Organometallic Hydrides as Reactants in Fullerene Chemistry. Synthesis and Configuration of $(\eta^2\text{–}C_n)RhH(CO)(PPh_3)_2$ (n = 60, 70) Complexes†

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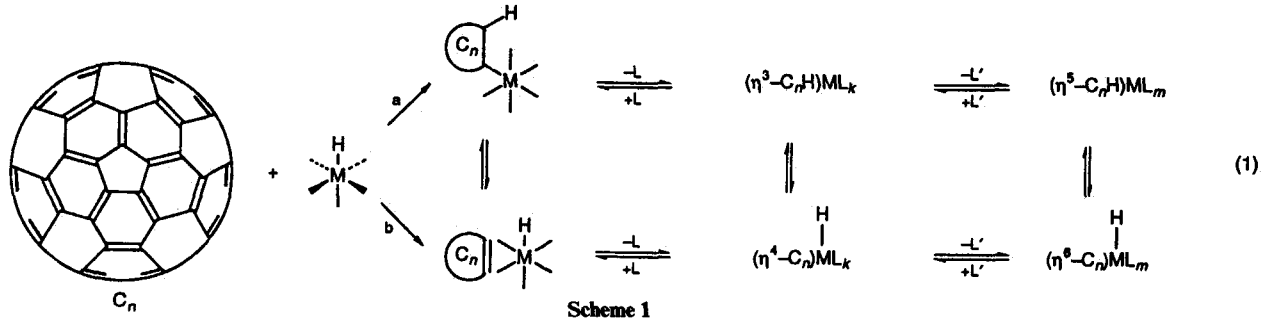
Rhodium hydride $HRh(CO)(PPh_3)_3$ reacts with fullerenes C_{60} and C_{70} yielding $(\eta^2\text{–}C_n)RhH(CO)(PPh_3)_2$ (n = 60, 70) complexes whose composition and configuration have been established by means of IR and NMR spectroscopy.



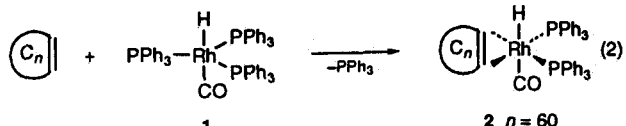
Scheme 1

Recent investigations[1–9] of fullerene reactivity towards various transition metal complexes have led to the synthesis of a series of exohedral organometallic derivatives of C_{60} and C_{70} with such metals as Ni, Pd, Pt, Ru and Ir. In most cases these complexes have been structurally characterized and it has been shown that they contain one or several (up to six) transition metal atoms coordinated with a fullerene moiety solely in an η^2-fashion. The use of organometallic hydrides for a study of the reactivity of such polyene strong acceptors as fullerenes seems to be rather promising for at least two reasons. First, they can react with fullerenes by two different ways: (i) by an addition of an M–H bond to a fullerene polyene system giving oddly-bonded complexes (of η^1-, η^3- and η^5-types) and (ii) by direct coordination with fullerene giving evenly-bonded π-complexes (of η^2-, η^4- and η^6-types) (see Scheme 1, pathways a and b). Second, a hydride ligand furnishes a way to distinguish between different reaction pathways and to determine the configuration of the hydride complexes (path b) from IR and/or NMR spectra.

In this paper we present the results of our study of the interaction of C_{60} and C_{70} fullerenes with $HRh(CO)(PPh_3)_3$ **1**. The latter is a highly efficient catalyst for such processes as hydrogenation, isomerisation, hydroformylation and hydrosilylation of alkenes.[10–12]

When an equimolar quantity of a yellow solution of **1** in benzene or toluene is added to a purple solution of C_{60} in the same solvent, a green solution is immediately produced. A dark-green $(\eta^2\text{-}C_{60})RhH(CO)(PPh_3)_2$‡ complex **2** can be precipitated from this solution with ether in 80–85% yield (Scheme 2). The electron spectrum of the reaction mixture in toluene obtained immediately after the mixing contains two new bands at 438 and 660 nm which were absent from the spectra of the initial compounds. The spectrum does not vary with time which is indicative of a high rate of formation of **2**. The absorption spectrum of the individual compound in THF solution contains the following bands: 255 (s), 327 (s), 390 (sh), 438(w), 618(w) and 659(w) nm. A dark-brown (almost black) $(\eta^2\text{-}C_{70})RhH(CO)(PPh_3)_2$‡ complex **3** whose electron spectrum in toluene [332 (s), 364 (sh), 380 (m), 464 (m) and 545 (sh) nm] varies very little (except for intensity) from that of the starting C_{70} can be obtained in the same manner.

The configuration of **2** and **3** is determined from IR and NMR



1

2 n = 60
3 n = 70

Scheme 2

data. The IR spectrum of the starting complex **1** contains a strong ν_{CO} band at 1921 cm^{-1} and a moderate ν_{RhH} band at 2038 cm^{-1}, which is typical for carbonyl hydride complexes of transition metals.[11] However, IR spectra of **2** and **3** both in the solid state (KBr pellets, Nujol mull) and in solutions ($CDCl_3$) are similar and rather unusual (see Fig. 1). One can see from this spectrum that ν_{RhH} bands at 2056 cm^{-1} (**2**) and 2060 cm^{-1} (**3**) are somewhat more intense than ν_{CO} bands at 1984 cm^{-1} (**2**) and 1986 cm^{-1} (**3**). This 'equalization' of intensities is due to the resonance coupling between two vibrations of the same symmetry with close frequencies. Such coupling between M–CO and M–H coordinates has been observed previously.[13,14] It can take place only when both bonds are in a *trans*-position

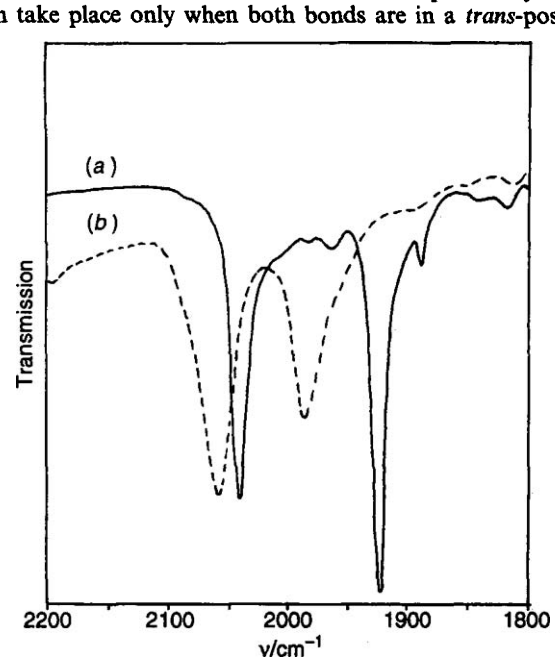


Fig. 1 IR spectra of (*a*) $HRh(CO)(PPh_3)_3$ in Nujol mull; (*b*) $\eta^2\text{–}(C_{60})RhH(CO)(PPh_3)_2$ in KBr pellet.

† Part of this material has been reported earlier – see A. V. Usatov, S. V. Suprunovich, E. V. Vorontsov and Yu. N. Novikov, Abstracts of the Xth FECHEM Conference on Organometallic Chemistry, Crete, Greece; 1993, p. 133.

‡ Satisfactory elemental analyses were obtained for compounds **2** and **3**.

relative to each other. A substantial shift of the ν_{CO} band in **2** and **3** as compared with **1** is due to the strong electron-acceptor nature of η^2-coordinated fullerene molecules and is typical for carbonyl complexes of transition metals with electron-deficient alkenes (TCNE, C_2F_4, *etc.*) as well as for carbonyl complexes of Ir with C_{60} and C_{70}.[2–7]

The results obtained are also confirmed by NMR data. The ^1H NMR spectra ($CDCl_3$, TMS) of both complexes contain a triplet at $\delta = -9.38$ ppm ($^2J_{HP} = 9.5$ Hz) (**2**) and at $\delta = -10.23$ ppm ($^2J_{HP} = 10$ Hz) (**3**) which is assigned to the hydride proton. The observed multiplicity and small value of the $^2J_{HP}$ spin-spin constant testify that two phosphines in **2** and **3** are in the *cis*-position[11,15] relative to the hydride proton. The hydride chemical shifts in the initial compound **1** (−9.5 ppm, bd) and both complexes **2** and **3** are almost the same which also indicates that H- and CO-ligands maintain their *trans*-position when coordinated with fullerene since the main contribution to a chemical shift in hydride complexes of transition metals is from the ligand in the *trans*-position.[11,15] A complex multiplet is observed in the spectra of both compounds at ~7.3 ppm which is assigned to phenyl protons. The ^{31}P NMR spectrum (toluene, 85% H_3PO_4) of **2** contains a single doublet at 39.7 ppm with $J_{P-Rh} = 143$ Hz which corresponds to a single isomer with equivalent phosphorous atoms. However, two doublets of doublets at 40.7 ppm ($J_{P1-Rh} = 142$ Hz; $^2J_{P1-P2} = 30$ Hz) and 43.9 ppm ($J_{P2-Rh} = 143$ Hz; $^2J_{P1-P2} = 30$ Hz) are observed in the ^{31}P NMR spectrum of **3**. These signals are assigned to two non-equivalent phosphorous atoms in a *cis*-position relative to each other as evidenced by the value of the $^2J_{P1-P2}$ constant.[11,15] Considering that the Rh atom in **2** and **3** seems to be bonded with fullerene through a 6-6 edge (in the way which is typical for each of the fullerenes[1,3–8]), the non-equivalence of phosphorous atoms in **3** is due to the non-symmetrical position of the C_{70} molecule in the complex. This has been observed in Ir complexes of C_{70} whose structure has been determined previously.[6,7] Thus, all the results obtained strongly support the structure of **2** and **3** with an η^2-coordinated fullerene moiety and *trans*-configuration of hydride and carbonyl ligands.

In addition, it should be noted that **1** reacts with such electron acceptor alkenes as tetracyanoethylene or tetrafluoroethylene giving solely associated σ-complexes,[11,16] due to the insertion of alkene to a Rh-H bond, whereas in the case of C_{60} and C_{70} fullerenes only η^2-derivatives of **2** and **3** are formed, as follows from our results. This is the first example of a fundamentally different reactivity of fullerenes towards metallocomplexes as compared to the conventional electron acceptor alkenes.

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