Sunlight induced synthesis of tricarbonylhexahaptobuckminsterfullerenetungsten

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Abstract. $[W(CO)_3(\eta^6\text{-}C_{60})]$ has been synthesized by sunlight irradiation of a benzene solution of C_{60} and $W(CO)_6$ or $[W(CO)_3(\eta^6\text{-}C_6H_6)]$ as a red-brown solid. This compound has been characterized by elemental analysis and by FAB mass spectroscopy (parent ion peak centred at 988 (30%)). Chemical reactivity and IR spectroscopy indicate a hexahapto mode of bonding in this complex according to the 18-electron rule. XPS and cyclic voltammetric data support the electron acceptor/donor properties of bonded C_{60} and the electron donor/acceptor properties of $W(CO)_3$ moiety respectively in this compound.

The inability of buckminsterfullerene C_{60} to bond as hexahapto (η^6) ligand is shown to be due to the poor orientation of its π orbitals (Haddon 1993). The ready formation of $\eta^2\text{-}C_{60}$ metal complexes (Balch *et al* 1991; Fagan *et al* 1992; Douthwaite *et al* 1993) is reported to be due to the need for strain relief in the spherical C_{60} (Haddon 1993). Relatively low ionization potential (Lichtenberger *et al* 1991) and high electron affinity (Curl and Smalley 1988) suggest the ability of C_{60} to participate in the synergic mode of bonding with appropriate metal fragments like $M(CO)_3$ (M = Cr, Mo, W), which are avid electron acceptors as well as good π-donors (Wilkinson *et al* 1982). The spatial extended $5d$ orbitals of tungsten may circumvent the problem of poor π-overlap of hybrid π-orbitals of spherical C_{60} (Haddon 1993; Rogers and Marynick 1993). Photo-excited C_{60} having lower symmetry might further alleviate this problem. Photo-polymerization (Rao *et al* 1993) and oxidative degradation (Taylor *et al* 1991; Juha *et al* 1993) of C_{60} have been shown to require prolonged irradiation with high wattage power but its skylight exposure in benzene for nine days did not show observable degradation (Arbogast and Foote 1991). We tested these conjectures and hereby report the photosynthesis of $[W(CO)_3(\eta^6\text{-}C_{60})]$ by sunlight irradiation of a benzene solution of C_{60} and $W(CO)_6$ or $[W(CO)_3(\eta^6\text{-}C_6H_6)]$ and its initial characterization.

C_{60}, prepared by electric arc process (Krätschmer *et al* 1990) and purified (Ajie *et al* 1990), and excess (tenfold) of $W(CO)_6$ were dissolved in degassed benzene in a Pyrex flask fitted with a water aspirator for slow evacuation. The flask was immersed in a cold water bath (10°C) and was exposed to midday sunlight (Kanpur, August–October) for 2 h under evacuation whereby the purple colour of the solution finally changed to reddish brown with a greenish tinge. The solution was flash chromatographed (silica
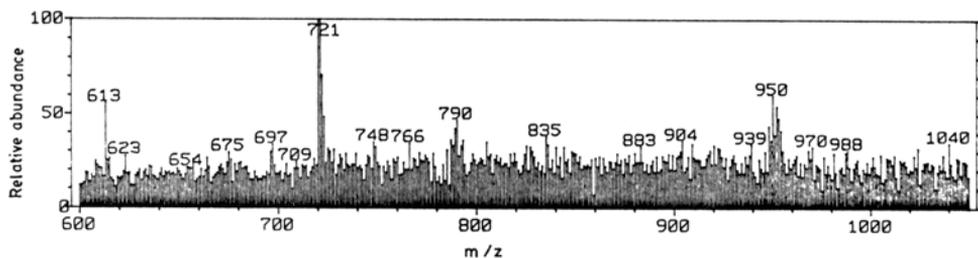
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Figure 1. Part of the FAB mass spectrum of the compound using xenon as the FAB gas in an *m*-nitrobenzyl alcohol (NBA) matrix.

gel), concentrated under vacuum and finally diluted with *n*-hexane to precipitate a red-brown solid, which was washed several times with *n*-hexane to remove unreacted $W(CO)_6$, $[W(CO)_3(\eta^6\text{-}C_6H_6)]$, and other related *n*-hexane-soluble derivatives, and finally dried under vacuum. The same compound was synthesized by reacting stoichiometric amounts of $[W(CO)_3(\eta^6\text{-}C_6H_6)]$ (Fischer *et al* 1958; King and Frozaglia 1966) and C_{60} in benzene under argon within 30 minutes of sunlight exposure. The elemental analysis of the complex has been done by the microanalytical technique. A known amount of the compound was burnt under oxygen, at a temperature of 950°C and the CO_2 thus formed was analyzed as per standard micro-analytical procedure. The residue left in the boat was cooled and weighed for WO_3. Elemental analyses from three batches of compounds showed C, 74·5, 74·5, 73·6%; W, 19·5, 19·2, 19·8%. Calculated for $C_{60}W(CO)_3$; C 76·5%, W 18·6%. The low carbon value may be due to the formation of some refractory material along with the formation of some tungsten oxides with lower oxygen contents resulting in high tungsten values. A part of the FAB mass spectrum is shown in figure 1. Besides peaks *m/z* 721 (100%), some of the prominent peaks are 988 (33%), 950 (58%), 904 (30%), 766 (30%), 748 (30%), 613 (60%), related to $C_{60}W(CO)_3$, $HC_{60}W(CO)OH$, $C_{60}W$, $HC_{60}(CO)OH$, $C_{60}(CO)$ and matrix (*m*-nitrobenzyl alcohol) tetramer, respectively. IR (KBr): ν cm^{-1} = 2083, 1957, 1460, 1425·6, 1182·3, 1167·5, 1095·5, 1075, 1021, 952, 935, 875, 804, 736, 700, 667·5, 616, 581, 564, 526, 484, 465, 444·6, 422, 404. For C_{60} the band at 1428 cm^{-1} shifted to 1425·6 cm^{-1} with the appearance of another band at 1460 cm^{-1} in the complex. Similarly 1181 cm^{-1} band of C_{60} shifted to 1182·3 cm^{-1} with the close appearance of another band at 1167·5 cm^{-1}. 527 cm^{-1} band remains almost unchanged in the derivative (526 cm^{-1}) relative to C_{60}. The 577 cm^{-1} vibration of C_{60} could not be assigned in the derivative due to overlapping vibrations mainly responsible for $\delta(WCO)$.

[W(CO)$_3$C$_{60}$] undergoes facile C_{60} displacement reactions with σ or π-donor ligands like CH_3CN, THF, PPh_3, or 2,2-bipyridine in solvents like C_6H_6, CH_2Cl_2, or CS_2 where even in neat solvent it slowly releases C_{60}. In the solid state it is relatively stable under an inert atmosphere but on aging slowly decomposes to yield C_{60} and metallic tungsten. The trend of these reactions is similar to the general reactivities of $[M(CO)_3(\eta^6\text{-arene})]$ (Wilkinson *et al* 1982) complexes suggesting the nature of bonding of C_{60} in this complex as $[W(CO)_3(\eta^6\text{-}C_{60})]$, satisfying the 18 electron rule. It shows IR bands at 2083 (A_1) and 1957 cm^{-1} (E) (split due to C_{60}, figure 2b) assignable to $\nu(CO)$'s of the bonded $W(CO)_3$ moiety and at 446·6 and 422 cm^{-1} assignable to A_1 and E modes of ν (WC)'s of bonded carbonyls respectively (Nakamoto 1986).
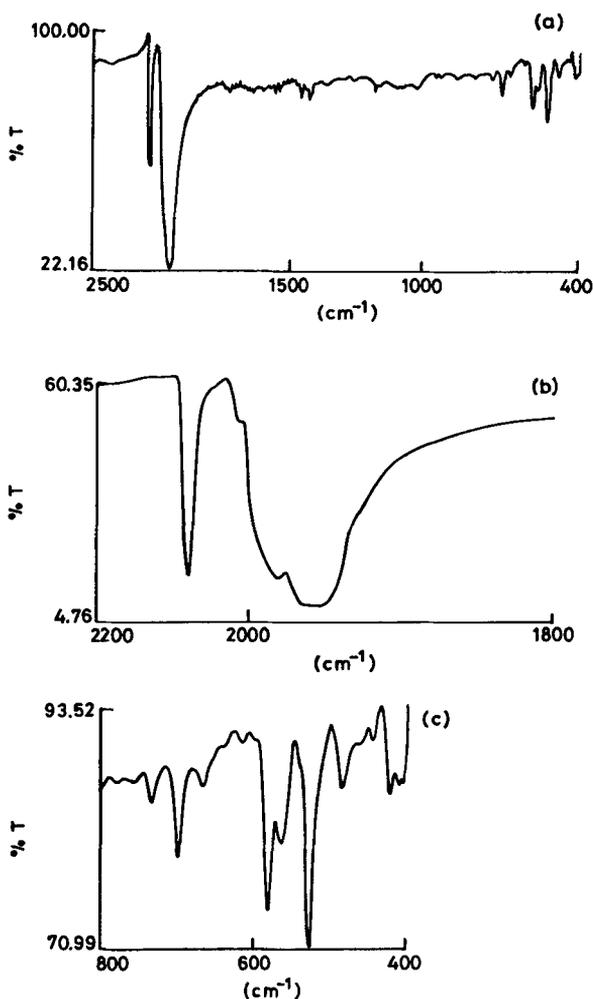
Figure 2. Fourier transform infrared (FTIR) transmission spectra of [W(CO)$_3$ (η^6-C$_{60}$)] in KBr matrix (curve **a**). Expanded spectrum in the carbonyl region showing splitting of the E band expected for perturbed C$_{3v}$ symmetry by C$_{60}$ (curve **b**). Expanded 800–400 cm^{-1} region (curve **c**).

Excluding the 550–600 cm^{-1} region mainly responsible for δ(WCO), the appearance of other bands strongly suggest reduced symmetry of the bonded C$_{60}$ (figure 2). In X-ray photoelectron spectra, (figure 3) the C$_{1s}$ binding energy of [W(CO)$_3$(η^6-C$_{60}$)] (curve 3b) and of C$_{60}$ (curve 3a), with the respective peak at 285·7 and at 286·3 eV suggests the electron withdrawing character of C$_{60}$. The shift of W$_{4f7/2}$ and W$_{4f5/2}$ binding energies to higher values compared to those of metallic tungsten (figure 3, curve c) supports the electron-donating property of the W(CO)$_3$ moiety. The presence of trace amounts of metallic tungsten is presumably due to partial decomposition of the compound under the high vacuum conditions of the XPS measurement. The larger full width at half maximum (FWHM) of 1·85 eV of the C$_{1s}$ peak of [W(CO)$_3$(η^6-C$_{60}$)] along with its asymmetry compared to the C$_{1s}$ peak of C$_{60}$ (FWHM), 1·51 eV) is due to the presence

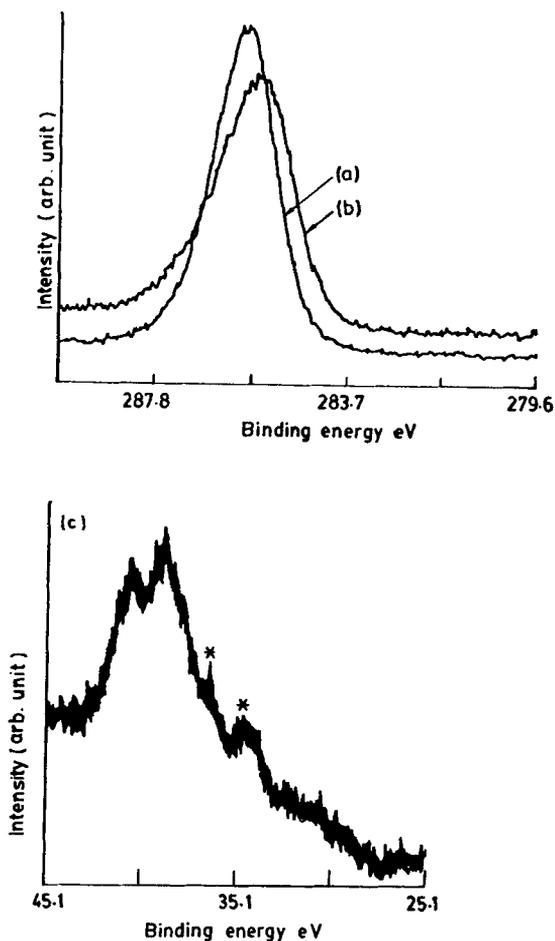**Figure 3.** X-ray (Mg K_α) photoelectron spectra of C_{1s} binding energy of (a) C_{60}, (b) $[W(CO)_3(\eta^6\text{-}C_{60})]$ and (c) $W_{4f7/2}$, $W_{4f5/2}$ binding energies of the complex. The intensity of (c) is magnified three times as-compared to that of (a) and (b). Peaks indicated by asterisks show the presence of metallic tungsten (see text). Compounds were deposited on In-foils.

of different sets of carbons in $[W(CO)_3(\eta^6\text{-}C_{60})]$. Solution instability of this compound beyond ~ 6 h in benzene has thwarted our attempts to probe this aspect by ^{13}C NMR method.

In contrast to the electron-withdrawing character of C_{60}, its electron-donating property towards the $W(CO)_3$ moiety is shown by cyclic voltammetry. The appearance of five successive reduction steps of $[W(CO)_3(\eta^6\text{-}C_{60})]$ within the less negative potential window compared to the three reductions of free C_{60} (figure 4) clearly shows the easier reduction of η^6-bonded C_{60} as compared to that of free C_{60} or η^2-bonded C_{60} (Lerke *et al* 1992). A metal centred one-step two-electron irreversible oxidation process is also observed. However, the necessary addition of CH_3 CN in benzene (1:4·5, v/v) for cyclic voltammetric measurements leads to solvolysis of $[W(CO)_3(\eta^6\text{-}C_{60})]$

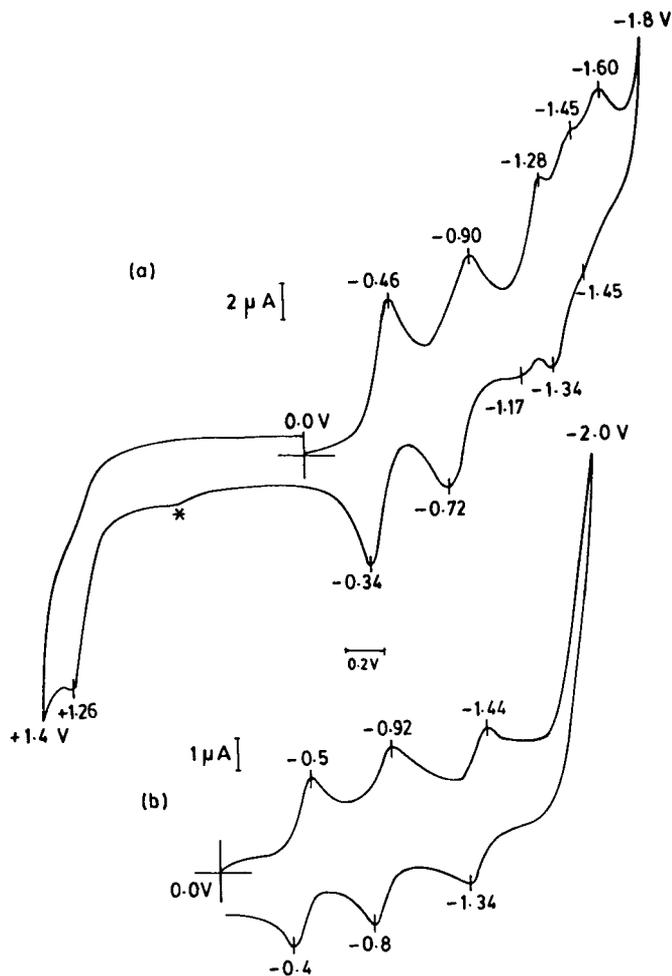**Figure 4.** Comparative cyclic voltammograms of (a) $[W(CO)_3(\eta^6\text{-}C_{60})]$ and (b) C_{60}; ($\sim$ 0·3 mM) in C_6H_6: CH_3CN (4·5 v:1v) with 0·1 M TBAP $(Bu_4N^+ClO_4^-)$ as supporting electrolyte; glassy carbon working and Pt-counter electrodes; Ag/AgCl/3M NaCl reference electrode; scan rate 50 mV/s; ambient conditions ($E_{1/2}$ of ferrocinium/ferrocene, 0·503 V vs Ag/AgCl). The arterisk indicates an unidentified peak.

with the release of C_{60} within 15 minutes. The solution placed in the electrochemical cell completely changed its colour from red-brown to purple within two hours which showed cyclic voltammogram identical to that of an 1:1 mixture of $[W(CO)_3(CH_3CN)_3]$ and C_{60} comprising two ill-defined oxidative peaks for $[W(CO)_3(CH_3CN)_3]$ and three reduction steps for free C_{60} respectively. The electronic spectrum of this complex in benzene shows absorption bands at λ (nm), 336, 431, 552 (br) 661 cm^{-1} which remained unchanged for a few hours. However, addition of any strong σ-donor like CH_3CN to the benzene solution changed the band profile with the appearance of prominent bands at 598, 540, 406 nm in the visible region within an hour confirming solvolysis of the complex during cyclic voltammetric studies.

The formation of $[W(CO)_3\eta^6\text{-}C_{60}]$ did not occur in the absence of light or under thermal conditions. The inability of $Cr(CO)_6$ or $Mo(CO)_6$ to form similar compounds with C_{60} in sunlight brings out the importance of the spatial character of the $5d$ orbitals of tungsten in bonding with photoexcited C_{60}. We have identified the 320–380 nm region as being the actually effective (using narrow band pass filters) solar radiation comprising only $\sim 5\cdot 5\%$ of the solar constant (Duffie and Beckman 1974). This opens up the possibility of derivatizing C_{60} photochemically under mild irradiating conditions.

Acknowledgements

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