Selective Insertion of Dioxygen into an (η^2-C_{60})−Ir Bond: Synthesis and Structure of the First Metallacyclic Complex with a σ-Coordinated Fullerene Molecule

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Oxidation of the carboranyliridium fullerene complex [(η^2-C_{60})Ir(*o*-$HCB_{10}H_9CCH_2PPh_2$-*B*,*P*)(*t*BuNC)$_2$] (**I**) in $CHCl_3$ solution by O_2 occurs by a selective insertion of the dioxygen molecule into the longest Ir–C bond (in the *trans*-position relative to the B-σ-carboranyl fragment) to give a new metal complex [σ-C_{60}OO-Ir(*o*-$HCB_{10}H_9CCH_2PPh_2$-*B*,*P*)(*t*BuNC)$_2$] (**II**). Complex **II** was isolated and characterized analytically and by UV, IR, ^{1}H and ^{31}P NMR spectroscopy. An X-ray diffraction study of **II** showed that this complex contains a cyclic iridaperoxide fragment in which the fullerene cage is σ-coordinated to the iridium atom.

Despite considerable advances in the synthesis of metal complexes of fullerenes and their derivatives, the reactivity of these interesting compounds has been studied rather scarcely.[1] The most interesting results obtained in this field are: (i) the discovery of an interaction between polymeric compounds [$C_{60}M_n$] (M = Pd, Pt) and various phosphanes and phosphites resulting in the known monomeric complexes [(η^2-C_{60})ML_2],[2,3] and (ii) insertion of two isocyanide molecules into the Pt−C(fullerene) bonds in the complex [(η^2-C_{60})Pt(CNR)$_2$] giving rise to a new five-membered metallacyclic complex [C_{60}(C=NR)$_2$Pt(CNR)$_2$].[4]

Recently,[5] we have reported the synthesis and structure of the iridium complex [(η^2-C_{60})Ir(*o*-$HCB_{10}H_9CCH_2PPh_2$-*B*,*P*)(*t*BuNC)$_2$] (**I**) containing both an η^2-coordinated C_{60} fullerene and a chelating carboranylphosphane fragment in the coordination sphere of the metal atom. A salient feature of this complex is a distorted η^2-coordination of the fullerene ligand, which is manifested in an appreciable lengthening of one Ir−C bond relative to the other one due to the strong *trans*-effect of the B-σ-carboranyl group. Having established this fact, we started to investigate the possibility of the selective insertion of various reagents into the most reactive elongated bond.

In studies of the oxidation of complex **I** in various solutions we found that bubbling dioxygen through a solution of **I** in $CHCl_3$ at room temperature led to a gradual disappearance of the absorption band at 460 nm in the UV/Vis spectrum of the reaction mixture (this band is characteristic of (η^2-C_{60})-type metal derivatives[5−7]). The reason for this is the formation of a new complex **II** that was isolated and characterized both analytically and spectroscopically.

The IR spectrum of complex **II** exhibits a strong stretching vibration band of *trans*-arranged isocyanide ligands at 2191 cm^{-1} similar to the IR spectrum of **I**. A rather large frequency shift of this band towards the high-frequency region [cf. ν(NC) = 2168 cm^{-1} for complex **I**][5] points to a considerably higher electron-deficient character of the iridium atom in **II**. The $^{31}P\{^1H\}$ NMR spectrum of **II** exhibits a singlet at δ_P = 20.9 ppm, which is shifted appreciably to high field (δ_P = 37.8 ppm for **I**).[5] The ^{1}H NMR spectral pattern of **II** is similar to that of **I**, exhibiting two singlets for the protons of the *tert*-butyl groups of the isocyanide ligands and an ABX pattern for the protons of methylene group of the five-membered ring. This points to a retention of the molecular chirality of the carborane polyhedron. However, these spectral characteristics are insufficient to draw an unambiguous conclusion about the mutual arrangement of the components in the complex **II** and, correspondingly, to determine the addition position of the dioxygen molecule [this can be either the Ir−C bond or one (or several) of the C=C bonds of the fullerene cage]. To establish the structure of this compound, we grew a single crystal of **II** from $CHCl_3$ solution and performed an X-ray diffraction study. The molecular structure of this complex is shown in Figure 1 while selected geometric parameters are listed in Table 1. Our X-ray diffraction study showed that complex **II** is a five-membered iridaperoxide derivative [σ-C_{60}OO-Ir(*o*-$HCB_{10}H_9CCH_2PPh_2$-*B*,*P*)(*t*BuNC)$_2$] with a σ bond between the Ir atom and fullerene cage. This complex is formed as a result of selective insertion of dioxygen

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molecule into the longest Ir−C bond of the metallacyclopropane fragment of complex **I** according to Scheme 1.

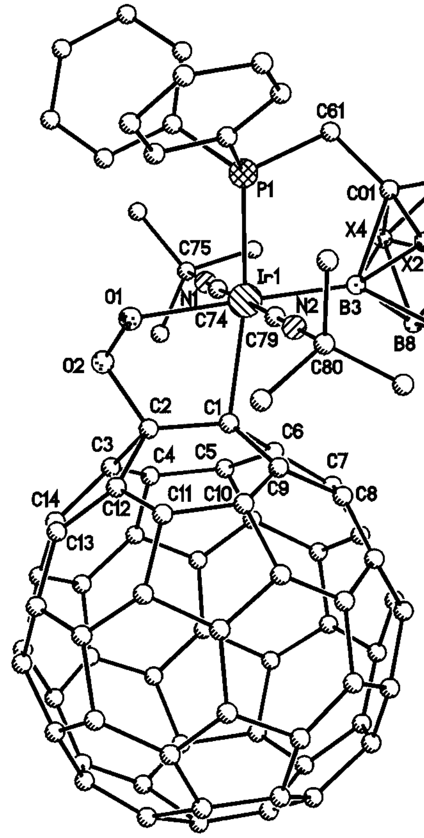


Figure 1. Molecular structure of **II**

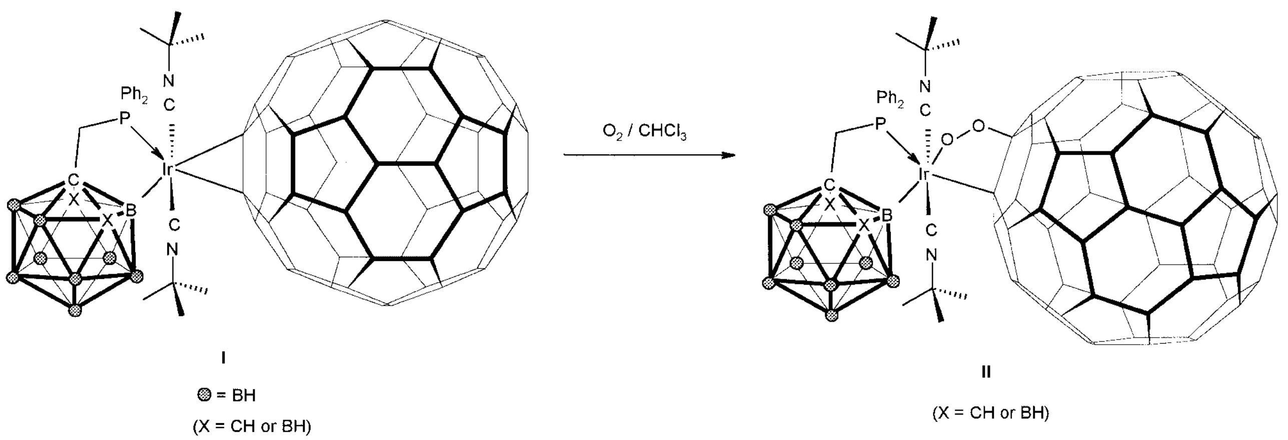
No significant changes were found in the geometry of the carboranylphosphane ligand of **II** relative to the initial compound **I** (this was also confirmed by the spectroscopic data). This ligand is coordinated to the iridium atom by the Ir(1)−B(3) σ-bond with the boron atom in position 3(6) and the Ir(1)−P(1) coordination bond involved in the five-membered metallacycle Ir(1)P(1)C(61)C(01)B(3). The both bond lengths in **I** and **II** are essentially identical. However, the metallacycle conformations in both compounds are appreciably different. In **I**, this cycle has a flattened envelope conformation with the P(1) atom deviating by 0.43 Å from the plane of other four atoms of the cycle. In **II**, the metallacycle adopts a flattened twist-conformation characterized by slight deviations of the P(1) and C(61) atoms in opposite directions from the plane passing through the Ir(1), B(3), and C(01) atoms; the Ir(1)−P(1)−C(61)−C(01) torsion angle is 13.8°. This points to a high lability of this metallacycle in the related complexes. The carbon and boron atoms in the 2- and 4-positions of the carborane polyhedron in both **I** and **II** are disordered with equal weights (labeled X2 and X4, see Figure 1). This is due to the fact that the crystal structure is comprised of both enantiomers differing in the mutual arrangement of these boron and carbon atoms with respect to the plane passing through the C(01), B(3), B(10), and B(12) atoms as a consequence of the molecular chirality of the substituted carborane polyhedron.

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

Bond lengths (Å)			
Ir(1)−P(1)	2.281(2)	C(01)−B(3)	1.826(9)
Ir(1)−B(3)	2.101(8)	O(1)−O(2)	1.417(8)
Ir(1)−O(1)	2.154(5)	O(2)−C(2)	1.48(2)
Ir(1)−C(1)	2.238(6)	O(2)−C(2′)	1.41(2)
Ir(1)−C(74)	1.982(6)	C(1)−C(2)	1.46(2)
Ir(1)−C(79)	1.982(6)	C(1)−C(2′)	1.67(2)
P(1)−C(61)	1.853(7)	N(1)−C(74)	1.135(7)
C(01)−C(61)	1.508(9)	N(1)−C(75)	1.480(8)
C(01)−X(4)	1.631(10)	N(2)−C(79)	1.146(7)
C(01)−X(2)	1.657(9)	N(2)−C(80)	1.466(7)
Bond angles (°)			
B(3)−Ir(1)−O(1)	177.0(2)	C(01)−B(3)−Ir(1)	116.8(4)
C(1)−Ir(1)−P(1)	171.74(17)	C(01)−C(61)−P(1)	112.4(4)
B(3)−Ir(1)−C(1)	103.3(2)	O(2)−O(1)−Ir(1)	103.8(4)
O(1)−Ir(1)−C(1)	76.4(2)	O(1)−O(2)−C(2)	94.2(9)
B(3)−Ir(1)−P(1)	84.90(18)	O(1)−O(2)−C(2′)	109.3(7)
O(1)−Ir(1)−P(1)	95.49(17)	C(74)−N(1)−C(75)	176.7(7)
C(74)−Ir(1)−C(79)	178.1(2)	C(79)−N(2)−C(80)	176.7(7)
C(61)−P(1)−Ir(1)	110.9(2)	N(1)−C(74)−Ir(1)	177.7(6)
C(61)−C(01)−B(3)	113.5(5)	N(2)−C(79)−Ir(1)	179.3(6)

A salient feature of complex **II** is the η^1-coordination of the fullerene ligand to the iridium atom through the Ir(1)−C(1) σ-bond. To the best of our knowledge, no structurally characterized mononuclear complexes with this type of fullerene coordination to the transition metal atom have been reported so far.[1] Although Balch et al.[8a] have suggested the formation of a σ-bond between the fullerene cage and a post transition metal atom (Ag), taking compound $C_{60}[Ag(NO_3)]_5$ as an example, a strong structural disorder (including orientation disordering of the fullerene fragment and a disordering of the silver atoms over several positions) does not allow us to use their results for a reliable description of the geometrical features of this type of fullerene coordination to metal atoms. Among polynuclear complexes, a series of triosmium cluster derivatives with μ_3-η^1:η^1:η^2-C_{60} [8b] and μ_3-η^1:η^2:η^1-C_{60} [8c,8d] ligands have been recently obtained and structurally characterized by Park and coworkers. In these complexes, one of the Os atoms has a π-type coordination with a 6/6 bond of a hexagon ring in the C_{60} moiety, whereas two other Os atoms are σ-bonded to this ring with an average Os−C(C_{60}) distance of 2.24 Å.

The Ir(1)−C(1) σ-bond length in **II** is 2.238(6) Å. This value somewhat exceeds the Ir−C(fullerene) bond lengths typical for a conventional η^2-coordination {cf. 2.228(4) and 2.162(4) Å in **I**[5] and 2.19 Å in $[(\eta^2\text{-}C_{60})Ir(CO)Cl(PPh_3)_2]$[1]}. A feature of the crystal structure of complex **II** is the unusual disordering of the fullerene cage due to the type of coordination to the metal atom. The Ir(1)−C(1) σ-bond defines a rigid axis about which the fullerene cage is rotated by about 10°. In this case, only two



Scheme 1

out of sixty fullerene carbon atoms are ordered, namely the C(1) atom and the C(60) atom occupying the diametrically opposite position. The remaining fifty eight carbon atoms are disordered over two equally populated positions. Figure 2 shows a fragment of the complex **II** to illustrate this disordering of the fullerene ligand.

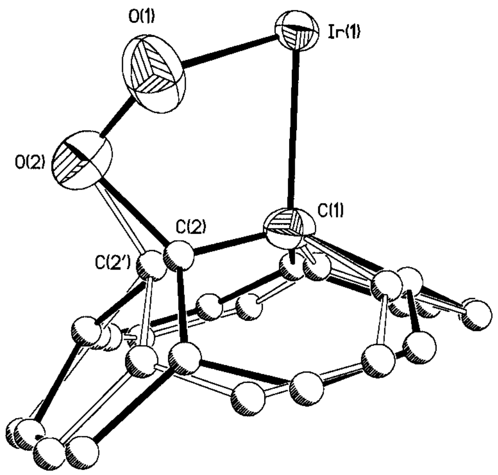


Figure 2. Disordered fragment of molecule **II**

The iridium atom in **II** is also bound to the fullerene cage through a peroxide bridge, which is part of the five-membered cycle Ir(1)−O(1)−O(2)−C(2)−C(1). The crystal structure (Figure 1) unambiguously shows that the dioxygen molecule has inserted into the longer Ir−C(fullerene) bond of the initial complex **I** [this bond is in a pseudo-*trans*-position relative to the Ir(1)−B(3) σ-bond]. As a result, the iridium atom in **II** is close to an octahedral coordination. Specifically, the O(1) atom is in a *trans*-position with respect to the B(3) atom while the C(1) atom is in a *trans*-position with respect to the phosphane ligand [the O(1)−Ir(1)−B(3) and C(1)−Ir(1)−P(1) angles are 177.0(2) and 171.7(2)°, respectively]. The M−O−O−R fragment is not uncommon in transition metal chemistry; however, five-membered metallacycles containing a peroxy group similar to that found in **II** are rarely observed, even though the formation of such compounds has been postulated for olefin oxidation catalyzed by metal complexes. The closest analog of this metallacyclic peroxide fragment is found in the platinum complex [(PPh$_3$)$_2$Pt(O-O-C(Me)$_2$-C(CN)$_2$] (**III**).[9] Only three structurally characterized iridium complexes containing an Ir−O−O−R fragment are known, where R = C(sp^3)[10,11] or a second Ir atom.[12] All these compounds are characterized by a very wide range of their Ir−O and O−O bond lengths (1.99−2.11 and 1.43−1.59 Å, respectively). In complex **II**, the Ir(1)−O(1) and O(1)−O(2) distances are 2.154(5) and 1.417(8) Å, respectively. The dioxairidacycle has an envelope conformation and the angle of folding along the Ir(1)···O(2) line is nearly 60° [the Ir(1)−O(1)−O(2)−C(2) and Ir(1)−O(1)−O(2)−C(2′) torsion angles are 67.1 and 65.8°, respectively]. The corresponding cycle in the platinum complex **III** also has a nonplanar structure with a Pt−O−O−C torsion angle of 53.5°. Disordering of the C(2) atom in the fullerene cage causes a disorder of the oxygen atoms in the peroxy group, increasing the thermal parameters of the O(1) and O(2) atoms (see Figure 2). However, we failed to resolve this disorder due to the spatial proximity of these positions.

A disorder of the fullerene cage and, correspondingly, a low accuracy of its geometric parameters in **II** precludes a detailed consideration of changes in the structure caused by σ-coordination to the iridium atom and peroxy group. In particular, substantially different C(1)−C(2) and C(1)−C(2′) distances [1.46(2) and 1.67(2) Å, respectively; av. 1.56 Å] were obtained for two equivalent positions, C(2) and C(2′), of the C atom bound to the oxygen atom of peroxy group. Nevertheless, both disordered C$_{60}$ cages display different distortions in the vicinity of the key atoms C(1) and C(2) [or C(2′)]. These distortions can be revealed by comparing the distances from the center of the C_{60} moiety to the carbon atoms along different directions.[13] In particular, in both disordered fullerene cages the distance to the C(1) atom bonded to Ir atom is, on average, 3.83 Å, whereas the distances to the C(2) [or C(2′)] atom bonded to the peroxy group are longer (av. 3.90 Å). The distances to other carbon atoms of the fullerene cage lie between 3.47 and 3.60 Å. Thus, bonding to an O-atom of the peroxy group leads to a greater distortion of the fullerene ligand than that caused by the σ-bond with the Ir atom. Much smaller distortions of the fullerene ligand were found for a conventional η^2-coordination to the iridium atom in **I**, where the average Ir−C distance to the key carbon atoms is 3.73 Å.

In the crystal, there are $3^2/_3$ solvate chloroform molecules per molecule of **II**. The crystal packing (Figure 3) is characterized by shortened Cl···Cl contacts between the solvate chloroform molecules (the shortest distances are 3.31 and 3.43 Å) and by shortened Cl···C distances involving the C(19), C(20), and C(55) atoms of the fullerene ligand (3.13, 3.25 and 3.22 Å, respectively). For comparison, the shortest van der Waals intermolecular contacts are 3.65 Å for Cl···Cl and 3.45 Å for Cl···C.[14] One solvate chloroform molecule forms a weak C−H···O hydrogen bond with the O(1) atom of the peroxy group of **II** [the O(1)···C(1S) distance is 3.02(2) Å and the O(1)···H(1S)−C(1S) angle is 159°].

Thus, we have established that selective insertion reactions can occur involving only one M−C(fullerene) bond in complexes of the (η^2-C_{60})-M type to give the corresponding metallacyclic derivatives with a σ-coordinated fullerene ligand. Oxidation of [(η^2-C_{60})Ir(*o*-$HCB_{10}H_9CCH_2PPh_2$-*B,P*)(*t*BuNC)$_2$] by dioxygen resulting in the complex [σ-C_{60}OO-Ir(*o*-$HCB_{10}H_9CCH_2PPh_2$-*B,P*)(*t*BuNC)$_2$] is a good example of such a process. To the best of our knowledge, this is not only the first stable mononuclear exohedral fullerene complex in which the fullerene cage is σ-coordinated to the transition metal atom, but also the first structurally characterized complex with a peroxoiridacycle.

Experimental Section

General: IR spectra were obtained on a Specord M80 spectrometer. ^{1}H NMR spectra (400.3 MHz) and ^{31}P{^{1}H} NMR spectra (160.02 MHz) were recorded on a Bruker AMX-400 spectrometer and are quoted relative to residual signals of the solvent (internal standard) and 85% H_3PO_4 (external standard), respectively.

Synthesis of Complex [σ-C_{60}OO-Ir(*o*-$HCB_{10}H_9CCH_2PPh_2$-*B,P*)(*t*BuNC)$_2$] (II): Dioxygen was slowly bubbled through a stirred solution of complex **I** (0.0562 g, 0.04 mmol) in dry chloroform (15 mL) at room temperature until disappearance of the absorption band at 460 nm in the UV spectrum of the reaction mixture (ca. 60 h). Chloroform was then removed under reduced pressure and the residue was extracted with THF. The extract was filtered, concentrated to approx. 1.5 mL, and hexane was added. The resulting precipitate was filtered off, washed with hexane, and dried in vacuo

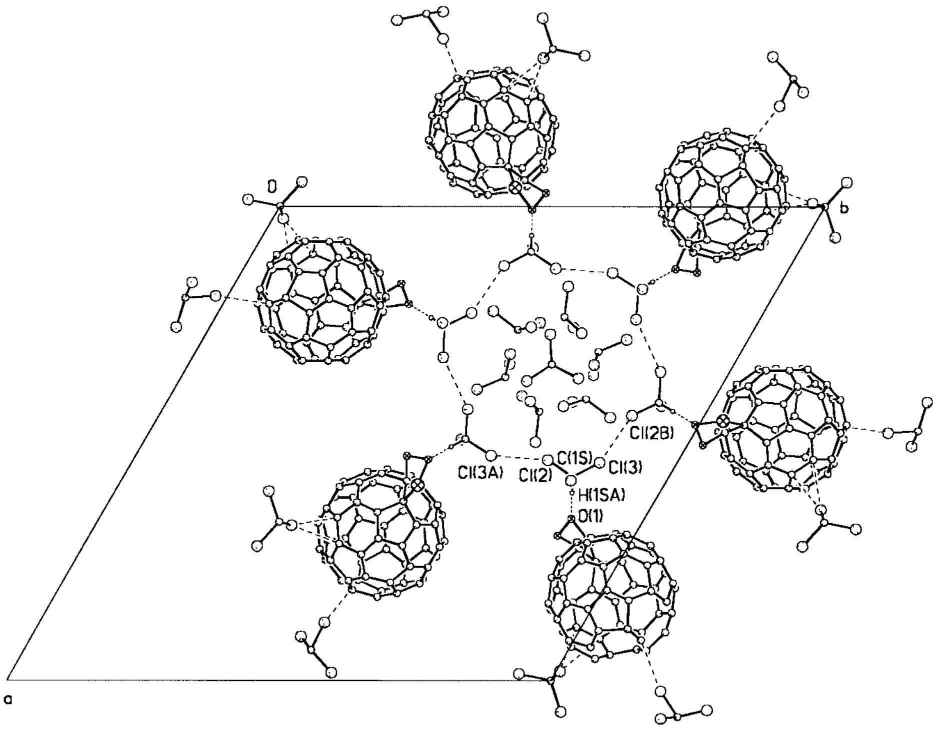


Figure 3. Fragment of crystal packing of solvate **II**·$3^2/_3CHCl_3$ viewed along the *c* direction with intermolecular contacts Cl···Cl, Cl···C and C−H···O (one of two possible orientations of fullerene moiety is shown); the ligand environment of the Ir atoms, apart from the fullerene and oxygen atoms of the peroxide bridge, has been omitted for clarity

to give the complex **II**·$6H_20$ (24.4 mg, 39%) as a dark-green powder. $C_{85}H_{40}B_{10}N_2O_2PIr\cdot 6H_20$ (1560.6): calcd. C 65.42, H 3.36; found C 65.53, H 3.73. UV/Vis ($CHCl_3$): λ = 329 nm, 404 (sh), 707. IR (Nujol): $\tilde{\nu}$ = 3568 cm^{-1} (OH), 2581 (BH), 2191 (NC). ^1H NMR ([D_8]THF): δ = 1.30 (s, 9 H, *t*Bu), 1.45 (s, 9 H, *t*Bu), 2.45 (s, 12 H, H_2O), 3.21 (dd, $^2J_{H,P}$ = 6.8, $^2J_{H,H}$ = 16.9 Hz, 1 H, CH_2), 3.50 (s, 1 H, CH^{carb}), 4.19 (dd, $^2J_{H,P}$ = 10.7, $^2J_{H,H}$ = 16.9 Hz, 1 H, CH_2), 7.48 (m, 6 H, Ph), 8.15 (m, 4 H, Ph) ppm. $^{31}P\{^1H\}$ NMR ([D_8]THF): δ = 20.9 ppm.

X-ray Structure Determination of II: Single crystals of **II**·$3^2/_3CHCl_3$ were grown from a chloroform solution of **II**·$6H_20$ at room temperature. The crystals are rhombohedral, space group $R\bar{3}$, a = 29.901(1), c = 42.955(2) Å, V = 33258(1) Å^3, Z = 18, $d_{calcd.}$ = 1.699 g/cm^3, and $\mu(\text{Mo-}K_\alpha)$ = 22.83 cm^{-1}. The intensities of 19332 independent reflections (R_{int} = 0.0635) were measured on a Bruker SMART 1000 CCD diffractometer (graphite monochromated Mo-K_α radiation, λ = 0.71073 Å, ω and scan technique with a 0.3° step in ω and 10 s per frame exposure, $\theta \leq 29.5°$) at 100.0(2) K. Reflection intensities were integrated using the SAINT software[15] and corrected for absorption semi-empirically (SADABS program)[16] based on multiple measurements of identical reflections and equivalents. The structure was solved by direct methods and refined by full-matrix least-squares against F^2. The uncoordinated carbon atom in the carborane polyhedron is disordered over two equally populated positions labeled X(2) and X(4). The carbon atoms of the C_{60} fullerene ligand [except for the C(1) and C(60) atoms] are disordered over two equally populated positions. The methyl groups of the *tert*-butyl isocyanide ligands are rotationally disordered over two positions with a 3:1 occupancy ratio. In the crystal structure, there are three solvate chloroform molecules in general positions (one of them is disordered) and three solvate chloroform molecules in special positions (one of them occupies a position on the 3 axis and the two others occupy the $\bar{3}$ axes). All disordered atoms in the crystal structure of complex **II** were refined with isotropic thermal parameters. All H atoms of the carborane polyhedron were located from the electron density difference synthesis, while the remaining H atoms were placed geometrically and included in the refinement using a riding model. The refinement converged to wR_2 = 0.1911 and GOF = 1.013 for all independent reflections]R_1 = 0.0649 was calculated against F for a total of 12640 observed reflections with $I > 2\sigma(I)$]; the number of refined parameters was 1013. All calculations were performed using the SHELXTL-97 program[17] on an IBM PC/AT computer.

CCDC-190946 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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