Fullerene and Carborane in One Coordination Sphere: Synthesis and Structure of a Mixed η^2-C_{60} and σ-Carboranyl Complex of Iridium

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The first representative of metal complexes containing two different polyhedral clusters (namely, a fullerene and a carborane) as ligands in the same coordination sphere of the metal atom, $[(\eta^2\text{-}C_{60})Ir(o\text{-}HCB_{10}H_9CCH_2PPh_2\text{-}B,P)(t\text{BuNC})_2]$ (**II**), was synthesized in the reaction of C_{60} with the metallacyclic carboranyliridium dihydride complex $[Ir(H)_2(o\text{-}HCB_{10}H_9CCH_2PPh_2\text{-}B,P)(PPh_3)(L)]$ (L = CO or PPh_3) by reflux in toluene in the presence of 2 equiv. of *t*BuNC. The compound obtained was characterized by analytical and spectroscopic (UV, IR, ^1H and ^{31}P NMR) data. The molecular structure of complex **II** was determined by single-crystal X-ray diffraction analysis, which showed that the most interesting structural feature of **II** is the distortion of the iridacyclopropane moiety due to the strong *trans* influence of the B-σ-carboranyl fragment.

Most of the currently obtained metal complexes of fullerenes are known to possess η^2-coordination due to both electron-acceptor properties and the weakly conjugated polyene character of the fullerene molecule. However, all the complexes known to date exhibit a "symmetrical" η^2-coordination, where the metal atom is equidistant from the carbon atoms of the double bond because of the *trans* arrangement of either identical ligands or ligands having similar *trans* influence with respect to these carbon atoms.[1,2] With the ligands substantially different in there *trans* influence, one would, however, expect the formation of metal complexes of fullerene with "nonsymmetric" or slip-distorted η^2-coordination. The aim of this work was to attempt the synthesis of the first representatives of slip-distorted metal η^2-complexes of fullerene.

The initial metal complexes were *cis*-dihydridoiridium complexes $[Ir(H)_2(o\text{-}HCB_{10}H_9CCH_2PPh_2\text{-}B,P)(PPh_3)(L)]$ (**Ia**, L = PPh_3; **Ib**, L = CO) chelated to the B-σ-carboranylphosphane fragment recently obtained by us.[3] Reductive elimination of a dihydrogen molecule from these complexes can result in an unsaturated Ir^+ intermediate capable of forming corresponding adducts with the electron-acceptor fullerene molecule. In addition, the bulky B-σ-carboranyl fragment should occupy a *trans* position with respect to the fullerene ligand that has a much stronger *trans* influence compared to phosphane.

We found that dihydrides chosen by us do not react with fullerene upon heating in toluene or chlorobenzene. This seems to be due to their unusual thermal stability, since these compounds do not undergo reductive elimination of dihydrogen, even upon heating in toluene or decane. It is well known that the presence of electron-acceptor ligands in the coordination sphere of a metal atom promotes the reductive elimination. To this end, we used the *t*BuNC ligand that combines the strong π-acceptor and σ-donor properties and can stabilize the complexes of transition metals both in low and high oxidation states. Such stabilisation is of great importance both for the reductive elimination and, especially, for the coordination of the intermediate metal complex to the electron-accepting fullerene molecule in the next stage of reaction. Indeed, in the presence of 2 equiv. of *t*BuNC, the dihydrido complexes **Ia** or **Ib** react smoothly with fullerene C_{60} in refluxing toluene by replacement of the triphenylphosphane or carbonyl ligand, respectively, by isocyanide with elimination of an H_2 molecule. The novel $(\eta^2\text{-}C_{60})Ir$ complex containing the B-σ-carboranyl group incorporated into the chelate metallacycle, viz. $[(\eta^2\text{-}C_{60})Ir(o\text{-}HCB_{10}H_9CCH_2PPh_2\text{-}B,P)(t\text{BuNC})_2]$ (**II**), was obtained in a high yield as shown in Scheme 1.

The complex obtained was characterized by elemental analysis as well as UV, IR, and ^1H and $^{31}P\{^1H\}$ NMR spectroscopy. Since the molecule contains no other chromophore groups, the UV/Vis spectrum of **II** is typical for η^2-complexes of C_{60} fullerene with transition metals[4,5] exhibiting characteristic bands at 258, 329, 400, 453, and 717 nm. The IR spectrum contains stretching vibration bands of the B−H bonds of the carborane moiety (at 2576 cm^{-1}), the C−C bonds of the fullerene cage (at 1432 and 1184 cm^{-1}),

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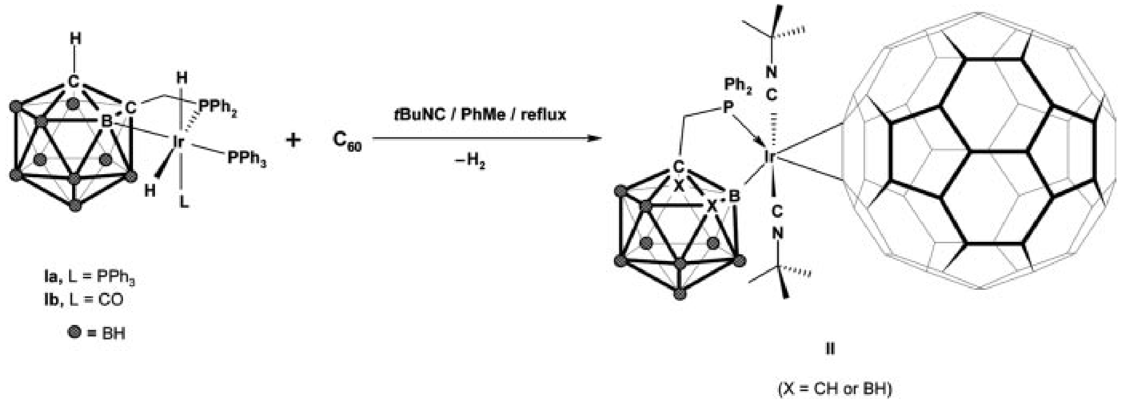

Scheme 1

and one strong, narrow absorption band of the isocyanide ligands [ν(NC)] at 2168 cm^{-1} corresponding to their mutual *trans* positions (*cis* arrangement of the ligands would require two IR-active stretching vibration bands) that completely determines the arrangement of all the ligands around the metal atom. The $^{31}P\{^{1}H\}$ NMR spectrum exhibits a singlet at $\delta_P = 37.8$ ppm, which points to the existence of only one isomer with η^2-coordination of the fullerene fragment at the 1−2 bond. Otherwise (coordination at the 1−9 bond), we would observe the formation of two geometric isomers (for discussion, see, for example, refs.[5,6]). As in the initial dihydride complexes **Ia** and **Ib**, the molecular chirality of the carborane polyhedron is responsible for inequivalence of two *tert*-butyl isocyanide ligands, which manifests itself as two singlets from protons of the corresponding *tert*-butyl groups in the ^{1}H NMR spectrum. Similarly, protons of the methylene group in the five-membered metallacycle are inequivalent and their signals appear as an ABX system with the coupling constants ^2J(HH) = 16.2 Hz and ^2J(HP) = 6.6 and 9.6 Hz. These results are consistent with the proposed structure of compound **II** when taken together.

The molecular structure of this complex, determined by single-crystal X-ray diffraction, is presented in Figure 1. Selected bond lengths and bond angles are listed in Table 1. There are four solvate toluene molecules for each of the complex molecules in the crystal of the **II**·4C_6H_5Me solvate whose crystal packing is characterized by the absence of specific interactions. All intermolecular distances correspond to the conventional van der Waals contacts. The carborane moiety involved in the five-membered metallacycle Ir(1)P(1)C(61)C(01)B(3) is bound to the iridium atom by a σ-bond through the boron atom in position 3(6) [Ir(1)−B(3) 2.101(5) Å]. The metallacycle adopts a flattened envelope conformation, with the P(1) atom deviating by 0.43 Å from the plane of the other four atoms in the cycle. A feature of the carborane ligand in complex **II** is disordering of the boron and carbon atoms in positions 2 and 4 of the carborane polyhedron (these positions are equally occupied and are denoted X2 and X4 in Figure 1). The disordering observed originates from the molecular chirality of the carborane moiety and points to the coexistence of both enantiomers in the crystal, differing in the mutual arrangement of these boron and carbon atoms with respect to the plane passing through the P(1), B(3), C(1), and C(2) atoms.

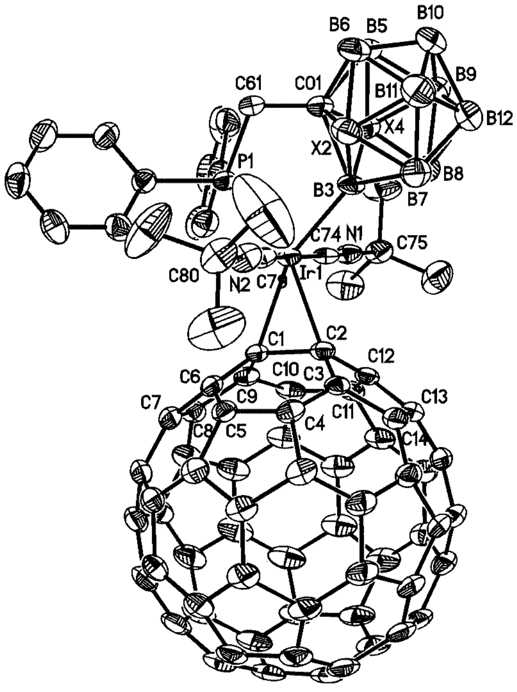

Figure 1. Molecular structure of **II** with numbering of key atoms (see text); hydrogen atoms are not shown

The iridium atom in **II** is coordinated to fullerene at the 6:6 bond C(1)−C(2), which is typical for η^2 complexes of fullerene with transition metals. As a result, the C(1)−C(2) coordination bond is appreciably lengthened as compared to the 6:6 bonds that are not involved in the coordination [cf. 1.525(6) and 1.394 Å, respectively) and is also very close to the corresponding bond length in the fullerene complex (η^2-C_{60})Ir(CO)Cl$(PPh_3)_2$ (**III**) (1.53 Å).[7] Distortion of the fullerene cage due to its coordination to the transition metal atom is also typical of this type of complex.[7,8] An important structural feature of complex **II** is strong distortion of the metallacyclopropane fragment C(1)−Ir(1)−C(2) due to

Table 1. Selected geometrical parameters for **II**

Bond lengths [Å]			
Ir(1)−C(1)	2.228(4)	C(01)−X(2)	1.656(8)
Ir(1)−C(2)	2.162(4)	C(01)−X(4)	1.653(8)
Ir(1)−P(1)	2.294(2)	C(01)−B(3)	1.814(7)
Ir(1)−B(3)	2.101(5)	C(1)−C(2)	1.525(6)
Ir(1)−C(79)	1.966(5)	C(1)−C(6)	1.480(6)
Ir(1)−C(74)	1.979(5)	C(1)−C(9)	1.454(6)
P(1)−C(61)	1.852(5)	C(2)−C(3)	1.477(6)
C(01)−C(61)	1.511(7)	C(2)−C(12)	1.482(6)
Bond angles [°]			
C(79)−Ir(1)−C(74)	172.3(2)	C(61)−P(1)−Ir(1)	109.0(2)
B(3)−Ir(1)−P(1)	84.5(2)	C(61)−C(01)−B(3)	112.9(4)
C(2)−Ir(1)−C(1)	40.6(2)	C(01)−B(3)−Ir(1)	116.8(3)
B(3)−Ir(1)−C(1)	158.0(2)	C(2)−C(1)−Ir(1)	67.4(2)
C(2)−Ir(1)−P(1)	157.9(1)	C(1)−C(2)−Ir(1)	72.0(2)

appreciable lengthening of the Ir(1)−C(1) bond compared to the Ir(1)−C(2) bond [2.228(4) vs. 2.162(4) Å, respectively] because of the strong *trans* influence of the other polyhedral ligand, i.e. the B-σ-carboranyl fragment. It should be mentioned that in the case of the symmetric ligand environment (e.g., in **III)** these bonds have the same length (2.19 Å).[7]

Thus, complex **II** is not only the first representative of metal complexes characterized by the simultaneous presence of two different polyhedral ligands in the coordination sphere of the metal atom, but also the first example of exohedral metallofullerenes with distorted η^2-coordination of fullerene to the transition metal atom. This can be both theoretically and practically valuable because of the possibility for selective insertion of various unsaturated substrates into the longer (and, correspondingly, more reactive) Ir−C bond.

Experimental Section

General: All experiments were carried out under dry, oxygen-free argon in deoxygenated solutions. IR spectra were obtained with a Specord M80 spectrometer. ^{1}H NMR spectra (400.3 MHz) and ^{31}P{^{1}H} NMR spectra (160.02 MHz) were recorded with a Bruker AMX-400 spectrometer relative to residual signals of the solvent (internal standard) and 85% H_3PO_4 (external standard), respectively.

Synthesis of [(η^2-C_{60})Ir(*o*-$HCB_{10}H_9CCH_2PPh_2$-*B,P*)(*t*BuNC)$_2$] (II): To a solution of C_{60} (0.0654 g, 0.09 mmol) in toluene (50 mL), dihydride complex **Ia** (0.0954 g, 0.09 mmol) and *t*BuNC (22 μL, 0.198 mmol) were added while stirring and the reaction mixture was refluxed for 3 h. After cooling, the reaction mixture was filtered, concentrated to 5 mL, and diluted with pentane. The precipitate formed was filtered off, washed successively with methanol and pentane, and dried in vacuo at 60°C to give 95.9 mg (70.5%) of complex **II** as 1:1 solvate with toluene. $C_{85}H_{40}B_{10}N_2PIr\cdot C_7H_8$ (1512.7): calcd. C 73.05, H 3.20, B 7.15; found C 72.53, H 3.34, B 7.15. UV/Vis (THF): λ = 258, 329, 400 (sh), 453, 717 nm. IR (KBr disc), $\tilde{\nu}$ = 2576 (BH), 2168 (NC) cm^{-1}. ^{31}P{^{1}H} NMR (CDCl$_3$): δ = 37.8 ppm. ^{1}H NMR (CDCl$_3$): δ = 1.22 (s, 9 H, *t*Bu), 1.24 (s, 9 H, *t*Bu), 2.35 (s, 3 H, Ph*CH$_3$*), 3.31 [dd, ^2J(HP) = 6.5, ^2J(HH) = 16.0 Hz, 1 H, CH$_2$], 3.60 (s, 1 H, CH^{carb}), 4.07 [dd, ^2J(HP) = 9.8, ^2J(HH) = 16.0 Hz, 1 H, CH$_2$], 7.17 (m, 3 H, *Ph*CH$_3$), 7.24 (m, 2 H, *Ph*CH$_3$), 7.44 (m, 6 H, Ph), 7.84 (m, 6 H, Ph) ppm.

X-ray Structure Determination of II: Single crystals of $\mathbf{II}\cdot 4C_6H_5CH_3$ were grown from a toluene solution of complex **II** at room temperature. The crystals were triclinic with the space group $P\bar{1}$, a = 15.317(8), b = 16.751(8), c = 19.317(10) Å, α = 88.10(3), β = 72.48(3), γ = 60.87(2)°, V = 4090(3) Å^3, Z = 2, $d_{calcd.}$ = 1.453 g/cm^3, μ(Mo-K_α) = 17.09 cm^{-1}. The intensities of 14417 independent reflections (R_{int} = 0.0687) were measured at 193(2) K with a Syntex P2$_1$ diffractometer (graphite-monochromated Mo-K_α radiation, λ = 0.71073 Å, ω-scan technique, θ ≤ 25°). The structure was solved by the direct methods and refined by the full-matrix least-squares method against F^2 in the anisotropic (isotropic for H atoms) approximation. All hydrogen atoms of the carborane cage were located from the electron density difference synthesis, while the other H atoms were placed geometrically and included in the refinement using the rigid motion model. The refinement converged to wR_2 = 0.1253 and GOF = 1.068 for all independent reflections [R_1 = 0.0446 was calculated against F for 13363 observed reflections with $I > 2\sigma(I)$]; the number of refined parameters was 1184. All calculations were performed using the SHELXTL-97 software[9] with an IBM PC/AT. CCDC-185865 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk]

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