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Structural Characterization of $\{(\eta^2\text{-}C_{60})RhH(CO)(PPh_3)_2\}$: Product of the Reaction of C_{60} with the Hydrogenation Catalyst $\{RhH(CO)(PPh_3)_3\}$

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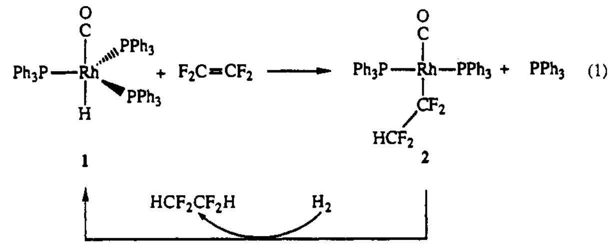
Since the discovery that C_{60} can be readily prepared in macroscopic quantities,[1] there has been considerable effort expended in preparing addition products of this truncated icosahedral molecule.[2] While there are a number of theoretical papers concerned with structures and stabilities of hydrogenated C_{60},[3] little experimental work on hydrogenation of the fullerenes is available. An early report claimed the existence of $C_{60}H_{36}$, which was obtained through Birch reduction.[4] However, it was not recognized at the time that ammonia, the solvent for the Birch reduction, is also reactive toward C_{60}.[5] Consequently, the true identity of "$C_{60}H_{36}$", which was identified through mass spectroscopy, is open to question. As part of our study of the reactivity of fullerenes with organometallic reagents,[6] we have explored the use of known homogeneous hydrogenation catalysts for their ability to react with C_{60}. Here we report studies using $\{RhH(CO)(PPh_3)_3\}$, **1**, a well-known catalyst of this sort.[7] We particularly chose this catalyst because its stoichiometric reactivity toward an electron deficient olefin (to which C_{60} has been likened) had previously been described. The reaction of **1** with tetrafluoroethylene produces the fluoroalkyl complex **2** (eq 1).[8] In the presence of dihydrogen, this mixture affects the hydrogenation of tetrafluoroethylene (and other olefins as well).[8]



Treatment of a dichloromethane solution of $\{RhH(CO)(PPh_3)_3\}$ with C_{60} results in the formation of a green solution. The $^{31}P\{^1H\}$ NMR spectrum of the solution shows the loss of the doublet at 41.1 ppm ($^1J(Rh, P) = 154$ Hz) that is due to the starting hydride complex, **1**, and the growth of a new doublet at 40.3 ppm ($^1J(Rh, P) = 138$ Hz) due to $\{(\eta^2\text{-}C_{60})RhH(CO)(PPh_3)_2\}$, **3**, and a singlet at −3.5 ppm due to free triphenylphosphine. The complex **3** can be isolated as green-black crystals in 75% yield. It redissolves in benzene, toluene, or dichloromethane to give green solutions. The ^1H NMR spectrum of **3** in dichloromethane-d_2 at 25 °C shows a broad singlet at −9.33 ppm due to the hydride ligand which remains bound to rhodium. On cooling to −60 °C, this resonance resolves into a 1:2:1 triplet with $^2J(P,H) = 8.4$ Hz. The infrared spectrum of **3** (fluorolube mull) shows ν(Rh–H) at 2082 cm^{-1} as well as ν(CO) at 1988 cm^{-1}. Thus, unlike $\{(\eta^2\text{-}C_{60})IrCl(CO)(PPh_3)_2\}$, which readily dissociates into C_{60} and $\{Ir(CO)Cl(PPh_3)_2\}$ when it is dissolved,[6] $\{(\eta^2\text{-}C_{60})RhH(CO)(PPh_3)_2\}$ is stable in solution.

The results of an X-ray crystallographic investigation of **3** are

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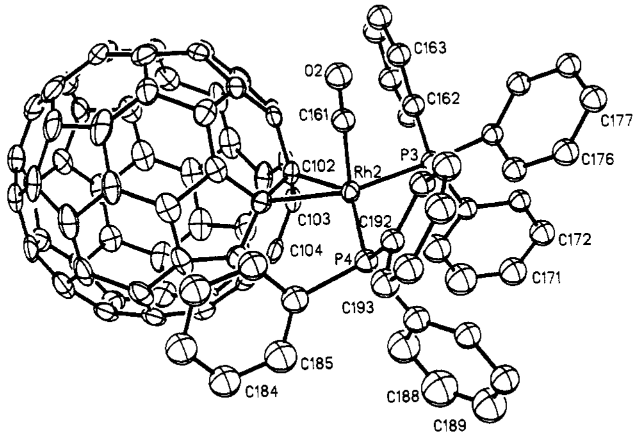


Figure 1. Perspective view of one molecule of $\{(\eta^2\text{-}C_{60})RhH(CO)(PPh_3)_2\}$ with 50% thermal contours for all atoms. The other molecule has a similar structure, but one of the triphenylphosphine ligands shows disorder in the position of two of its phenyl rings.

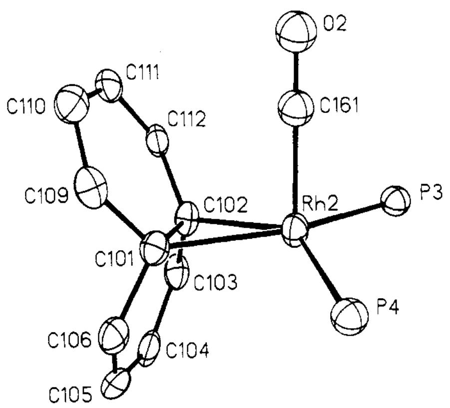
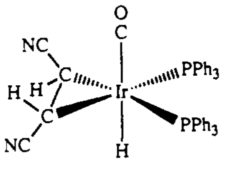


Figure 2. View of the inner coordination about rhodium in $\{(\eta^2\text{-}C_{60})RhH(CO)(PPh_3)_2\}$. Selected interatomic distances (Å) with corresponding values for the other molecule in brackets: Rh(2)–C(101), 2.165(8) [2.167(7)]; Rh(2)–C(102), 2.151(8) [2.168(7)]; Rh(2)–C(161), 1.934(9) [1.924(8)]; Rh(2)–P(3), 2.333(2) [2.337(2)]; Rh(2)–P(4), 2.318(2) [2.322(2)]; C(101)–C(102), 1.479(11) [1.496(10)]. Selected angles (deg): C(101)–Rh(2)–C(102), 40.1(3) [40.4(3)]; P(3)–Rh(2)–P(4), 113.60(8) [113.09(8)].

shown in Figures 1 and 2.[9] There are two molecules of the complex and disordered molecules of dichloromethane in the asymmetric unit. The geometries of the two rhodium complexes are similar. As seen in Figure 2, the C_{60} moiety is bound to the rhodium in an η^2 fashion through a 6:6 ring fusion. Similar η^2 coordination at the 6:6 ring fusion has been seen for the $\{(Ph_3P)_2Pt\}$[10] and $\{Ir(CO)Cl(PR_3)_2\}$[6] adducts of C_{60}. The hydride ligand was not located directly in the crystallographic study but its position can be inferred to be the apparently vacant site opposite the carbonyl ligand.[11] With that site occupied, the rhodium ion has approximate trigonal bipyramidal geometry with the carbonyl and hydride ligands in axial positions and the η^2-C_{60} and the triphenylphosphine ligands in the equatorial plane. The dihedral angles between the P_2Rh and C_2Rh planes in the two molecules are 22.3 and 21.9°. The structure of **3** is similar to that of $\{(trans\text{-}C_2H_2(CN)_2)IrH(CO)(PPh_3)_2\}$, **4**.[12] However in **4** the dihedral angle between the P_2Ir plane and the IrC_2 plane (0.2(9)°) is much smaller than the corresponding dihedral angles found for **3**.



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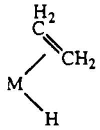
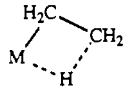
There has been considerable recent interest on the relationships between terminal ethylene hydride complexes (**A**), agostic ethyl species (**B**), and alkyl complexes (**C**).[13] In the case of **3**, the spectroscopic and crystallographic data indicate that the ethylene hydride form A is present. So far, attempts to hydrogenate C_{60} using $\{RhH(CO)(PPh_3)_3\}$ have led only to the formation of **3**, but efforts on catalytic hydrogenation are continuing.



A



B

$M{-}CH_2CH_3$

C

Since this manuscript was submitted reports on the hydrogenation of C_{60} by 9,10-dihydroanthracene[14] and by BH_3 (to form $C_{60}H_2$)[15] have appeared. A reviewer called attention to two reports on the hydrogenation of fullerenes with ruthenium on carbon as a catalyst.[16,17]

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Supplementary Material Available: Tables of atomic parameters and isotropic thermal parameters for non-hydrogen atoms, bond distances, bond angles, anisotropic thermal parameters, hydrogen atom coordinates, and crystal data for $\{(\eta^2\text{-}C_{60})RhH(CO)(PPh_3)_2\}_2\cdot 6.55CH_2Cl_2$ (30 pages). Ordering information is given on any current masthead page.

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(9) Green-black shards of $\{(\eta^2\text{-}C_{60})RhH(CO)(PPh_3)_2\}_2\cdot 6.55CH_2Cl_2$, $C_{200.55}H_{75.1}Cl_{13.1}Rh_2O_2P_4$, crystallize in the monoclinic space group $P2_1/c$ with $a = 13.355(2)$ Å, $b = 34.661(4)$ Å, $c = 27.329(4)$ Å, and $\beta = 92.28(2)°$ at 123 K with $Z = 4$. Refinement of 15 437 independent reflections gave $R_w(F^2) = 0.223$; for 11 378 reflections with $F_o > 4\sigma F_o$, it gave the conventional $R(F) = 0.072$.

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