Palladium-catalysed [3 + 2] Cycloaddition of Trimethylenemethane (TMM) and Fullerene. Observation of the Room-temperature Fluorescence Spectrum of the TMM–C_{60} Adduct

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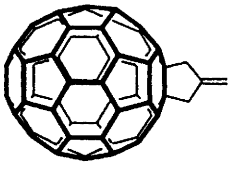
The first synthesis of the parent TMM–C_{60} adduct **1** was achieved by means of Pd°-mediated [3 + 2] cycloaddition and its structure was unambiguously proved by spectroscopic means (^{1}H and ^{13}C NMR and MS); a pentane solution of the adduct **1** exhibited a fluorescence emission spectrum with λ_{max} 704 nm and vibronic fine structure at ambient temperature.

Since the discovery of the multigram synthesis of C_{60},[1] a number of organic and organometallic derivatives have been prepared.[2–4] Late transition metals such as nickel triad and iridium can readily form stable complexes with C_{60}.[2] Cycloaddition reactions so far may be one of the most successful tools to derivatize C_{60}.[3] A recent report concerning the synthesis and biological activities of the derivatives of trimethylenemethane (TMM) adducts[4] prompted us to report a convenient synthesis of the parent TMM–C_{60} adduct **1** by means of the transition metal-mediated organic reaction of C_{60}.

Palladium-catalysed [3 + 2] cycloaddition of $CH_2{=}C(CH_2OAc)CH_2SiMe_3$ **2** *via* a TMM–palladium intermediate with alkenes having electron-withdrawing substituent has been proved to be particularly useful for the synthesis of methylenecyclopentanes.[5] It is well documented that C_{60} is an electron deficient species and the reduction potential (*e.g.* the second or third wave)[6] of C_{60} is compatible with that of an α,β-unsaturated carbonyl compound.[7] Accordingly, palladium-catalysed cycloaddition or **2** with C_{60} would provide a useful entry to prepare the parent TMM–C_{60} adduct **1**. However, treatment of C_{60} with **2** in the presence of a catalytic amount of palladium catalysts under various conditions[5] resulted in the recovery of C_{60}. On the other hand, when C_{60} was first mixed with a stoichiometric amount of $[Pd(PPh_3)_4]$ and 1 equiv. of $Ph_2PCH_2CH_2PPh_2$ in benzene, a green solution was formed immediately, presumably, the corresponding palladium–C_{60} complex being formed.[2l] A benzene solution of **2** (3 equiv.) was then added slowly and the mixture was allowed to reflux under N_2 for 72 h. A reddish brown mixture was obtained. The solvent was removed and the residue was chromatographed on silica gel using hexane as the eluent; the TMM–C_{60} adduct **1** was obtained in 25% yield. The parent peak at *m/z* 774 for **1** was observed by desorption chemical ionization mass spectrometry in the negative ion mode and by the FAB method.

The ^{1}H NMR spectrum of **1** exhibited a two-proton



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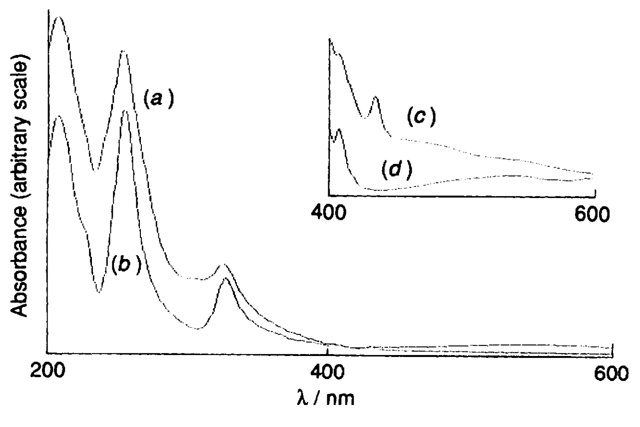


Fig. 1 The UV–VIS spectra of (*a*) 1.1 × 10^{-5} mol dm^{-3} **1** in pentane (*b*) 5.2 × 10^{-6} mol dm^{-3} C_{60} in pentane, (*c*) 1.0 × 10^{-4} mol dm^{-3} **1** in benzene and (*d*) 1.0 × 10^{-4} mol dm^{-3} C_{60} in benzene. The molar absorptivities (in 10^4 dm^3 mol^{-1} cm^{-1}) are 7.6 at 207, 6.9 at 254 and 2.1 at 326 nm in (*a*), and 5.3 at 406 and 3.7 at 433 nm in (*c*)

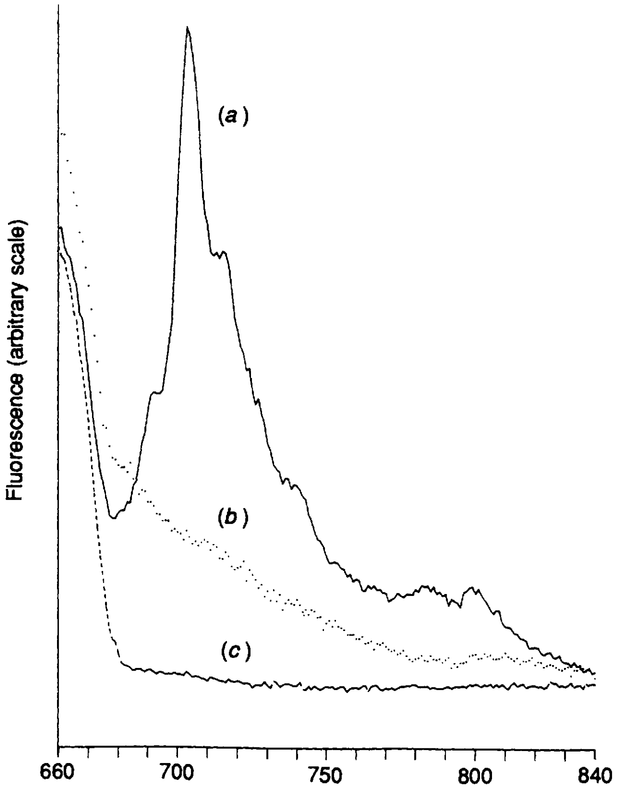
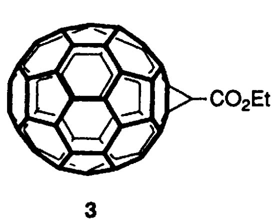


Fig. 2 Fluorescence emission spectra of **1** (*a*) and C_{60} (*b*) in pentane (5.2 μmol dm^{-3}) at 25°C. Excitation wavelength 295 nm with band pass 16 nm and mission bandpass 2 nm. Each curve was the average of five scans, (*c*) shows the background of solvent pentane



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multiplet centred at δ 5.63 and a four-proton multiplet at δ 4.31 due to the TMM moiety. The ^{13}C NMR spectrum was acquired at 75 MHz in CS_2–$CDCl_3$ with 0.03 mol dm^{-3} $[Cr(acac)_3]$ (acac = acetylacetonate) added as a relaxant. All twenty lines were observed.† The fullerene region (δ 135–160) of the spectrum has three peaks corresponding to two carbon atoms and 13 corresponding to four carbon atoms in addition to the absorption attributed to the quaternary olefinic carbon of the substituent. The terminal olefinic carbon exhibited an absorption at δ 110.3. The sp^3 carbon of the fullerene skeleton appeared as a single peak at δ 69.0 and the CH_2 group at δ 48.4. This result indicated that **1** has C_{2v} symmetry and the cycloaddition occurred at a two six-membered ring junction site.

The UV–VIS spectrum of **1** showed broad absorptions similar to those of many other C_{60} derivatives (Fig. 1). Intriguingly, the fluorescence emission spectrum of **1** (Fig. 2) appeared at λ_{max} 704 nm with vibronic fine structure (694, 704, 714, 725, 739 nm) which is quite similar to those observed for C_{60} in methylcyclohexane glass at 77 K.[9d] The spectral characteristics obtained were independent of the excitation wavelength used (*e.g.* spectra obtained using excitation at 295 or 312 nm gave almost identical emission spectrum). This is the first fluorescence spectrum of a solution sample of a C_{60} derivative measured at ambient temperature.‡ It is interesting that the methanofullerene **3**[8] also exhibited similar emission spectrum with λ_{max} 702 nm.

Attempts to obtain a single crystal of **1** was only partially successful. The highly disordered tetragonal crystal with a = 10.05, b = 10.05 and c = 30.32 Å exhibited similar dimensions in the a and b axes as those in C_{60}.[1]

Support from the National Science Council of the Republic of China is gratefully acknowledged.

Received, 28th October 1993; Com. 3/06472G

Footnotes

† Spectroscopic data for **1**. ^{13}C NMR δ 156.2, 147.0, 145.8, 145.7, 145.3, 145.2, 144.9, 144.8, 144.2, 142.7, 142.6, 142.2, 141.8, 141.6, 141.4, 139.7, 135.1, 110.3, 69.0, 48.4; IR ν/cm^{-1} (KBr) 2913w, 2846w, 1667w, 1630w, 1507w, 1461w, 1424w, 1263w, 1181br, 895w, 865w, 803w, 768s, 707s, 584s, 574vs, 526vs; UV–VIS (*n*-hexane, nm) 207, 254, 326, 406, 433.

‡ The fluorescence emission spectrum of C_{60} has been reported.[9]

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