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Metalation of C_{60} with Pentacarbonylrhenium Radicals. Reversible Formation of $C_{60}\{Re(CO)_5\}_2$

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Abstract: Xenon lamp flash photolysis or continuous sunlamp irradiation of $Re_2(CO)_{10}$ with C_{60} in benzene produces a new species with IR (ν_{CO}) bands at 2134, 2130 (sh), 2036, and 1993 cm^{-1}. This product is assigned as $C_{60}\{Re(CO)_5\}_2$ primarily on the basis of a quantitative IR study of its formation stoichiometry. Similar results are obtained from the thermal reaction of C_{60} with a known source of rhenium pentacarbonyl radicals, viz., $(\eta^3\text{-}Ph_3C)Re(CO)_4$, in the presence of CO. The compound $C_{60}\{Re(CO)_5\}_2$ is unstable and decomposes to $Re_2(CO)_{10}$ and C_{60} with a first-order rate constant at room temperature of $7.3(6) \times 10^{-5}$ s^{-1}. When the decomposition is allowed to proceed in the presence of carbon tetrachloride, $Re(CO)_5Cl$ and C_{60} are the only products formed.

Introduction

The organometallic chemistry of C_{60} is becoming a flourishing subdiscipline of the fast expanding fullerene research.[1,2] The first structurally characterized C_{60} derivative, an osmate ester with C–O–Os bonds, $(^tBuC_5H_5N)_2Os(=O)_2O_2(C_{60})$, confirmed the predicted C_{60} framework.[3] Subsequently, X-ray diffraction studies of complexes with direct C–M bonding, e.g., $(Ph_3P)_2Pt(\eta^2\text{-}C_{60})$[4a] and $(Ph_3P)_2(CO)(Cl)Ir(\eta^2\text{-}C_{60})$,[5a] as well as related derivatives[4b,5b] provided detailed metric data. In these complexes and the related $(\eta^5\text{-}C_9H_7)(CO)Ir(\eta^2\text{-}C_{60})$,[6] C_{60} behaves as an electron-deficient olefin, interacting with the transition metal center via π-bonds. However, recent reports have illustrated the susceptibility of C_{60} to carbon radical[7] as well as halogen addition.[8] This prompted us to investigate the interaction of C_{60} with transition metal radicals in anticipation of discovering a different mode of bonding the transition metal center to C_{60}, that is, via formation of a C–M σ-bond.

The photodissociation of the M–M σ-bond in dinuclear metal carbonyl compounds to form metal carbonyl radicals has been thoroughly investigated.[9] We have applied photochemical reaction conditions appropriate to generate metal carbonyl radicals to a solution system containing $Re_2(CO)_{10}$ and C_{60} and have used IR and UV/vis spectroscopic methods to follow the progress of the reactions. The radical $^\bullet Re(CO)_5$ can also be generated thermally from the complex $(\eta^3\text{-}Ph_3C)Re(CO)_4$ in the presence of CO.[10] We observe the same product, characterized as $C_{60}\{Re(CO)_5\}_2$, from the reaction of C_{60} with $^\bullet Re(CO)_5$ radicals generated either photochemically or thermally.

Experimental Section

All experiments handling reaction solutions were carried out in an atmosphere of purified argon by employing Schlenk techniques or by utilizing a glovebox. Infrared spectra were recorded on a Perkin-Elmer 1710 FTIR spectrometer (2-cm^{-1} resolution) by using either 1.0- or 0.1-mm KCl cells with Teflon stoppers. EPR experiments were performed on a Bruker ESP 300 instrument at X-band frequencies.

C_{60} was obtained from the carbon soot purchased from Texas Fullerenes Corp. by first using toluene to extract the fullerene mixture and then applying HPLC with a Pirkle column to separate C_{60} and C_{70}.[11] $Re_2(CO)_{10}$ (Strem Chemical Co.) was used as received. $(\eta^3\text{-}Ph_3C)Re(CO)_4$ was prepared according to the literature.[10] Benzene (Fisher Scientific) was distilled over CaH_2 under argon, degassed by three freeze–pump–thaw cycles, and stored over freshly activated 4-Å molecular sieves in a flask fitted with a threaded Teflon stopcock. Carbon tetrachloride (Fisher Scientific) was used as received. Carbon monoxide (Matheson Gas Products, Matheson purity grade, 99.99+%) was purified as previously described.[12] Argon (research grade, Linde Specialty Gas Co.) was purified by passing through activated MnO and 4-Å molecular sieve columns.

The photolysis reactions were carried out on a 5-mm quartz tube fitted with a threaded Teflon stopcock, or they were carried out directly in KCl IR cells. The light source used was either a 275-W General Electric sunlamp (predominantly 366-nm radiation) or a conventional flash photolysis apparatus composed of two linear high-pressure xenon-flash

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Table I. IR Data for C_{60} and $Re_2(CO)_{10}$ in Benzene Solution

	band positions, cm^{-1} (ϵ, mm^{-1} M^{-1})			
C_{60}	1429 (22)	1183 (12)	578 (40)	528 (102)
$Re_2(CO)_{10}$	2070 (561)	2011 (1850)	1969 (442)	

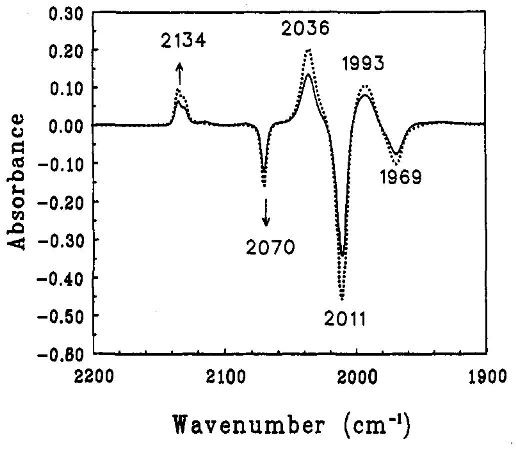

Figure 1. Difference IR (ν_{CO}) spectra of C_{60} and $Re_2(CO)_{10}$ in benzene during photolysis. Positive values show the growth of new bands due to **P**, whereas negative values show the loss of bands due to $Re_2(CO)_{10}$.

tubes (radiation from 300 to 900 nm).[13] Progress of the reaction between C_{60} and $Re_2(CO)_{10}$ was monitored by using IR spectroscopy.

Results

Infrared Monitoring of C_{60} and $Re_2(CO)_{10}$. Both C_{60} and $Re_2(CO)_{10}$ exhibit characteristic absorption bands in the infrared, which provides a method of monitoring their concentrations by using IR spectroscopy. Table I lists the appropriate IR bands of C_{60} and $Re_2(CO)_{10}$ in benzene solution together with their experimentally determined extinction coefficients. Beer's law plots were linear for both C_{60} and $Re_2(CO)_{10}$ over the concentration ranges 0.10–1.55 and 0.41–2.05 mM, respectively. However, measurements of changes in [C_{60}] are difficult due to the low solubility of C_{60}, the relatively low intensities of its IR bands (see Table I), and band overlaps. The band at 1183 cm^{-1} for C_{60} is obscured by solvent absorption when a cell with 1.0-mm path length is employed, which is required to obtain spectra with good signal to noise ratios. The band at 578 cm^{-1} overlaps with a CO deformation band of $Re_2(CO)_{10}$ at 591 cm^{-1}. In these studies, calculation of [C_{60}] was based on the band intensities at 1429 and 528 cm^{-1}, whereas measurement of [$Re_2(CO)_{10}$] was based on the absorbance at 2070 cm^{-1}. The latter value is generally more accurate than the former.

Photochemical Reaction of $Re_2(CO)_{10}$ with C_{60}. Flash photolysis or sunlamp irradiation of $Re_2(CO)_{10}$ in the presence of C_{60} in benzene solution caused a color change from magenta to grayish brown. Formation of a new species, **P**, was indicated from the decrease of IR band intensities for both $Re_2(CO)_{10}$ and C_{60} and the appearance of new CO stretching bands at 2134, 2130 (sh), 2036, and 1993 cm^{-1} (see Figure 1). Further observations regarding the new species include the following: (a) The formation of **P** upon photolysis of $Re_2(CO)_{10}$ + C_{60} was not suppressed when the solution was saturated at 1 atm with carbon monoxide. (b) **P** did not exhibit an ESR signal either in benzene solution at room temperature or in frozen benzene at 110 K.[14] (c) A solution containing **P** showed generally higher absorption in the visible region (400–700 nm) compared to C_{60} (see Figure 2) as seen for other C_{60} derivatives.[6a,15] However, there was no evidence for absorption in the near-IR region (800–2000 nm) as seen for the C_{60} radical anion.[16]

Stoichiometry of the Reaction between $Re_2(CO)_{10}$ and C_{60}. Figure 3 shows the low-frequency region of the spectrum before and after ca. 90% reaction. The band at 528 cm^{-1} is strongest for C_{60}; however, the reaction product, **P**, also absorbs at this position, with the extinction coefficient estimated to be 32 mm^{-1} M^{-1}. When the progress of the photolysis reaction was controlled by the number of flashes, the consumption of C_{60} and $Re_2(CO)_{10}$ was calculated at various stages on the basis of the IR band absorbances. Figure 4 shows a plot of the ratio of [C_{60}]/[$Re_2(CO)_{10}$] consumed vs the percentage of $Re_2(CO)_{10}$ consumed due to reaction. The points in the early stage of the reaction (<50%) were obtained using a longer path length (1.0 mm) cell, and the last point (90%) was obtained using a shorter path length (0.1 mm) cell with higher initial [C_{60}] and [$Re_2(CO)_{10}$]. The results indicate that the stoichiometry of the reaction is [C_{60}]/[$Re_2(CO)_{10}$] = 1/1, which establishes the formula of **P** as $C_{60}\{Re(CO)_5\}_2$.

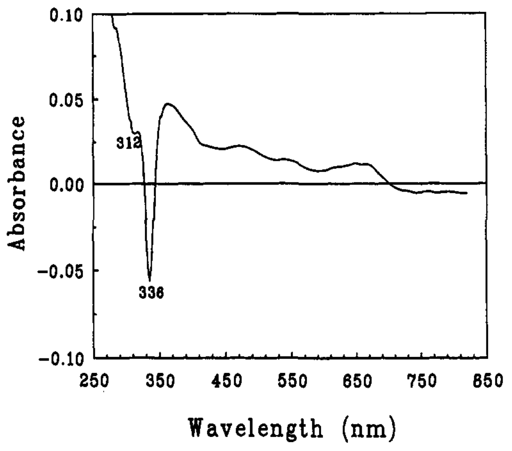

Figure 2. Difference UV/vis spectrum of C_{60} + $Re_2(CO)_{10}$ in benzene, 1 min after one xenon lamp flash in a 0.1-mm KCl cell.

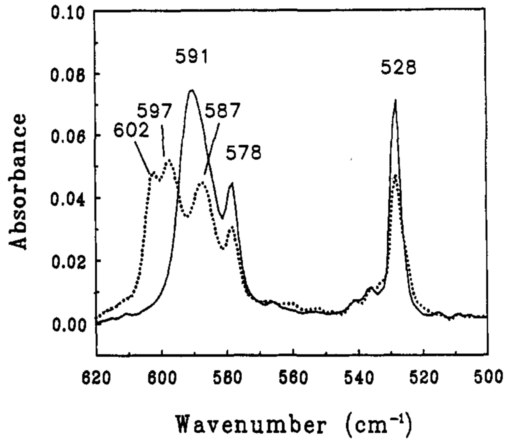

Figure 3. Low-frequency IR spectra of C_{60} + $Re_2(CO)_{10}$ in benzene before (solid line) and after (dotted line) ca. 90% reaction.

Formation of $C_{60}\{Re(CO)_5\}_2$ via Reaction of (η^3-Ph_3C)$Re(CO)_4$ with C_{60} under CO. The reaction of (η^3-Ph_3C)$Re(CO)_4$ with CO is known to produce $^\bullet Re(CO)_5$, presumably via homolysis of a

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[14] In a typical experiment, a benzene solution of C_{60} and $Re_2(CO)_{10}$ (≈5 mM) was introduced into a quartz EPR tube under argon. Photolysis was performed directly on the solution sealed inside the tube. EPR traces were recorded typically about 10–15 min after beginning irradiation (at this point the color of the solution was still grayish brown and the IR bands were mainly those of species **P**). For low-temperature measurements, the solution was frozen in liquid nitrogen immediately after photolysis, and then the tube was transferred to the precooled cavity. Traces were recorded at a range of microwave power settings from 200 mW to 200 μW with temperatures ranging from -100 to +25 °C.

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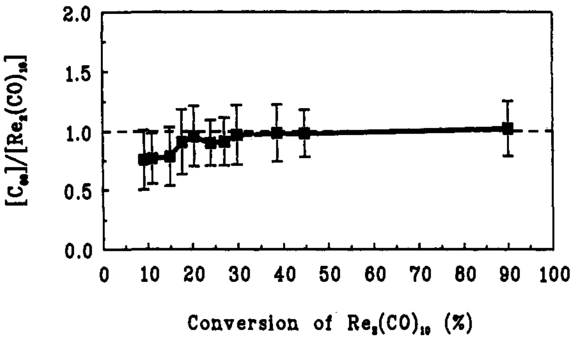

Figure 4. Plot of the consumption ratio of $[C_{60}]/[Re_2(CO)_{10}]$ vs the percentage of $Re_2(CO)_{10}$ reacted. The points in the early stage of the reaction (<50%) were obtained with a 1.0-mm KCl cell with $[C_{60}]_0$ = 1.51 mM and $[Re_2(CO)_{10}]_0$ = 0.58 mM. The last point (90%) was obtained with a 0.1-mm KCl cell with $[C_{60}]_0$ = 6.6 mM and $[Re_2(CO)_{10}]_0$ = 3.2 mM.

weak Re–C bond in a η^1-Ph_3C–$Re(CO)_5$ intermediate.[10] The reaction of (η^3-Ph_3C)$Re(CO)_4$ with C_{60} in the presence of carbon monoxide resulted in a color change in the solution from magenta to grayish brown over the course of a few hours. IR monitoring of the reaction at intermediate times showed a decrease in the concentration of (η^3-Ph_3C)$Re(CO)_4$ and the formation of a product with IR absorptions at 2134 (w), 2036 (s), and 1993 (w) cm^{-1}. This pattern matches well with the absorption bands of the product from photolysis of C_{60} and $Re_2(CO)_{10}$. Prolonged exposure of the mixture to CO resulted in the appearance of additional bands at 2095 (w) and 2018 (s) cm^{-1}. Since excess (η^3-Ph_3C)$Re(CO)_4$ was used (≈6 equiv), the appearance of new bands may suggest the formation of higher $Re(CO)_5$ derivatives of C_{60}. However, in neither case were the products stable, and over a span of several hours they decomposed to C_{60} and $Re_2(CO)_{10}$, as indicated by color change and IR spectra.

Decomposition of Photogenerated $C_{60}\{Re(CO)_5\}_2$. Although the photochemical production of $C_{60}\{Re(CO)_5\}_2$ from C_{60} and $Re_2(CO)_{10}$ could be driven to greater than 90% conversion of $Re_2(CO)_{10}$, we were unable to isolate the product. The solutions containing $C_{60}\{Re(CO)_5\}_2$ decomposed over the course of a day to regenerate C_{60} and $Re_2(CO)_{10}$. This process is demonstrated in Figure 5. Figure 5a shows the disappearance of bands 2134, 2036, and 1993 cm^{-1} for $C_{60}\{Re(CO)_5\}_2$ and recovery of $Re_2(CO)_{10}$ as indicated by the disappearance of the negative peaks at 2070, 2011, and 1969 cm^{-1}. Figure 5b shows the recovery of C_{60}, as indicated by the disappearance of the negative band at 528 cm^{-1}. Figure 6 shows plots of absorbance vs time for $C_{60}\{Re(CO)_5\}_2$ (P) at 2134 cm^{-1} and C_{60} at 528 cm^{-1}. The data were fitted with an exponential function, and the inset shows that plots of $\log(A_t - A_\infty)$ vs time were linear. The kinetics of the decomposition reaction are first order with a rate constant of (4.4 ± 0.3) × 10^{-3} min^{-1} ((7.3 ± 0.6) × 10^{-5} s^{-1}).

Decomposition of $C_{60}\{Re(CO)_5\}_2$ in the Presence of CCl_4. After $C_{60}\{Re(CO)_5\}_2$ in benzene was produced photochemically, CCl_4 was added to the solution ($[CCl_4]$ ≈ 50 mM). The IR spectral changes clearly indicated the formation of $ClRe(CO)_5$ at the expense of $C_{60}\{Re(CO)_5\}_2$ (see Figure 7). There was no evidence for formation of $Re_2(CO)_{10}$ under these conditions.

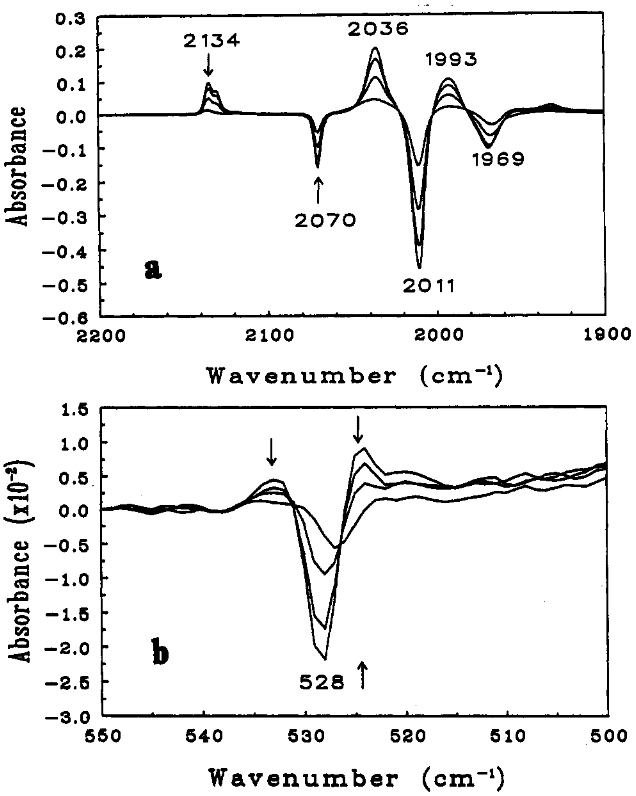

Figure 5. Difference IR spectra taken during decomposition of $C_{60}\{Re(CO)_5\}_2$ in benzene. The spectra correspond to 1 min, 2 h, 5 h, and 20 h after photolysis of a solution containing C_{60} (6.6 mM) + $Re_2(CO)_{10}$ (3.1 mM); the spectrum before photolysis is taken as the reference.

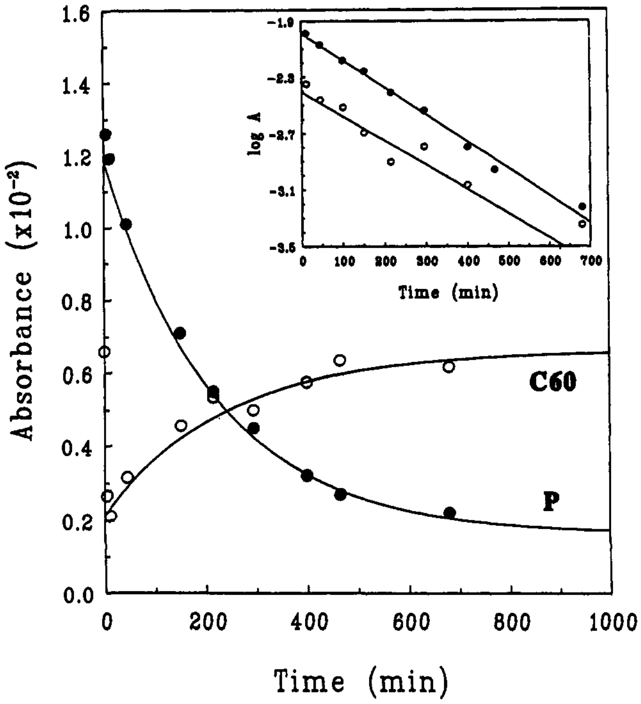

Figure 6. Plots of absorbance vs time for $C_{60}\{Re(CO)_5\}_2$ (P) at 2134 cm^{-1} and C_{60} at 528 cm^{-1}. The data were fitted with an exponential function. The inset shows plots of $\log(A_t - A_\infty)$ vs time.

Discussion

Formation of $C_{60}\{Re(CO)_5\}_2$. When $Re_2(CO)_{10}$ is irradiated in the presence of C_{60}, a relatively simple set of new carbonyl IR bands, attributed to the species P, is produced. It is well established that the photochemistry of metal–metal-bonded carbonyl compounds, such as $Re_2(CO)_{10}$, involves both homolysis of the metal–metal bond, which generates 17-electron radicals (eq 1), and cleavage of a metal–CO bond, which produces an unsaturated intermediate (eq 2).[9] The fact that formation of P is not suppressed by CO argues against involvement of the CO-loss intermediate, $Re_2(CO)_9$. Therefore, P is most likely formed via reaction of C_{60} with the metal carbonyl radical, •$Re(CO)_5$. Observation of the same new IR bands from the thermal reaction

$$Re_2(CO)_{10} \rightarrow 2\ {}^\bullet Re(CO)_5 \tag{1}$$

$$Re_2(CO)_{10} \rightarrow (CO)_5Re\text{–}Re(CO)_4 + CO \tag{2}$$

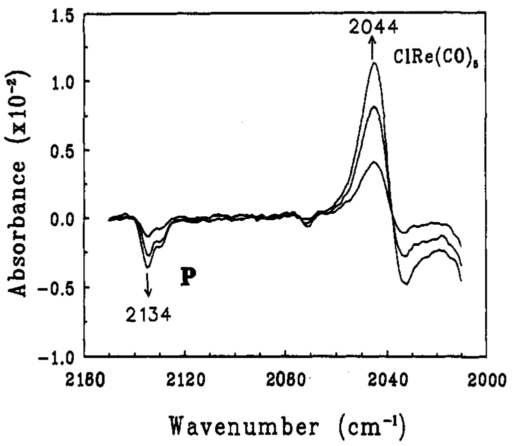

Figure 7. Difference IR spectra taken during the decomposition of $C_{60}\{Re(CO)_5\}_2$ in the presence of CCl_4. The spectra correspond to 18, 43, and 330 min after CCl_4 was added to the solution.

of C_{60} with $(\eta^3\text{-}Ph_3C)Re(CO)_4$[10] in the presence of CO provides further support for the involvement of $^{\bullet}Re(CO)_5$ radicals in the formation of **P**.

The infrared spectral pattern observed for **P** is characteristic of a species with the local structure X–Re(CO)$_5$, with X moderately electronegative.[17,18] This is consistent with the established electronegative character of C_{60}.[19] On the basis of the stoichiometry studies, product **P** is assigned to $C_{60}\{Re(CO)_5\}_2$, i.e., a C_{60} molecule σ-bonded to two $Re(CO)_5$ fragments. Therefore, no ESR signal, e.g., for $^{\bullet}C_{60}\{Re(CO)_5\}_n$, $n = 1$, 3, or 5,[7] would be expected for **P**.

The possibility must be considered that a photochemically excited C_{60} is involved in the reaction observed, since triplet-state C_{60} ($E_T \approx 35$ kcal/mol) is sufficiently oxidizing to induce electron transfer from amines.[20] A reviewer has suggested that the initial photochemical step is formation of a radical ion pair $[C_{60}^{-}]$-$[Re_2(CO)_{10}^{+}]$, followed by fragmentation of the Re–Re bond and formation of the disubstituted product $C_{60}\{Re(CO)_5\}_2$. A qualitative argument against such an electron-transfer pathway is based on our observations that neither $Mn_2(CO)_{10}$ nor $Cp_2Fe_2(CO)_4$ appears to form any photoproduct when irradiated in the presence of C_{60}. Each of these dimers, and especially the latter, should be more easily ionized than $Re_2(CO)_{10}$. Furthermore, the $\sigma \rightarrow \sigma^*$ transition that is important for M–M bond homolysis is effectively "filtered" by the strong C_{60} absorption in the cases of $Mn_2(CO)_{10}$ ($\lambda_{max} = 336$ nm) and $Cp_2Fe_2(CO)_4$ ($\lambda_{max} = 346$ nm), whereas the analogous transition for $Re_2(CO)_{10}$ ($\lambda_{max} = 312$ nm) is not appreciably shielded.

A more direct indication that the $^{\bullet}Re(CO)_5$ radical is the active intermediate in the observed reaction is provided by a laser flash photolysis experiment. The $^{\bullet}Re(CO)_5$ radical exhibits strong absorbance at 550 nm.[21] In the absence of C_{60}, photogenerated (excimer XeCl laser at 308 nm) $^{\bullet}Re(CO)_5$ radicals from a 0.3 mM solution of $Re_2(CO)_{10}$ in benzene will recombine to form $Re_2(CO)_{10}$ over a period of 10–20 μs. However, in the presence of 0.5 mM C_{60} the 550-nm transient decays in <2 μs. It is unlikely that the observed transient decay is due to $^3C_{60}$, since the spectrum for this species exhibits strong bands at 740 and 680 nm (sh) but only weak absorption at 550 nm.[22] Furthermore, neither C_{60}^{-} nor C_{60}^{+} shows significant absorption in this region.[16,20,23] Recent studies reported values of the bimolecular rate constant for carbon radical (methyl or trichloromethyl) addition to C_{60} of ca. 5×10^8 M^{-1} s^{-1}.[23,24] If the rate for $^{\bullet}Re(CO)_5$ radical addition to C_{60} is comparable, this process will certainly compete favorably with the recombination of $^{\bullet}Re(CO)_5$ radicals ($k = 3.7 \times 10^9$ M^{-1} s^{-1} at 22 °C in hexane).[21]

One possible pathway leading to the formation of $C_{60}\{Re(CO)_5\}_2$ is shown in eqs 3–5. This involves dimerization of the initial

$$^{\bullet}Re(CO)_5 + C_{60} \rightarrow {}^{\bullet}C_{60}Re(CO)_5 \qquad (3)$$

$$2\ {}^{\bullet}C_{60}Re(CO)_5 \rightarrow \{C_{60}Re(CO)_5\}_2 \qquad (4)$$

$$\{C_{60}Re(CO)_5\}_2 \rightarrow C_{60}\{Re(CO)_5\}_2 + C_{60} \qquad (5)$$

$^{\bullet}Re(CO)_5$ radical adduct of C_{60}, as has been observed for some alkyl radical adducts.[7d] On the other hand, a sequential process such as shown in eq 6 cannot be eliminated.

$$^{\bullet}C_{60}Re(CO)_5 + Re_2(CO)_{10} \rightarrow C_{60}\{Re(CO)_5\}_2 + {}^{\bullet}Re(CO)_5 \qquad (6)$$

Stability of $C_{60}\{Re(CO)_5\}_2$. In many ways, the moiety $Re(CO)_5$ can be considered as a pseudohalogen.[25] It is therefore of interest to consider the potential stability of $C_{60}\{Re(CO)_5\}_2$ within the context of the approach previously adopted for estimating the stability of dihalogen adducts of C_{60}.[26a] Thus, the ΔE for eq 7

$$C_{60} + X_2 \rightarrow C_{60}X_2 \qquad (7)$$

$$C_{60} + X\text{–}CH_2CH_2\text{–}X \rightarrow C_{60}X_2 + C_2H_4 \qquad (8)$$

$$C_2H_4 + X_2 \rightarrow X\text{–}CH_2CH_2\text{–}X \qquad (9)$$

is estimated by considering the sum of the energy changes for eqs 8 and 9. The advantages of this cycle are, firstly, that eq 8 is isodesmic (i.e., the group of bonds being formed is essentially the same as the group being broken), which is likely to make calculations of the energy difference more reliable, and, secondly, that the energy (enthalpy) change for eq 9 can be calculated from known thermochemical data in the case of X = halogen (or hydrogen). However, since $\Delta H_f°$ data are not available for X–CH$_2$CH$_2$–X in the case of X = Re(CO)$_5$, we have placed the three cases of X = Br, I, and Re(CO)$_5$ on an equal basis by using general X–X and C–X bond dissociation values to calculate the energy changes for eq 9. As shown in Table II, the results of this approach are roughly comparable with the previous results for X = Br and I. The energy changes for eq 8 are based on specific calculations that also are not available for X = Re(CO)$_5$. However, the values calculated for X = Br and X = I are very close, so if we assume a similar value for X = Re(CO)$_5$, the estimate for eq 7 can be completed. Interestingly, this analysis suggests that the $C_{60}X_2$ species should be even less stable for X

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Table II. Bond Energy Data (kcal/mol)

X	E(H–X)[a]	E(H$_3$C–X)[a]	E(X–X)[a]	ΔE(9)[b]	ΔE(8)[c]	ΔE(7)[d]
Br	87	70	46	−32 (−29)	39	7 (10)
I	71	56	36	−14 (−12)	38	24 (27)
Re(CO)$_5$	75	53	45	1	38	39

[a] Values for X = Br and I from ref 27, p 624. Values for HRe(CO)$_5$ from ref 28 and for H$_3$CRe(CO)$_5$ and Re(CO)$_{10}$ from ref 29. [b] Calculated for eq 9 according to $\Delta E(9) = E(\text{C=C}) + E(\text{X—X}) - E(\text{C—C}) - 2E(\text{C—X})$. Values of $E(\text{C=C}) = 141$ and $E(\text{C—C}) = 79$ are from ref 27, p 23. Values in parentheses are based on experimental thermochemical data as reported in ref 26a. [c] Values calculated for eq 8 as reported in ref 26a for X = Br and I. An analogous value is assumed for X = Re(CO)$_5$. [d] $\Delta E(7) = \Delta E(9) + \Delta E(8)$.

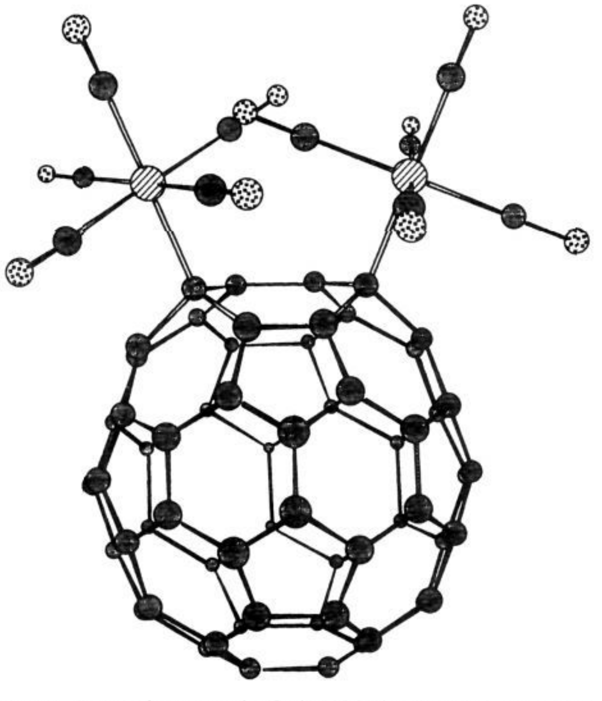


Figure 8. Proposed structure for $C_{60}\{Re(CO)_5\}_2$, based on 1,4-addition.

= Re(CO)$_5$ than for X = I. This is apparently due to the relatively low C–Re bond strength. However, the most recent analysis of the uncertainties in the values of the H$_3$C–Re(CO)$_5$ and the Re$_2$(CO)$_{10}$ bond dissociation energies suggests that the quoted values may be somewhat low.[29] Thus, this analysis of relative stabilities is best considered only as a semiquantitative comparison.

The isosbestic points shown in Figure 5 indicate that the only net reaction from the decomposition of $C_{60}\{Re(CO)_5\}_2$ is that shown in eq 10. However, we may consider two possible pathways

$$C_{60}\{Re(CO)_5\}_2 \rightarrow C_{60} + Re_2(CO)_{10} \qquad (10)$$

for this reaction: (i) Re$_2$(CO)$_{10}$ is formed first on the C$_{60}$ "surface" and then released into solution or (ii) a C$_{60}$–Re bond undergoes cleavage to release a ${}^{\bullet}$Re(CO)$_5$ radical, which ultimately recombines to form Re$_2$(CO)$_{10}$.

A trapping experiment with CCl$_4$ supports the second mechanism, as shown in eqs 11–13. It is known that the chlorine atom transfer reaction between ${}^{\bullet}$Re(CO)$_5$ and CCl$_4$ to produce ClRe(CO)$_5$ (eq 13) takes place readily ($k = 4.9 \times 10^7$ M^{-1} s^{-1} at 22 °C in hexane).[30] Under the adopted reaction conditions ([CCl$_4$] $\approx$ 50 mM, [${}^{\bullet}$Re(CO)$_5$] $\ll$ 0.7 mM), the ${}^{\bullet}$Re(CO)$_5$ radical recombination cannot compete with the chlorine atom transfer, consistent with the result that no Re$_2$(CO)$_{10}$ was observed.

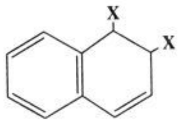
$$C_{60}\{Re(CO)_5\}_2 \rightarrow {}^{\bullet}C_{60}Re(CO)_5 + {}^{\bullet}Re(CO)_5 \qquad (11)$$

$${}^{\bullet}C_{60}Re(CO)_5 \rightarrow C_{60} + {}^{\bullet}Re(CO)_5 \qquad (12)$$

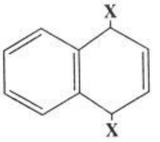
$$CCl_4 + {}^{\bullet}Re(CO)_5 \rightarrow ClRe(CO)_5 \qquad (13)$$

Our direct observation of $C_{60}\{Re(CO)_5\}_2$ implies a significant kinetic barrier to its decomposition. If the primary barrier is due to homolysis of a C–Re bond, then the observed rate of decomposition may be taken as an estimate of the rate of dissociation. From the rate constant one calculates $\Delta G^{\ddagger} = 23.1$ kcal/mol. Since the value of $\Delta S^{\ddagger}$ is unknown, this serves as a very rough estimate of $\Delta H^{\ddagger}$ and in turn of the bond dissociation energy. However, it is appropriately larger than the value of ca. 15 kcal/mol that has been estimated for the bond energy in η^1-Ph$_3$C–Re(CO)$_5$, the putative precursor to the ${}^{\bullet}$Re(CO)$_5$ radical under thermal conditions.[10]

Structure of $C_{60}\{Re(CO)_5\}_2$. Calculations of the relative stabilities of various possible isomers generated by addition of X$_2$ (X = H, F, Cl, Br, I) to the conjugated double bonds of C$_{60}$ to form C$_{60}$X$_2$ have indicated a strong preference for 1,2-addition (see **I**) with X = H, F, and Cl but a preference for 1,4-addition (see **II**) with X = Br and I.[26,31] The latter pattern is supported by the structure determined for C$_{60}$Br$_{24}$,[8c] and the former, by the recent isolation and characterization of C$_{60}$H$_2$.[31b] The next lowest energy isomer for C$_{60}$H$_2$ was calculated to be that for addition at the 2,6-positions of a "naphthalene" moiety (see **III**).[31a] The 1,2-isomer will clearly be destabilized by steric interactions as X becomes larger, whereas the more separated 1,4- and 2,6-isomers will be less affected by the size of X. On the other hand, these isomers have the disadvantage that one and two double bonds, respectively, are localized within the more highly strained five-membered rings. In the case of X = Re(CO)$_5$, molecular modeling clearly shows that the 1,2-isomer is very crowded and is unlikely to be stable. However, the 1,4-isomer appears feasible, on the basis of structural data for R–Re(CO)$_5$ derivatives;[32] a structural diagram of this isomer is shown in Figure 8. At this time it does not appear possible to make meaningful calculations to determine the relative energy of this 1,4-isomer in comparison with the 2,6-isomer or other reasonable configurations.



I



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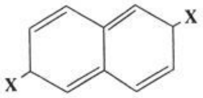

III

The IR spectra of $C_{60}\{Re(CO)_5\}_2$ provide little information regarding the possible presence of isomers, since a basic X–Re(CO)$_5$ pattern is observed. However, the presence of a shoulder on the highest frequency (A$_1$) mode is intriguing. This could be taken to indicate a slight resolution of different environments. On the other hand, since this mode is largely due to stretching of the axial Re–CO group,[18] the splitting may be due to coupling between these oscillators. This interpretation would certainly favor the 1,4-isomer over the 2,6-isomer, not only in terms of a shorter distance apart but also in terms of a smaller angle between the axial vectors. Unfortunately, there do not seem to be stable, known Re(CO)$_5$ derivatives that could model this stereochemical situation.

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