# Letters to the Editor

## Synthesis of the first ruthenium-iridium bimetallacarborane cluster

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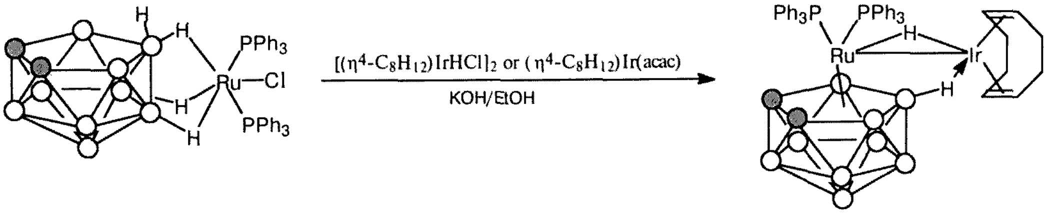
Binuclear metallacarborane clusters containing unusual B—H...M aghostic bonds (where M is a metal) or new B—M—H σ-bonds with the terminal hydride at the metal atom (formed therefrom on intramolecular oxidative addition) attract considerable attention in the chemistry of metallacarboranes.[1,2] In this family of carborane clusters of platinum group metals, compounds incorporating Rh—Rh,[3,4] Rh—Ir,[4] Rh—Ru,[5] and Rh—Pt,[6,7] are already known, and their properties are being intensely studied. In the present paper, we synthesized the first ruthenium—iridium bimetallacarborane $(\eta^4\text{-}C_8H_{12})IrRu(\mu\text{-}H)(PPh_3)_2(\eta^5\text{-}C_2B_9H_{11})$ (**1**), which is an electron-deficient cluster (32 valence electrons) wherein the bond is formed due to B—H...Ir aghostic interaction and to formation of an Ru—H—Ir bridged system.

We found that the reaction of *exo-nido*-5,6,10-$[Cl(Ph_3P)_2Ru]$-5,6,10-$(\mu\text{-}H)_3$-10-H-7,8-$C_2B_9H_8$ (see Ref. 8) with an equimolar amount of dimeric complex $[(\eta^4\text{-}C_8H_{12})IrHCl]_2$ (**2**) in ethanol in the presence of excess KOH at 22 °C followed by recrystallization of the product from a $CH_2Cl_2$—$C_6H_{14}$-*n* mixture affords mixed-metal cluster **1** in 74 % yield. Analytically pure complex **1** was obtained, though in a lower yield (55 %), when starting dimer **2** in the above reaction was replaced by $(\eta^4\text{-}C_8H_{12})Ir(acac)$ (Scheme 1).

The composition of cluster **1** was confirmed by the data of elemental analysis. Found (%): C, 50.11; H, 5.11; B, 8.73; P, 5.63. $C_{46}H_{54}B_9P_2RuIr \cdot 0.5CH_2Cl_2$. Calculated (%): C, 50.68; H, 5.00; B, 8.83; P, 5.63. The structure of complex **1** is in good agreement with the data of $^1H$, $^{13}C$, $^{31}P$, and $^{11}B$ NMR spectroscopy and with the IR spectra. For example, the $^1H$ NMR spectrum of cluster **1** in $C_6D_6$ exhibits two high-field signals with a 1 : 1 integral intensity ratio. These are a broad quadruplet-like signal at −2.95 ppm ($J_{B-H}$ ≈

**Scheme 1**



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80 Hz) and a narrow triplet at −10.70 ppm ($J_{\mathrm{H-P}}$ = 19.2 Hz), which were assigned to the protons of B—H...Ir and Ru—H—Ir fragments, respectively. The signals of the H and C atoms of the coordinated diene ligand are exhibited in the $^1$H NMR spectrum (in $C_6D_6$) and $^{13}C\{^1H\}$ NMR spectrum (in $CD_2Cl_2$) at $\delta$ 4.88 (br.s, 4 H, CH=CH), 2.06 (m, 4 H, $CH_2$), 1.54 (br.q, 4 H, $CH_2$) and at $\delta$ 67.3 (s, CH=CH), 32.0 (s, $CH_2$); the signals corresponding to the carborane ligand are observed as separate broadened singlets at $\delta$ 2.84 and 41.2, respectively. The signals of the phenyl groups of the phosphine ligands are observed in their normal regions: at $\delta$ 6.90—7.90 (m, 30 H) in the $^1$H NMR spectra and at $\delta$ 127.6—137.3 ($C_o$, $C_m$, $C_p$, and $C_{\mathrm{key}}$) in the $^{13}$C NMR spectra. The IR spectrum of cluster **1** (pellets with KBr) exhibits a characteristic ν(B—H) band at 2580 cm$^{-1}$ and ν(C—H) band at 3070 cm$^{-1}$; no absorption band corresponding to the bridged hydride was found in the spectrum. The magnetic equivalence of the carbon and hydrogen nuclei in the 1,5-cyclooctadiene and carborane ligands as well as the two equivalent phosphine ligands at the Ru atom [$^{31}P\{^1H\}$ NMR spectrum ($C_6D_6$), $\delta$: 50.42 (s)] indicate the presence of symmetry in cluster **1** and suggests that the B(8) atom of the pentagonal open plane of the carborane cage participates in the B—H...Ir aghostic interaction. The typical low-field signal at +6.45 ppm ($J_{\mathrm{B-H}} \approx$ 90 Hz) in the $^{11}$B NMR spectrum of the cluster in $CH_2Cl_2$ evidences the existence of this interaction; the signals of the other boron atoms of the carborane ligand are observed in a substantially higher field, namely, in the region from −8.0 to −25.0 ppm.

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# 1,3-Dipolar tris-cycloaddition of *tert*-butylphosphaacetylene to 2,4,6-triazido-3-chloro-5-cyanopyridine

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It has been shown recently that 1,3-cycloaddition even of such a reactive dipolarophile as norbornene to 2,4,6-triazido-3-chloro-5-cyanopyridine (**1**) occurs regioselectively to the azido group at position 4 of the pyridine cycle.[1,2] It has been established that considerable weakening of the properties of the α-azido groups in compound **1** as 1,3-dipoles is caused by their strong conjugation with the electron-acceptor pyridine system.[3] In this connection, study of the reaction of **1** with *tert*-butylphosphaacetylene (**2**) as the dipolarophile with

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