Geometric and electronic structure of metal-cage fullerenes, $C_{59}M$ (M = Pt, Ir) obtained by laser ablation of electrochemically deposited films

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Laser ablation of electrochemically deposited $C_{60}M_n$ [M = Pt, $Ir(CO)_2$] films produces $[C_{59}M]^+$ whose electronic and geometric structures have been investigated by density functional theory.

A number of clusters based on a fullerene-like cage with heteroatoms incorporated into the cage framework have been observed in mass spectrometric studies. These clusters include examples where boron,[1] nitrogen,[2] silicon,[3] and niobium[4] are incorporated into the cages. The dimer, $\{C_{59}N\}_2$, has been prepared *via* a chemical route and isolated.[5] Recently, Branz *et al.* reported gas phase studies that generated $C_{60}M_x$ and $C_{70}M_x$ by evaporation of the metal into the fullerene vapor.[6] Subsequent photofragmentation of $C_{60}M_x$ and $C_{70}M_x$ produced clusters with the compositions, $C_{59-2n}M$ and $C_{69-2n}M$ with M = Fe, Co, Ni, Rh, Ir and n = 0, 1, 2. Here we report complementary studies that show that $C_{59-2n}M$ and $C_{69-n}M$ can be formed by laser ablation of electrochemically deposited films that are believed to contain polymeric, covalently bound chains: $\cdots C_{60}ML_nC_{60}ML_nC_{60}ML_n\cdots$, where ML_n = $Ir(CO)_2$ or Pt.[7]

Fig. 1 shows the results of laser ablation studies of the electrochemically deposited $C_{60}\{Ir(CO)_2\}_n$ film, which was obtained by electrochemical reduction of a toluene–acetonitrile (4 : 1 v/v) solution of C_{60} and $Ir(CO)_2Cl(NH_2C_6H_4Me\text{-}p)$ as described previously.[7] The lower trace shows the entire spectrum in the positive ion mode from laser desorption with a 340 nm N_2 laser from a film of $C_{60}\{Ir(CO)_2\}_n$. The spectrum reveals a strong $[C_{60}]^+$ peak at *m/z* 720 with the usual set of lower mass peaks due to loss of C_2 units from the fullerene. At higher mass the second most intense feature in the spectrum is a multiplet that is indicative of the presence of $[C_{59}Ir]^+$. Additionally a feature is seen at *m/z* 877 that corresponds to the presence of $[C_{57}Ir]^+$. Inset 1 shows an expansion of the spectroscopic multiplets for the $[C_{59}Ir]^+$ and $[C_{57}Ir]^+$ features and comparison with the calculated spectra based on the natural abundances of isotopes of C and Ir. No other iridium containing peaks are seen in the spectrum, the other peaks in the spectrum between those of $[C_{57}Ir]^+$ and $[C_{60}]^+$ correspond to the fullerene ions, $[C_{70-2n}]^+$. There is also no evidence in this spectrum for the presence of the $[C_{60}Ir_n]^+$ ions which were a prominent feature of the mass spectra that were obtained by Branz *et al.*[6] in their studies of the reactions of C_{60} and iridium vapors that led to the prior detection of $[C_{59}Ir]^+$.

Fig. 2(a) shows the corresponding spectral features for formation of $[C_{69}Ir]^+$ that was obtained by desorption from a film prepared by electrochemical reduction of a solution of C_{70} and $Ir(CO)_2Cl(NH_2C_6H_4Me\text{-}p)$. Fig. 2(b) shows the spectral features for the formation of $[C_{59}Pt]^+$ which was obtained by desorption from a film of $C_{60}Pt_n$ prepared by electrochemical reduction of a solution of C_{60} and $PtCl_2(pyridine)_2$. In the negative ion mode, the spectra from all three films show only the features due to $[C_{60}]^-$ and its fragmentation products; no evidence for the existence of $[C_{59}Ir]^-$, $[C_{69}Ir]^-$ or $[C_{59}Pt]^-$ was seen. We believe that the ions, $[C_{59}Ir]^+$, $[C_{69}Ir]^+$ and $[C_{59}Pt]^+$, are formed during the laser ablation process from $(\eta^2\text{-}C_{60})M$ units that are present in the electrochemically deposited films.

In order to understand the electronic and geometrical structures of these heterofullerenes, the optimal geometries have been computed by means of DFT calculations† under the

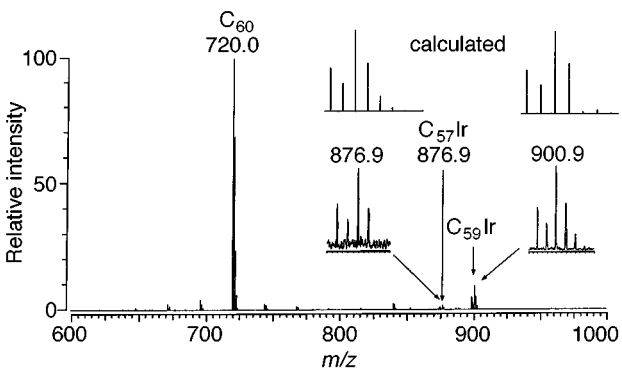


Fig. 1 Mass spectra (positive ion mode) obtained by laser ablation of electrochemically deposited films from C_{60} and $Ir(CO)_2Cl(NH_2C_6H_4Me\text{-}p)$. Inserts show expansions of the multiplets observed for $[C_{59}Ir]^+$ and $[C_{57}Ir]^+$ and comparisons with the calculated spectra.

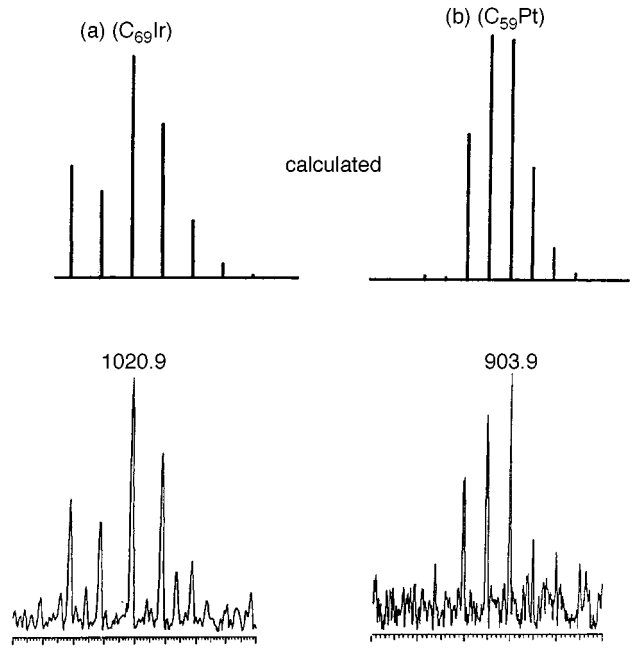
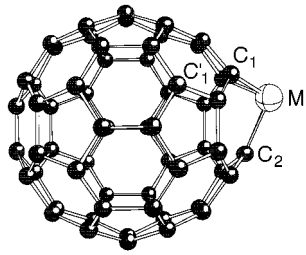


Fig. 2 Mass spectra (positive ion mode) obtained by laser ablation of electrochemically deposited films from (a) C_{70} and $Ir(CO)_2Cl(NH_2C_6H_4Me\text{-}p)$; and (b) C_{60} and $PtCl_2(py)_2$.



$C_{59}Ir$, $C_{59}Pt$

Fig. 3 A drawing of the geometric structure of $C_{59}Ir$ (and $C_{59}Pt$) obtained from density functional calculations. Selected bond lengths (Å) and angles (°): C_1–Pt 1.992, C_2–Pt 1.934, C_1–Pt–C_1' 78.5, C_1–Pt–C_2 96.7, C_1–Ir 1.954, C_2–Ir 1.905, C_1–Ir–C_1' 81.7, C_1–Ir–C_2 92.3.

Table 1 Computed energies (in eV) of C_{60} and metal–fullerene compounds

	C_{60}	$C_{59}Pt$	$C_{59}Ir$	$(\eta^2\text{-}C_{60})\text{-}Pt(PH_3)_2$	$(\eta^2\text{-}C_{60})\text{-}\{Pt(PH_3)_2\}_2$
IP	8.28	7.39	7.10	7.35	6.82
EA	3.49	3.56	3.71	3.08	2.73
E(LUMO)	−5.37	−5.34	−5.08	−4.86	−4.45
E(HOMO)	−7.03	−6.05	−5.64	−6.22	−5.97

restrictions of C_s symmetry. The computed geometries, which correspond to the substitution of one carbon atom by a metal atom, are similar for M = Pt and Ir. The optimization yields a geometry with a local distortion in the vicinity of the metal atom (Fig. 3). The computed M–C bond lengths are 1.954 and 1.905 Å for $C_{59}Ir$ and 1.992 and 1.934 Å for $C_{59}Pt$.

The electronic configuration of $C_{59}Pt$ is a closed-shell singlet in which the HOMO–LUMO gap was computed to be 0.7 eV. The triplet structure with one electron in the HOMO and another in the LUMO was also optimized but its relative energy with respect to the singlet structure was quite high (10.1 kcal mol^{-1}). Mulliken population analysis indicates that there is significant charge transfer from metal to the carbon fragment, since the net charge on platinum is +1.3 e. The electronic populations of the s, p and d platinum orbitals are 2.38, 6.03 and 8.24 e, respectively. Other models of space partitioning predict less charge transfer. Hirshfeld and Voronoi procedures assign a net charge of +0.5 e to the platinum atom.[8,9] The metal orbitals in $C_{59}Pt$ are spread through a range of molecular orbitals and each of the molecular orbitals in the metallofullerene has a low metal contribution. Specifically, the participation of the metal orbitals is 19% in the HOMO and 17% in the LUMO. The ground state for the analog iridium cluster is a doublet of symmetry A′ in which the spin density is quite delocalized with 0.22 e on the metal center, 0.27 e on C(2) and the rest of the spin density delocalized through the carbon cage in smaller increments. Hirshfeld and Voronoi population analyses suggest that the charge on the iridium atoms is *ca.* 0.35 e, and that the charge transfer from the metal to fullerene is somewhat lower than in the platinum analog.

In order to get more information about the physical properties of these clusters we have also computed the vertical ionization potentials (IP) and electron affinities (EA). These data and the energies of the HOMOs and LUMOs are presented in Table 1 for C_{60}, $C_{59}Pt$, $C_{59}Ir$, $(\eta^2\text{-}C_{60})Pt(PH_3)_2$ and $(\eta^2\text{-}C_{60})\{Pt(PH_3)_2\}_2$. Substitution of a carbon by a metal increases the energy of the HOMO in both $C_{59}Pt$ and $C_{59}Ir$ relative to C_{60}. As a consequence of this increase, the IP's of the substituted fullerenes are lower than those of C_{60} itself.

Smalley and coworkers[10] estimated from photoelectron spectra an EA of *ca.* 2.60–2.80 eV for C_{60}. Although present DFT calculations probably predict an excessively high value for C_{60}, the computed relative EAs for $(\eta^2\text{-}C_{60})\{Pt(PH_3)_2\}_n$ (n = 1 and 2) are in very good concordance with the electrochemical studies of Fagan and coworkers who proposed that coordination of one $Pt(PR_3)_2$ group to C_{60} lowers the EA of the carbon cluster by 0.34 eV while coordination of two groups to C_{60} decreases the EA by 0.70 eV.[11]

The energies of the LUMOs in $C_{59}Pt$ and C_{60} are very similar, −5.34 and −5.37 eV, respectively. Consequently, the difference between the EAs of C_{60} and $C_{59}Pt$ was computed to be very small (0.05 eV). The added electron in $C_{59}Ir$ goes to a half-filled orbital at an energy of −5.64 eV, which is 0.27 eV lower than the energy of the LUMO of C_{60}. Thus, the EA of $C_{59}Ir$ is 0.22 eV higher than the EA of C_{60}.

The ability of $C_{59}Pt$ to coordinate PH_3 or CO was also analyzed. For both molecules, the DFT calculations yielded an optimal geometry in which the metal has a tetrahedral coordination with three quasi identical Pt–C bond lengths. The new computed Pt–ligand bond distances are 2.409 Å for PH_3 and 1.983 Å for CO. The corresponding bonding energies were calculated to be 14.2 and 6.2 kcal mol^{-1}, respectively. In the case of $C_{59}PtCO$, the ground state is a triplet since the HOMO and LUMO are quasi degenerate orbitals.

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Notes and references

† *Computation*: gradient corrected DFT calculations were carried out with the ADF program.[12] We used the local density approximation with Vosko–Wilk–Nusair parametrization for correlation.[13] Becke's non-local corrections to the exchange energy and Perdew's non-local corrections to the correlation energy were added.[14] Slater basis sets of double-ζ + polarization quality were used to describe the valence electrons of C, O, P and H. For iridium and platinum, the 5sp electrons were described by double-ζ Slater functions, 5d and 6s by triple-ζ functions, and 6p by a single orbital.

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