

## Black Spots on a Cluster Face: Synthesis and Characterization of $\text{Ru}_3(\text{CO})_9(\mu_3\text{-}\eta^2,\eta^2,\eta^2\text{-C}_{60})$ , $\text{Ru}_3(\text{CO})_9(\mu_3\text{-}\eta^2,\eta^2,\eta^2\text{-C}_{70})$ , and Related Face-Capped Derivatives

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Fullerenes were discovered by Smalley et al. in 1985.<sup>1</sup> Subsequently, the macroscopic synthesis<sup>2</sup> of the two most abundant fullerenes,  $\text{C}_{60}$  and  $\text{C}_{70}$ , initiated the development of the organometallic chemistry of fullerenes. Early approaches to forming metal complexes were based on the view dating to the original report on  $\text{C}_{60}$  that the molecule was highly aromatic.<sup>1</sup> However, well-known arene-coordinating reagents failed to form the expected  $\eta^6\text{-C}_{60}$  derivatives, and these notions were swept aside by the synthesis and structural determination of  $\text{Pt}(\text{PPh}_3)_2(\eta^2\text{-C}_{60})$ .<sup>3</sup> Subsequent metal  $\pi$ -complex chemistry<sup>4</sup> has reinforced the idea that  $\text{C}_{60}$  reacts primarily as a moderately electronegative olefin. However, fullerene complexes with tetrahapto coordination of adjacent  $\pi$  bonds to two connected metal centers have been reported.<sup>5</sup> The failure to form stable  $\text{M}(\eta^6\text{-C}_{60})$  compounds has been attributed to the bending away ( $10^\circ$ )<sup>6</sup> of the  $p_\pi$ -orbitals of the six-membered ring from the perpendicular to the face of the ring; both calculations and experiment indicate that  $\text{C}_{60}$  is a weaker ligand than benzene toward a single metal. However, benzene and related arenes can also bond to triangular faces of metal clusters, and geometric considerations suggest that a metal triangle should provide for effective overlap with the  $\text{C}_{60}$   $p_\pi$  orbitals.

After many attempts, conditions were found under which the reaction of  $\text{Ru}_3(\text{CO})_{12}$  with  $\text{C}_{60}$  gave the novel hexahapto  $\text{C}_{60}$  compound,  $\text{Ru}_3(\text{CO})_9(\mu_3\text{-}\eta^2,\eta^2,\eta^2\text{-C}_{60})$  (Figure 1).<sup>7</sup> 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  $\text{Ru}_3(\text{CO})_9(\mu_3\text{-}\eta^2,\eta^2,\eta^2\text{-C}_6\text{H}_6)$ .<sup>8</sup>

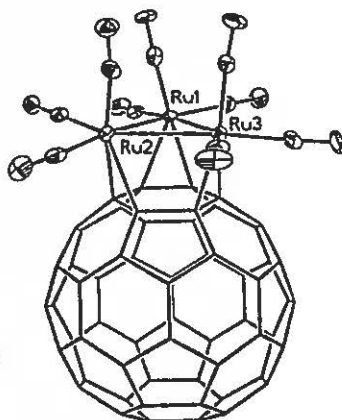
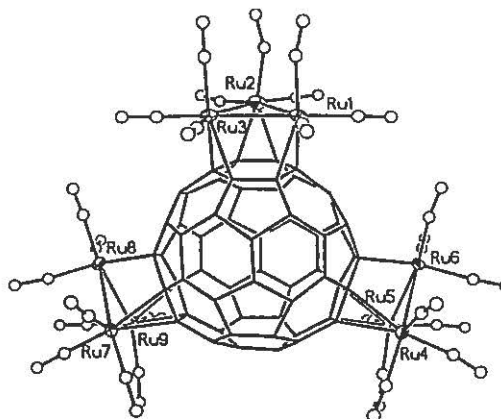


Figure 1. A perspective view of  $\text{Ru}_3(\text{CO})_9(\mu_3\text{-}\eta^2,\eta^2,\eta^2\text{-C}_{60})$ .

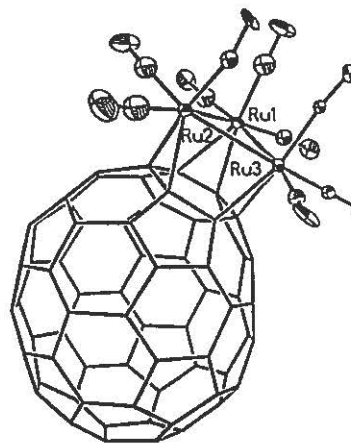
The stability of  $\text{Ru}_3(\text{CO})_9(\mu_3\text{-}\eta^2,\eta^2,\eta^2\text{-C}_{60})$  toward elevated temperatures ( $> 130\text{ }^\circ\text{C}$ ) and CO pressures (ca. 4 atm) indicates strong interaction between the  $\text{Ru}_3$  triangle and the  $\text{C}_6$  ring. The carbonyl ligands can be replaced by triphenylphosphine ligands 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 complexes. Detailed  $^{31}\text{P}$  and  $^{13}\text{C}$  NMR studies on the  $\text{Ru}_3(\text{CO})_{9-n}(\text{PPh}_3)_n(\mu_3\text{-}\eta^2,\eta^2,\eta^2\text{-C}_{60})$  derivatives 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 (Figure 2). The steric availability of further reacting sites seems to be the dominant factor in determining the isomer distribution with this special bonding mode.



**Figure 2.** A perspective view of  $\{\text{Ru}_3(\text{CO})_9\}_3(\mu_3\text{-}\eta^2,\eta^2,\eta^2\text{-C}_{60})$ .

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 (Figure 3).<sup>9</sup> 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.



**Figure 3.** A perspective view of  $\text{Ru}_3(\text{CO})_9(\mu_3\text{-}\eta^2,\eta^2,\eta^2\text{-C}_{70})$ .

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  $95^\circ\text{C}$ , 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 (Figure 4).<sup>10</sup> The dppm ligand bridges two Ru atoms not bonded to  $\text{C}_{60}$ .

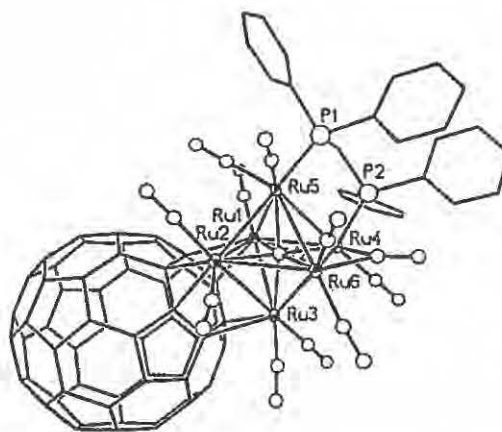


Figure 4. A perspective view of  $\text{Ru}_6\text{C}(\text{CO})_{12}(\text{dppm})(\mu_3\text{-}\eta^2,\eta^2,\eta^2\text{-C}_{60})$ .

Although two possible bonding modes were observed in mono-arene  $\text{Ru}_6\text{C}$  complexes,<sup>11</sup> it is found that the  $\text{C}_{60}$  coordinates to a ruthenium triangle face of  $\text{Ru}_6\text{C}$  framework.

## References

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