of 2.73 (2) Å is unexceptional, being similar to that found in dimeric amides[2-5] but significantly shorter than that in dimeric halides, e.g. 3.004 (9) Å in $[\{Li(\mu\text{-}Cl)(2\text{-methylpyridine})_2\}_2]$,[8] as expected on the basis of incorporating two third-row atoms into a four-membered-ring system. In general, the bonding in dimeric lithium compounds containing second-row groups is now regarded as highly ionic,[19] and replacing one of the anionic centers by chlorine as in **1** would result in even greater ionic character.

Acknowledgment. We gratefully acknowledge support of this work by the Australian Research Council.

Supplementary Material Available: Tables listing atomic positional parameters, thermal parameters, ligand hydrogen parameters, extended metal core geometries, and ligand non-hydrogen geometries (10 pages); a listing of structure factor amplitudes (9 pages). Ordering information is given on any current masthead page.

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Accumulating Evidence for the Selective Reactivity of the 6-6 Ring Fusion of C_{60}. Preparation and Structure of $(\eta^2\text{-}C_{60})Ir(CO)Cl(PPh_3)_2\cdot 5C_6H_6$

The recent discovery that C_{60} (buckminsterfullerene) can be isolated in macroscopic quantities[1,2] has led to widespread interest in its chemical and physical properties.[3] C_{60} has icosahedral D_{5h} symmetry with 20 six-membered rings that are interconnected with 12 five-membered rings. There are two types of C-C bonds within this cluster: one type occurs at the 6-6 ring fusions, while the other occurs at the 6-5 ring fusions. There are no 5-5 ring fusions. Two crystalline derivatives of C_{60} have been obtained by addition of transition-metal complexes to the cluster. Addition of osmium tetraoxide and *tert*-butylpyridine produces $C_{60}O_2OsO_2(NC_5H_4CMe_3)_2$ in which an O_2Os unit has added across a 6-6 ring fusion in the carbon cluster.[4] Addition of C_{60} to $(Ph_3P)_2Pt$(ethylene) results in displacement of ethylene and formation of $(\eta^2\text{-}C_{60})Pt(PPh_3)_2$. In this complex, the platinum atom is bound to carbon atoms again at a 6-6 ring junction of the carbon cluster.[5] Here we report another case of reactivity that involves addition to a C-C bond of a 6-6 ring fusion.

Under a dinitrogen atmosphere, addition of an equimolar amount of a purple solution of C_{60}[6] in benzene to a yellow benzene solution of $Ir(CO)Cl(PPh_3)_2$ immediately forms a deep brown solution from which black-brown crystals of $(\eta^2\text{-}C_{60})Ir(CO)Cl(PPh_3)_2\cdot 5C_6H_6$ (**1**) precipitate in 45% yield within a matter of minutes. The infrared spectrum of the solid dispersed in a Fluorolube mull shows $\nu(CO)$ at 2014 cm^{-1} (versus 1953 cm^{-1} for $Ir(CO)Cl(PPh_3)_2$). Crystals suitable for X-ray diffraction have been obtained by slow diffusion of benzene solutions of the reactants into one another.[7] Figure 1 shows a view of the molecule with appropriate atomic labels, while Figure 2 shows a stereoscopic view of the molecule from a different angle. The iridium is attached to the soccer ball shaped C_{60} moiety in an η^2 fashion through a 6-6 ring fusion. The geometry of the complexed C_{60} portion is similar to that observed in the osmium tetraoxide[4] and platinum diphosphine[5] adducts. Carbon atoms C(1) and C(2) are pulled away from the C_{60} unit toward the iridium. This is best seen by comparing the local structure at C(1) and C(2) with that about C(59) and C(60) at the opposite end of the molecule. The C(1)-C(2) distance of 1.53 (3) Å is at the extreme long end of the range of C-C distances found in **1**. The two triphenylphosphine ligands have folded back into a nearly cis geometry from their trans positions in the starting complex, $Ir(CO)Cl(PPh_3)_2$. The carbonyl and chloride ligands retain their trans disposition. The coordination about iridium closely resembles that seen earlier for the tetracyanoethylene (TCNE) complex $(TCNE)IrBr(CO)(PPh_3)_2$ (**2**).[8,9] Thus the Ir-C(C_{60}) distances in **1** (2.19 (2) Å) are similar to those in **2** (2.146 (11), 2.151 (11) Å), as are the C-Ir-C angles (41.0 (8)° in **1**; 41.0 (4)° in **2**) and the P-Ir-P angles (113.3 (2)° in **1**; 110.4 (1)° in **2**). The benzene molecules show no unusual contacts with the iridium complex but fill what would otherwise be voids between the molecules (see supplementary material). However, efficient packing within this particular benzene solvate may contribute significantly to the low solubility and isolation of this relatively weakly bound adduct.

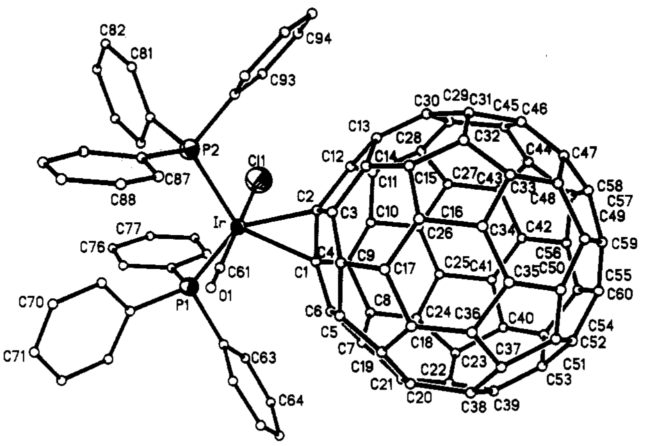

Figure 1. Perspective view of $(\eta^2\text{-}C_{60})Ir(CO)Cl(PPh_3)_2$ with 50% thermal contours for Ir, Cl, and P and uniform, arbitrarily sized circles for C and O. C-C distances within the C_{60} range from 1.35 (3) to 1.53 (3) Å. Other bond lengths (Å): Ir-P(1), 2.382 (6); Ir-P(2), 2.385 (7); Ir-Cl, 2.401 (7); Ir-C(1), 2.19 (2); Ir-C(2), 2.19 (2). Bond angles (deg): C(1)-Ir-C(2), 41.0 (8); P(1)-Ir-P(2), 113.3 (2); Cl(1)-Ir-C(61), 179.6 (4).

Formation of **1** is reversible. Dissolution of the crystalline complex in dichloromethane gives a solution whose infrared spectrum shows $\nu(CO)$ at 1965 cm^{-1} due to the presence of $Ir(CO)Cl(PPh_3)_2$. No absorption due to **1** is present in the 2100-2000-cm^{-1} region. The electronic spectrum of this dichloromethane solution is simply a superposition of the spectral features of C_{60}[1] and $Ir(CO)Cl(PPh_3)_2$. The ^{31}P NMR spectrum of the complex dissolved in chloroform shows only a resonance at 24.5 ppm, which is the same as that observed for $Ir(CO)Cl(PPh_3)_2$.

The formation of **1** adds confirmatory evidence to the suggestion of Fagan and co-workers[5] that C_{60}, with its high electron affinity

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(7) Deep purple plates of $(\eta^2\text{-}C_{60})Ir(CO)Cl(PPh_3)_2\cdot 5C_6H_6$ crystallize in the monoclinic space group $P2_1/n$ with a = 14.624 (6) Å, b = 19.902 (12) Å, c = 28.388 (16) Å, and β = 100.67 (4)° at 130 K with Z = 4. Refinement of 4939 reflections with $F > 4.0\sigma(F)$ and 487 parameters yielded R = 0.085, R_w = 0.067.

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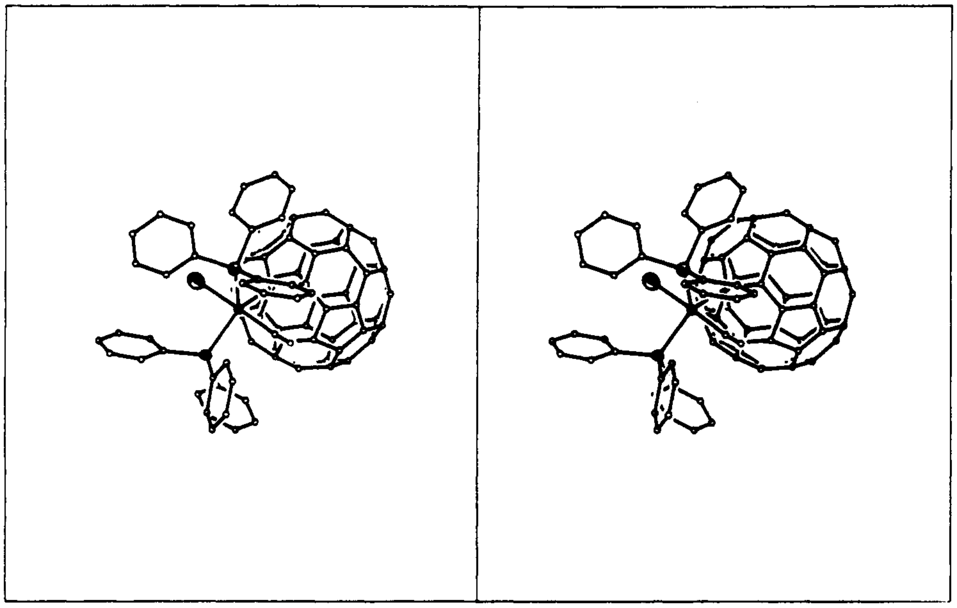

Figure 2. Stereoscopic view of $(\eta^2\text{-}C_{60})Ir(CO)Cl(PPh_3)_2$.

(2.8 eV),[10] will react like an electron-deficient alkene. $Ir(CO)Cl(PPh_3)_2$ is known to react with electron-deficient olefins (tetracyanoethylene, tetrafluoroethylene) to form stable η^2 adducts.[11] The carbon monoxide stretching frequency in these adducts can be used to monitor the degree of electron withdrawal from the metal in the adducts. For both the tetracyanoethylene and tetrafluoroethylene adducts, ν(CO) has increased considerably more than found for **1** (ν(CO): 2052 cm^{-1} for the C_2F_4 adduct, 2057 cm^{-1} for the TCNE adduct).[11] This indicates that C_{60} is less effective in removing electron density from iridium in its adduct than these electron-deficient olefins are. The degree of electron withdrawal is similar to that seen for the dioxygen adduct, $O_2Ir(CO)Cl(PPh_3)_2$ (ν(CO): 2015 cm^{-1}).[11] Vaska[11] has noted a correlation between the reversibility of adduct formation and ν(CO) of the adduct. Both $(\eta^2\text{-}C_{60})Ir(CO)Cl(PPh_3)_2$ and $O_2Ir(CO)Cl(PPh_3)_2$ fall into the category of "easily reversible" on the basis of their spectroscopic and chemical properties. These similarities lead to the suggestion that transition-metal complexes that are known to bind dioxygen may also bond to C_{60}. The fact that low-valent metal centers like Ir^I and Pt^0 add to the carbon atoms at 6–6 ring fusions in C_{60} is consistent with the predictions of bond localization energy calculations.[12]

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Supplementary Material Available: A stereoview of **1** showing the crystal packing and tables of structure determination data, atomic coordinates, bond distances and angles, anisotropic thermal parameters, and hydrogen atom positions for **1** (13 pages); a listing of observed and calculated structure factors (21 pages). Ordering information is given on any current masthead page.

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