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Ligand Exchange Reactions of Bis(cyclo-octa-1,5-diene)platinum; Synthesis of Trisethyleneplatinum and Molecular Structure of Tris-μ-(t-butyl isocyanide)-tris-(t-butyl isocyanide)-*triangulo*-triplatinum, [$Pt_3(Bu^tNC)_6$]

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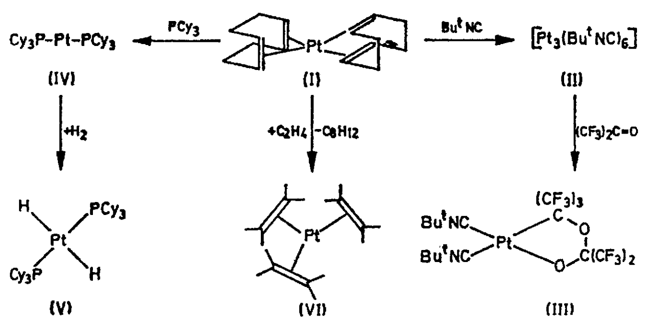
Summary The reaction of [$Pt(1,5\text{-}C_8H_{12})_2$] with Bu^tNC yields [$Pt_3(Bu^tNC)_6$], structurally identified by *X*-ray crystallography, and with tricyclohexylphosphine and ethylene affords [$Pt(PCy_3)_2$] and [$Pt(C_2H_4)_3$] respectively (Cy = cyclohexyl); the 14-electron phosphine complex reacts with hydrogen to give *trans*-[$PtH_2(PCy_3)_2$].

The synthesis of bis(cyclo-octa-1,5-diene)nickel and *trans,-trans,trans*-cyclododeca-1,5,9-trienenickel has led to important advances in the chemistry of nickel.[1] However, although it would be interesting to develop related platinum chemistry, this has not been possible owing to the absence of a convenient synthetic route to labile olefin-substituted Pt^0 complexes. Zerovalent platinum chemistry has so far been dominated by the less versatile phosphine, phosphite,[2,3] and diphenylpenta-1,4-dien-3-one[4] substituted complexes.



Scheme

Bis(cyclo-octa-1,5-diene)platinum (I) can be conveniently prepared in good yield (30—50%) as a white crystalline material [^1H n.m.r. resonances (C_6H_6) at τ 5·80 (J_{HPt} 55 Hz) and 7·81], by treating ($-20°$) $Li_2C_8H_8$ with [$PtCl_2(1,5\text{-}C_8H_{12})$] in Et_2O in the presence of excess of cyclo-octa-1,5-diene. This complex has been obtained[5] before by u.v. irradiation of [$PtPr^i_2(1,5\text{-}C_8H_{12})$] in the presence of 1,5-C_8H_{12}; however, variable results are obtained with this two-step (from $PtCl_2C_8H_{12}$) synthesis, a fact which has undoubtedly inhibited studies of this potentially interesting complex. Both cyclo-octa-1,5-diene ligands in (I) are readily displaced and this is illustrated by the reactions with isocyanides, phosphines and olefins† (see Scheme).

Treatment of [$Pt(C_8H_{12})_2$] with an excess of Bu^tNC in light petroleum affords red-orange crystals of (II) [i.r. bands (Nujol) at 2150vs, 2095sh, 1730sh, and 1710vs cm^{-1}] structurally characterised by single crystal *X*-ray crystallography. *Crystal data:* monoclinic, $P2_1/n$, $Z = 4$ in a unit cell of dimensions $a = 18{\cdot}213(7)$, $b = 11{\cdot}811(7)$, $c = 21{\cdot}996(6)$ Å; $\beta = 110{\cdot}21(3)°$; $R = 0{\cdot}061$ for 3680 reflections (Syntex $P2_1$ four-circle diffractometer). The molecular structure of (II), which crystallises with inclusion of toluene, is shown in the Figure, the solvent of crystallization (4 molecules per unit cell) being omitted for clarity.

The structure consists of an approximately equilateral triangle, mean Pt–Pt distance 2·632 Å, with three bridging and three terminal t-butylisocyanide ligands. The terminal groups form an almost linear Pt–C(1)–N–C(2) chain [mean angle at C(1) 176°, mean angle at N 170°], whereas the

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† Reactions also occur with 1,2- and 1,3-dienes, to be published elsewhere.

bridging groups show considerable bending (mean $\angle$ CNC 143°). The bridging carbon atoms lie almost in the plane of the Pt_3 triangle, and each are symmetrically related to two Pt atoms, within the errors given, [mean Pt–C bridge distance 2·10(3) Å, $\angle$ Pt–C–Pt 77°]. The nitrogen and distal carbon atoms of these isocyanides show a greater deviation from the plane. The triangular Pt–Pt distance in (II) compares favourably with the average value of 2·65 Å found[6] in the phosphine-substituted complexes [Pt_3L_3-(μ_2-CO)$_3$] (L = phosphine).

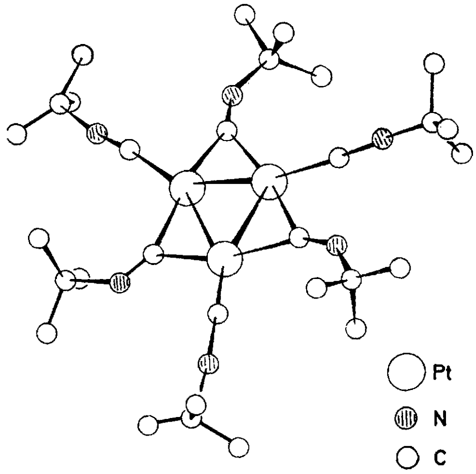

Figure. Structure of [$Pt_3(Bu^tNC)_6$], hydrogen atoms omitted for clarity.

Formation in this reaction of a stable Pt_3 species is in contrast with the ill defined nature of the related palladium species [$Pd(Bu^tNC)_2$].[7] However, it is interesting that the Pt_3 array is easily broken in oxidative-addition reaction, for example, treatment with hexafluoroacetone affords (III).

Reaction of (I) with tricyclohexylphosphine afforded a 14-electron two-co-ordinate platinum(0) species (IV), an observation which is of interest in view of recent studies[8,9] which have established the structural identity of the analogous palladium species. The complex (IV), which dissolves in toluene to give an orange-yellow solution, reacts (on bubbling) with molecular hydrogen to form a stable dihydride (V) [i.r. (Nujol) 1710 cm^{-1}, ^{1}H n.m.r. resonance (C_6H_6) at τ 13·10 (t with ^{195}Pt satellites, J_{HPt} 796, J_{HP} 17 Hz), ^{31}P resonance at −52·76 p.p.m. (w.r.t. H_3PO_4 extn.) (J_{PPt} 2872 Hz)] formulated as the *trans*-isomer. It is interesting that a rather insoluble material obtained from the reaction of [$Pt(acac)_2$] with $AlEt_3$ and PCy_3 and showing a high Pt-H stretching frequency at 1910 cm^{-1}, has been assigned the same structure.[10]

Ethylene (1 atmos.) displaces (room temperature) cycloocta-1,5-diene from (I) in light petroleum solution to give tris-ethyleneplatinum (VI) as a white crystalline solid, unstable in solution except under ethylene [^{1}H n.m.r. (C_6H_6; 20 °C) resonance at τ 6·83 (J_{PtH} 57·0 Hz); ^{195}Pt resonance (INDOR) + 1609 p.p.m. (w.r.t. 21·4 MHz) shows the central 9 lines with the correct relative intensity of the expected 13-line multiplet]. The recently reported[11] complex [$Ni(C_2H_4)_3$] is apparently less stable than the platinum analogue and shows a ^{1}H n.m.r. signal (−30 °C) at τ 6·89, which is shifted downfield in the presence of C_2H_4. It is suggested that [$Pt(C_2H_4)_3$] has the illustrated trigonal-planar structure, rather than a structure in which the C:C double bonds are perpendicular to the co-ordination plane. This assumption which is based on the structure established[12] by *X*-ray crystallography for tris(bicyclo[2,2,1]-heptene)nickel, receives support from a theoretical study[13] of the complexes [$Ni(C_2H_4)_n$] (n = 2, 3, 4).

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