

## Recent developments in organometallic chemistry

M.L.H.Green

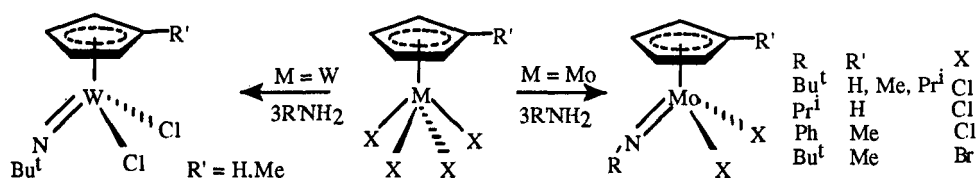
Inorganic Chemistry Laboratory, South Parks Road, Oxford, OX1 3QR, UK

**Abstract:** New cyclopentadienyl-imido compounds of molybdenum (and tungsten) have been prepared. They have an extensive chemistry in which the imido group behaves as a 4-electron donor spectator ligand. The structure of the bis- $\eta$ -cyclopentadienyl compound  $[\text{Mo}(\eta\text{-C}_5\text{H}_4\text{R})_2(\text{NBU}^t)]$  shows the  $\eta$ -cyclopentadienyl rings are partially displaced from the metal by the  $p\pi$ -donor electron pair on the imido nitrogen. In consequence a  $\eta$ -cyclopentadienyl ring can be readily displaced. The *ansa*-sandwich compounds  $[\text{M}(\eta\text{-C}_5\text{H}_4\text{-CMe}_2\text{-}\eta\text{-C}_5\text{H}_4)\text{X}_2]$ , where  $\text{M} = \text{Mo}$  or  $\text{W}$  and  $\text{X}_2 = \text{Cl}_2, \text{H}_2, \text{Me}_2, \text{HPh}, \text{HMe}$  have been prepared. These *ansa* bridged compounds are much more resistant to reductive elimination reactions than their non-*ansa* analogues. New transition metal compounds of the fullerene  $\text{C}_{60}$  have been prepared.

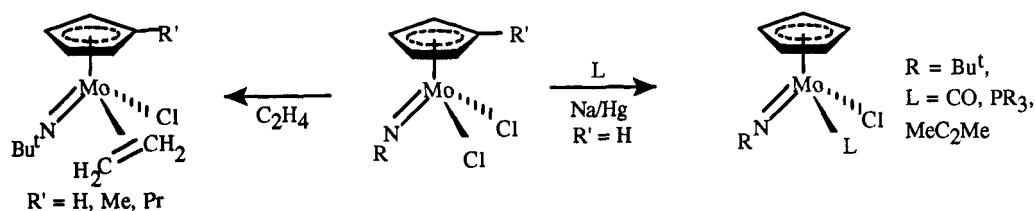
### STUDIES IN $\eta$ -CYCLOPENTADIENYL-IMIDO-MOLYBDENUM CHEMISTRY

Both the imido ligands  $\text{NR}$  and the  $\eta$ -cyclopentadienyl ligands  $\eta\text{-C}_5\text{R}_5$  have an extensive chemistry. The mission of this research was to learn more about the properties of imido ligands in general and, more specifically, the chemistry of the combination of both ligands in  $\eta$ -cyclopentadienyl-imido-molybdenum (and tungsten) compounds. References to previous chemistry of  $\eta$ -cyclopentadienyl-imido transition metal compounds are available (1,2).

The 17-electron compounds  $[\text{Mo}(\eta\text{-C}_5\text{H}_4\text{R})(\text{NR}')\text{X}_2]$ , where, typically,  $\text{R} = \text{H}$  or alkyl,  $\text{R}' = \text{Bu}^t, \text{Pr}^i$ , or  $\text{Ph}$  and  $\text{X} = \text{Cl}, \text{Br}$  or  $\text{I}$ , (1,2) may be prepared by the reactions shown below:-



The  $d^1$  compounds  $[\text{Mo}(\eta\text{-C}_5\text{H}_4\text{R})(\text{NR}')\text{Cl}_2]$  readily undergo a reductive substitution reaction giving the 18-electron  $d^2$  compounds  $[\text{Mo}(\eta\text{-C}_5\text{H}_4\text{R})(\text{NR}')\text{LCl}]$ , where  $\text{L} = \text{CO}, \text{PR}_3, \text{C}_2\text{H}_4, \text{MeC}_2\text{Me}$ , viz:-



The compound  $[\text{Mo}(\eta\text{-C}_5\text{H}_4\text{R})(\text{NR}')(\eta\text{-C}_2\text{H}_4)\text{Cl}]$  readily undergoes substitution of the chloride ligand by hydrocarbonyl ligands and this is shown in Fig. 1. We have also prepared the imido- $\eta$ -allyl compound  $[\text{Mo}(\eta\text{-C}_5\text{H}_4\text{Me})(\text{NBu}^t)(\eta^3\text{-C}_3\text{H}_5)]$  since there were no previous example of the ligand combination and there has been speculation that the oxidative amination of propene to acrolein might proceed by intermediates with an imido- $\eta$ -allyl moiety. However, thermolysis or photolysis reactions of  $[\text{Mo}(\eta\text{-C}_5\text{H}_4\text{Me})(\text{NBu}^t)(\eta^3\text{-C}_3\text{H}_5)]$  with donor ligands failed to provide evidence for products containing a nitrogen-carbon bond.

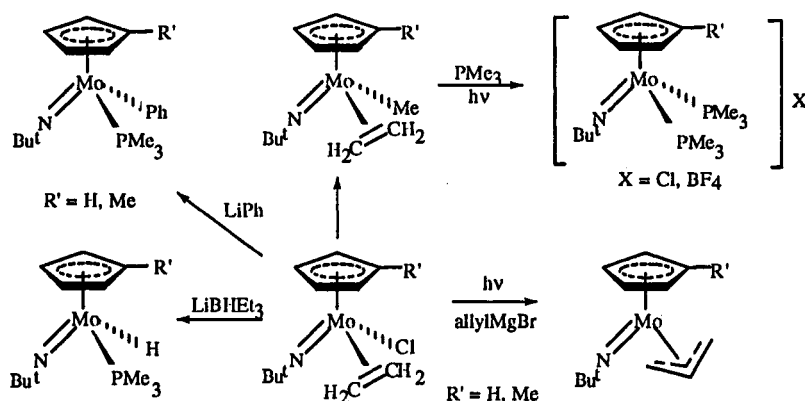


Fig. 1. Synthesis of allyl, alkyl, aryl and hydrido derivatives.

The bis- $\eta$ -cyclopentadienyl-imido compounds  $[\text{Mo}(\eta\text{-C}_5\text{H}_4\text{R})_2(\text{NR}')]_2$  have been prepared by a one-pot reductive cyclopentadienylation of the 17-electron compounds  $[\text{Mo}(\eta\text{-C}_5\text{H}_4\text{R})(\text{NR}')\text{X}_2]$  (see Fig. 2) (3). The crystal structure of the compound  $[\text{Mo}(\eta\text{-C}_5\text{H}_5)_2(\text{NBu}^t)]$  shows interesting features. The Mo-N-C linkage is effectively linear ( $177.7(2)^\circ$ ) and the metal-carbon distances of both  $\text{C}_5$ -rings are unequal and clearly indicate a distortion such that the planer  $\eta$ -cyclopentadienyl rings are tilted back and away from the molybdenum-imido group. These features can be accounted for by invoking a donor role for the out-of-plane  $p\pi$ -electrons of the imido nitrogen (3). Calculations support this proposal and indicate there is an interaction between the nitrogen  $p\pi$ -electrons and the  $b_2$  metal based orbital. The overall effect of this interaction is to destabilise the metal- $\eta$ -cyclopentadienyl bonding and thereby to labilise a cyclopentadienyl ring. For example, treatment of  $[\text{Mo}(\eta\text{-C}_5\text{H}_5)_2(\text{NBu}^t)]$  with trimethylphosphine gives the salt  $\{[\text{Mo}(\eta\text{-C}_5\text{H}_5)(\text{NBu}^t)(\text{PMe}_3)_2][\text{C}_5\text{H}_4\text{Me}]\}^+$  and the crystal structure of this compound is represented in Fig. 2 (3).

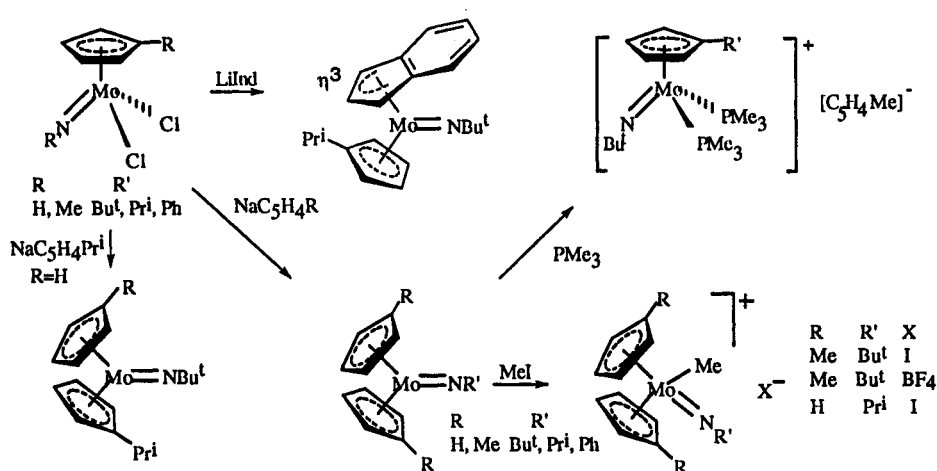


Fig. 2. Synthesis and some reactions of bis- $\eta$ -cyclopentadienyl-imidomolybdenum compounds.

The mechanism of formation of the compounds  $[\text{Mo}(\eta\text{-C}_5\text{H}_4\text{R})_2(\text{NR}')]$  from  $[\text{Mo}(\eta\text{-C}_5\text{H}_4\text{R})(\text{NR}')\text{X}_2]$  is unknown but NMR studies of the products of the reaction between  $[\text{Mo}(\eta\text{-C}_5\text{H}_4\text{Pr}^i)(\text{NBu}^t)\text{X}_2]$  and  $\text{NaC}_5\text{H}_5$  showed the presence of a mixture of the three compounds  $[\text{Mo}(\eta\text{-C}_5\text{H}_4\text{Pr}^i)_2(\text{NBu}^t)]$ ,  $[\text{Mo}(\eta\text{-C}_5\text{H}_5)_2(\text{NBu}^t)]$  and  $[\text{Mo}(\eta\text{-C}_5\text{H}_4\text{Pr}^i)(\eta\text{-C}_5\text{H}_5)(\text{NBu}^t)]$  (4). Clearly ring exchange processes are occurring. In the light of the facile exchange of  $\eta$ -cyclopentadienyl rings noted above it was decided to attempt to synthesise *ansa*-bis- $\eta$ -cyclopentadienyl molybdenum derivatives, for example,  $[\text{Mo}(\eta\text{-C}_5\text{H}_4\text{-CMe}_2\text{-}\eta\text{-C}_5\text{H}_4)\text{X}_2]$ .

Treatment of  $[\text{Mo}(\eta\text{-C}_5\text{H}_4\text{R})(\text{NR}')\text{X}_2]$  with  $\text{Li}_2(\text{C}_5\text{H}_4\text{-CMe}_2\text{-C}_5\text{H}_4)$  gives a smooth reaction and the NMR spectra of the resulting red oil showed resonances consistent with the presence of the compound  $[\text{Mo}(\eta\text{-C}_5\text{H}_4\text{-CMe}_2\text{-}\eta\text{-C}_5\text{H}_4)(\text{NBu}^t)]$  and, surprisingly,  $[\text{Mo}(\eta\text{-C}_5\text{H}_5)_2(\text{NBu}^t)]$ . The mixture could not be separated (4). However, having established that the new class of *ansa* compounds  $[\text{Mo}(\eta\text{-C}_5\text{H}_4\text{-CMe}_2\text{-}\eta\text{-C}_5\text{H}_4)\text{X}_2]$  were stable an alternative synthesis was sought.

It was found that treatment of  $[\text{MoCl}_4(\text{dme})]$  with  $\text{Li}_2(\text{C}_5\text{H}_4\text{-CMe}_2\text{-C}_5\text{H}_4)$  gives the dichloro compound  $[\text{Mo}(\eta\text{-C}_5\text{H}_4\text{-CMe}_2\text{-}\eta\text{-C}_5\text{H}_4)\text{Cl}_2]$  in 52% yield. The red-brown tungsten analogue  $[\text{W}(\eta\text{-C}_5\text{H}_4\text{-CMe}_2\text{-}\eta\text{-C}_5\text{H}_4)\text{Cl}_2]$  was prepared similarly in 64% from  $[\text{WCl}_4(\text{dme})]$  (5). Starting from these *ansa*-dichloro compounds, the dihydrides  $[\text{M}(\eta\text{-C}_5\text{H}_4\text{-CMe}_2\text{-}\eta\text{-C}_5\text{H}_4)\text{H}_2]$ , the dimethyl derivatives  $[\text{M}(\eta\text{-C}_5\text{H}_4\text{-CMe}_2\text{-}\eta\text{-C}_5\text{H}_4)\text{Me}_2]$ , where  $\text{M} = \text{Mo}$  or  $\text{W}$ , and the methylhydride  $[\text{W}(\eta\text{-C}_5\text{H}_4\text{-CMe}_2\text{-}\eta\text{-C}_5\text{H}_4)\text{MeH}]$  have been prepared as shown in Fig. 3.(6).

We were interested to explore the effect of the presence of an *ansa*-bridge on the chemistry of bent metallocenes. Therefore, we have studied the properties of the *ansa*-compounds shown in the Fig. 3 with that of the long known non-*ansa* analogues (7).

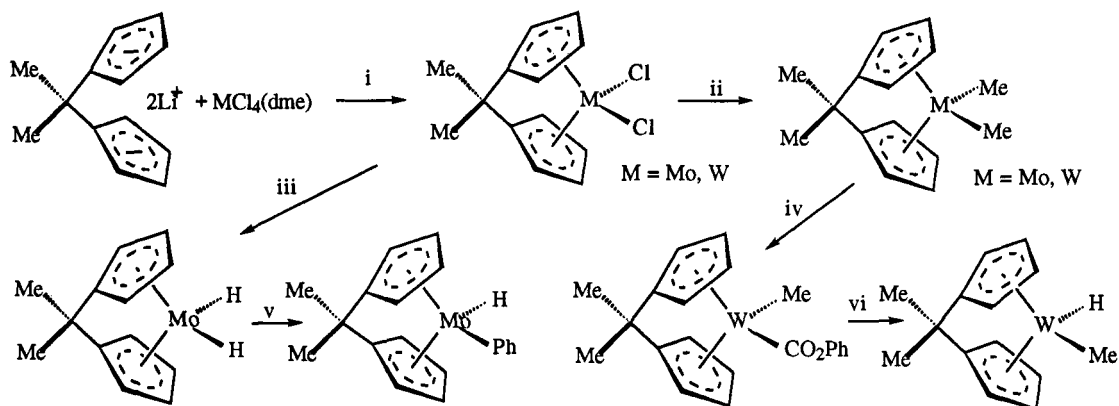


Fig. 3. i In  $\text{Et}_2\text{O}$  at r.t. ii  $\text{ZnMe}_2$  in toluene,  $-78^\circ\text{C}$ . iii  $\text{LiAlH}_4$  in  $\text{Et}_2\text{O}$  at  $-78^\circ\text{C}$ . iv  $\text{PhCOOH}$  at reflux in petroleum ether (b.p.  $100 - 120^\circ\text{C}$ ). v  $h\nu$ , in benzene. vi  $\text{Na}[\text{AlH}_2(\text{OCH}_2\text{CH}_2\text{OMe})_2]$  in benzene at r.t.

Striking differences in the reactivities were observed. For example, photolysis of  $[\text{Mo}(\eta\text{-C}_5\text{H}_5)_2\text{H}_2]$  in benzene gives only the dimer  $[\text{Mo}(\eta\text{-C}_5\text{H}_5)(\mu\text{-}\sigma\text{-}\eta\text{-C}_5\text{H}_4)]_2$  (8). The expected phenyl hydride  $[\text{Mo}(\eta\text{-C}_5\text{H}_5)_2\text{PhH}]$  was not formed, neither can this compound be made by alternative routes available to the tungsten analogue. However, photolysis of  $[\text{W}(\eta\text{-C}_5\text{H}_4\text{-CMe}_2\text{-}\eta\text{-C}_5\text{H}_4)\text{Cl}_2]$  under the same conditions gives the *ansa* phenyl hydride  $[\text{Mo}(\eta\text{-C}_5\text{H}_4\text{-CMe}_2\text{-}\eta\text{-C}_5\text{H}_4)\text{PhH}]$ . In contrast, whilst photolysis of  $[\text{W}(\eta\text{-C}_5\text{H}_5)_2\text{H}_2]$  in benzene readily gives the phenyl hydride  $[\text{W}(\eta\text{-C}_5\text{H}_5)_2\text{PhH}]$  (9), under the same conditions the *ansa* dihydride analogue is completely unreactive. Further the methyl-hydride  $[\text{W}(\eta\text{-C}_5\text{H}_5)_2\text{MeH}]$  is thermally unstable above *ca.*  $40^\circ\text{C}$  and decomposes with evolution of methane and formation of the intermediate compound tungstenocene. Tungstenocene is a very reactive (10) which can insert into carbon-hydrogen bonds (9,10). For example, thermolysis of  $[\text{W}(\eta\text{-C}_5\text{H}_5)_2\text{MeH}]$  in benzene give the phenyl

hydride  $[W(\eta-C_5H_5)_2PhH]$ . In contrast, the *ansa*- $[W(\eta-C_5H_4-CMe_2-\eta-C_5H_4)MeH]$  is stable in benzene at 110 °C for a week. These observations show that the *ansa*-bridged compounds  $[M(\eta-C_5H_4-CMe_2-\eta-C_5H_4)AB]$  have a much greater stability towards reductive elimination of the ligands AB than the corresponding non-*ansa* bis- $\eta$ -cyclopentadienyl analogues  $[M(\eta-C_5H_5)_2AB]$ .

The crystal structures of some of the new *ansa* compounds have been determined and selected data are given in Table 1. The data in Table 1 show that the bending angle  $\theta$  is substantially reduced for the *ansa*-bridged compounds compared to the non-*ansa* analogues and, therefore, the structures of intermediate 16-electron fragments  $M(\eta-C_5H_4-CMe_2-\eta-C_5H_4)$  would be substantially different from the parallel ring structure found for the corresponding unbridged  $[M(\eta-C_5H_5)_2]$ , where  $M = Cr, W$  [14]. In contrast the Cl-M-Cl angles ( $\phi$ ) are closely similar in both the *ansa* and non-*ansa* dichloride compounds. Further, the photoelectron spectrum of  $[W(\eta-C_5H_4-CMe_2-\eta-C_5H_4)H_2]$  shows that the ionisation energy associated with the  $d^2$  electron is 6.47 eV and this value is similar to that of the non-bridged analogue (15) It appears that the electron energies associated the X-M-X grouping are essentially independent of  $\theta$  (16).

TABLE 1. The angles  $\theta$  and  $\phi^a$ .

| Compound <sup>a</sup>            | X-M-X<br>( $\phi$ ) <sup>o</sup> | bending angle ( $\theta$ ) <sup>o</sup> | Ref  |
|----------------------------------|----------------------------------|---|------|
| $[Mo(\eta-C_5H_5)_2Cl_2]$        | 82.0(2)                          | 130.9                                   | (11) |
| $[Mo(\eta-C_5H_5)_2H_2]$         | 75.5(3)                          | 145.8                                   | (12) |
| $[Mo\{C(C_4H_8)(C_5H_4)_2\}Cl]$  | 82.66(2)                         | 114.6                                   | (6)  |
| $[Mo\{C(CH_3)_2(C_5H_4)_2\}H_2]$ | 80.3(2.8)                        | 121                                     | (13) |
| $[W\{C(CH_3)_2(C_5H_4)_2\}Cl_2]$ | 81.85(8)                         | 115.2                                   | (6)  |
| $[W\{C(CH_3)_2(C_5H_4)_2\}H_2]$  | 95.5(4.0)                        | 120.3                                   | (13) |

<sup>a</sup> The angles are defined in structure Fig. 4.

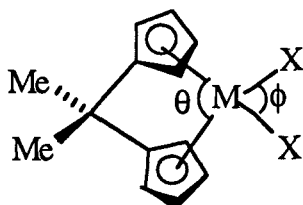


Fig. 4 Showing the angles  $\theta$  and  $\phi$ .

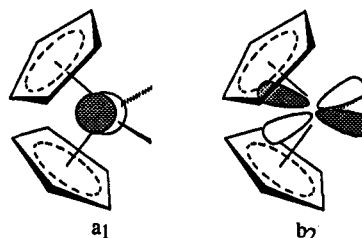


Fig. 5. The  $a_1$  and  $b_2$  metal based orbitals.

Fig. 5 shows two of the metal orbitals principally involved in the bonding to ligands in the X-M-X systems. For the bent compounds  $[Mo(\text{and } W(\eta-C_5H_5)_2X_2)]$  the  $a_1$  orbital is the HOMO and has largely metal character and is occupied by the  $d^2$  electrons. The  $b_1$  orbital takes part in both  $MX_2$  bonding and also metal-ring bonding. The  $a_1$  orbital lies normal to the metallocene principle axis and, in consequence, changes in the angle  $\theta$  will cause little change in the energy of  $a_1$ , as shown by the ionisation energy data. However, the  $b_1$  orbital clearly interacts with the two  $\eta$ -cyclopentadienyl rings and this orbital increases in energy with decrease in  $\theta$ . Extended Huckel calculations show that this orbital is raised about 0.24 eV on bending from 130° to 120°.

In conclusion, the marked increase in the stability of the *ansa*-bridged compounds towards reductive elimination reactions compared to the related non-*ansa* compounds may be associated with the higher energy of the bent metallocene structure compared with the lower energy parallel ring structure. A schematic representation of the energetics for reductive elimination reactions of *ansa* and non-*ansa* metallocenes is given

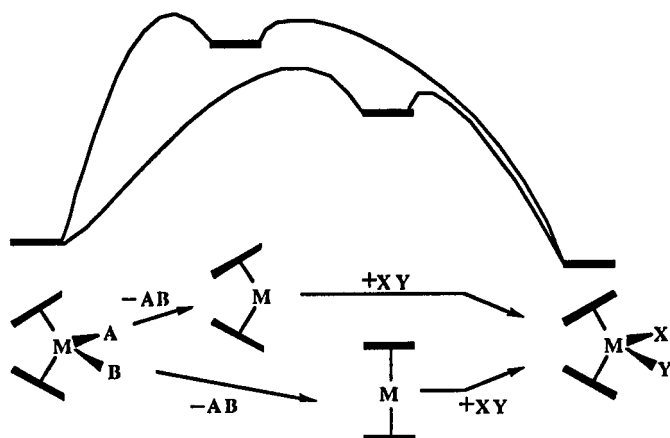


Fig. 6.

Hypothetical energy diagram for reductive elimination of AB.

Showing the higher transition state required for a bent metallocene structure.

in Fig. 6. We note that in 1981 Brintzinger observed that the *ansa* compound  $\{\text{Ti}[(\eta\text{-C}_5\text{H}_4\text{-(CH}_2)_2\text{-}\eta\text{-C}_5\text{H}_4)]\text{Cl}\}$  cannot be reduced to the divalent bent metallocene intermediate  $\{\text{Ti}[(\eta\text{-C}_5\text{H}_4\text{-(CH}_2)_2\text{-}\eta\text{-C}_5\text{H}_4)]\}$  under conditions where the non-*ansa*  $\{\text{Ti}[(\eta\text{-C}_5\text{H}_5)]_2\text{Cl}\}$  reduces to the intermediate divalent  $\{\text{Ti}[(\eta\text{-C}_5\text{H}_5)]_2\}$  (17); this difference can be associated with the increased energy of the  $b_1$  orbital in the *ansa* titanium compound consequent upon the decrease of  $\theta$ .

### SOME INORGANIC CHEMISTRY OF THE FULLERENE C<sub>60</sub>

Early studies of the chemistry of the fullerene C<sub>60</sub> have shown that it forms adducts with transition metals in low oxidation states where the metal-C<sub>60</sub> bonding is formally analogous to the metal-olefin bond (18). C<sub>60</sub> also react with osmium tetroxide in a manner analogous to an olefin forming an osmate ester derivative (19).

The hexa-platina compound  $\{\text{C}_{60}[\text{Pt}(\text{Et}_3\text{P})_2]_6\}$  has been described (18) and has six platinum atoms bonded to the six 6,6 carbon-carbon double bonds which lie on the octahedral coordinates. This compound clearly demonstrates a multi-functional nature for C<sub>60</sub> and the preference for metal bonding with the 6,6 C-C bonds rather than the 6,5 double bonds.

We set out to further develop the organometallic chemistry of C<sub>60</sub> and simple strategy we employed was the react C<sub>60</sub> with transition metal fragments which are known to form stable olefin derivatives.

The first transition metal carbonyl derivatives of C<sub>60</sub> have been prepared by direct reaction of C<sub>60</sub> with  $[\text{Fe}_2(\text{CO})_9]$  or  $[\text{Ru}(\text{CO})_4(\eta^2\text{-H}_2\text{C}=\text{CHCO}_2\text{Me})]$  in benzene which gave the deep red microcrystalline mononuclear compounds  $[\text{C}_{60}\text{M}(\text{CO})_4]$  M = Fe or Ru respectively (Fig. 7). The <sup>13</sup>C nmr spectra of these two compounds clearly show the 17 bands expected for a 6,6-monosubstituted C<sub>60</sub> molecule bonded to a metal fragment with C<sub>2v</sub> symmetry. Both compounds slowly decompose in solution at ambient temperature with release of C<sub>60</sub>.

The first  $\eta$ -cyclopentadienyl-transition metal derivatives of C<sub>60</sub> have also been prepared. Thus, treatment of C<sub>60</sub> in toluene at ambient temperature with  $[\text{Mo}(\eta\text{-C}_5\text{H}_4\text{R})_2\text{H}_2]$ , where R = H or Bu<sup>n</sup>, gives the mononuclear adducts  $[\text{C}_{60}\text{Mo}(\eta\text{-C}_5\text{H}_4\text{R})_2]$ . The analytical and spectroscopic data suggest the structures given in Fig. 7. The related tantalum compound  $[\text{C}_{60}\text{TaH}(\eta\text{-C}_5\text{H}_5)_2]$  has also been prepared (Fig. 7) and the presence of the Ta-hydrogen group is confirmed by the <sup>1</sup>H nmr spectrum (20).

The co-ordination compounds of cobalt, rhodium and ruthenium, namely  $[\text{CoC}_{60}(\text{PPh}_3)_2(\text{CO})\text{H}]$  and  $[\text{MC}_{60}(\text{PPh}_3)_2\text{NO}]$ , M = Co or Rh, and the nitrosyl  $[\text{RuC}_{60}(\text{PPh}_3)_2(\text{NO})\text{Cl}]$  are also readily prepared. The rhodium compound has been independently prepared (21). The molecular structure of the ruthenium compound has been determined and shows the ruthenium is bonded to a 6,6 C-C "double bond" of the C<sub>60</sub> ligand (22).

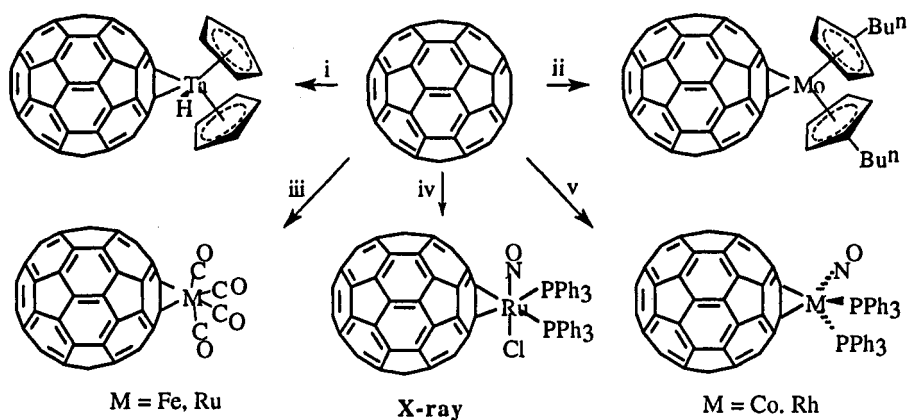


Fig. 7. Synthesis of  $C_{60}$  transition metal compounds. i  $[Ta(\eta-C_5H_5)_2H_3]$  in benzene, >90%. ii  $[Mo(\eta-C_5H_4Bu^n)_2H_2]$  in toluene, >80%. iii  $[Fe_2(CO)_9]$  or  $[Ru_3(CO)_{12}]$  in benzene, >89%. iv  $[Ru(PPh_3)_3(NO)Cl]$  in toluene >95%. v  $[M(PPh_3)_3NO]$ , where  $M = Co$  or  $Rh$ , in toluene, >60% (21).

In a further development of  $C_{60}$  chemistry we set out to prepare organic derivatives of  $C_{60}$  which had functionalities suitable for further coordination with metals. We chose to employ the well established (23) Diels-Alders reaction of  $C_{60}$  with suitable dienes and we have prepared the the hydroxy-anthraquinone derivatives shown in Fig. 8 (24). The anthraquinone moiety is strongly bound to the  $C_{60}$  and these  $C_{60}$  derivatives survive deprotonation and also can undergo further coordination to a transition metal, as shown for the ruthenium compound shown in Fig. 8 (25).

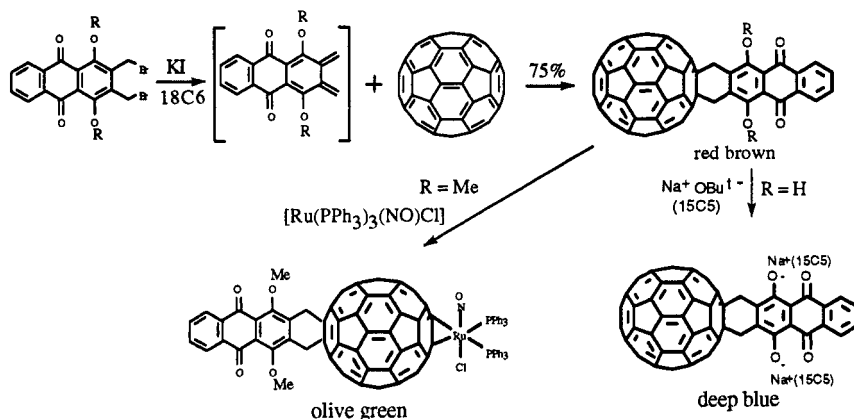


Fig. 8. Some di-hydroxy anthraquinone derivatives of  $C_{60}$

### Inclusion compounds, charge-transfer compounds and salts of $C_{60}$ .

There have been reports of the anion  $[C_{60}]^-$  formed by electrochemical reduction (26), by electrocrystallization  $(PPh_4(Ph_4PCl))^+C_{60}^-$  and  $N(PPh_3)_2^+C_{60}^-$  (27,28) and the charge transfer compounds  $\{Cr(TTP)^+[C_{60}]^-(THF)_3\}$ , where TTP = teraphenylporphyrin and  $\{[Fe(\eta^5-C_5H_5)(\eta-C_6Me_6)_2]_n^+C_{60}^{n-}\}$  ( $n=1-3$ ) have been characterised (29,30). We have identified a simple selective synthesis of the sodium salt of the  $C_{60}$  monoanion  $\{Na^+[C_{60}]^-(THF)_5\}$  by reduction of  $C_{60}$  in toluene with  $Na[Mn((\eta-C_5Me_5)_2)]$  (31) in THF solution as dark purple microcrystalline solid in *ca.* 80% yield (32).

The compound  $\text{Na}[\text{Mn}(\eta\text{-C}_5\text{Me}_5)_2]$  was chosen as the reducing agent since the anion  $[\text{Mn}(\eta\text{-C}_5\text{Me}_5)_2]^-$  has oxidation couples at  $-0.17\text{V}(-1/0)$  and  $-0.56(0/+1)$  and solution in THF may be added to toluene without causing precipitation. The salt  $\text{Me}_4\text{N}[\text{C}_{60}]\cdot\text{thf}$  has been prepared by reacting  $\{\text{Na}^+[\text{C}_{60}^-]\cdot(\text{THF})_5\}$  with  $[\text{Me}_4\text{N}]\text{F}$  in acetonitrile (33).

Also, we have shown that the known salts  $\text{K}_x[\text{C}_{60}]$ , where  $x = 3, 4$  and  $\text{M}_x[\text{C}_{60}]$   $\text{M} = \text{Rb}, \text{Cs}$ , and  $x = 1, 3, 4$ , can be prepared readily using a microwave plasma induced methodology. For example, when a mixture of  $\text{C}_{60}$  and sodium metal in a alumina tube under  $10^{-5}$  mbar of argon is irradiated with a 500W source at 2.45GHz for 30-60 seconds the compounds  $\text{K}_x[\text{C}_{60}]$  are formed according to the chosen stoichiometry (34). Synthesis of the same compounds by thermal reaction requires *ca.*  $350^\circ\text{C}$  for 10-14 days.

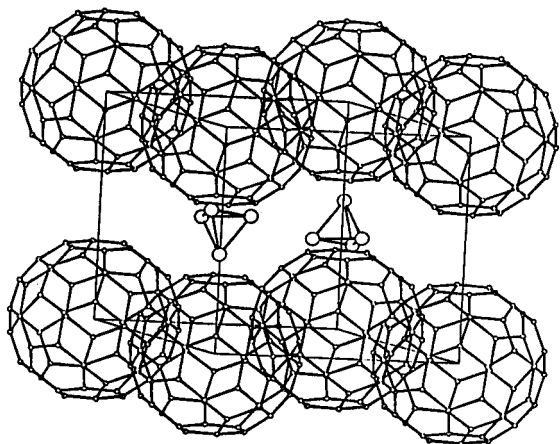


Fig. 9. Structure of  $\{(P_4)_2C_{60}\}$ . Note that only one orientation of the  $P_4$  tetrahedron at each trigonal prismatic site is shown, corresponding to the space group  $P\bar{3}$  (38).

Inclusion compounds of the fullerene  $\text{C}_{60}$  without net electron transfer have been described. Previously reported examples include  $\{[\text{Fe}(\eta\text{-C}_5\text{H}_5)_2]_2\text{C}_{60}\}$  (35),  $\{(\text{I}_2)_2\text{C}_{60}\}$  (36), and the benzene solvate  $[\text{C}_{60}\cdot 4\text{C}_6\text{H}_6]$  (37). Recently we have prepared an inclusion compound of white phosphorus, namely,  $\{(P_4)_2\text{C}_{60}\}$  as a black-blue solid by treatment of a toluene solution of  $\text{C}_{60}$  with white phosphorus in  $\text{CS}_2$  (38). The X-ray powder diffraction data could be indexed on a hexagonal/trigonal cell ( $a = b = 10.09\text{\AA}$ ,  $c = 10.11\text{\AA}$ ), which suggested an AAA stacking of close packed  $\text{C}_{60}$  layers. A Rietveld analysis led to a structural model in which a  $P_4$  tetrahedron occupies each trigonal prismatic site with one of its  $\text{C}_3$  axes parallel to the  $[001]$  direction (Fig. 9): the tetrahedra are disordered randomly over these sites, with the apical phosphorus either lying above or below the  $z = 1/2$  plane. Solid state  $^{31}\text{P}$  MAS NMR spectroscopy shows the  $P_4$  molecules are dynamic and render the phosphorus atoms equivalent.

## REFERENCES

1. M.L.H.Green, P.C. Konidaris, P.Mountford and S.J. Simpson, *J. Chem. Soc., Chem. Commun.*, 256 (1992).
2. M.L.H.Green, P.C. Konidaris, P.Mountford and S.J. Simpson, *J. Chem. Soc., Dalton Trans.*, in press (1994).
3. J.C. Green, M.L.H.Green, J.T. James, P.C. Konidaris, G.H. Maunder and P. Mountford, *J. Chem. Soc., Chem. Commun.*, 1361 (1992).
4. D. Michaelidou, D. Phil thesis, Oxford (1993).
5. C. Persson and C. Andersson, *Organometallics*, **12**, 2370 (1993).
6. L. Labella, A. Chernega and M.L.H.Green, *J. Organomet. Chem.*, in press.
7. C. R. Davis and L.A.P. Kane-Maguire, in *Comprehensive Organometallic Chemistry*, G. Wilkinson, F.G.A. Stone and E.W. Abel, Eds., Pergamon Press, Oxford, 1982, Vol. 3.
8. M. Berry, N.J. Cooper, M.L.H. Green and S.J. Simpson, *J. Chem. Soc. Dalton Trans.*, 29 (1980).

9. M.L.H. Green, *Pure & Appl. Chem.*, **50**, 27 (1978).
10. N.J.Cooper, M.L.H. Green and R. Mahtab., *J. Chem. Soc. Dalton Trans.*, 1557 (1978).
11. K.Prout, T.S. Cameron, R.A. Forder, S.R. Critchley, B. Denton and G.V. Rees, *Acta. Crystallogr. Sect. B*, **30**, 2290 (1974).
12. A.J. Schultz, K.L. Stearley, J.M. Williams, R. Mink and G.D. Stucky, *Inorg. Chem.*, **16**, 3303 (1977).
13. L. Labella, A. Chernega and M.L.H. Green, unpublished observation.
14. P. Grebenik, A.J. Downs, M.L.H. Green and R.N. Perutz, *J. Chem. Soc., Chem. Commun.*, 742 (1979).
15. J.C. Green, S.E. Jackson, B. Higginson, *J. Chem. Soc. Dalton Trans.*, 403 (1975).
16. J. W. Lauher and R. Hoffman, *J. Am. Chem. Soc.*, **98**, 1728 (1976).
17. J.A. Smith, and H.H. Brintzinger, *J. Organomet. Chem.*, **218**, 159 (1981).
18. P.J. Fagan, J.C. Calabrese and B. Malone, *Acc. Chem. Res.*, **25**, 134 (1992) and references therein.
19. J.M. Hawkins, A. Meyer, T.A. Lewis, S. Loren, F.J. Hollander, *Science*, **252**, 312 (1991).
20. R.E. Douthwaite, M.L.H. Green, A.H.H. Stephens and J.F.C. Turner, *J.Chem. Soc., Chem. Commun.*, 1522 (1993).
21. A. L. Balch, J. N. Lee, B.C. Nou, N.M. Olmstead, *Inorg. Chem.*, **32**, 3577 (1993).
22. M.L.H. Green, J. Haggitt and A.H.H. Stephens, unpublished observation.
23. F. Wudl, *Acc. Chem. Res.*, **25**, 157 (1992); Y.Rubin, S. Kahn, D.I. Freedberg and C. Yerezian, *J. Am. Chem. Soc.*, **115**, 344 (1993); see also refs 1 and 2 in ref 24.
24. W. Bidell, R.E. Douthwaite, M.L.H. Green, A.H.H. Stephens and J.F.C. Turner, *J. Chem. Soc., Chem. Commun.*, 1641 (1994).
25. W. Bidell, M.L.H. Green and A.H.H. Stephens, unpublished observation.
26. D. Dubois, T.M. Jones, K.M. Kadish, *J. Am. Chem. Soc.*, **114**, 6446 (1992).
27. P-M, Allemand, G. Srdanov, A. Koch, K. Khemani, F. Wudl, Y. Rubin, F. Diederich, M.M. Alvarez, S.J. Anz and R.L. Whetten, *J. Am. Chem. Soc.*, **113**, 2780 (1991).
28. H. Moriyama, H. Kobayashi, A. Kobayashi and T. Watanabe, *J. Am. Chem. Soc.*, **115**, 1185 (1993).
29. A. Penicaud, J. Hsu, C.A. Reece, A. Koch, K.C. Khemani, P.M. Allemand and F. Wudl, *J. Am. Chem. Soc.*, **113**, 6698 (1991)
30. C. Bossard, S. Rigaut, D. Astruc, M-H. Delville, G. Felix, A. Fevrier-Bouvier, J. Amiell, S. Flandrois, and P. Delhaes, *J. Chem. Soc., Chem. Commun.*, 333 (1993).
31. J.L. Robbins, N.M. Edelstein, S.R. Cooper and J.C. Smart, *J. Am. Chem. Soc.*, **101**, 3853 (1979).
32. R.E. Douthwaite, A.R. Brough and M.L.H. Green, *J. Chem. Soc., Chem. Commun.*, 267 (1994).
33. R.E. Douthwaite and M.L.H. Green, unpublished observation
34. R.E. Douthwaite and M.L.H. Green, *J.Chem. Soc., Chem. Commun*, (1994) in press.
35. J.D. Crane, P.B. Hitchcock, H.W. Kroto, R. Taylor and D.R.M. Walton, *J. Chem. Soc., Chem. Commun.*, 1764 (1992).
36. Q. Zhhu, D.E. Cox, J.E. Fischer, K. Kniaz, A.R. McGhie and D. Zhou., *Nature*, **355**, 712 (1992).
37. a) M.F. Meidine, P.B. Hitchcock, H.W. Kroto, R. Taylor and D.R.M. Walton, *J. Chem. Soc., Chem. Commun.*, 1534 (1992); b) A.L. Balch, J.W. Lee, B.C. Noll and M.M.Olmstead, *J. Chem. Soc., Chem. Commun.*, 56 (1993).
38. R.E. Douthwaite, M.L.H. Green, S.J. Heyes, M.J. Rosseinsky and J.F.C. Turner, *J.Chem. Soc., Chem. Commun.*, 1367 (1994).