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, olefinic complexes having a functional group on one pyrazole ring. Thus, currently, 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, 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, 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.

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(η²-C₇₀)Ir(CO)(PPh₃)₂: The Synthesis and Structure of an Organometallic Derivative of a Higher Fulleren

Alan L. Balch,* Vincent J. Catalano, Joong W. Lee, Marilyn M. Olimstead, and Sean R. Parkin

Department of Chemistry, University of California

Davis, California 95616

Received August 12, 1991

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chloride ligands are disordered, as frequently seen in such complexes.20


at 2010 cm⁻¹. The increase in 6:6 ring fusions.17 Here we report on the synthesis and structural refinement of methanol into a benzene solution of the complex. They occurred at 6:6 ring fusions and those at 6:6 ring fusions. For c₆₀ the 6:6 ring fusion. The additions of (Ph₃P)₂Pt and Ir(CO)CI(PPh₃)₂ both occur at 6:6 ring fusions to give π²-C₆₀ adducts,65 and osmium tetroxide attacks at the same site to form a cis-diindol chelate ring.5 Theoretical work has indicated that the bonds at the 6:6 ring fusions in C₆₀ 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 C₆₀.

Mixing equal volumes of dioxygen-free benzene solutions of Ir(CO)(Cl(PPh₃)₂) (2 mM) and C₇₀ (2 mM) gives a brown solution, from which brown crystals of (π²-C₆₀)Ir(CO)(Cl(PPh₃)₂)·2.5C₆H₆ (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 ν(CO) over that in Ir(CO)(Cl(PPh₃)₂ (ν(CO), 1965 cm⁻¹) is consistent with partial oxidation of the metal and is characteristic 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 and 3, which shows a schematic view of the molecule from a different perspective. The core structure of the C₇₀ 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-e, 1.37 (2) Å; e-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 π² 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 (π²-C₆₀)Ir(CO)(Cl(PPh₃)₂)² and that of the olefin 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 π² 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 (π²-C₆₀)Ir(CO)(Cl(PPh₃)₂)² and that of the olefin

(17) Deep brown crystals of (π²-C₆₀)Ir(CO)(Cl(PPh₃)₂)·2.5C₆H₆, were obtained by diffusion of methanol into a benzene solution of the complex. They form in the triclinic space group P1 with a = 13.439 (6) Å, b = 17.208 (7) Å, c = 18.195 (8) Å, α = 113.50 (4)°, β = 95.00 (4)°, γ = 105.37 (4)° at 120 K with Z = 2. Refinement of 5107 reflections with F > 4σ(F) and 440 parameters yielded R = 0.074 and Rw = 0.068. The carbon monoxide and chloride ligands are disordered, as frequently seen in such complexes.²⁰

Allylboration in Organic Synthesis: Unprecedented α-Selective and Stereoselective Allylation of Carbonyl Compounds

Akira Yanagisawa, Shigeki Habaue, and Hisashi Yamamoto*

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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 stereoselectivity.


(3) Allylboration has, as yet, been prepared only by transmetalation with diallylmercury or tetraallylithium in THF.


(6) Anhydrous BaI₂ was prepared by drying commercially available BaI₂·2H₂O with a heat gun under reduced pressure (3 Torr).

(7) Highly reactive calcium has been prepared by the lithium biphénylide reduction of CaBr₂ or CaI₂; see: Wu, T.-C.; Xiong, H.; Rieke, R. D. J. Org. Chem. 1990, 55, 5045.

(8) α:γ ratios of the products obtained by the reaction of benzaldehyde with germallactones: M = Mg, γ:α < 1; 9% (yield); M = Ca, γ:α = 8:92 (38% yield); M = Li, γ:α = 47:53 (36% yield); M = Ce, γ:α = 72:28 (52% yield); preliminary results by A. Yanagisawa, S. Habaue, and H. Yamamoto.

Table 1. Regio- and Stereoselective Allylation of Carbonyl Compounds with Allylic Barium Reagents Prepared from Allylic Chlorides

<table>
<thead>
<tr>
<th>allylic chlorides</th>
<th>carbonyl</th>
<th>yield, %</th>
<th>α:γ</th>
<th>E:Z*</th>
</tr>
</thead>
<tbody>
<tr>
<td>(E)-CH₂=CHCH₂Cl</td>
<td>PhCHO</td>
<td>70</td>
<td>&gt;99 1</td>
<td></td>
</tr>
<tr>
<td>(Z)-CH₂=CHCH₂Cl</td>
<td>PhCHO</td>
<td>90</td>
<td>92:8</td>
<td>2:98</td>
</tr>
<tr>
<td>(E)-CH₂=CHCH₂Cl</td>
<td>C₅H₅CHO</td>
<td>90</td>
<td>94:6</td>
<td>&gt;99 1</td>
</tr>
<tr>
<td>(Z)-CH₂=CHCH₂Cl</td>
<td>C₅H₅CHO</td>
<td>89</td>
<td>96:4</td>
<td>&lt; 1:99</td>
</tr>
</tbody>
</table>

*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.

1Stereocinally pure (>99%) allylic chlorides were used.

2Isolated yield. Determined by GC analysis. *1,4-Adduct was also obtained in 14% yield.

Highly reactive barium was readily prepared by the reduction of barium iodide with 2 equiv of lithium biphénylide 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 allylboration. The reaction is slow at -78 °C, but it can be accelerated by heating to room temperature. The reaction was invesigated thoroughly by the reaction of in situ generated barium metal with various allylic chlorides, and regio- and stereolective allylation of carbonyl compounds using these allylmetals (eq 1).

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