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closo-3-(η^3-4,6-Dimethylbicyclo[3.3.0]oct-1-en-2-yl)-1,2-dimethyl-3,1,2-dicarbollyliridium with an agostic C—H...Ir bond

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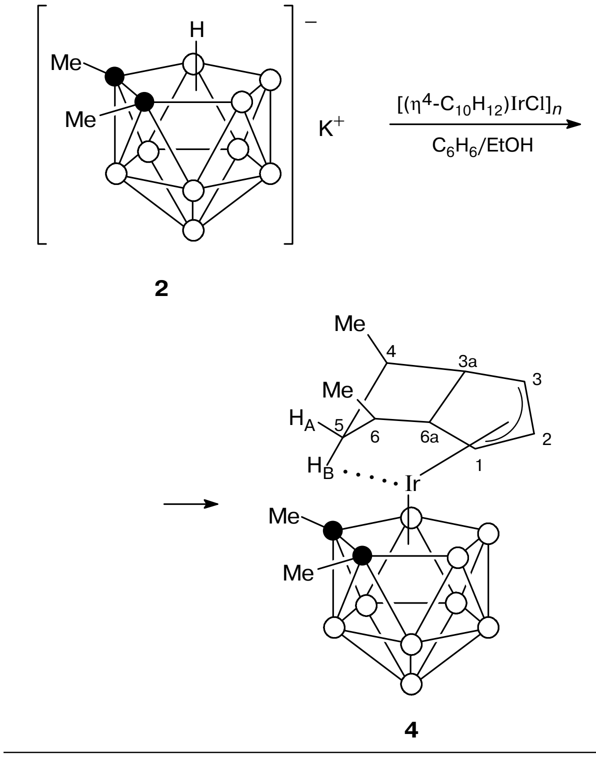
Recently, we have developed a procedure for the synthesis of *closo*-metallacarboranes of rhodium and iridium with cyclodiene-based π-ligands,[1] which allowed us to substantially extend the range of *closo*-iridacarborane complexes.[1,2] Most of the known compounds of this family contain the hydride and phosphine ligands[3—8] or the η^5-Cp* ligands[9] at the metal atom. The procedure is based on the reactions of potassium salts of *nido*-dicarbaundecaborates [*nido*-7-R^1-8-R^2-$C_2B_9H_{10}$]$^-$ (R^1 and R^2 = H, Alk, or ArAlk) with the [(η^4-diene)MCl]$_2$ dimers (**1**) in a C_6H_6—EtOH mixture. The reactions of the rhodium or iridium complexes containing the COD ligands afford *closo*-(η-enyl/dienyl)metallacarboranes. In the resulting complexes, the organic ligands can be bound to the metal center in the η^3-, $\eta^{2,3}$-, or $\eta^{1,2}$-coordination mode,[2] whereas the C_8 skeleton remains unchanged in all cases without either opening[10,11] or closure[12] of the ring.



Using complexes **1** (diene = dicyclopentadiene ($C_{10}H_{12}$); M = Rh (**a**)[13] or Ir (**b**)[14]) as the starting compounds, we found that the reaction of rhodium dimer **1a** with [*nido*-7,8-Me_2-7,8-$C_2B_9H_{10}$]$^-$K$^+$ (**2**) gave rise to the $\eta^{1,2}$-dicyclopentenyl complex with an agostic C—H...Rh interaction, *viz*., *closo*-3,3,3-($\eta^{1,2}$-$C_{10}H_{13}$)-1,2-Me_2-3,1,2-$RhC_2B_9H_9$ (**3**),[1] whereas the reaction of complex **1b** with **2** was accompanied by the deep transformation of the dicyclopentadiene ligand to form *closo*-3-(η^3-$Me_2C_8H_9$)-1,2-Me_2-3,1,2-$IrC_2B_9H_9$ (**4**), which also contains an agostic C—H...Ir bond.

Although complex **4** was prepared in low yield (22%), the result obtained is of fundamental importance be-

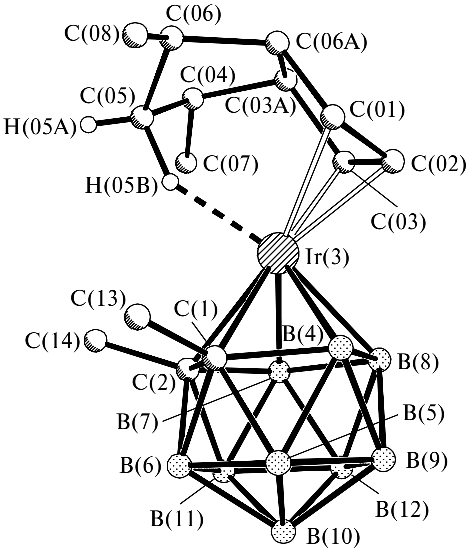


Fig. 1. Molecular structure of complex **4**. Selected bond lengths (*d*):

Bond	*d*/Å	Bond	*d*/Å
Ir(3)—C(01)	2.230(2)	C(05)—H(05b)	1.15(3)
Ir(3)—C(02)	2.134(3)	Ir(3)—C(1)	2.210(2)
Ir(3)—C(03)	2.170(2)	Ir(3)—C(2)	2.171(3)
Ir(3)—H(05b)	1.89(4)	Ir(3)—B(4)	2.160(3)
C(01)—C(02)	1.420(4)	Ir(3)—B(7)	2.242(2)
C(02)—C(03)	1.428(4)	Ir(3)—B(8)	2.162(3)
C(05)—H(05a)	0.81(3)		

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cause the transformation of the η^4-dicyclopentadiene ligand into the η^3-pentalenyl ligand in the coordination sphere of the metal atom was observed for the first time.

The structure of complex **4**, the mode of coordination of the hydrocarbon ligand to the Ir atom, and the presence of the agostic bond were established by X-ray diffraction analysis (Fig. 1). Crystals of **4** are monoclinic, space group $P2_1/n$, at 100 K a = 8.459(2), b = 13.326(3), c = 17.207(3) Å, β = 103.64(3)°, V = 1884.8(7) Å^3, Z = 4, M = 487.87, d_{calc} = 1.719 g cm^{-3}, μ(MoKα) = 70.75 cm^{-1}, F(000) = 944. The intensities of 5755 independent reflections (R_{int} = 0.0388) were measured on an automated Bruker SMART 1000 CCD diffractometer (MoKα radiation, λ = 0.71073 Å, graphite monochromator, T = 100 K, $2\theta_{\text{max}}$ = 62°, the ω scan step was 0.3°, the time per scan step was 10 s). The positions of all hydrogen atoms were revealed from difference electron density syntheses and included in the refinement with isotropic thermal parameters. The final R factors were as follows: R_1 = 0.0229 (based on F for 5209 observed reflections with $I > 2\sigma(I)$) and wR_2 = 0.0509 (based on F^2 for all reflections); 337 parameters were refined. All calculations were carried out using the SHELXTL-97 program package.[15]

The results of X-ray diffraction analysis of complex **4** are in complete agreement with the data from elemental analysis, mass spectrometry, and ^{1}H, ^{13}C, and ^{11}B NMR spectroscopy (the assignments of the signals in the ^{1}H and ^{13}C NMR spectra of complex **4** were made based on the correlation 2D ^{1}H-^{13}C NMR spectrum). The ^{1}H, ^{13}C, and ^{11}B NMR spectra were recorded on a Bruker AMX-500 spectrometer (^{1}H, 500.13 MHz; ^{13}C, 125.77 MHz; ^{11}B, 160.46 MHz) in CD_2Cl_2.

***closo*-3-(η^3-4,6-Dimethylbicyclo[3.3.0]oct-1-en-2-yl)-1,2-dimethyl-3,1,2-dicarbollyliridium (4).** ^{1}H NMR, δ: 5.91 (t, 1 H, H(2), J = 3.0 Hz); 5.54 (dd, 2 H, H(1), H(3), J_1 = 3.0 Hz, J_2 = 1.5 Hz); 3.56 (dt, 1 H, H(5a), J_{gem} = 12.8 Hz, ^3J = 2.9 Hz); 3.29 (m, 2 H, H(3a), H(6a)); 2.66 (s, 6 H, 2 Me$_{\text{carb}}$); 1.71 (m, 2 H, H(4), H(6)); 1.27 (d, 6 H, 2 Me, J = 6.7 Hz); −5.82 (dt, 1 H, H(5b), J_{gem} = 12.8 Hz, J_{t} = 11.1 Hz). ^{13}C{^{1}H} NMR, δ: 108.82 (C(2)); 81.35 (2 C$_{\text{carb}}$); 81.19 (C(5)); 80.83 (C(1), C(3)); 54.60 (C(3a), C(6a)); 44.42 (C(4), C(6)); 34.04 (2 Me$_{\text{carb}}$); 16.78 (2 Me). ^{11}B NMR, δ: 3.42 (1 B, $J_{^{11}\text{B},^1\text{H}}$ = 146 Hz); −6.27 (1 B, $J_{^{11}\text{B},^1\text{H}}$ = 159 Hz); −7.70 (2 B, $J_{^{11}\text{B},^1\text{H}}$ = 158 Hz); −13.24 (2 B, $J_{^{11}\text{B},^1\text{H}}$ = 140 Hz); −15.76 (2 B, $J_{^{11}\text{B},^1\text{H}}$ = 147 Hz); −16.50 (1 B, $J_{^{11}\text{B},^1\text{H}}$ = 141 Hz). Found (%): C, 34.69; H, 6.14; B, 19.89. $C_{14}H_{30}B_9Ir$. Calculated (%): C, 34.46; H, 6.15; B, 19.94. FAB MS, m/z: 488 [M]$^+$.

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