within statistical error, identical corresponding bond lengths except for slight differences in Co(3)–C(1) and Co(3)–B(8) between **1α** and **2**. Moreover, in all three structures the cage carbon atoms are somewhat displaced toward the polyhedral center and the metal-bonded C_2B_3 face is accordingly buckled, as has been noted before.[14]

The folding of the C_2B_3 face of an icosahedral metallacarborane may be described by two angular parameters, ϕ and θ; the slip distortion Δ of a metal atom across that face is, however, best referred to the more regular B_5 pentagonal ring B(5,6,11,12,9).[1h] With the possibility of indenyl as well as cage slipping in **1** it is necessary to define slip and fold parameters for the hydrocarbon as well as the polyhedron. Thus ϕ^h, θ^h, and Δ^h refer to the former and ϕ^p, θ^p, and Δ^p the latter. For Δ^h no suitable reference plane exists, and here we simply use the best (least-squares) plane of η^5 ring.

A refinement of this geometrical description has recently been proposed,[3j] in which an additional parameter, σ, is introduced to define the direction of slip with respect to a suitable in-plane reference vector. For an indenyl ligand the reference vector is obviously from the centroid of the η^5 ring to C(22). In η^5-C_5H_5 complexes we propose that the reference vector be chosen from the ring centroid to that carbon atom (identified by a subscript following σ) made unique by the envelope folding. Moreover, the sign of σ is chosen to be positive when the angle taken from reference to slip vectors is anticlockwise viewed from the metal atom.

Table VII lists the slip and fold parameters for **1α**, **1β**, and **2**. There is excellent agreement between corresponding entries for **1α** and **1β**. In **2** the slip parameter Δ^p and the fold parameters ϕ^h and θ^h are so small as to render the σ values practically meaningless. A much greater hydrocarbon slip is noted for the indenyl complex, resulting in significantly longer Co–C(24,25) than Co–C(21-23) distances.

In both **1α** and **1β** the conformation of the indenyl six-membered ring with respect to the polyhedral carbon atoms is cisoid. This corresponds to the theoretical minimum energy conformation (α = 36°) obtained on rigid rotation of the C_9H_7 ligand about the Co–B(10) vector of the idealized model, as shown in Figure 3. The local minima and maxima of the curve are staggered and ec-

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[23] Several derivatives of **2** and of its iron analogue have, however, been subject to crystallographic studies. See, for example: Totani, T.; Nakai, H.; Shiro, M.; Nakagawa, T. *J. Chem. Soc., Dalton Trans.* **1975**, 1938. Zakharkin, L. I.; Kobak, V. V.; Yanovsky, A. I.; Struchkov, Yu. T. *J. Organomet. Chem.* **1982**, *228*, 119.

Table II. Fractional Coordinates of Atoms for 1α

	x	y	z
C(21)	0.39054 (6)	−0.08527 (22)	0.15197 (7)
C(22)	0.37263 (7)	0.10884 (24)	0.12341 (8)
C(23)	0.38623 (7)	0.23351 (20)	0.18100 (8)
C(24)	0.41776 (6)	0.11826 (18)	0.24882 (7)
C(25)	0.42046 (6)	−0.08045 (18)	0.23045 (7)
C(26)	0.44587 (6)	−0.23058 (19)	0.28628 (7)
C(27)	0.46710 (7)	−0.18098 (23)	0.35586 (8)
C(28)	0.46513 (8)	0.01635 (23)	0.37426 (8)
C(29)	0.44098 (7)	0.16376 (21)	0.32282 (8)
C(1)	0.23901 (6)	0.13308 (17)	0.16036 (7)
C(2)	0.26198 (6)	−0.09446 (17)	0.18739 (6)
Co(3)	0.31053 (1)	0.02141 (2)	0.15021 (1)
B(4)	0.21196 (7)	0.16937 (19)	0.07148 (7)
B(5)	0.14631 (7)	0.15540 (20)	0.08553 (8)
B(6)	0.18073 (8)	−0.00947 (20)	0.16195 (8)
B(7)	0.25176 (7)	−0.23537 (18)	0.11887 (7)
B(8)	0.21633 (7)	−0.06898 (20)	0.03990 (7)
B(9)	0.13043 (8)	0.02371 (19)	0.00889 (8)
B(10)	0.11146 (7)	−0.08675 (21)	0.06481 (8)
B(11)	0.18701 (7)	−0.24293 (19)	0.13374 (7)
B(12)	0.15529 (7)	−0.22582 (19)	0.03855 (7)
H(21)	0.3824 (9)	−0.204 (3)	0.1217 (11)
H(22)	0.3506 (10)	0.141 (3)	0.0731 (11)
H(23)	0.3775 (8)	0.3739 (24)	0.1752 (8)
H(26)	0.4457 (9)	−0.357 (3)	0.2716 (9)
H(27)	0.4847 (10)	−0.281 (3)	0.3938 (11)
H(28)	0.4777 (11)	0.048 (3)	0.4237 (12)
H(29)	0.4381 (8)	0.294 (3)	0.3340 (9)
H(1)	0.2636 (8)	0.2274 (22)	0.2006 (8)
H(2)	0.2980 (8)	−0.1164 (22)	0.2409 (9)
H(4)	0.2198 (8)	0.3095 (23)	0.0550 (9)
H(5)	0.1196 (8)	0.2863 (22)	0.0819 (8)
H(6)	0.1772 (11)	0.0213 (21)	0.2062 (11)
H(7)	0.2842 (8)	−0.3673 (23)	0.1370 (8)
H(8)	0.2206 (8)	−0.0917 (24)	−0.0035 (9)
H(9)	0.0872 (9)	0.071 (3)	−0.0492 (10)
H(10)	0.0594 (8)	−0.1095 (25)	0.0448 (8)
H(11)	0.1846 (9)	−0.3712 (25)	0.1599 (10)
H(12)	0.1263 (8)	−0.3413 (23)	−0.0015 (8)

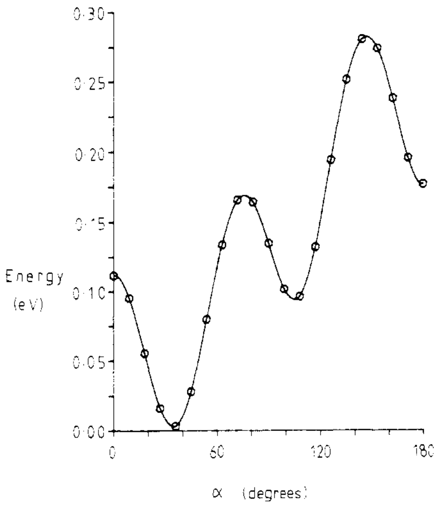

Figure 3. Plot of relative energy vs. α, the angle of rotation of the η^5-C_9H_7 ligand of 1 about the Co–B(10) axis.

Table III. Fractional Coordinates of Refined Atoms for 1β

	x	y	z
Co(3)	−0.15322 (9)	−0.07052 (6)	−0.39252 (3)
C(21)	0.0933 (9)	−0.5416 (6)	−0.0051 (3)
C(22)	−0.0683 (9)	−0.5228 (6)	−0.0470 (3)
C(23)	−0.0299 (10)	−0.4268 (6)	−0.0960 (3)
C(24)	0.1542 (8)	−0.3791 (5)	−0.08220 (25)
C(25)	0.2285 (9)	−0.4493 (5)	−0.0252 (3)
C(26)	0.4155 (10)	−0.4244 (6)	−0.0021 (3)
C(27)	0.5123 (10)	−0.3333 (6)	−0.0333 (3)
C(28)	0.4381 (10)	−0.2644 (6)	−0.0898 (3)
C(29)	0.2636 (10)	−0.2847 (6)	−0.1134 (3)
C(1)	0.2427 (8)	−0.5746 (5)	−0.2068 (3)
C(2)	0.4006 (8)	−0.6183 (5)	−0.1500 (3)
B(4)	0.0343 (10)	−0.6493 (7)	−0.1949 (4)
B(5)	0.1962 (10)	−0.6892 (7)	−0.2629 (4)
B(6)	0.4275 (12)	−0.6640 (7)	−0.2349 (4)
B(7)	0.3159 (11)	−0.7273 (6)	−0.0943 (4)
B(8)	0.0781 (11)	−0.7553 (7)	−0.1223 (4)
B(9)	0.0917 (11)	−0.8082 (7)	−0.2101 (4)
B(10)	0.3298 (11)	−0.8167 (6)	−0.2363 (3)
B(11)	0.4703 (11)	−0.7669 (7)	−0.1641 (4)
B(12)	0.2645 (11)	−0.8548 (7)	−0.1486 (4)
H(1)	0.234 (11)	−0.489 (8)	−0.225 (4)
H(2)	0.522 (10)	−0.548 (6)	−0.144 (4)
H(4)	−0.116 (11)	−0.607 (7)	−0.213 (4)
H(5)	0.158 (10)	−0.659 (6)	−0.313 (3)
H(6)	0.561 (11)	−0.632 (7)	−0.263 (4)
H(7)	0.366 (9)	−0.749 (6)	−0.040 (3)
H(8)	−0.038 (11)	−0.783 (6)	−0.089 (3)
H(9)	−0.041 (10)	−0.858 (6)	−0.233 (3)
H(10)	0.394 (11)	−0.892 (7)	−0.269 (4)
H(11)	0.650 (10)	−0.783 (6)	−0.152 (4)
H(12)	0.249 (11)	−0.954 (6)	−0.133 (4)

Table IV. Fractional Coordinates for 2

	x	y	z
C(21)	0.0823 (3)	0.3164 (5)	0.1817 (6)
C(22)	0.0902 (3)	0.3241 (5)	0.3696 (7)
C(23)	0.0913 (3)	0.1959 (5)	0.4369 (6)
C(24)	0.08421 (22)	0.1095 (4)	0.2956 (5)
C(25)	0.0779 (3)	0.1819 (5)	0.1349 (6)
C(1)	0.2846 (3)	0.1199 (4)	0.3613 (4)
C(2)	0.27585 (25)	0.1120 (4)	0.1438 (5)
Co(3)	0.18936 (3)	0.22517 (4)	0.26388 (5)
B(4)	0.2847 (3)	0.2766 (6)	0.4362 (4)
B(5)	0.3802 (3)	0.1816 (5)	0.4207 (5)
B(6)	0.37175 (23)	0.0745 (3)	0.2379 (6)
B(7)	0.2688 (3)	0.2646 (6)	0.0520 (5)
B(8)	0.27877 (22)	0.3766 (3)	0.2383 (6)
B(9)	0.3786 (3)	0.3439 (4)	0.3394 (6)
B(10)	0.43099 (23)	0.2203 (4)	0.2170 (5)
B(11)	0.3636 (3)	0.1700 (5)	0.0420 (5)
B(12)	0.3679 (3)	0.3361 (5)	0.1036 (6)
H(21)	0.088 (3)	0.386 (5)	0.110 (6)
H(22)	0.092 (3)	0.399 (5)	0.442 (6)
H(23)	0.094 (3)	0.179 (4)	0.545 (5)
H(24)	0.0843 (25)	0.018 (4)	0.326 (5)
H(25)	0.060 (3)	0.154 (4)	0.020 (5)
H(1)	0.259 (3)	0.044 (5)	0.425 (5)
H(2)	0.257 (3)	0.036 (5)	0.099 (5)
H(4)	0.2702 (25)	0.299 (4)	0.575 (5)
H(5)	0.409 (3)	0.152 (4)	0.540 (5)
H(6)	0.3935 (22)	−0.026 (3)	0.260 (6)
H(7)	0.2340 (25)	0.274 (4)	−0.074 (5)
H(8)	0.2556 (22)	0.494 (3)	0.218 (6)
H(9)	0.412 (3)	0.416 (4)	0.402 (6)
H(10)	0.5026 (24)	0.216 (4)	0.206 (4)
H(11)	0.375 (3)	0.123 (4)	−0.091 (5)
H(12)	0.397 (3)	0.405 (5)	0.034 (5)

lipsed forms, respectively. Note that $\alpha = 0$ is the cis-eclipsed form and $\alpha = 180°$ corresponds to the trans-staggered conformation. The average calculated barrier to rotation between staggered and eclipsed forms in 1 is 12.1 kJ mol^{-1}. This is more than twice the similarly calculated barrier in 2, 5.34 kJ mol^{-1}, and may represent increased repulsion between the H atoms on the upper polyhedral face and the π-electron density associated with the C–C bonds of the six-membered ring of 1 vs. the σ-electron density in the C–H bonds of 2. The time-averaged molecular symmetry suggested by the room-temperature NMR spectra of 1 is C_s. This does not distinguish between partial or complete rotation of the C_9H_7 ligand relative to the cage, and no significant change in the ^{1}H NMR spectrum was noted on cooling to −80 °C. The chemical shift of the carborane CH protons (2.50 ppm) lies ca. 1.7 ppm to low frequency of those[22] in 2; possibly this is because

Table V. Parameters Used in EHMO Calculations

orbital	H_{ii}, eV	ζ_1	ζ_2	c_1	c_2
Co 3d	−13.18	5.55	2.10	0.567 86	0.605 86
Co 4s	−9.21	2.00			
Co 4p	−5.29	2.00			
C 2s	−21.40	1.625			
C 2p	−11.40	1.625			
B 2s	−15.20	1.30			
B 2p	−8.50	1.30			
H 1s	−13.60	1.30			

Table VI. Comparison of Bond Lengths (Å)

	1α	1β	2
C(21)–C(22)	1.4164 (23)	1.417 (9)	1.415 (7)
C(21)–C(25)	1.4294 (21)	1.437 (8)	1.421 (6)
C(22)–C(23)	1.4147 (24)	1.426 (9)	1.404 (7)
C(23)–C(24)	1.4345 (22)	1.432 (8)	1.384 (6)
C(24)–C(25)	1.4365 (20)	1.431 (8)	1.417 (6)
C(24)–C(29)	1.4248 (22)	1.415 (8)	
C(25)–C(26)	1.4261 (20)	1.428 (9)	
C(26)–C(27)	1.3562 (22)	1.341 (9)	
C(27)–C(28)	1.4237 (25)	1.415 (10)	
C(28)–C(29)	1.3568 (24)	1.340 (10)	
Co(3)–C(21)	2.0211 (15)	2.034 (6)	2.030 (5)
Co(3)–C(22)	2.0298 (17)	2.023 (7)	2.028 (5)
Co(3)–C(23)	2.0502 (16)	2.037 (6)	2.044 (5)
Co(3)–C(24)	2.1240 (14)	2.122 (5)	2.055 (4)
Co(3)–C(25)	2.1055 (14)	2.118 (6)	2.059 (4)
Co(3)–C(1)	2.0182 (14)	2.010 (6)	1.991 (4)
Co(3)–C(2)	1.9955 (13)	2.007 (6)	2.005 (4)
Co(3)–B(4)	2.0623 (15)	2.061 (7)	2.054 (5)
Co(3)–B(7)	2.0622 (15)	2.065 (7)	2.065 (5)
Co(3)–B(8)	2.0885 (16)	2.084 (8)	2.106 (4)
C(1)–C(2)	1.6314 (19)	1.634 (8)	1.637 (6)
C(1)–B(4)	1.6962 (21)	1.703 (9)	1.697 (6)
C(1)–B(5)	1.6993 (22)	1.671 (9)	1.698 (6)
C(1)–B(6)	1.7193 (22)	1.717 (10)	1.724 (6)
C(2)–B(6)	1.7217 (22)	1.712 (10)	1.717 (6)
C(2)–B(7)	1.7131 (20)	1.700 (9)	1.709 (6)
C(2)–B(11)	1.6925 (20)	1.700 (10)	1.692 (6)
B(4)–B(5)	1.7969 (22)	1.792 (10)	1.800 (6)
B(4)–B(8)	1.8133 (2))	1.828 (10)	1.803 (6)
B(4)–B(9)	1.7835 (23)	1.786 (10)	1.792 (6)
B(5)–B(6)	1.7640 (24)	1.752 (11)	1.758 (6)
B(5)–B(9)	1.7737 (24)	1.796 (10)	1.768 (6)
B(5)–B(10)	1.7735 (23)	1.748 (10)	1.770 (6)
B(6)–B(10)	1.7682 (24)	1.789 (10)	1.768 (5)
B(6)–B(11)	1.7648 (23)	1.781 (11)	1.768 (6)
B(7)–B(8)	1.8062 (22)	1.801 (10)	1.812 (6)
B(7)–B(11)	1.7880 (22)	1.783 (10)	1.778 (7)
B(7)–B(12)	1.7719 (22)	1.765 (10)	1.772 (7)
B(8)–B(9)	1.7915 (23)	1.780 (10)	1.784 (6)
B(8)–B(12)	1.7940 (22)	1.779 (10)	1.783 (6)
B(9)–B(10)	1.7785 (24)	1.770 (10)	1.768 (6)
B(9)–B(12)	1.7885 (23)	1.776 (10)	1.777 (6)
B(10)–B(11)	1.7758 (23)	1.792 (10)	1.766 (6)
B(10)–B(12)	1.7839 (23)	1.793 (10)	1.766 (6)
B(11)–B(12)	1.7752 (22)	1.770 (10)	1.761 (7)

Table VII. Slip and Fold Parameters for 1α, 1β, and 2

	1α	1β	2
ϕ^p, deg	0.49	0.31	1.18
θ^p, deg	2.35	2.33	2.61
Δ^p, Å	0.028	0.034	0.005
σ^p, deg	−46.3	−39.6	89.5
ϕ^h, deg	2.78	2.81	0.46
θ^h, deg	1.03	1.05	0.20
Δ^h, Å	0.089	0.099	0.033
σ^h, deg	16.6	1.7	114.1_{25}

of the magnetic anisotropy of the six-membered indenyl ring[3j] and is consistent with 1 being mostly in the cisoid conformation in solution.

Faller and co-workers have recently rationalized the conformation and slipping distortion in a number of structurally studied indenyl complexes.[3j] They suggest that the trans influence of the functions opposite the indenyl ligand largely control the conformation. Only when the bridging atoms C(24,25) are opposite ligands of greatest trans influence can the relatively weak M–C(indenyl) bonding be compensated by stabilization of the otherwise underused pπ atomic orbitals in the six-membered aromatic ring. Previous analysis of the structures of bis(phosphine)platinacarboranes has suggested that the trans influence of boron in a metallacarborane is greater than that of carbon,[24] a phenomenon that may be understood in terms of the established[1e,h] localization of the frontier orbitals of a *nido*-carborane ligand onto the boron atoms in the open face. Thus the observed cisoid conformation of 1 is readily understood.

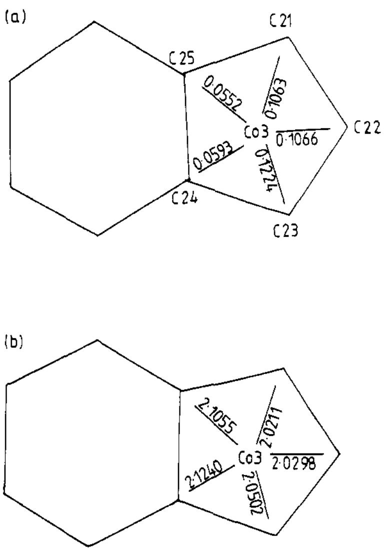

Figure 4. Comparison of (a) computed overlap populations and (b) observed bond lengths (Å) for the metal–hydrocarbon bonds of 1.

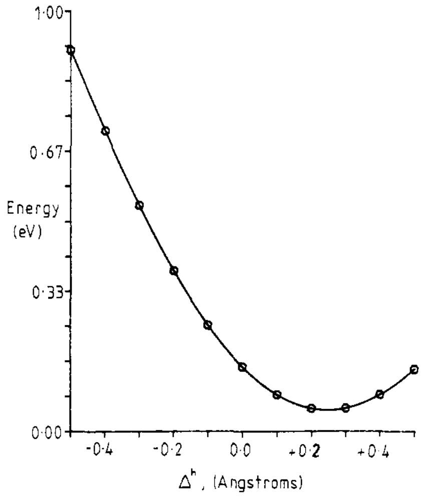

Figure 5. Plots of relative energy vs. Δ^h, the slipping parameter of the η^5-C_9H_7 ligand of 1.

EHMO-calculated overlap populations for 1 computed at α = 36° (Figure 4) successfully reproduce the relative weakness of the Co–C(24,25) bonds, and slipping of the indenyl ligand away from the facial boron atoms follows logically from these weak bonds. Figure 5 plots the energy of 1 vs. slip of the indenyl ligand with α = 36° and σ^h = 0° and suggests an optimum slip of Δ^h = 0.25 Å. This

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[24] Barker, G. K.; Garcia, M. P.; Green, M.; Pain, G. N.; Stone, F. G. A.; Jones, S. K. R.; Welch, A. J. *J. Chem. Soc., Chem. Commun.* **1981**, 652 and references therein.

prediction is in modest agreement with the observed values of 0.09 (1α) and 0.10 Å (1β).

Although 1 is the first reported example of an indenylmetallacarborane, there exist in the literature[11,25] examples of polycyclic (arene)ferracarboranes. Structural studies of 1-(η^6-Ar)-2,3-Et_2-1,2,3-$FeC_2B_4H_4$ (Ar = $C_{10}H_8$ and $C_{14}H_{10}$) have both shown cisoid conformations of the carbon atoms in the C_2B_3 face relative to the bridge atoms of the polycyclic arene. Clearly these apparent conformational preferences could be related to those in indenylmetallacarboranes. In addition, the naphthalene complex shows a distinct slipping distortion in the expected direction.[25] The enhanced reactivity toward arene substitution by CO or $P(OMe)_3$ in [3-(η^6-$C_{10}H_8$)-1,2-Me_2-3,1,2-$FeC_2B_9H_9$] over its C_6H_6 analogue has, moreover, been ascribed to naphthalene slippage.[11] It is interesting, however, that no slipping distortion is apparent in the structure of 1-(η^6-$C_{14}H_{10}$)-2,3-Et_2-1,2,3-$FeC_2B_4H_4$.[25]

Electrochemical studies on 1 reveal two reversible one-electron reductions at −0.8 and −1.82 V. The difference between these potentials is the same as that reported by Geiger et al.[26] for 2, suggesting that the reductions are metal-based. The electrochemical synthesis of the 19ve monoanion of 1 may prove to be feasible, but the formation of the 20ve dianion is clearly a less attractive proposition and the analogous system 3-(η^5-C_9H_7)-3,1,2-$NiC_2B_9H_{11}^-$ seems a more realistic target.

The 19- and 20ve analogues of 1 are important because of potential conformational changes, cf. bis(carborane) complexes, and selective or concerted slipping distortions. Complexes of this type will be subject to future contributions in this series.

Acknowledgment. We are very grateful to Dr. G. A. Heath for performing the electrochemical studies and for related discussion. D.E.S. thanks the S.E.R.C. for the award of a research studentship.

Registry No. 1, 100839-11-0; 2, 37100-20-2; $Co(acac)_3$, 21679-46-9; $Tl_2C_2B_9H_{11}$, 97102-40-4; Li[C_9H_7], 32334-19-3.

Supplementary Material Available: Tables of calculated H atom coordinates, thermal parameters, bond distances involving H atoms, bond angles, and least-squares plane data, packing diagrams, and lists of observed and calculated structure factors (69 pages). Ordering information is given on any current masthead page.

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Some Chemistry of Alkyl Complexes of Bis(1,2-bis(diphenylphosphino)ethane)iridium(I)

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New five-coordinate Ir(I) alkyl complexes have been prepared by the addition of LiR (R = CH_3, C_5H_5) to [Ir(dppe)$_2$]Cl (dppe = 1,2-bis(diphenylphosphino)ethane). IrMe(dppe)$_2$ is found to be very reactive toward acid, forming *cis*-IrH(Me)(dppe)$_2^+$, and toward CO and CO_2. In contrast, the cyclopentadienyl complex [Ir(dppe)$_2$]Cp is ionic and shows the reactivity of the Ir(dppe)$_2^+$ cation. That this complex is ionic is apparently not a result of steric constraints. A X-ray structural study of IrMe(dppe)$_2$ indicates that the coordination geometry about the Ir center is that of a distorted trigonal bipyramid with the Me group in an axial position; Ir–Me = 2.189 (8) Å.

Introduction

Transition-metal alkyl complexes play a large role in organo-transition-metal catalyzed transformations of organic molecules. These complexes are involved in such processes as hydrogenation,[1,2] hydroformylation,[3] olefin isomerization,[4] and polymerization.[5]

The square-planar, four-coordinate ions Ir(P–P)$_2^+$, P–P = dppe (1,2-bis(diphenylphosphino)ethane), dmpe (1,2-bis(dimethylphosphino)ethane), and depe (1,2-bis(diethylphosphino)ethane), have shown remarkable activity toward a variety of small molecules, including hydrogen, oxygen, carbon monoxide, hydrogen halides, and carbon dioxide.[6-11] But there appear to be no reports of the reactions of these ions with alkyl groups. Here we report the preparation, structure, and some reaction chemistry of Ir(Me)(dppe)$_2$; we also contrast the chemistry of the Me complex with the corresponding Cp complex, which is the ionic compound [Ir(dppe)$_2$]Cp.

Experimental Section

All reactions were performed under purified dinitrogen with the use of standard Schlenk-line techniques. Manipulations of

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(1) For a general survey of homogeneous catalysis see: (a) Parshall, G. W. "Homogeneous Catalysis"; Wiley-Interscience: New York, 1980. (b) Schrauzer, G. N. "Transition Metals in Homogeneous Catalysis"; Marcel Dekker: New York, 1971. (c) Taqui Kahn, M. M.; Martell, A. E. "Homogeneous Catalysis by Metal Complexes"; Academic Press: New York, 1974.

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