A Platinum-promoted Ring-opening Reaction of Hexakistrifluoromethylbenzene involving Carbon–Carbon Bond Cleavage; Crystal and Molecular Structure of Bis(t-butyl isocyanide)platinacyclohepta-*cis*-2,*cis*-4,*cis*-6-triene

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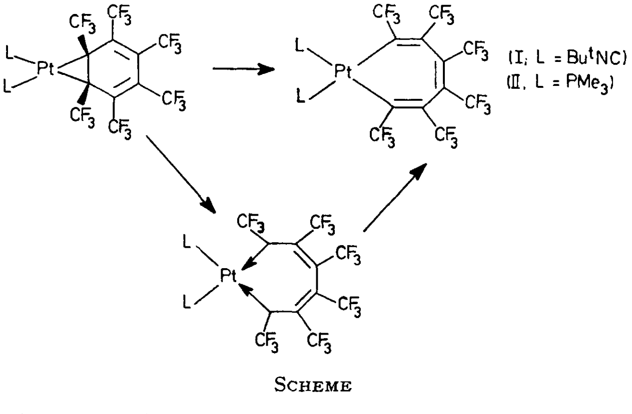
Summary Reaction of hexakis(trifluoromethyl)benzene with *triangulo*-$[Pt_3(Bu^tNC)_6]$ or *trans*-stilbenebis(trimethylphosphine)platinum affords the metallacyclohepta-*cis*,*cis*,-*cis*-trienes $[\overline{PtC(CF_3):C(CF_3)C(CF_3):C(CF_3)C(CF_3):C}(CF_3)L_2]$; the bis(t-butylisocyanide) complex has been identified structurally by *X*-ray crystallography.

THE fluxional 1,2-η bonded arene complexes $[M\{1,2\text{-}\eta\text{-}C_6(CF_3)_6\}L_2]$ ($M = Ni$, $L = PPh_3$; $M = Pt$, $L = PEt_3$) are readily formed on reaction of hexakis(trifluoromethyl)benzene with the d^{10} species $[Ni(C_2H_4)(Ph_3P)_2]$ or $[Pt(\textit{trans}\text{-stilbene})(Et_3P)_2]$.[1] In exploring this reaction further we have observed an unusual ring-opening of the arene.

Treatment (4 h, room temperature, toluene) of the *triangulo*-complex $[Pt_3(Bu^tNC)_6]$[2] with hexakis(trifluoromethyl)benzene afforded a white crystalline complex (I) [15%, m.p. 123°, ^{19}F n.m.r. resonances (rel. CCl_3F in $CDCl_3$) at 55·6 (q, 6F, J_{FF} 12·0, J_{PtF} 120·0 Hz), 56·5 (q, 6F, J_{FF} 12·0 Hz), and 58·7 p.p.m. (q, 6F, J_{FF} 2·4 Hz)]. It was expected that this complex was the fluxional 1,2-η bonded species $[Pt\{C_6(CF_3)_6\}(Bu^tNC)_2]$; however, this was clearly not borne out by the observation of a temperature independent ^{19}F spectrum. Treatment of *trans*-stilbenebis(trimethylphosphine)platinum[3] with hexakis(trifluoromethyl)benzene gave a related complex (II) [42%, m.p. 250°, ^{19}F resonances at 52·6, 57·1, and 57·2 p.p.m. (temperature invariant)]; comparison of the i.r. spectra of (I) and (II) indicated that these molecules were isostructural. This was supported by the observation that (I) is converted into (II) by treatment (60°, diethyl ether) with trimethylphosphine. At room temperature only one isocyanide ligand was displaced by trimethylphosphine.



SCHEME

In order to identify structurally these complexes, a single crystal *X*-ray diffraction study on (I) was undertaken.

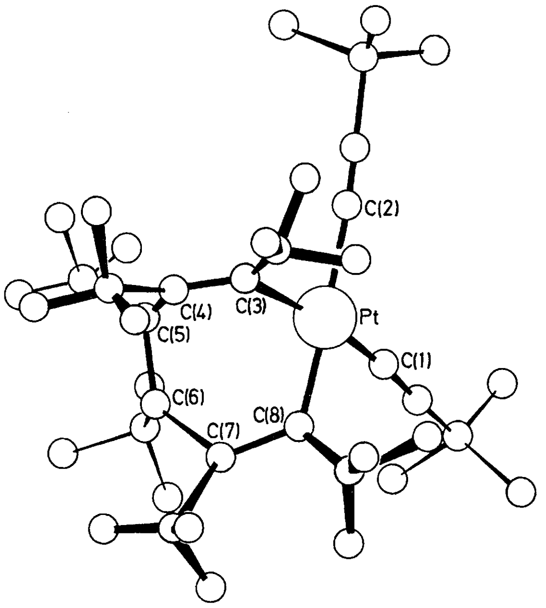


Figure The complex [*cis,cis,cis*-PtC(CF_3) : C(CF_3)C(CF_3) : -C(CF_3)C(CF_3) : C(CF_3)(Bu^tNC)$_2$] projected on the *a*, *b* plane.

Crystal data: orthorhombic, space group *Pbca*, $Z = 8$ in a unit cell of dimensions, $a = 16{\cdot}754(13)$, $b = 23{\cdot}211(20)$, $c = 16{\cdot}295(8)$ Å; $R = 0{\cdot}098$ for 1900 reflections (Syntex $P2_1$ four-circle diffractometer). The results established the molecular structure shown in the Figure, and showed the surprising result that (I) is a platinacyclohepta-*cis,cis,cis*-triene. The platinum atom is σ-bonded to atoms C(3) and C(8) at distances of 2·01(8) and 2·05(9) Å, respectively. The C(3)–C(8) distance is 2·61(11) Å, which precludes any significant bonding between these two atoms. The seven-membered ring is considerably distorted from planarity, adopting a boat conformation. The platinum atom has square-planar co-ordination with angles C(2)–Pt–C(1) 89(3)°, C(8)–Pt–C(3) 80(3)°, and C(3)–Pt–C(2) 97(3)°.

Thus, platinum(0) species can promote an unusual ring-opening reaction of hexakis(trifluoromethyl)benzene. It is reasonable to suggest that in reaction with [Pt(*trans*-stilbene)(Me_3P)$_2$] an initially formed 1,2-η bonded species undergoes a ring-opening reaction, and if such an intermediate is depicted in valence bond terms as a platinacyclopropane then the reaction may be considered to be formally analogous to a disrotatory norcaradiene–cycloheptatriene rearrangement. An alternative explanation is that a 1,2-η bonded species rearranges with C–C cleavage to form a Pt^0 dicarbene complex, which transforms electronically to a platinacyclohepta-*cis,cis,cis*-triene (see Scheme). That the ring-opening reaction is very dependent upon the nature of the ligands co-ordinated to platinum is shown by the absence of ring-opening in the reaction of $C_6(CF_3)_6$ with [Pt(*trans*-stilbene)(Et_3P)$_2$], and it is interesting that the crystallographically characterised complex [Pt-{1,2-η-C_6(CF_3)$_6$}(Et_3P)$_2$][1] does not rearrange to a seven-membered ring complex on heating (140°, 14 h).

We have previously reported[1] that [Pt{1,2-η-$C_6(CF_3)_6$}-(Et_3P)$_2$] reacts with an excess of hexafluorobut-2-yne to form a platinacyclohepta-*cis,trans,cis*-triene; however, the *cis,cis,cis*-triene cannot be converted thermally into the *cis,trans,cis*-isomer or *vice-versa*. The formation of a metallacyclohepta-*cis,cis,cis*-triene from a benzene derivative is particularly interesting in the context of the Reppe reaction,[4] in which nickel complexes promote the conversion of acetylene into benzene and cyclo-octatetraene. A metallacyclohepta-*cis,cis,cis*-triene is clearly a possible precursor of the C_8 ring system *via* insertion of an acetylene molecule and subsequent reductive-elimination. Previously a metallacyclopentadiene was the obvious, although unproved, precursor of a metallacycloheptatriene, but the demonstration of the conversion of an arene into the complexes (I) and (II) suggests an alternative reaction path.

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