Synthesis of Co-ordinated *trans*-1,2-Di(cycloheptatrienyl)ethylene, a New Cyclo-Octatetraene Dimer, and the *X*-Ray Crystal Structure of an Intermediate Bis-phosphonium Salt $[Fe_2(CO)_6\{\eta^4,\eta'^4\text{-}C_{16}H_{16}(PPh_3)_2\}][PF_6]_2$

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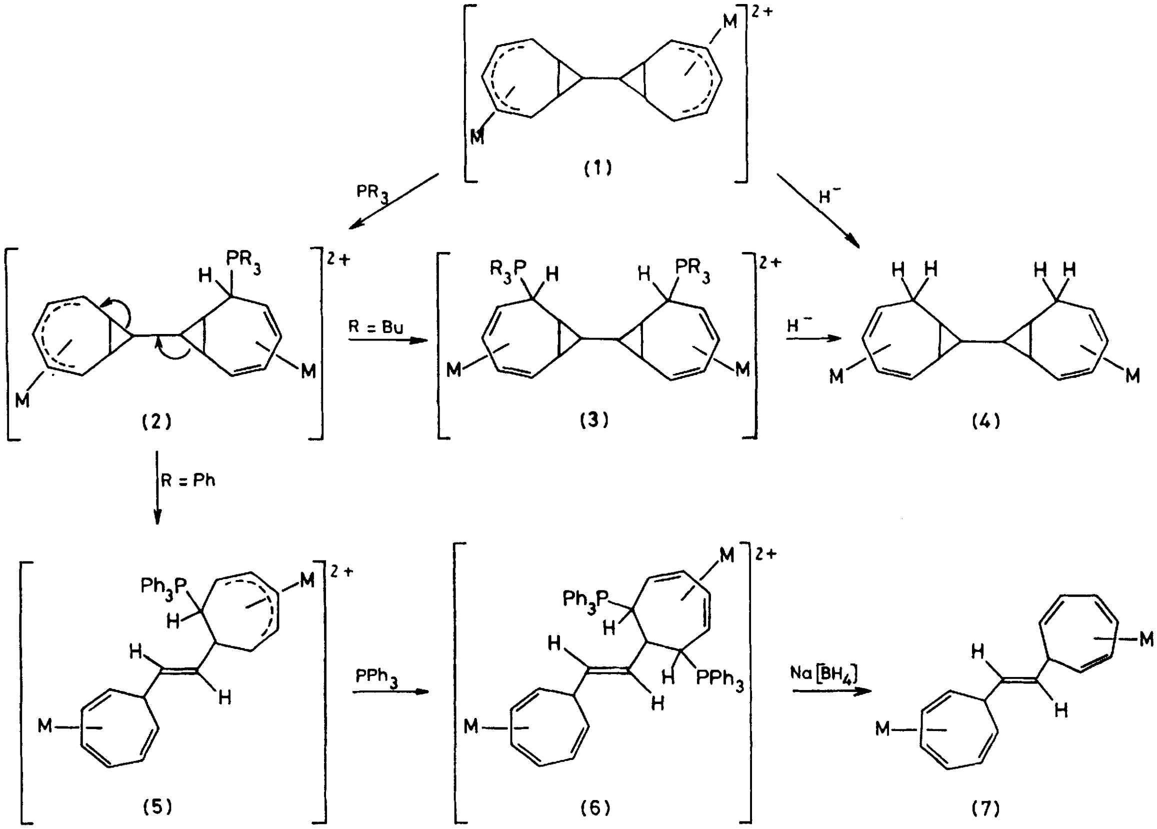
Summary The dication (**1**) obtained from tricarbonyl(η^4-cyclo-octatetraene)iron and PPh_3 afford the bis-phosphonium salt (**6**), *X*-ray structural studies on which reveal both phosphorus atoms attached to one of the C_7-rings; reduction of (**6**) with $Na[BH_4]$ gives (**7**), a complex of the cyclo-octatetraene dimer, *trans*-1,2-di(cycloheptatrienyl)ethylene.

We have previously shown[1] that oxidative dimerisation of $[Fe(CO)_3(\eta^4\text{-cot})]$ (cot = cyclo-octatetraene) affords the dication (**1**, Scheme). The reactions of (**1**) with phosphine ligands lead to the synthesis of novel polycyclic hydrocarbon ligands including the cot dimer *trans*-1,2-di(cycloheptatrienyl)ethylene *via* an unusual bis-phosphonium salt in which two PPh_3 groups are attached to one seven-membered ring.

Addition of 2 mol. equiv. of PBu^n_3 to (**1**) in acetone at −93 °C, followed by slow warming to room temperature affords (Scheme) the dimeric bis-phosphonium salt (**3**) [53%, yellow crystals, $\tilde{\nu}(CO)(CH_2Cl_2)$ 2 049, and 1 985 cm^{-1}]. On treatment with $Na[BH_4]$, hydride addition and phosphine displacement affords $[Fe_2(CO)_6(\eta^4,\eta'^4\text{-}C_{16}H_{18})]$ (**4**) which may also be made directly from (**1**) and $Na[BH_4]$.

By contrast, (**1**) and PPh_3 react (1:2 ratio, acetone, −78 °C) to give a yellow crystalline bis-adduct (**6**, 85%) with spectral properties very different from those of (**3**) [*e.g.* $\tilde{\nu}(CO)(CH_2Cl_2)$ 2 069, 2 051, 2 003(sh), 1 991, and 1 971(sh) cm^{-1}]. The ^1H and ^{13}C n.m.r. spectra† of (**6**) show the dimeric structure of (**3**) to be absent; an *X*-ray diffraction analysis reveals the presence of the unusual bis-phosphonium dication shown in the Figure.

Crystal data: $C_{58}H_{46}F_{12}Fe_2O_6P_4\cdot\frac{1}{2}C_7H_8$, $M = 1\,348$, monoclinic, space group $P2_1/c$, $Z = 8$, $a = 26{\cdot}795(13)$, $b = 19{\cdot}699(25)$, $c = 26{\cdot}297(23)$ Å, $\beta = 116{\cdot}37(6)°$, $U = 12\,436$-



Scheme. M = Fe(CO)$_3$.

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† For the sake of brevity ^1H and ^{13}C n.m.r. spectral data, and the results of ^1H–^1H decoupling experiments which verify the structures shown, are not given.

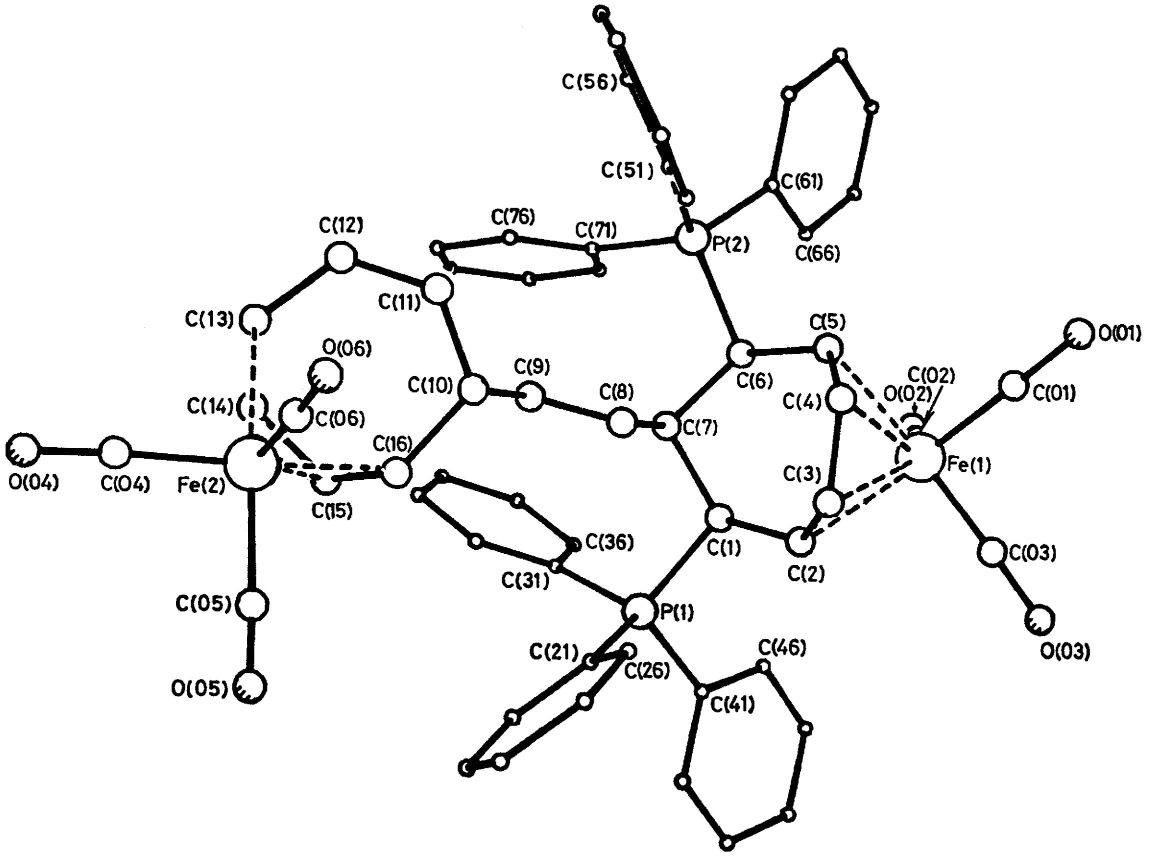

FIGURE. Molecular structure of $[Fe_2(CO)_6\{\eta^4,\eta'^4\text{-}C_{16}H_{16}(PPh_3)_2\}]^{2+}$.

(21) Å^3, $F(000) = 5\,495$. The structure was solved by heavy-atom methods from data collected at 220 K to $2\theta = 50°$ on a Syntex $P2_1$ diffractometer with monochromatised Mo-K_α X-radiation. For the 6 436 observed reflections $[I \geqslant 2{\cdot}0\sigma(I)]$, and with anisotropic thermal parameters for Fe, P, and F, $R = 0{\cdot}142$, $R' = 0{\cdot}136$.‡ The asymmetric unit of the structure comprises two molecules of complex (**6**), four $[PF_6]^-$ counter-ions, and two half-molecules of solvent (toluene), one of which is disordered.

The structure of the dication is illustrated in the Figure together with the atom numbering system. The two C_7 rings are joined by an ethylenic bridge comprising four coplanar carbon atoms, and the two phosphine ligands are both bonded to the carbon atoms adjacent to the bridgehead of *one* C_7 ring. The other four carbon atoms of this ring [C(2)—C(5)] and the corresponding four carbon atoms of the other C_7 ring [C(13)—C(16)] are η^4-bonded to an $Fe(CO)_3$ group and are themselves coplanar.

The diffraction study shows that the bicyclo[5·1·0]octadienyl group can undergo rearrangement to a cycloheptatriene ring with one exocyclic carbon atom and, therefore, that co-ordinated cyclo-octatetraenes can be converted into cycloheptatriene derivatives. The proposed mechanism for the formation of (**3**) and (**6**) is shown in the Scheme. After co-ordination of the first phosphine ligand to one pentadienyl unit of (**1**), to give (**2**), either rearrangement or addition of the second phosphine can occur. For PBu^n_3, a stronger nucleophile than PPh_3 and for which a faster rate of addition would be expected,[2] formation of the symmetric bis-phosphonium salt (**3**) is preferred. For PPh_3, rearrangement of (**2**) affords the intermediate (**5**) in which a new pentadienyl unit is generated; co-ordination of the second PPh_3 ligand then yields (**6**).

The reaction of (**6**) with $Na[BH_4]$ contrasts with that of (**3**); reduction, rather than hydride addition, and phosphine elimination gives $[Fe_2(CO)_6(\eta^4,\eta'^4\text{-}C_{16}H_{16})]$ (**7**) (Scheme) [yellow needles, 22%, $\tilde{\nu}(CO)(CH_2Cl_2)$ 2 041 and 1 975 cm^{-1}, *m/e* 488, m.p. 128—130 °C]. ^1H and ^{13}C N.m.r. spectroscopy clearly reveals (**7**) to be an enantiomeric mixture§ of a complex of *trans*-1,2-di(cycloheptatrienyl)ethylene, a new dimer of cot.

We thank Dr. R. J. Goodfellow of this Department for assistance with the ^1H n.m.r. spectroscopy. M. W. W. and R. M. M. thank the S.R.C. for Research Studentships.

(*Received, 22nd September* 1980; *Com.* 1033.)

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‡ The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Rd., Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

§ One form of (**7**) preferentially crystallises at −20 °C from n-heptane; in solution enantiomerisation occurs.

[1] N. G. Connelly, M. D. Kitchen, R. F. D. Stansfield, S. M. Whiting, and P. Woodward, *J. Organomet. Chem.*, 1978, **155**, C34.
[2] G. R. John and L. A. P. Kane-Maguire, *J. Chem. Soc., Dalton Trans.*, 1979, 873.