

Preliminary communication

REDUCTION—OXIDATION PROPERTIES OF ORGANOTRANSITION METAL COMPLEXES

VII\*. THE DIMERISATION OF COORDINATED CYCLOOCTATETRAENE VIA SILVER(I) OXIDATION, AND THE X-RAY CRYSTAL STRUCTURE OF  $[\text{Fe}_2(\text{CO})_4\{\text{P}(\text{OPh})_3\}_2(\eta^5, \eta'^5\text{-C}_{16}\text{H}_{16})][\text{PF}_6]_2$

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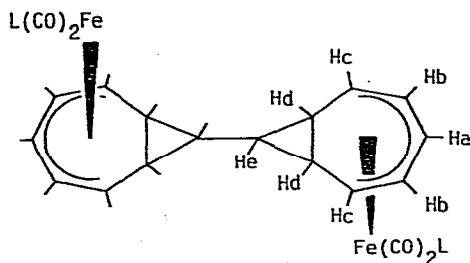
Summary

The complex  $[\text{Fe}(\text{CO})_2\text{L}(\eta^4\text{-C}_8\text{H}_8)]$  ( $\text{L} = \text{CO}$ ,  $\text{PPh}_3$ , or  $\text{P}(\text{OPh})_3$ ) reacts with  $[(p\text{-BrC}_6\text{H}_4)_3\text{N}][\text{PF}_6]$  or with  $\text{AgPF}_6$  to give, via one-electron oxidation followed by dimerisation,  $[\text{Fe}_2(\text{CO})_4\text{L}_2(\eta^5, \eta'^5\text{-C}_{16}\text{H}_{16})][\text{PF}_6]_2$ , the structure of which has been elucidated by X-ray crystallography ( $\text{L} = \text{P}(\text{OPh})_3$ ).

The dimerisation of coordinated cyclic polyolefins is uncommon and requires vigorous reaction conditions. In the case of cyclooctatetraene (COT), for example complexes of coordinated COT dimers are formed in the reaction between COT and  $[\text{H}_4\text{Ru}_4(\text{CO})_{12}]$  in boiling heptane [2, 3], by prolonged irradiation of  $[\text{Fe}(\text{CO})_5]$  with excess COT [4], and in the reaction of  $[\text{Fe}(\text{CO})_3(\eta^4\text{-COT})]$  with  $\text{WCl}_6$ ,  $\text{EtAlCl}_2$  and ethanol in toluene [5]. We now report that the facile, room temperature reaction of  $[\text{Fe}(\text{CO})_2\text{L}(\eta^4\text{-COT})]$  ( $\text{L} = \text{CO}$ ,  $\text{PPh}_3$ , or  $\text{P}(\text{OPh})_3$ ) with one-electron oxidants such as  $[(p\text{-BrC}_6\text{H}_4)_3\text{N}][\text{PF}_6]$  or  $\text{AgPF}_6$  gives  $[\text{Fe}_2(\text{CO})_4\text{L}_2(\eta^5, \eta'^5\text{-C}_{16}\text{H}_{16})][\text{PF}_6]_2$  via the unprecedented dimerisation of an organotransition metal cation radical viz.  $[\text{Fe}(\text{CO})_2\text{L}(\text{C}_8\text{H}_8)]^+$ .

The addition of  $[(p\text{-BrC}_6\text{H}_4)_3\text{N}][\text{PF}_6]$  to  $[\text{Fe}(\text{CO})_3(\eta^4\text{-COT})]$  in  $\text{CH}_2\text{Cl}_2$  immediately gives essentially quantitative yields of an orange precipitate which microanalytical and conductance data suggest to be  $[\{\text{Fe}(\text{CO})_3(\text{C}_8\text{H}_8)\}_2][\text{PF}_6]_2$  (I). The double-irradiated  $^1\text{H}$  NMR spectrum of I [ $\text{CD}_3\text{NO}_2$ ,  $\tau$  2.32 ppm (1H, t,  $J(\text{H}_a\text{H}_b)$  6 Hz,  $\text{H}_a$ ), 4.32 (2H, d.d,  $J(\text{H}_a\text{H}_b)$  6 Hz,  $J(\text{H}_b\text{H}_c)$  10 Hz,  $\text{H}_b$ ), 4.90 (2H m,  $\text{H}_c$ ), 6.86 (2H, m,  $\text{H}_d$ ), 8.02 (1H, m,  $\text{H}_e$ )] is consistent with the structure shown in Fig. 1.

\*For part VI see ref. 1.



(I)  $L = \text{CO}$ ; (II)  $L = \text{PPh}_3$  or  $\text{P(OPh)}_3$

Fig. 1.

Derivatives of I,  $[\{\text{Fe}(\text{CO})_2\text{L}(\text{C}_8\text{H}_8)\}_2][\text{PF}_6]_2$  (II,  $L = \text{PPh}_3$  or  $\text{P(OPh)}_3$ ) are prepared by the addition of  $[(p\text{-BrC}_6\text{H}_4)_3\text{N}][\text{PF}_6]$  or  $\text{AgPF}_6$  to  $\text{CH}_2\text{Cl}_2$  solutions of  $[\text{Fe}(\text{CO})_2\text{L}(\eta^4\text{-COT})]$ . At  $60^\circ\text{C}$  the  $^{31}\text{P}$ -decoupled  $^1\text{H}$  NMR spectrum of II ( $L = \text{P(OPh)}_3$ ) is very similar to that of I but at room temperature the spectrum is more complex; restricted rotation of the  $\text{Fe}(\text{CO})_2\{\text{P(OPh)}_3\}$  groups relative to the organic ring system destroys the effective mirror symmetry observed at the higher temperature.

An X-ray crystallographic study on II ( $L = \text{P(OPh)}_3$ ) has been carried out.

*Crystal data.*  $\text{C}_{56}\text{H}_{46}\text{Fe}_2\text{O}_{10}\text{P}_4\text{F}_{12}$ ,  $M$  1342.5, orthorhombic, space group  $Pccn$  (No. 56),  $a$  18.760(15),  $b$  21.605(10),  $c$  14.486(5) Å,  $U$  5872(6) Å<sup>3</sup>,  $Z = 4$ ,  $F(000)$  2728, Mo- $K_\alpha$  X-radiation,  $\lambda$  0.71069 Å,  $\mu(\text{Mo-}K_\alpha)$  6.3 cm<sup>-1</sup>.

Recrystallisation from dichloromethane/hexane at  $0^\circ\text{C}$  yielded yellow needles. The structure was solved by conventional heavy-atom methods from 2378 independent intensities [ $2\theta_{\text{max}}$ ,  $50^\circ$ ;  $|F| \geq 3\sigma(F)$ ] collected on a Syntex  $P2_1$  four-circle diffractometer. Current  $R$  0.11, the high value being due to poor crystal quality and internal disorder among the fluorine atoms of the  $[\text{PF}_6]^-$  anion.

The molecular structure (Fig. 2) shows a dimeric cation of the expected structure with 2-fold symmetry crystallographically imposed. A view along the Fe-Fe vector shows the two three-membered rings edgewise and the two seven-membered rings almost eclipsed. Atoms C(21–25) are coplanar within 0.04 Å and are  $\eta^5$ -bonded to the Fe atom, while atoms C(21), C(25–27) are also coplanar (0.007 Å) at a dihedral angle of  $143^\circ$  with the first plane. A further fold in the same sense (dihedral angle  $113^\circ$ ) occurs between the second plane and the three-membered ring C(26–28). The structure is related to that reported [5] for  $[\text{Fe}_2(\text{CO})_6(\eta^4, \eta'^4\text{-C}_{16}\text{H}_{16})]$ ; in the latter the atom equivalent to C(21) is bonded across the 2-fold axis to its dimeric counterpart (thereby creating a central 6-membered ring) instead of to the iron atom. In the title compound C(21)---C(21)' is ca. 3.6 Å.

We have previously shown [6] that  $[\text{Fe}(\text{CO})_2\text{L}(\eta^4\text{-COT})]$  undergoes an irreversible one-electron oxidation at the platinum electrode in  $\text{CH}_2\text{Cl}_2$ . It is clear that chemical oxidation, by one-electron oxidants, also generates the radical cation  $[\text{Fe}(\text{CO})_2\text{L}(\text{C}_8\text{H}_8)]^+$  in which the electron spin density is localised on the  $\text{C}_8\text{H}_8$  ligand and the positive charge on the metal atom. Dimerisation of the

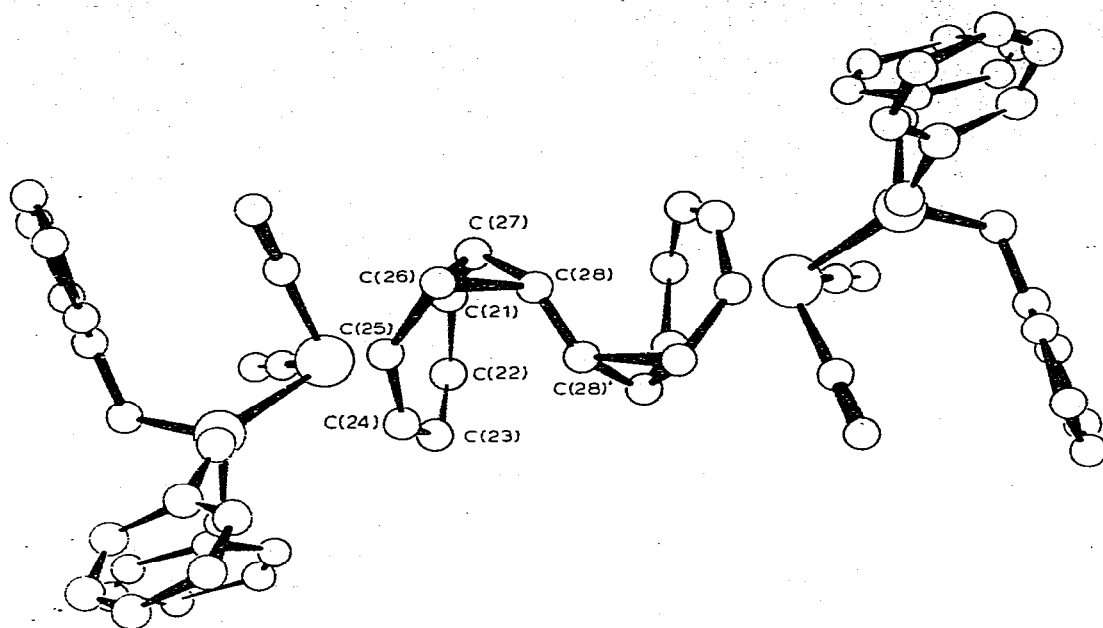


Fig. 2. Molecular structure of  $[\text{Fe}_2(\text{CO})_4\{\text{P}(\text{OPh})_2\}_2(\eta^5, \eta'^5\text{-C}_{16}\text{H}_{16})][\text{PF}_6]_2$ ; Fe—C(21), 2.30(2); Fe—C(22), 2.11(1); Fe—C(23), 2.14(2); Fe—C(24), 2.12(2), Fe—C(25), 2.24(2) Å.

radical, via carbon—carbon bond formation, clearly occurs after closure of the  $\text{C}_8\text{H}_8$  ring to the 5.1.0-bicyclic form.

Radical cations generated by one-electron oxidation do not always dimerise. The complex  $[\text{Fe}(\text{CO})_3(\eta^4\text{-CHPT})]$  (CHPT = cycloheptatriene) reacts with  $\text{AgPF}_6$  or  $[(p\text{-BrC}_6\text{H}_4)_3\text{N}][\text{PF}_6]$  in  $\text{CH}_2\text{Cl}_2$  to give  $[\text{Fe}(\text{CO})_3(\eta^5\text{-C}_7\text{H}_9)][\text{PF}_6]$  by oxidation followed by hydrogen radical addition whereas  $[\text{Mo}(\text{CO})_3(\eta^6\text{-CHPT})]$  affords  $[\text{Mo}(\text{CO})_3(\eta^7\text{-C}_7\text{H}_7)][\text{PF}_6]$  via hydrogen elimination.

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