

# Platinum Group Metal Fullerenes

## SOME RECENT STUDIES ON SYSTEMS CONTAINING C<sub>60</sub>

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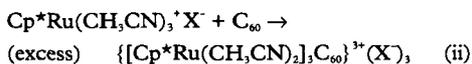
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The C<sub>60</sub> molecule, named 'buckminsterfullerene', is very stable physically, and its potential as a source of a number of useful materials has been suggested. For example, nonhydrostatic compression of C<sub>60</sub> transforms it into bulk polycrystalline diamond at room temperature (1); and when doped with alkali metals C<sub>60</sub> gives the highest temperature organic superconductors seen to date (2-4). The soot deposits from arc evaporation contain near perfect nanotubes with potentially outstanding electronic and mechanical properties, and encapsulated palladium can act as the seed for the growth of a worm-like nanostructure (4, 5). The biological activity of unsubstituted buckminsterfullerene is also being investigated using C<sub>60</sub> labelled with radioactive carbon-14 (6, 7). Potential biological applications for fullerenes are being sought in areas ranging from drug metabolism to agrochemicals.

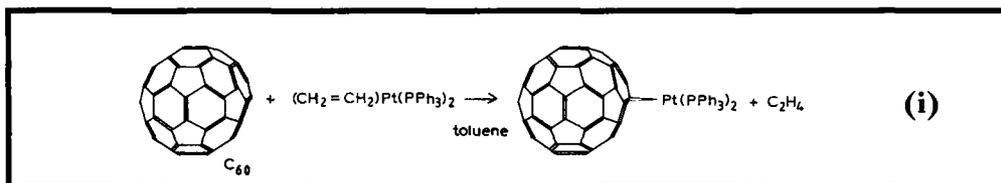
In spite of its physical robustness, C<sub>60</sub> readily undergoes chemical reactions and its organic chemistry has been widely investigated. In recent years there have also been reports of its reactions with inorganic species, including platinum group metals systems. These have given rise to the preparation of a number of platinum group metals complexes, the first such compound being: C<sub>60</sub>(OsO<sub>4</sub>)(4-Bu<sup>t</sup>C<sub>5</sub>H<sub>4</sub>N)<sub>2</sub>, an osmate ester with C-O-Os bonds, which was reported by Hawkins and co-workers (8, 9). The first example of a compound with a direct metal-C<sub>60</sub> bond, Pt(η<sup>2</sup>-C<sub>60</sub>)(PPh<sub>3</sub>)<sub>2</sub> was described in 1991 (10), see Equation (i), below.

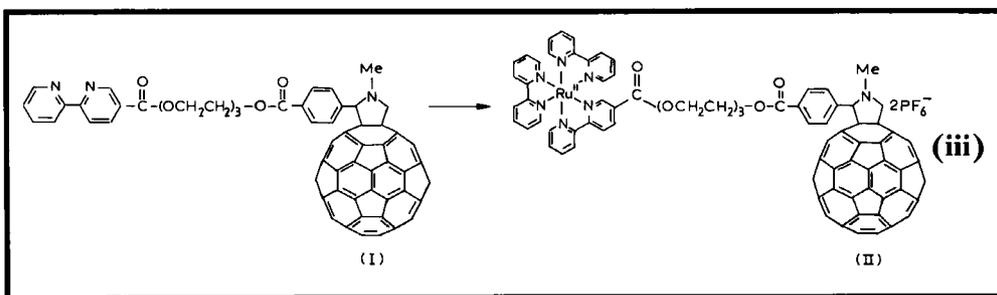
Addition of Pt(η<sup>2</sup>-C<sub>2</sub>H<sub>4</sub>)(PPh<sub>3</sub>)<sub>2</sub> to C<sub>60</sub> in toluene under nitrogen gave the C<sub>60</sub> platinum complex indicated in Equation (i) as black microcrystals in 85 per cent yield; Pt(η<sup>2</sup>-C<sub>60</sub>)(PEt<sub>3</sub>)<sub>2</sub> could be prepared by reaction with Pt(PEt<sub>3</sub>)<sub>4</sub> (11). The triethylphosphine complex was obtained in 68 per cent yield after purification by column chromatography on silica gel. The triphenylphosphine complex is also formed when fullerene-60 reacts with a binuclear heterometallic compound with a mercury-platinum bond, *trans*-Ph<sub>2</sub>CHCH<sub>2</sub>HgPt(PPh<sub>3</sub>)<sub>2</sub>Br, or *cis*-(CF<sub>3</sub>)<sub>2</sub>CFHgPt(PPh<sub>3</sub>)<sub>2</sub>CH=CPh<sub>2</sub> (12).

[60]Fullerene complexes have now been reported for all the platinum group metals. The reaction of C<sub>60</sub> with excess Cp<sup>\*</sup>Ru(CH<sub>3</sub>CN)<sub>3</sub><sup>+</sup>X<sup>-</sup> (Cp<sup>\*</sup> = η<sup>5</sup>-C<sub>5</sub>Me<sub>5</sub>; X<sup>-</sup> = O,SCF<sub>3</sub><sup>-</sup>) proceeds as follows (13):



The first ruthenium carbonyl derivative of fullerene, (η<sup>2</sup>-C<sub>60</sub>)Ru(CO)<sub>4</sub>, was prepared by the reaction between Ru(CO)<sub>5</sub> and C<sub>60</sub> in toluene solution under nitrogen. The product is more stable than the equivalent iron compound (14). The synthesis of a [60]fullerene derivative covalently linked to a ruthenium(II) tris(bipyridine) complex has been reported (15). [Ru(bpy)<sub>3</sub>]<sup>2+</sup> complexes are photoactive (2), known to transfer energy in the excited state, and [60]fullerene has a high electron affinity and can reversibly accept up to six electrons in solution. Due to solubility problems, however, the reaction of





$\text{Ru}(\text{bpy})_2(\text{bpy}-5\text{-COCl})(\text{PF}_6)_2$  with the parent N-H fulleropyrrolidine gave a very insoluble stone-like material which could not be characterised (16); but when the fulleropyrrolidine(I) was synthesised and treated with  $\text{Ru}(\text{bpy})_2\text{Cl}_2 \cdot 2\text{H}_2\text{O}$  in refluxing 1,2-dichloroethane, in the presence of  $\text{NH}_4\text{PF}_6$ , compound (II) was produced, see Equation (iii), above.

Compound (II) is now being studied as a model for long-lived charge separated states, and is being compared with compounds which have conventional rigid spacers less flexible than the triethylene glycol chain.

A number of isomers of the *bis*-complex  $\text{C}_{60}[\text{OsO}_4(\text{py})_2]_2$  have been prepared (17); and  $\text{C}_{60}$  triosmium cluster compounds have been obtained from the reaction between a toluene solution of  $\text{Os}_3(\text{CO})_{11}(\text{NCMe})$  and one equivalent of  $\text{C}_{60}$  by heating at  $80^\circ\text{C}$  for 5 minutes. The products have the formulae  $(\eta^2\text{-C}_{60})\text{Os}_3(\text{CO})_{11}$ ,  $(\eta^2\text{-C}_{60})\text{Os}_3(\text{CO})_{10}(\text{NCMe})$ ,  $(\eta^2\text{-C}_{60})\text{Os}_3(\text{CO})_{10}(\text{PPh}_3)$  and  $(\eta^2\text{-C}_{60})\text{Os}_3(\text{CO})_9(\text{PPh}_3)_2$  (9).

A  $\text{C}_{60}$  rhodium complex  $\text{Rh}(\eta^2\text{-C}_{60})\text{H}(\text{CO})(\text{PPh}_3)_2$ , which is a dark green powder, has been prepared by the addition of one equivalent of  $\text{RhH}(\text{CO})(\text{PPh}_3)_3$  in toluene to  $\text{C}_{60}$  in toluene (18). This rhodium complex may also be prepared in dichloromethane solution and obtained and isolated as green-black crystals (19). This product is more stable in solution than

$\text{Ir}(\eta^2\text{-C}_{60})\text{Cl}(\text{CO})(\text{PPh}_3)_2$  which readily dissociates into  $\text{C}_{60}$  and  $\text{IrCl}(\text{CO})(\text{PPh}_3)_2$ . 'Naked metal' complexes  $\text{M}(\text{C}_{60})$  have been prepared for a number of metals including rhodium – the general approach involves the formation of  $\text{M}^+$  ions from pure metal targets by laser desorption, followed by interaction with  $\text{C}_{60}$  in the vapour state (20).

$\text{Ir}(\eta^2\text{-C}_{60})\text{Cl}(\text{CO})(\text{PPh}_3)_2 \cdot 5\text{C}_6\text{H}_6$ , was obtained as brown-black crystals when a purple solution of  $\text{C}_{60}$  in the dangerous solvent, benzene, was added to a yellow benzene solution of  $\text{IrCl}(\text{CO})(\text{PPh}_3)_2$  (21). The indenyl  $\text{C}_{60}$  complex  $\text{Ir}(\eta^5\text{-C}_9\text{H}_7)(\eta^2\text{-C}_{60})(\text{CO})$  was obtained by refluxing the indenyl cyclooctene complex  $\text{Ir}(\eta^5\text{-C}_9\text{H}_7)(\eta^2\text{-C}_8\text{H}_{14})$  and  $\text{C}_{60}$  in dichloro-methane (22).  $\text{C}_{60}[\text{IrCl}(\text{CO})(\text{PMe}_2\text{Ph})_2]_2$  has been obtained in two conformational isomers (20, 23), and  $\text{C}_{60}[\text{Ir}_2\text{Cl}_2(1,5\text{-COD})_2]_2 \cdot 2\text{C}_6\text{H}_6$  has been prepared by mixing solutions of  $\text{C}_{60}$  and  $\text{Ir}_2\text{Cl}_2(1,5\text{-COD})_2$  in benzene (24).

$\text{Pd}(\eta^2\text{-C}_{60})(\text{PPh}_3)_2$  has been reported (25) and the reaction between  $\text{C}_{60}$  and  $\text{M}(\text{PEt}_3)_4$ , where M is nickel, palladium or platinum, gives  $(\eta^2\text{-C}_{60})\text{M}(\text{PEt}_3)_2$  compounds. Addition of  $\text{Pt}(\text{PEt}_3)_4$  to a solution of  $\text{C}_{60}$  in benzene produced  $\text{C}_{60}[\text{Pt}(\text{PEt}_3)_2]_6$  (26), and analogous compounds of nickel and palladium have also been prepared (27). In the palladium product the molecule has a  $\text{C}_{60}$  core bearing six octahedrally-disposed  $\text{Pt}(\text{PEt}_3)_2$  groups (26).

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## Platinum Nanochannel Replica Membranes

Nanoscale materials are widely used in electronic and optical devices, and for filtration and biological applications; so there is clearly a need for suitable production and patterning techniques, and some have been discussed here before, *Platinum Metals Rev.*, 1993, **37**, (2), 101.

Researchers at the Naval Research Laboratory, Washington D.C., U.S.A., now report the preparation of thin platinum membranes using nanochannel glass replica membrane technology (D. H. Pearson and R. J. Tonucci, *Science*, 1995, **270**, (5233), 68–70).

The thin membranes produced, which can be fabricated from platinum, gold, tungsten and molybdenum, contain uniform, nanometre-scale, patterned voids. The metal membranes are formed on nanochannel glass (NCG) wafer substrates. The NCG material is fabricated by a draw process similar to the preparation of optical fibres and the fibres are packed together in a hexagonal close-packed arrangement. The fibres are then repacked and redrawn to achieve the desired packing density and element size, made into wafers, polished and etched. Other packing schemes enable more complex void patterns to be achieved.

The usual deposition techniques are employed to deposit an easily dissolved buffer layer of aluminium onto the NCG, followed by a 75 nm thick layer of platinum by magnetron sputter-

ing. The buffer layer is dissolved in sodium hydroxide and the platinum replica membrane floated off. Thin platinum membranes having a uniform, hexagonal pattern of voids as small as 40 nm in diameter, and possibly less, have been formed. The membranes, displaying good mechanical properties, can be used as masks in pattern deposition onto substrates. This method is said to be an improvement on the usual lithographic techniques and involves fewer steps.

### Increased Catalytic Activity

Clearly, it would be advantageous if the catalytic activity and/or the selectivity of a heterogeneous catalyst could be varied by a signal given to the catalyst.

Recent studies by scientists at the Nagaoka University of Technology, Japan, have led them to conclude that remarkable enhancements in the catalytic activity of a thin film palladium catalyst supported on ferroelectric lead strontium zirconium titanate and lithium niobate substrates can result from resonance oscillation of the material (Y. Inoue and Y. Ohkawara, *J. Chem. Soc., Chem. Commun.*, 1995, (20), 2101–2102).

Using the resonance oscillations generated by low-frequency voltages of the ferroelectric substrates, remarkable 250 to 300 fold increases in activity of the catalyst surfaces were found during ethanol oxidation. I.E.C.