Synthesis and Crystal Structure of Bis(triethylphosphine)[hexakis(trifluoromethyl)benzene]platinum, and of a Nickelacycloheptatriene Complex

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Summary Reaction of [Pt(PEt$_3$)$_3$] with hexakis(trifluoromethyl)benzene affords [Pt{C$_6$(CF$_3$)$_6$}(PEt$_3$)$_2$], with a 1,2-*hapto*-structure; reaction of the nickel analogue with more hexafluorobut-2-yne gives a new kind of complex, a nickelahexakis(trifluoromethyl)cyclohepta-*cis,trans,cis*-triene; both structures have been established by *X*-ray crystal analysis.

Reaction of bis(cyclo-octa-1,5-diene)nickel with hexafluorobut-2-yne or treatment of ethylenebis(triphenylphosphine)nickel with hexakis(trifluoromethyl)benzene affords complexes of type [Ni{C$_6$(CF$_3$)$_6$}L$_2$] [L$_2$ = 1,5-C$_8$H$_{12}$; L = PPh$_3$, P(OMe)$_3$, AsMe$_2$Ph]; the phosphite and arsine compounds being derived from the cyclo-octa-1,5-diene complex by ligand exchange.[1] The ^{19}F n.m.r. spectra of these compounds showed a single sharp signal suggesting a fluxional system, but attempts to obtain crystals suitable for *X*-ray crystallography were unsuccessful. Hence attention was directed at related platinum chemistry.

Reaction of tris(triethylphosphine)platinum[2]‡ with hexakis(trifluoromethyl)benzene in toluene at −50° afforded orange crystals of (I) [Pt{C$_6$(CF$_3$)$_6$}(PEt$_3$)$_2$], m.p. 203°. The ^{19}F n.m.r. spectrum (30°) showed a single resonance at 51·2 p.p.m. [18F, apparent t with ^{195}Pt satellites, J_{PF} 3·0 Hz, J_{PtF} 27·5 Hz, CF$_3$], rel. to CCl$_3$F. However, at −90° the spectrum shows two unresolved multiplets at 47·7 and 52·5 p.p.m. (ratio 1 : 2). An *X*-ray crystallographic study of this fluxional molecule was therefore undertaken [monoclinic space group $P2_1/c$; R = 0·057 for 2154 reflections].

The molecule is illustrated in Figure 1 which shows that the Pt(PEt$_3$)$_2$ part is bonded to two adjacent carbon atoms of the non-planar benzene ring. The dihedral angle between the mean plane of this ring and the group PtC(7)-C(12) is 102°.

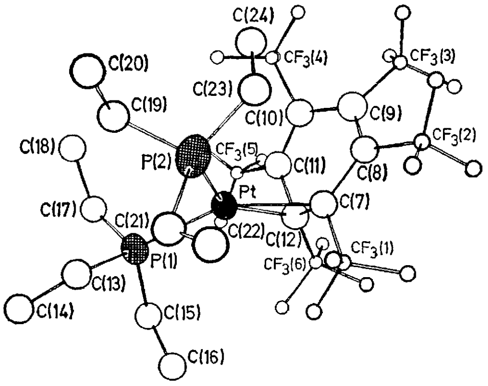

Figure 1. *A general view of one molecule* [(Et$_3$P)$_2$Pt{C$_6$(CF$_3$)$_6$}], *with all atoms labelled individually except for the* CF$_3$ *groups.*

Relevant bond lengths and angles are: Pt–P 2·331(5), 2·295(6); Pt–C(7) 2·15(2); Pt–C(12) 2·14(2); C(7)–C(8) 1·50(2); C(8)–C(9) 1·36(3); C(9)–C(10) 1·48(3); C(10)–C(11) 1·36(3); C(11)–C(12) 1·48(3); C(7)–C(12) 1·51(3) Å; C(7)–Pt–C(12) 41·2(7); P(1)–Pt–P(2) 101·6(2)°. Thus the C–C bond distances of the ring alternate between average values of

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‡ Prepared more conveniently by treating Pt(π-C$_3$H$_5$)(π-C$_5$H$_5$) with PEt$_3$ followed by heating the resultant tetrakis Pt^0 complex.

1·49 and 1·36 Å (consistent with single and double bonds) with the exception of C(7)–C(12) which has been significantly lengthened as a result of co-ordination to the platinum atom.

This kind of bonding for an arene–transition metal complex has not been previously found and contrasts with the 1,2,3,4-h^4 bonding mode established[3] for [hexakis-(trifluoromethyl)benzene](π-cyclopentadienyl)rhodium. It is clear from the variable-temperature ^{19}F n.m.r. results that (I) undergoes a degenerate intramolecular rearrangement with very low activation energy. The availability of a low-energy reaction path is in striking contrast to both $[Rh(\pi\text{-}C_5H_5)\{C_6(CF_3)_6\}]$[4] and $[Rh(\pi\text{-}C_5Me_5)\{C_6(CO_2Me)_6\}]$;[5] the latter showing dynamic behaviour at 155°.

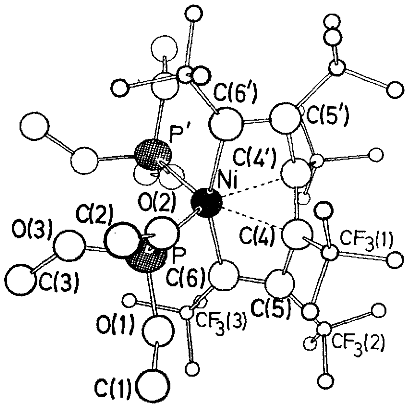

FIGURE 2. *A general view of one molecule of* $[\{(MeO)_3P\}_2Ni\{(CF_3)_2C_2\}_3]$ *with all atoms labelled individually except for the* CF_3 *groups.*

Complex (I) reacts slowly with more $CF_3C{\equiv}CCF_3$; however, the nickel analogues $[Ni\{C_6(CF_3)_6\}\{P(OMe)_3\}_2]$ and $[Ni\{C_6(CF_3)_6\}(AsMe_2Ph)_2]$ react at room temperature with three molar equivalents of the acetylene to afford a new type of organometallic. For example, the phosphite compound is transformed into an isomer (II), m.p. 140—141° [^{19}F n.m.r. resonances 56·6 p.p.m. (6F, q, J_{FF} 8·0 Hz), 57·3 (6F, m), and 65·2 (6F, m); double irradiation of the high-field signal reduced the low-field signal to a singlet and the other signal to a triplet (J_{PF} 11·0 Hz); ^{1}H n.m.r. resonance at τ 6·29 (18H, apparent t, $|J|_{POCH}$ 10·0 Hz, CH_3OP)]. These data did not establish a structure for (II), and therefore, an *X*-ray crystal structure determination was undertaken [R = 0·050 for 804 reflections].

The molecule, with symmetry C_2 imposed by the orthorhombic space group *Pbcn*, is illustrated in Figure 2. This shows that (II) may be formally described as a nickelahexakis(trifluoromethyl)cyclohepta-*cis,trans,cis*-triene, a kind of co-ordination compound not previously observed. Preliminary experiments suggest that the reaction path leading to the formation of (II) is not a simple isomerisation reaction.

Relevant bond lengths and angles are: Ni–P 2·215(3); Ni–C(6) 1·96(1); C(4)–C(4′) 1·41(2); C(4)–C(5) 1·51(1); Ni–C(4) 2·04(1); C(5)–C(6) 1·28(1) Å; C(4)–Ni–C(6) 66·8(4); C(6)–Ni–C(6′) 157·1(6); P–Ni–P′ 113·7(2); P–Ni–C(6) 93·3(1); C(4)–Ni–C(4)′ 40·4(5); P(1)–Ni–C(4) 105·9(2)°. Relevant dihedral angles are: NiC(4)C(5)C(6)–PNiP′ 90°; NiC(4)C(5)C(6)–C(4)NiC(4′) 58°; PNiP′–C(4)NiC(4′) 34°.

The interatomic distances indicate that there is a significant interaction between nickel and the formally double bond C(4)–C(4′) and if we take the centre of this bond as being one point of attachment of the triene, the co-ordination geometry about nickel closely approximates that of a trigonal bipyramid.

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