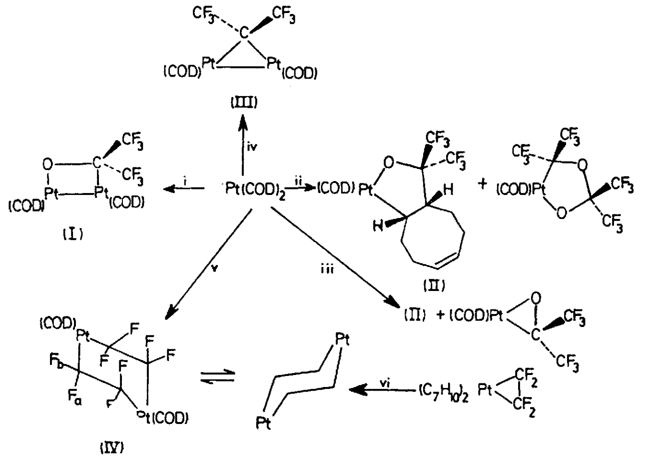
Reactions of Hexafluoroacetone, Hexafluoropropene, and Tetrafluoroethylene with Bis(cyclo-octa-1,5-diene)platinum; Molecular Structure of $[Pt_2\{(CF_3)_2CO\}(1,5\text{-}C_8H_{12})_2]$

By MICHAEL GREEN, JUDITH A. K. HOWARD, ANTONIO LAGUNA, MARTIN MURRAY, JOHN L. SPENCER, and F. GORDON A. STONE*

(*Department of Inorganic Chemistry, The University, Bristol* BS8 1TS)

Summary Treatment of $[Pt(COD)_2]$ (COD = cyclo-octa-1,5-diene) with hexafluoroacetone affords dinuclear or mononuclear platinum complexes, whereas tetrafluoroethylene gives a stereochemically non-rigid octafluoro-1,4-diplatinacyclohexane, and hexafluoropropene yields a dinuclear carbene-bridged complex.

THE course of the reaction between bis(cyclo-octa-1,5-diene)platinum[1] and unsaturated fluorocarbon molecules differs significantly from the chemistry of the corresponding nickel species.[2] Treatment (18°) of $[Pt(COD)_2]$ with hexafluoroacetone (HFA) (1 : 1 molar ratio) in diethyl ether solution led to rapid formation of the yellow crystalline dinuclear complex (I), which was characterised by single crystal *X*-ray crystallography.



SCHEME (i) Et_2O, HFA–$[Pt(COD)_2]$1 : 1; (ii) Et_2O, HFA–$[Pt(COD)_2]$ 20 : 1; (iii) C_6H_6, HFA–$[Pt(COD)_2]$1 : 1; (iv) $CF_3CF{=}CF_2$), petroleum ether; (v) C_2F_4, Et_2O; (vi) COD in petroleum ether.

Crystal data: monoclinic, $P2_1/c$, $Z = 4$, $a = 9{\cdot}917(3)$, $b = 14{\cdot}957(6)$, $c = 13{\cdot}358(3)$ Å; $\beta = 102{\cdot}18(2)°$; $R = 0{\cdot}040$ for 2215 reflections (Syntex $P2_1$ four-circle diffractometer). The molecular structure is shown in the Figure.

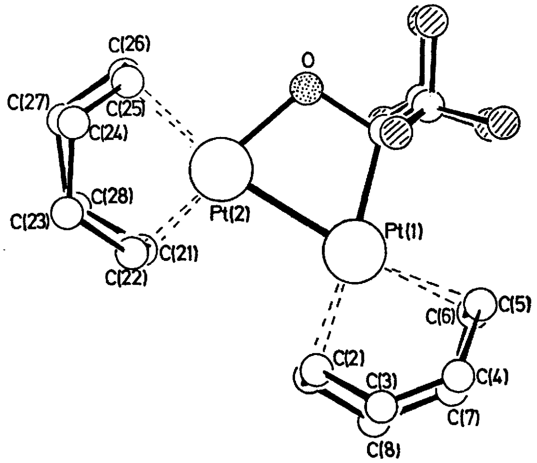


FIGURE. Molecular structure of $[Pt_2\{C(CF_3)_2O\}(COD)_2]$

The two platinum atoms [Pt–Pt, 2·585(1) Å] form a four-membered ring with the carbon and oxygen atoms of the HFA [Pt–C, 2·08(2) Å; Pt–O, 1·96(1) Å; C–O, 1·40(2) Å], the mean plane of which is an approximate mirror plane for the whole molecule. The cyclo-octa-1,5-diene ligands are symmetrically co-ordinated in the tub conformation to each platinum atom with three distinct Pt–C bond distances. The mean Pt–C distance *trans* to the Pt–Pt bond [C(5),-C(6),C(25),C(26)] is 2·29(2) Å, in contrast to the carbon atoms *trans* to the carbon and oxygen of the HFA, whose Pt–C distances are 2·25(2) Å and 2·13(2) Å respectively. This variation in Pt–C distances is reflected in the C=C bond lengths which are 1·37(3) Å *trans* to Pt and 1·43(3) Å *trans* to C and O.

The ^{19}F n.m.r. spectrum ($CDCl_3$) of (I) consists of a sharp singlet at 67·9 p.p.m. [rel. ext. CCl_3F], with two pairs of satellite peaks due to coupling with ^{195}Pt [J_{PtF} 115·9 and

11·5 Hz] consistent with the presence of two platinum atoms in the molecule. The spectrum contains four further peaks assigned to molecules in which both platinum atoms are ^{195}Pt. These show second order effects indicating that the two platinum nuclei have relatively similar chemical shifts. This is confirmed by the ^{19}F{^{195}Pt} INDOR spectra,,which give two ^{195}Pt chemical shifts at 190 and 824 p.p.m., and a value for J_{PtPt} of 5355 Hz.† This is the first value of a one-bond platinum–platinum coupling constant to be measured.

The products of reacting HFA with [Pt(COD)$_2$] are very dependent on the choice of reaction conditions (Scheme). For example, a high HFA concentration gives the platinaheterocyclic complex (II)[^{19}F n.m.r. (CH$_2$Cl$_2$) 72·04 p.p.m. (3F, q, J_{FF} 10) and 77·80 (3F, q, J_{FF} 10, J_{PtF} 11 Hz)]. The small ^{195}Pt–^{19}F couplings suggest that the C(CF$_3$)$_2$ group is not bonded directly to the platinum. The oxidative linking of HFA to a co-ordinated olefinic system has previously only been observed[3] with tricarbonyl(1,3-diene)iron and (1,3-diene)(η^5-cyclopentadienyl)rhodium complexes.

Treatment of [Pt(COD)$_2$] with hexafluoropropene in petroleum ether leads to an unusual fluorine migration to give the dinuclear complex (III) [^{19}F n.m.r. (CH$_2$Cl$_2$) 48·2 p.p.m. (5 peak multiplet ratio 1 : 8 : 18 : 8 : 1 consistent with coupling to two equivalent ^{195}Pt nuclei, J_{PtF} 153 Hz), irradiation at 21·4053 MHz reduced the multiplet to a singlet]. Fluorine migration has been previously observed in reactions of C$_2$F$_4$ with [Co$_2$(CO)$_8$][4] and C$_2$F$_3$H with[Fe(CO)$_3$(η^4-C$_4$Me$_4$)].[5] It is interesting that (III) may be considered to be a bridging carbene complex.

In contrast, tetrafluoroethylene reacts with Pt(COD)$_2$ in diethyl ether to give the octafluoro-1,4-diplatinacyclohexane (IV). The ^{19}F n.m.r. spectrum of (IV) is temperature dependent. At +90° in C$_6$D$_6$–toluene it consists of a single line (86·2 p.p.m.) about 30 Hz broad with two pairs of satellite peaks (J_{PtF} 388 and 98 Hz) indicative of coupling through two and three bonds, respectively. On cooling the sample the spectrum broadens and below 0° splits into an AB pattern, with the following parameters (in CD$_2$Cl$_2$ at −60°): $\delta_A = 81{\cdot}6$, $\delta_B = 93{\cdot}4$ p.p.m., J_{AB} 225 Hz; J_{APt} 390 Hz, J'_{APt} 80 Hz, J_{BPt} 350 Hz, J'_{BPt} 133 Hz. These observations are consistent with the presence of a $\overline{\text{Pt.CF}_2\text{.CF}_2\text{.Pt.CF}_2\text{.CF}_2}$ ring system, where F_a and F$_b$ are axial and equatorial fluorine atoms in a six-membered ring presumably in a chair conformation. At room temperature (IV) undergoes rapid ring inversion (chair–chair interconversion) thereby averaging the axial and equatorial fluorine environments. Complex (IV) is also produced by treating the platinacyclopropane ring complex tetrafluoroethylenebis(bicyclo[2,2,1]heptene)platinum with excess of cycloocta-1,5-diene.‡

We thank U.S.A.F. Office of Scientific Research for partial support and the Royal Society for a European Exchange Fellowship (to A.L.).

(*Received*, 24*th March* 1975; *Com.* **344**.)

---

† Referred to 21·4 MHz (Me$_4$Si = 100 MHz); positive values to high frequency. We thank Dr. R. J. Goodfellow for this measurement.

‡ We thank Rosemary R. Giles for preliminary studies on this reaction.

[1] M. Green, J. A. K. Howard, J. L. Spencer, and F. G. A. Stone, *J.C.S. Chem. Comm.*, 1975, **3**.
[2] J. Browning, C. S. Cundy, M. Green, and F. G. A. Stone, *J. Chem. Soc.* (*A*), 1969, **20**.
[3] M. Green and B. Lewis, *J.C.S. Chem. Comm.*, 1973, **114**; *J.C.S. Dalton*, in the press;
[4] B. L. Booth, R. N. Haszeldine, P. R. Mitchell, and J. J. Cox, *J. Chem. Soc.* (*A*), 1969, **691**; A. D. Beveridge and H. C. Clark, *J. Organometallic Chem.*, 1968, **11**, **601**.
[5] A. Bond, M. Green, and S. H. Taylor, *J.C.S. Chem. Comm.*, 1973, **112**.