

# SYNTHESIS AND CHARACTERIZATION OF MONONUCLEAR AND POLYNUCLEAR METAL-FULLERENE COMPLEXES

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The fullerene complexes  $M(\text{CO})_3(\text{dppe})(\eta^2\text{-fullerene})$  (fullerene =  $\text{C}_{60}$ ,  $M = \text{Mo}$  and  $\text{W}$ ; fullerene =  $\text{C}_{70}$ ,  $M = \text{Mo}$ ) as well as an analogous complex of dimethyl fumarate (dmf),  $\text{W}(\text{CO})_3(\text{dppe})(\eta^2\text{-dmf})$ , have been prepared by photolysis of  $M(\text{CO})_4(\text{dppe})$  and the respective olefin. The local coordination geometries prove to be very similar for all four compounds as observed in their single crystal X-ray structures, but the  $\text{C}_{60}$  complexes display significant secondary interactions between the fullerene moiety and the phenyl groups of the diphosphine ligand. The isomer distribution of the double addition  $\text{C}_{60}$  adducts have been probed by  $^{31}\text{P}$  NMR spectroscopy. For the compound  $\text{Mo}(\text{CO})_3(\text{dppe})(\eta^2\text{-C}_{70})$ , two isomers (ratio 4:1) are indicated by its  $^{31}\text{P}$  NMR spectrum.

The reaction of  $\text{Ru}_3(\text{CO})_{12}$  with  $\text{C}_{60}$  gave a novel hexahapto  $\text{C}_{60}$  compound,  $\text{Ru}_3(\text{CO})_9(\mu_3\text{-}\eta^2, \eta^2, \eta^2\text{-C}_{60})$ . The molecular structure of  $\text{Ru}_3(\text{CO})_9(\mu_3\text{-}\eta^2, \eta^2, \eta^2\text{-C}_{60})$  shows that the  $\text{Ru}_3$  triangle is positioned centrally over a ring of six carbons in the fullerene framework and the two planes are essentially parallel. The carbon-carbon bonds in the six-membered ring alternate in length and the Ru-C distances also show a short-long pattern at each metal center, which reflects a slight twist about the idealized threefold axis linking the  $\text{Ru}_3$  triangle and the  $\text{C}_6$  ring. The structural features seen for  $\text{Ru}_3(\text{CO})_9(\mu_3\text{-}\eta^2, \eta^2, \eta^2\text{-C}_{60})$  are closely comparable to those reported for the benzene complex  $\text{Ru}_3(\text{CO})_9(\mu_3\text{-}$

$\eta^2, \eta^2, \eta^2\text{-C}_6\text{H}_6$ ). The stability of  $\text{Ru}_3(\text{CO})_9(\mu_3\text{-}\eta^2, \eta^2, \eta^2\text{-C}_{60})$  toward temperature up to  $136^\circ\text{C}$  and CO pressures up to 4 atm indicates strong interaction between the  $\text{Ru}_3$  triangle and the  $\text{C}_6$  ring. However, the carbonyl ligands can be replaced by triphenylphosphine to give  $\text{Ru}_3(\text{CO})_{9-n}(\text{PPh}_3)_n(\mu_3\text{-}\eta^2, \eta^2, \eta^2\text{-C}_{60})$  ( $n = 1, 2$ ) and the  $\text{C}_{60}\text{-Ru}_3$  cluster interaction is interrupted by extended heating of these phosphine derivatives, which leads to the formation of mononuclear derivatives. Detailed  $^{31}\text{P}$  and  $^{13}\text{C}$  NMR studies on  $\text{Ru}_3(\text{CO})_{9-n}(\text{PPh}_3)_n(\mu_3\text{-}\eta^2, \eta^2, \eta^2\text{-C}_{60})$  indicate localized ligand rotation at each metal center. The multiple addition adducts,  $\{\text{Ru}_3(\text{CO})_9\}_n(\mu_3\text{-}\eta^2, \eta^2, \eta^2\text{-C}_{60})$  ( $n = 2, 3, 4$ ), were obtained by raising the ratio of  $\text{Ru}_3(\text{CO})_{12}$  to  $\text{C}_{60}$ . One of two isomers of the 3:1 adduct has been structurally defined. The availability of further reacting sites seems to be the dominant factor for the isomer distribution with this special bonding mode.

The first hexahapto complex of  $\text{C}_{70}$ ,  $\text{Ru}_3(\text{CO})_9(\mu_3\text{-}\eta^2, \eta^2, \eta^2\text{-C}_{70})$ , has been prepared and structurally defined. The  $\text{Ru}_3$  triangle is bonded to a six-membered ring next to one of the poles of  $\text{C}_{70}$ . In addition, the expected three isomers of the double substitution product,  $\{\text{Ru}_3(\text{CO})_9\}_2(\mu_3\text{-}\eta^2, \eta^2, \eta^2\text{-C}_{70})$ , were also obtained and separated, and the structure of one isomer has been determined. The two  $\text{Ru}_3$  units are each bonded to six-membered rings but adjacent to opposite poles of the ellipsoidal  $\text{C}_{70}$  unit. The phosphine derivatives of  $\text{Ru}_3(\text{CO})_9(\mu_3\text{-}\eta^2, \eta^2, \eta^2\text{-C}_{70})$  were prepared and studied by  $^{31}\text{P}$  and  $^{13}\text{C}$  NMR spectroscopy. For the monophosphine derivative,  $\text{Ru}_3(\text{CO})_8(\text{PPh}_3)(\mu_3\text{-}\eta^2, \eta^2, \eta^2\text{-C}_{70})$ , two isomers are observed in the  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum at room temperature and no evidence for rotation of  $\text{C}_{70}$  versus the  $\text{Ru}_3$  triangle is observed up to  $60^\circ\text{C}$ . However, in the parent compound,  $\text{Ru}_3(\text{CO})_9(\mu_3\text{-}\eta^2, \eta^2, \eta^2\text{-C}_{70})$ , the two carbonyl signals due to axial and equatorial carbonyl

ligands coalesce at 95°C, which can be attributed possibly to rotation or to a scrambling process equilibrating all the carbonyl ligands.

The reaction of  $\text{Ru}_6\text{C}(\text{CO})_{17}$  with  $\text{C}_{60}$  followed by carbonyl substitution with bis(diphenylphosphino)methane gave  $\text{Ru}_6\text{C}(\text{CO})_{12}(\text{dppm})(\mu_3\text{-}\eta^2, \eta^2, \eta^2\text{-C}_{60})$ , in which the  $\text{C}_{60}$  ligand occupies one face of the octahedral  $\text{Ru}_6$  unit. The dppm ligand bridges two Ru atoms not bonded to  $\text{C}_{60}$ . A related arene- $\text{Ru}_6\text{C}$  compound,  $\text{Ru}_6\text{C}(\text{CO})_{13}\{\text{PPh}_2(\mu\text{-}\eta^6\text{-C}_6\text{H}_6)\}$ , was obtained by thermolysis of  $\text{Ru}_6\text{C}(\text{CO})_{16}\text{PPh}_3$ . The tendency of the  $\text{Ru}_6\text{C}$  framework to form arene complexes is extended to include a coordinated triphenylphosphine moiety, evidenced by (reversible) coordination of a phenyl ring to an adjacent ruthenium center in the cluster unit.