

Figure 3. Molecular model of the dimer  $[tert\text{-butyl-C}_{60}]_2$ .

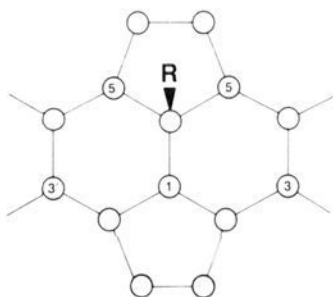
did eventually result in some reduction in signal intensity. Other radical adducts exhibited similar behavior, but in markedly different temperature ranges (Figure 1). Temperature dependence of this type is indicative of an equilibrium between a radical and its dimer, as typified by the behavior of the classical Gomberg radical  $(C_6H_5)_3C$ .<sup>13</sup>

The dependence of signal intensity on temperature and dilution at a fixed temperature (Figure 2) clearly established that the radical adducts of  $C_{60}$  exist in equilibrium with their dimers and that the dimer bond strength depends strongly on the size of the alkyl group R.



Upon dilution, the ESR signal strength decrease was less than expected for an inert radical and followed the curve (Figure 2) anticipated<sup>14</sup> for the dissociation of a dimer. On the assumption of a small degree of dissociation, the enthalpy change for the above equilibrium, and therefore the dimer bond strength, can be obtained from the slope of the van't Hoff plot in which  $\ln(T \times \text{intensity})$  is plotted against  $1000/T$  (Figure 1).<sup>15</sup>

The estimated bond strengths (Table I) of the dimers show a correlation with the size of R, which suggests that bonding in the dimer is greatly influenced by steric effects. This, in turn, strongly suggests that the constituents of the dimer bind at a carbon close to that bearing the substituent R, i.e., head-to-head, rather than head-to-tail as in the Gomberg radical dimer.<sup>13</sup> In such an arrangement, the near equality of the bond strengths for the *tert*-butyl and 1-adamantyl dimers would be expected from the similar steric constraints near the point of attachment. These observations support our conclusion<sup>8</sup> that the unpaired electron in  $RC_{60}$  radicals is essentially confined to the three carbon atoms ortho and the two carbon atoms para to the point of attachment of R, namely, C1, C3, C3', C5, and C5'. The resulting radical structure, having  $C_s$  symmetry, closely resembles two fused cyclohexadienyls:



Molecular graphics calculations<sup>16</sup> show that steric hindrance

(13) McBride, J. M. *Tetrahedron* **1974**, *30*, 2009.

(14)  $[r] = 0.5(0.25K^2 + 4K[d])^{0.5} - 0.25K$ , where  $[r]$  and  $[d]$  are the radical and undissociated dimer concentrations, respectively, and  $K$  is the equilibrium constant. ESR signal intensities were adjusted to give the required slope of 2 at zero concentration.

(15) Plotting  $\ln(\text{intensity} \times T)$  instead of simply  $\ln(\text{intensity})$  corrects for loss of signal due to the change in the Boltzmann distribution. "Intensity" means  $(\Delta B)^2 \ell$ , where  $\Delta B$  is the maximum-slope line width and  $\ell$  is the amplitude of the first-derivative presentation of the signal.

(16) Insight II Molecular Modelling Software, Biosym Technologies Inc., San Diego, CA 92121.

prevents the dimerization of *tert*-butyl- $C_{60}$  at C1, C5, or C5', but indicate that dimerization at C3 or C3' is feasible (Figure 3).

Our failure to detect ESR spectra from the reaction of small radicals ( $R = H, F, CH_3$ ) with  $C_{60}$  is presumably due to the unhindered access of secondary radicals to the spin-bearing carbons of the adduct. It could also be argued that the dimers of such radicals are so thermally stable that the equilibrium is overwhelmingly in favor of the dimer in the accessible temperature range.

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### Supramolecular Aggregation of an $(\eta^2-C_{60})$ Iridium Complex Involving Phenyl Chelation of the Fullerene

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The past 18 months have seen extraordinary interest in the chemical and physical properties of  $C_{60}$  and the higher fullerenes.<sup>1,2</sup> Samples of the fullerenes suitable for X-ray diffraction studies have been difficult to obtain due to poor crystal quality and orientational disorder.<sup>3-6</sup> However, organometallic derivatives in which a metal complex is bonded to the outer surface of the fullerenes have produced crystalline samples of good quality.<sup>7-11</sup> These have demonstrated preferential reactivity of the 6:6 ring fusions in both  $C_{60}$ <sup>7-9,11</sup> and  $C_{70}$ .<sup>10</sup> Not unexpectedly, the packing of these fullerenes and their derivatives produces cavities within the solid that can be occupied by occluded molecules. CocrySTALLIZATION of  $C_{60}$  or  $C_{70}$  with pentane causes a modification of their crystal structures in order to accommodate solvent occlusion.<sup>12</sup> Additionally,  $(\eta^2-C_{60})Ir(CO)Cl(PPh_3)_2$  crystallizes with five molecules of benzene,<sup>9</sup>  $(\eta^2-C_{70})Ir(CO)Cl(PPh_3)_2$  with 2.5 molecules of benzene,<sup>10</sup>  $C_{60}O_2OsO_2(4\text{-}tert\text{-butylpyridine})$  with 2.5 molecules of toluene,<sup>7</sup> and  $(\eta^2-C_{60})Pt(PPh_3)_2$  with a molecule of tetrahydrofuran.<sup>8</sup> In those structures, both intra- and intermolecular interactions of aromatic rings with the fullerenes occur. These are provided by one pair of phenyl rings bonded to the phosphines and, for example, by a benzene of the  $(\eta^2-C_{70})Ir(CO)Cl(PPh_3)_2$  structure which is squeezed between the sides of two adjacent  $C_{70}$  moieties.

These observations suggest that it might be possible to construct molecules that provide a host (a molecular egg crate) into which  $C_{60}$  (and other fullerenes) might nest. To explore this idea we

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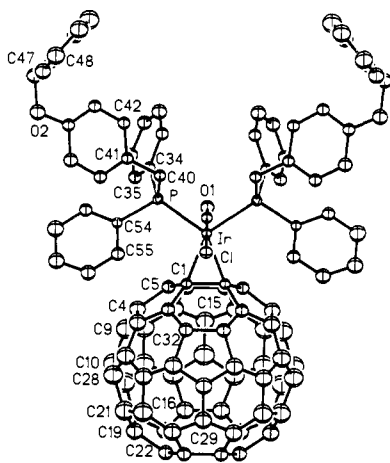
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**Figure 1.** Perspective view of  $(\eta^2\text{-C}_{60})\text{Ir}(\text{CO})\text{Cl}(\text{bobPPh}_2)_2$  with 50% thermal contours. Bond distances (Å): Ir–C(1), 2.194 (10); Ir–P, 2.370 (3); Ir–C(33), 1.834 (15); Ir–Cl, 2.398 (4); C–C (6:6 ring junctions) av, 1.383; C–C (6:5 ring junctions) av, 1.449. Bond angles (deg): P–Ir–P', 106.3 (1); Cl–Ir–C(33), 177.9 (5); C(1)–Ir–C(1)', 39.5 (5); C(1)–C(1)–C(2), 117.0 (6); C(1)–C(1)–C(5), 117.2 (6); C(2)–C(1)–C(5), 103.3 (9).

have begun modifying the phosphine ligands used to prepare Vaska-type iridium compounds,  $\text{Ir}(\text{CO})\text{Cl}(\text{PR}_3)_2$ , which are known to readily and reversibly bind to the fullerenes.<sup>9,10</sup> We sought to prepare new ligands that would have flat aromatic rings connected with sufficient flexibility to accommodate  $\pi\text{-}\pi$  interactions with the curved exterior of  $\text{C}_{60}$ .

To this end we prepared  $\text{C}_6\text{H}_5\text{CH}_2\text{OC}_6\text{H}_4\text{CH}_2\text{P}(\text{C}_6\text{H}_5)_2$  ( $\text{bobPPh}_2$ ). This was obtained by the addition of a solution of 4-(benzyloxy)benzyl chloride in tetrahydrofuran to a solution of  $\text{NaPPh}_2$  in liquid ammonia at  $-78^\circ\text{C}$ . After evaporation of the solvent, the residue was dissolved in dichloromethane. Addition of ethanol caused the phosphine to precipitate as colorless crystals.<sup>13</sup> Treatment of  $\text{Ir}(\text{CO})\text{Cl}(\text{AsPh}_3)_2$  with 2 equiv of  $\text{bobPPh}_2$  in dichloromethane yielded a yellow solution, from which  $\text{Ir}(\text{CO})\text{Cl}(\text{bobPPh}_2)_2$  was obtained in 75% yield by addition of methanol and evaporation of the solvent.<sup>14</sup> Mixing equal volumes of 2 mM benzene solutions of  $\text{Ir}(\text{CO})\text{Cl}(\text{bobPPh}_2)_2$  and  $\text{C}_{60}$  in benzene followed by the addition of diethyl ether produced black crystals of  $(\eta^2\text{-C}_{60})\text{Ir}(\text{CO})\text{Cl}(\text{bobPPh}_2)_2$  (**2**). The infrared spectrum of the solid shows  $\nu(\text{CO})$  at  $2037\text{ cm}^{-1}$  (fluorolube mull).

The results of an X-ray crystallographic study<sup>15</sup> of **2**, which crystallizes without occlusion of solvent molecules, are presented in Figures 1–3. Figure 1 shows a view of a single molecule. It lies on a crystallographic mirror plane that bisects the  $\text{C}_{60}$  unit and passes through the *trans*- $\text{ClIr}(\text{CO})$  group. The  $\text{C}_{60}$  molecule is bound to the iridium atom in an  $\eta^2$  fashion through a 6:6 ring junction as expected. The overall geometry closely resembles that of  $(\eta^2\text{-C}_{60})\text{Ir}(\text{CO})\text{Cl}(\text{PPh}_3)_2$  (**1**).<sup>9</sup> In both **1** and **2**, two of the phenyl rings are positioned near the  $\text{C}_{60}$  unit. In **2**, the closest contact (3.10 Å) involves C(55) and C(2). In **1**, the shortest distance of this type is 3.26 Å.

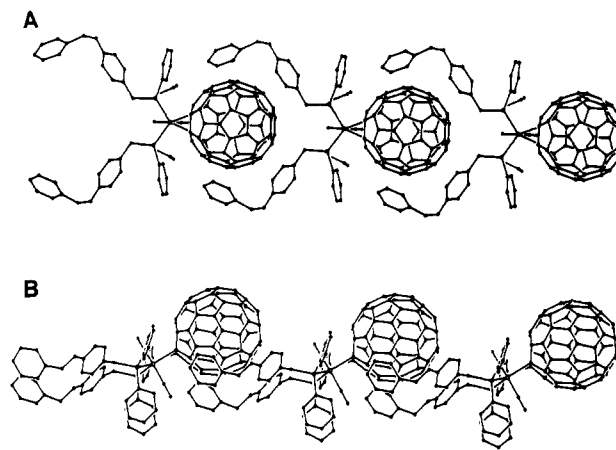
As seen in Figure 2, the two arms of the phosphine ligands in **2** reach out to cradle the  $\text{C}_{60}$  portion of an adjacent molecule of **2**. These interactions continue on to the next molecule so that an infinite chain results.

The interactions between the phosphine side chains and  $\text{C}_{60}$  are shown in Figure 3. Each phenyl ring lies above a 5:6 ring fusion

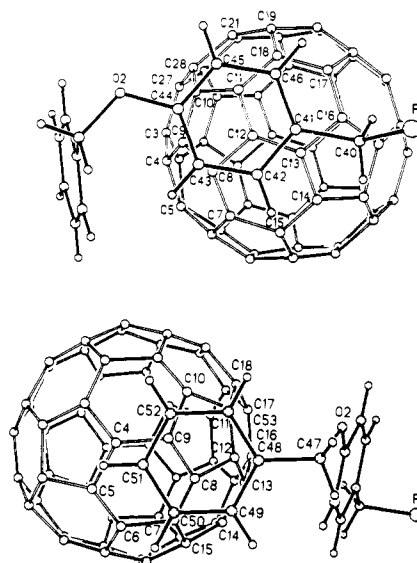
(13) Colorless crystals from hot ethanol: mp  $125^\circ\text{C}$  with resolidification;  $^{31}\text{P}\{\text{H}\}$  NMR  $\delta$  –10.5 ppm (toluene);  $^1\text{H}$  NMR methylene singlets 3.34, 4.97 ppm, phenylene AB doublet, 6.79, 6.95 ppm, phenyl multiplet, 7.28–7.4.

(14) Yellow crystals: mp 164–166  $^\circ\text{C}$ ;  $^{31}\text{P}\{\text{H}\}$  NMR  $\delta$  23.7 ppm (toluene); IR  $\nu(\text{CO})$  1964  $\text{cm}^{-1}$  (benzene solution).

(15) Black shards of  $(\eta^2\text{-C}_{60})\text{Ir}(\text{CO})\text{Cl}(\text{bobPPh}_2)_2$  were obtained by diffusion of diethyl ether into a benzene solution of the complex. They form in the orthorhombic space group *Pnma* with  $a = 19.879$  (4) Å,  $b = 24.885$  (6) Å, and  $c = 13.841$  (3) Å at 130 K with  $Z = 4$ . Refinement of 3389 reflections with  $F > 4.0\sigma(F)$  and 260 parameters yielded  $R = 0.066$  and  $R_w = 0.071$ .



**Figure 2.** Two views of **2** (A, B) which show the chelation of one molecule by another. The propagation of molecules occurs by translation along the *c* axis.



**Figure 3.** Top: view of the adjacent  $\text{C}_{60}$  through the plane of the phenyl ring C(41)–C(46). Shortest distances (Å): C(13)–C(41), 3.31; C(12)–C(42), 3.49; C(12)–C(41), 3.50; C(11) to ring plane, 3.82; C(12) to ring plane, 3.36. Bottom: view through ring C(48)–C(53). Shortest distances (Å): C(4)–C(51), 3.36; C(9)–C(52), 3.39; C(9)–C(51), 3.45; C(9) to ring plane, 3.35; C(8) to ring plane, 3.80.

in the chelated  $\text{C}_{60}$ . The two ring fusions that are chelated by one arm of the ligand are part of a single pentagonal face of the  $\text{C}_{60}$ . The two pentagonal faces that are involved in this chelation by the two side arms have a meta relationship to one another.<sup>16</sup> The shortest contacts between the  $\text{C}_{60}$  moiety and the two phenyl rings are given in the figure caption. These are in the 3.3–3.4 Å range and are typical of the separations found in graphite and between planar aromatic systems. For comparison, the contacts between the benzene molecules and the  $\text{C}_{60}$  in **1** are in the 3.6–3.7 Å range. The offset geometry, where the phenyl rings lie over the 5:6 ring fusions, appears consistent with the Hunter/Sanders rules for  $\pi\text{-}\pi$  interactions.<sup>17</sup> These 5:6 ring fusions represent centers of positive charge on the  $\text{C}_{60}$  surface.

Despite the fact that the arms of the two phosphine ligands surround an adjacent  $\text{C}_{60}$  unit, the P–Ir–P angle in **2** ( $106.3$  ( $1^\circ$ )) is actually *narrower* than the corresponding angles in **1** ( $113.3$  ( $2^\circ$ )) and in  $(\eta^2\text{-C}_{70})\text{Ir}(\text{CO})\text{Cl}(\text{PPh}_3)_2$  ( $114.9$  ( $2^\circ$ )). This nar-

(16) We define the relationship of parallel pentagonal faces in  $\text{C}_{60}$  as para; the five pentagonal faces that are only one C–C bond away from one of these are ortho to one another. Pentagonal faces that are separated by four bonds have a meta relationship to one another.

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rowing further suggests that an attractive interaction exists between the phosphine side arms and the fullerene.

In summary, this work shows that the guest/host nature of fullerene/phenyl interactions can be chemically manipulated to produce novel solid-state aggregates. The phenyl-X-Y-phenyl unit (X, Y are first row atoms) has the proper geometry to chelate a portion of C<sub>60</sub>.

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**Supplementary Material Available:** Tables of atomic coordinates, bond distances, bond angles, anisotropic thermal parameters, and hydrogen atom positions for **2** (10 pages); listings of observed and calculated structure factors for **2** (16 pages). Ordering information is given on any current masthead page.

### Hole Transfer Promoted Hydrogenation: One-Electron Oxidation as a Strategy for the Selective Reduction of $\pi$ Bonds

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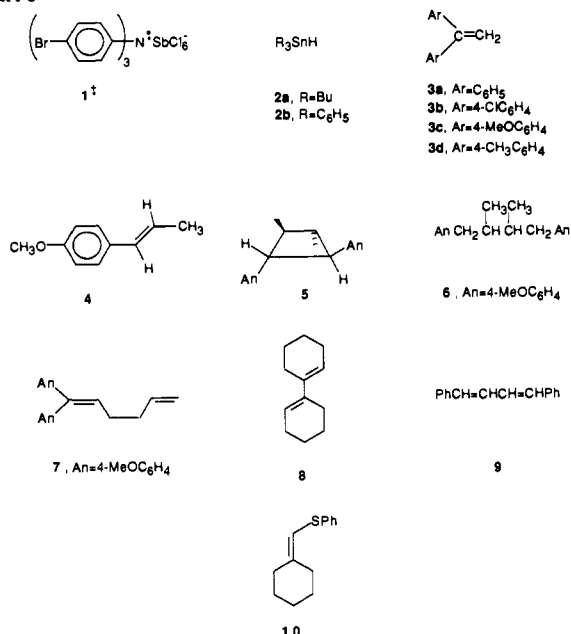
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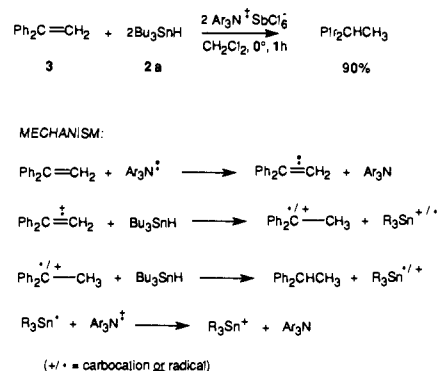
One-electron oxidation (hole formation) is increasingly being exploited as a fundamental option for activating molecules toward synthetically useful chemistry mediated by cation radicals.<sup>1-5</sup> In the context of multifunctional molecules, reactivity can be specifically directed to the most oxidizable functionality through the use of mild hole-transfer agents such as tris(4-bromophenyl)aminium hexachloroantimonate (**1**<sup>+</sup>) (Chart I). This strategy has recently been used to develop an efficient epoxidation procedure in which selectivity is based solely upon, and is highly sensitive to, relative oxidizability.<sup>6</sup> The present communication describes a similarly selective method for the dihydrogenation of relatively oxidizable ( $E_{ox} \leq 1.5$  V) functionalities, including conjugated dienes, styrenes, electron-rich alkenes, aromatics, and even strained  $\sigma$  bonds.

The reduction of an alkene cation radical to an alkane formally requires the transfer of one hydrogen atom and one hydride ion to the cation radical. The hydrogen-transfer agents found most effective in this work were tributyltin hydride (**2a**) and triphenyltin hydride (**2b**). The concept of promoting alkene reduction by initial one-electron oxidation is illustrated by the reduction of 1,1-diphenylethene (**3a**,  $E_{ox} = 1.22$  V, Scheme I, 90% yield). The important mechanistic issue of the sequence of hydrogen atom and hydride transfer, i.e., whether the initial product of hydrogen transfer is a carbocation or a free radical, has not yet been resolved but is currently under investigation. The ability of **1**<sup>+</sup> to ionize **3a** under the present reaction conditions has previously been established, and the generation of **3a**<sup>+</sup> is further confirmed by the observation of minor amounts of the cyclodimer of **3a** in the product.<sup>5</sup> A major substituent effect appropriate to the ionization of **3a** is suggested by the complete unreactivity of the corresponding *p,p'*-dichloro derivative (**3b**) during a reaction time of 1 h. In contrast to both **3a** and **3b**, the *p,p'*-dimethoxy derivative (**3c**) was completely reduced within 1 min (93%). A quantitative study

Chart I



Scheme I



of the competitive reduction of **3a** and its corresponding 4,4'-dimethyl derivative (**3d**) revealed a relative reaction rate of 1:167, corresponding to a  $\rho$  value of ca. -7.2 (using  $\sigma_p^+$ ) or -3.6 (using  $\Sigma\sigma_p^+$ ). A  $\rho$  value of -4.0 per aryl ring has been found to correspond to full carbocation formation in the equilibrium protonation of 1,1-diarylethenes.<sup>7</sup> The possibility of a Bronsted acid catalyzed mechanism is ruled out by the observation that excess 2,6-di-*tert*-butylpyridine fails to suppress the reaction.<sup>1,2,8</sup> Moreover, the reduction of 2,4-dimethyl-1,3-pentadiene yields, as a byproduct, the cyclodimer resulting from hole transfer catalyzed Diels-Alder cycloaddition but none of the acid-catalyzed cyclodimerization product.<sup>1,2</sup> Similarly, the hydrogenations of 1,3-cyclohexadiene and 1,1'-bicyclohexenyl also yield the well-known hole transfer catalyzed cyclodimers as byproducts.<sup>1,2</sup>

In the case of *trans*-anethole (**4**), hole transfer catalyzed cyclodimerization strongly predominates, affording the cyclobutadimer (**5**).<sup>9</sup> However, **5** is also readily oxidizable, and the proposed long bond<sup>9,10</sup> of **5**<sup>+</sup> is then reductively cleaved to afford **6** (80%). The dihydrogenation of **4** was achieved, nevertheless, by using the more reactive triphenyltin hydride (**2b**) as the reductant (55%). The selectivity of hole transfer promoted hydrogenation is illustrated by the reduction of **7**, which occurs exclusively at the more ionizable double bond (95% yield). Simple double bonds such as those in norbornene and 1-octene are not

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