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$(\eta^2\text{-C}_{70})\text{Ir}(\text{CO})\text{Cl}(\text{PPh}_3)_2$: the synthesis and structure of an iridium organometallic derivative of a higher fullerene

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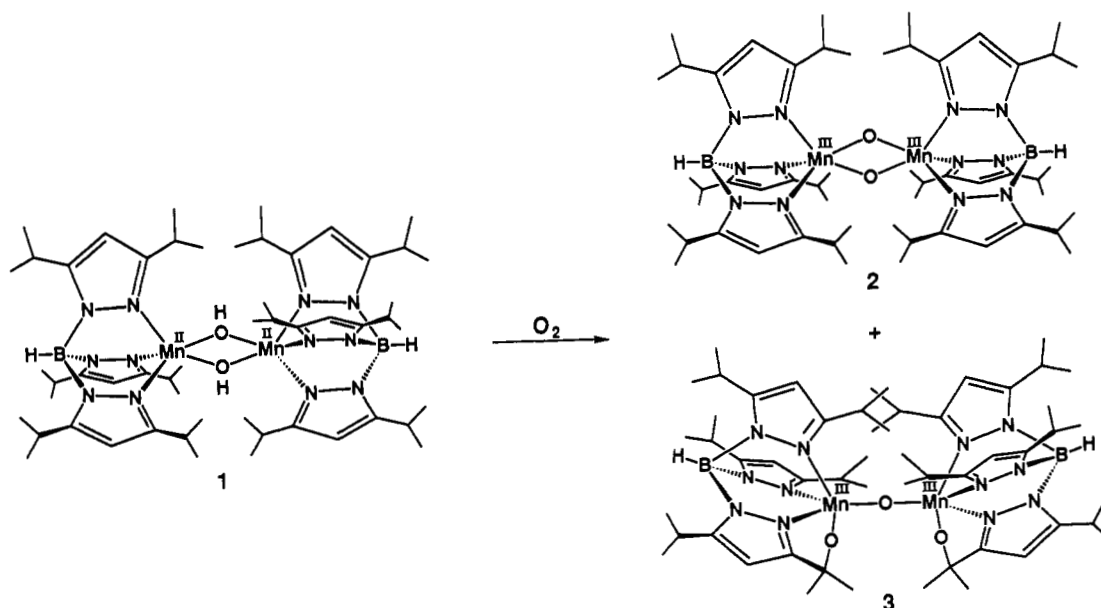
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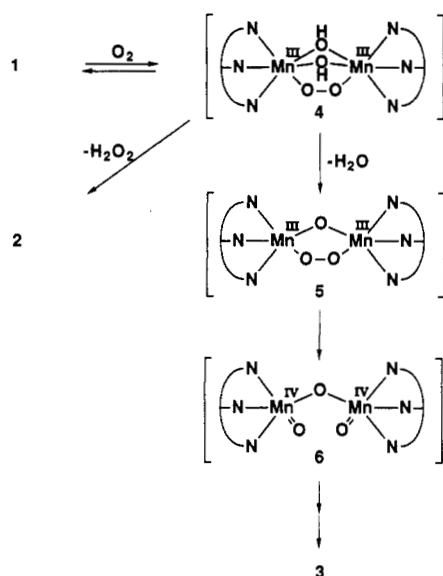
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Scheme I



Scheme II



the appropriate orientation and proximity of the isopropyl groups to the reactive oxo ligands in **6** is also an important factor for the present intramolecular reaction.

A few examples of aerobic ligand oxidations of transition-metal complexes have previously been reported. These include the oxidations of aromatic rings in dinuclear Cu complexes,¹⁰ olefinic ligand oxidation in an Ir complex,¹¹ and aliphatic CH bond oxidation in a Ni complex.¹²

The present ligand oxidation may provide us with a useful method to prepare a new type tris(pyrazolyl)borate ligand containing a functional group on one pyrazole ring. Thus, currently,

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efforts are being made to remove the manganese ions from **3**.

Acknowledgment. We thank Prof. Y. Fukuda of Ochanomizu University for the magnetic susceptibility measurement. Partial support of this research by Grant-in-Aid for Scientific Research from the Ministry of Education, Science and Culture, Japan (02750589) is gratefully acknowledged.

Supplementary Material Available: Tables of crystal data, atomic coordinates with isotropic thermal parameters, anisotropic thermal parameters for non-hydrogen atoms, and bond distances and angles (17 pages); listing of observed and calculated structure factors (28 pages). Ordering information is given in any current masthead page.

(η^2 -C₇₀)Ir(CO)Cl(PPh₃)₂: The Synthesis and Structure of an Organometallic Derivative of a Higher Fullerene

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Received August 12, 1991

The availability of macroscopic quantities of C₆₀¹⁻⁴ has rapidly led to remarkable discoveries of its chemical (formation of crystalline, structurally characterized transition-metal complexes,⁵⁻⁷ hydrogenation,⁴ fluorination⁸) and physical (metallic conductivity,^{10,11} superconductivity^{12,13} and soft ferromagnetism¹³ in

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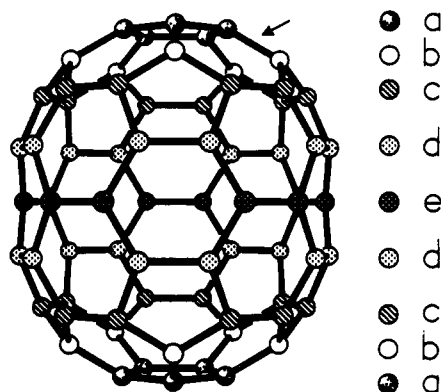


Figure 1. Schematic drawing of the ideal D_{5h} structure of C_{70} . The 5-fold axis passes through the pentagonal faces on the top and bottom sides. Sets of identical carbon atoms are labeled a–e. The arrow shows one of the 10 a–b bonds.

n-doped C_{60} properties. The higher fullerenes (e.g., C_{70} , C_{84} , etc.), which are available in smaller quantities, have naturally received less attention, but based on the results obtained for C_{60} , their properties clearly deserve attention.

For C_{70} , spectroscopic^{2,3} and theoretical considerations^{14–16} have focused on a D_{5h} structure, shown in Figure 1, which consists of 12 pentagonal faces fused to 25 hexagonal faces. In this structure there are five types of carbon atoms (labeled a–e in Figure 1) and eight distinct types of C–C bonds. Four of these (a–b, c–c, d–e, and e–e) are formed at fusions of two six-membered rings while the other four (a–a, b–c, c–d, and d–d) occur at fusions of five- and six-membered rings. In contrast, C_{60} , with I_h symmetry, has only one type of carbon atom and two types of C–C bonds: those at 6:6 ring fusions and those at 6:5 ring fusions. For C_{60} the reactivity noted so far toward transition-metal reagents occurs at the 6:6 ring fusion. The additions of $(Ph_3P)_2Pt$ and $Ir(CO)Cl(PPh_3)_2$ both occur at 6:6 ring fusions to give η^2-C_{60} adducts,^{6,7} and osmium tetroxide attacks at the same site to form a *cis*-diol chelate ring.⁵ Theoretical work has indicated that the bonds at the 6:6 ring fusions in C_{60} will be more reactive than those at the 6:5 ring fusions.¹⁷ Here we report on the synthesis and structural characterization of an iridium complex of C_{70} .

Mixing equal volumes of dioxygen-free benzene solutions of $Ir(CO)Cl(PPh_3)_2$ (2 mM) and C_{70} (2 mM) gives a brown solution, from which brown crystals of $(\eta^2-C_{70})Ir(CO)Cl(PPh_3)_2 \cdot 2.5C_6H_6$ (**1**) can be obtained by either slow evaporation or gradual addition of methanol. The infrared spectrum of **1** in a fluorolube mull shows a carbonyl stretching vibration at 2002 cm^{-1} with a shoulder at 2010 cm^{-1} . The increase in $\nu(CO)$ over that in $Ir(CO)Cl(PPh_3)_2$ ($\nu(CO)$, 1965 cm^{-1}) is consistent with partial oxidation of the metal and is characteristic of addition of an electron-withdrawing moiety (i.e., an electron-deficient olefin).¹⁸

The results of an X-ray crystallographic study are presented in Figure 2^{19,20} and Figure 3, which shows a stereoscopic view of

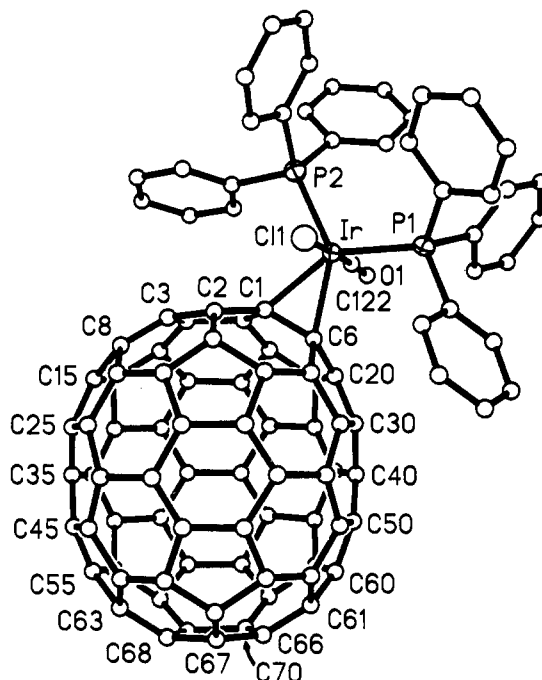


Figure 2. A perspective view of $(\eta^2-C_{70})Ir(CO)Cl(PPh_3)_2$ with 50% thermal contours for Ir and P and arbitrarily sized circles for C, Cl, and O. Only one orientation of the disordered CO and Cl units is shown. Bond distances (Å): Ir–P(1), 2.376 (5); Ir–P(2), 2.389 (6); Ir–C(1), 2.19 (2); Ir–C(6), 2.18 (2); C(1)–C(6), 1.46 (3). Bond angles (deg): P(1)–Ir–P(2), 114.9 (2); C(1)–Ir–C(6), 39.0 (7).

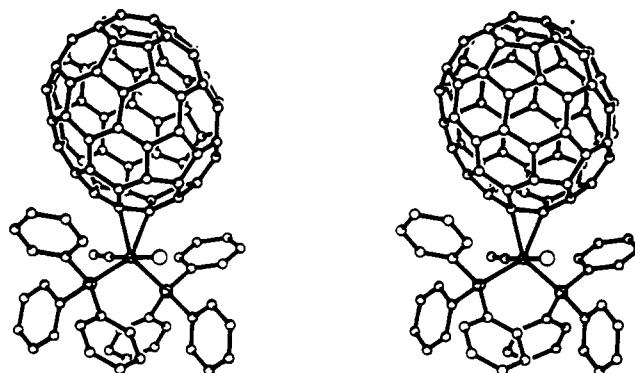


Figure 3. A stereoscopic drawing of $(\eta^2-C_{70})Ir(CO)Cl(PPh_3)_2$.

the molecule from a different perspective. The core structure of the C_{70} portion confirms earlier expectations (i.e., Figure 1). It has a spheroidal shape with a 7.90-Å distance along the major axis and a 6.82-Å diameter. Average C–C bond distances are as follows: a–a, 1.46 (3) Å; a–b, 1.38 (1) Å (C(1)–C(6) distance excluded); b–c, 1.45 (3) Å; c–c, 1.37 (2) Å; c–d, 1.43 (2) Å; d–d, 1.44 (1) Å; d–e, 1.42 (3) Å; e–e, 1.46 (2) Å. These lengths, with their admittedly large experimental errors, generally follow the trend of recent calculations,²¹ which predict the equatorial e–e bonds to be the longest and the c–c and a–b bonds to be the shortest. The pentagonal and hexagonal faces are nearly planar. The largest deviations from planarity involve the hexagons adjacent to the C(1)–C(6) bond and the hexagons along the equator. These are concave while the hexagons of the next band are convex. The iridium ion is bound in an η^2 fashion with the connection made at one of the a–b bonds (i.e., at a 6:6 ring fusion). The C(1)–C(6) distance (1.46 (3) Å) is elongated relative to the average of the other a–b bonds (1.38 Å). The geometry about the iridium is similar to that of $(\eta^2-C_{60})Ir(CO)Cl(PPh_3)_2$ ⁷ and that of the olefin

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(19) Deep brown crystals of $(\eta^2-C_{70})Ir(CO)Cl(PPh_3)_2 \cdot 2.5C_6H_6$ were obtained by diffusion of methanol into a benzene solution of the complex. They form in the triclinic space group $P\bar{1}$ with $a = 13.439$ (6) Å, $b = 17.208$ (7) Å, $c = 18.195$ (8) Å, $\alpha = 113.50$ (4)°, $\beta = 95.00$ (4)°, $\gamma = 105.37$ (4)° at 120 K with $Z = 2$. Refinement of 5107 reflections with $R = 4.0\sigma(F)$ and 440 parameters yielded $R = 0.074$ and $R_w = 0.068$. The carbon monoxide and chloride ligands are disordered, as frequently seen in such complexes.²⁰

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complex (tetracyanoethylene)Ir(CO)Cl(PPh₃)₂.^{22,23} All have acute C–Ir–C angles, linear Cl–Ir–CO units, and P–Ir–P angles near 115°.

The finding that the iridium ion is bound to an a–b edge of C₇₀ is not unexpected in light of the structural information on (η²-C₆₀)Pt(PPh₃)₂⁶ and (η²-C₆₀)Ir(CO)Cl(PPh₃)₂.⁷ In both of those structures it was noted that metal binding was accompanied by local distortion of the C₆₀ so that the two carbon atoms involved in coordination were pulled out from the C₆₀ surface. In the idealized C₇₀ structure, simple geometric considerations show that the a–b bond is the most accessible bond for coordination of this sort. The other C–C bonds at 6:6 ring fusions (c–c, d–e, and e–e) all have a more flattened local structure, which would require much larger distortion to accommodate metal coordination. Thus while eight isomeric forms of (η²-C₇₀) coordination by metal centers are possible, we suspect that coordination at the a–b bond will be most favored as found here. Given the success of our efforts in obtaining ordered crystals of (η²-C₆₀)Ir(CO)Cl(PPh₃)₂ and a single isomer of (η²-C₇₀)Ir(CO)Cl(PPh₃)₂, it appears that Ir(CO)Cl(PPh₃)₂ will be a useful reagent for obtaining crystalline samples of the higher fullerenes whose structures remain to be determined.²⁴

Acknowledgment. We thank the National Science Foundation (CHE 894209 and CHE 9022909) for support, Johnson Matthey Inc. for a loan of iridium chloride, and J. Mayer for experimental assistance.

Supplementary Material Available: Drawings of **1** showing atomic numbering, details of the data collection and refinement of the structure, and tables of atomic coordinates, bond distances and angles, anisotropic thermal parameters, and hydrogen atom positions of **1** (16 pages); listing of observed and calculated structure factors for (η²-C₇₀)Ir(CO)Cl(PPh₃)₂ (34 pages). Ordering information is given on any current masthead page.

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Allylbarium in Organic Synthesis: Unprecedented α-Selective and Stereospecific Allylation of Carbonyl Compounds

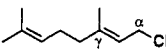
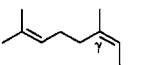
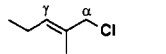
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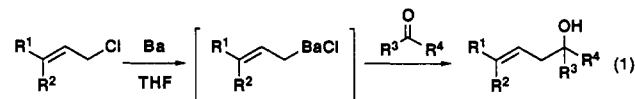
The organometallic compounds of heavier alkaline-earth metals have found little application in organic synthesis, since they do not offer any advantages over Grignard reagents.¹ We have been interested in using barium or strontium reagents with the anticipation that such species should exhibit stereochemical stability

Table I. Regio- and Stereoselective Allylation of Carbonyl Compounds with Allylic Barium Reagents Prepared from Allylic Chlorides^a

allylic chlorides ^b	carbonyls	yield, % ^c	α : γ ^d	E : Z ^d
(E)- ^γ C ₇ H ₁₅ CH=CHCH ₂ Cl	PhCHO	80	97 : 3	> 99 : 1
	^γ C ₈ H ₁₁ CHO	82	98 : 2	97 : 3
	(E)-PhCH=CHCHO	73 ^e	94 : 6	98 : 2
	Cyclohexanone	95	99 : 1	99 : 1
(Z)- ^γ C ₇ H ₁₅ CH=CHCH ₂ Cl	Acetophenone	94	96 : 4	99 : 1
	^γ C ₈ H ₁₁ CHO	75	86 : 14	2 : 98
	Cyclohexanone	89	75 : 25	2 : 98
(Z)- ^γ CH ₃ CH=CHCH ₂ Cl	^γ C ₈ H ₁₁ CHO	56	77 : 23	1 : 99
	PhCHO	90	92 : 8	98 : 2
	^γ C ₈ H ₁₁ CHO	90	94 : 6	> 99 : 1
	Cyclohexanone	98	89 : 11	> 99 : 1
	PhCHO	89	94 : 6	2 : 98
	^γ C ₈ H ₁₁ CHO	73	96 : 4	< 1 : 99
	Cyclohexanone	98	91 : 9	< 1 : 99
	^γ C ₈ H ₁₁ CHO	64	94 : 6	> 99 : 1
	Cyclohexanone	92	96 : 4	99 : 1

^a Allylation was carried out by using an allylic chloride, barium, and carbonyl compound (2, 2, and 1 equiv, respectively) at –78 °C for 30 min. ^b Stereochemically pure (>99%) allylic chlorides were used. ^c Isolated yield. ^d Determined by GC analysis. ^e 1,4-Adduct was also obtained in 14% yield.

markedly different from that of the ordinary magnesium reagent.² Herein, we disclose the first direct preparation of allylbarium by reaction of in situ generated barium metal with various allylic chlorides,³ and regio- and stereoselective allylation of carbonyl compounds using these allylmetals (eq 1).



Highly reactive barium was readily prepared by the reduction of barium iodide⁶ with 2 equiv of lithium biphenylide⁷ in dry THF at room temperature for 30 min. The dark brown suspension thus obtained was exposed to allylic chlorides at –78 °C. A slightly exothermic reaction takes place immediately to give a reddish suspension of allylic barium. The barium reagent reacts with a variety of carbonyl compounds cleanly at –78 °C in a few minutes to produce the homoallylic alcohol with remarkably high α-selectivity and retention of stereochemistry of the starting halides. It is well established that the corresponding magnesium or calcium reagent gave the γ-substituted product predominantly and the allylation with the lithium reagent was less selective.⁸ Table I summarizes the results obtained for the reaction of a variety of carbonyl compounds with barium reagents generated from E- or Z-allylic chlorides in THF at –78 °C. All reactions resulted in high yields with remarkable α-selectivities not only with aldehydes but also with ketones. In marked contrast to the allylmagnesium or allyllithium, the double-bond geometry of the allylbarium was

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