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Preliminary communication

FORMATION OF THE η^5-BICYCLO[5.1.0]OCTADIENYL LIGAND BY REACTION OF CYCLOOCTATETRAENE WITH A RUTHENIUM(II) HYDRIDE COMPLEX: MOLECULAR STRUCTURE OF [Ru(2—6-η-bicyclo[5.1.0]octadienyl)($PMe_2Ph)_3$][PF_6]

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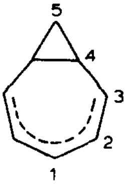
Summary

[Ru(2—6-η-bicyclo[5.1.0]octadienyl)($PMe_2Ph)_3$][PF_6], formed from the reaction of cyclooctatetraene with [RuH(COD)($PMe_2Ph)_3$][PF_6] (COD = cycloocta-1,5-diene), has been characterised spectroscopically from ^1J(CH) coupling constants and an X-ray structural analysis; the bicyclic ligand contains an elongated bridging C—C bond (1.63 Å).

Protonation of cyclooctatetraene (COT) complexes of transition metals often leads to complexes containing the C_8H_9 fragment, for which several bonding modes are possible [1]. In particular, protonation of [Fe(CO)$_3$(1-4-η-COT)] at −120°C gives a product containing a 1—5-η-cyclooctatrienyl ligand which undergoes ring closure above −60°C to give a stable complex of the 2—6-η-bicyclo-[5.1.0]octadienyl ligand I [2].



(I)

Although I has been reported [3,4] to form during protonation reactions of COT complexes of other metals, e.g. Co, Rh and Ir, there is some doubt of its stabilization by coordination to a ruthenium ion; an earlier proposal [5] of the

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detection of I bonded to a $Ru(CO)_3$ fragment has been disputed by Bennett [6] who has established by X-ray crystallographic studies that the C_8H_9 fragment bonds to areneruthenium moieties as a 1—5-η-C_8H_9 or a 1—3,6,7-η-C_8H_9 ligand. An alternative route to C_8H_9 complexes is by addition of COT to metal-hydride complexes [7], and we have now used this method to obtain the first unequivocal example of coordination of I to a ruthenium centre as well as the first X-ray structural study of I bound to a transition metal.

A suspension of $[RuH(COD)(PMe_2Ph)_3][PF_6]$ (II, COD = cycloocta-1,5-diene) [8] in methanol containing an excess of cyclooctatetraene dissolved on heating to 60°C and subsequently gave a pale yellow precipitate (15 min, 70%) of analytically pure $[Ru(2\text{-}6\text{-}\eta\text{-bicyclo}[5,1,0]\text{octadienyl})(PMe_2Ph)_3][PF_6]$ (III) which was characterised by IR and NMR spectroscopy* and single crystal X-ray crystallography**.

The molecular structure of the cation of 3 is shown in Fig. 1, together with the atom numbering scheme. The structure reveals a 2—6-η-bicyclo[5.1.0]octadienyl ligand bonded to a $Ru(PMe_2Ph)_3^+$ fragment. The carbon atoms bonded to ruthenium are coplanar (within 0.03(3) Å) with Ru—C bond lengths varying from 2.195(5) to 2.315(5) Å; the bond lengths to C(41) and C(45) being ca. 0.1 Å longer than those to C(42), C(43) and C(44). The cyclopropyl ring lies in a position *exo* to the ruthenium atom. A remarkable structural feature is the elongated bond (1.63 Å) between C(46) and C(48) indicating considerable weakening of the bond common to the three- and the seven-membered rings; much shorter bond lengths of 1.53(4) and 1.44(2) Å were found in the compounds $[Nb(\eta^4\text{-}C_8H_8)\{\eta^5\text{-}C_8H_8(C_6H_5)\}\{(CH_3)_2AsC_6H_4As(CH_3)_2\}]$ [9] and $[Fe_2(CO)_4\{P(OPh)_3\}_2(\eta^5{:}\eta^5\text{-}C_{16}H_{16})][PF_6]_2$ [10], respectively, both of which contain substituents on the apical carbon of the cyclopropyl ring.

On dissolution of III in CD_2Cl_2 two species are observed by ^1H and ^{13}C NMR techniques. The spectra of the major species are invariant with temperature and are consistent with the presence of the bicyclic moiety I. In view of the necessarily complex ^1H NMR spectra, where overlapping of resonances of different protons occurred, we were reluctant to rely solely on methods used previously by others [2—4, 9—11] to characterize the presence of a cyclopropyl ring, viz. the detection of a geminal H—H coupling constant of ca. 5 Hz. We chose rather to use $^1J(CH)$ coupling constants as a definitive method of structural assignment for these systems. This method has the additional advantage of being applicable

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*NMR data for III: $^1H\text{-}\{^1H\}$ and selective $^{13}C\text{-}\{^1H\}$ at 500 MHz established the assignments: ^{13}C: δ 94.7 (2CH, $^1J(CH)$ 163 Hz, C(2)), 87.7 (CH, $^1J(CH)$ 167 Hz, C(1)), 80.2 (2CH, $^1J(CH)$ 156 Hz, C(3)), 32.4 (2CH, $^1J(CH)$ 165 Hz, C(4)), 37.7 (CH_2, $^1J(CH)$ 162 Hz, C(5)). ^1H: δ 5.86 (t, 1H, H(1)), 4.62 (m, 2H, H(2)), 3.39 (m, 2H, H(3)), 1.54 (m, 1H, H(5 *exo*)), 1.10 (m, 1H, H(5 *endo*)).

***Crystal data for III*: $C_{32}H_{42}F_6P_4Ru$, M = 765.64, orthorhombic, space group *Pbca*, a 23.522(5), b 14.937(3), c 19.019(4) Å, U 6682(4) Å^3, $Z = 8$, D_c 1.522 Mg m^{-3}, $F(000)$3136, μ(Mo-K_α) 0.632 mm^{-1}. The structure was solved by Patterson and electron density map methods using SHELX [12] and was refined by least-squares procedures. Anisotropic temperature factors were used for all non-H atoms; all the H atom positions were located and refined. The refinement converged with $R = 0.0432$ and R_w = 0.0379 for 3356 unique reflections with $F_o \geqslant 6\sigma(F_o)$ measured in the range $3 \leqslant \theta \leqslant 23°$ at 293 K on a Philips PW1100 4-circle diffractometer (N.P.R.L., CSIR), using a crystal of dimensions 0.25 X 0.25 X 0.20 mm grown from dichloromethane/ethanol solution. The atomic coordinates for this structure are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical, Laboratory Lensfield Road, Cambridge CB2 1IW. Any request should be accompanied by the full literaturc citation for this communication.

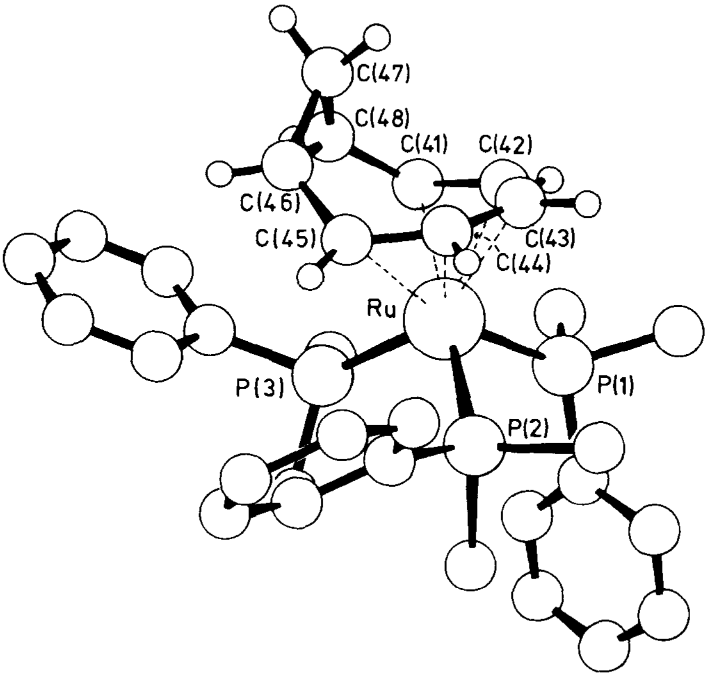

Fig. 1. A perspective view of the cation of III showing the atom numbering scheme. The H atoms on the phosphine ligands have been omitted for clarity. Bond lengths (Å) and angles (°): Ru—P(1) 2.359(1), Ru—P(2) 2.341(1), Ru—P(3) 2.349(1), Ru—C(41) 2.293(7), Ru—C(42) 2.204(6), Ru—C(43) 2.214(6), Ru—C(44) 2.195(5), Ru—C(45) 2.315(5), C(41)—C(42) 1.390(9), C(42)—C(43) 1.425(9), C(43)—C(44) 1.415(8), C(44)—C(45) 1.398(8), C(45)—C(46) 1.482(9), C(46)—C(47) 1.478(12), C(46)—C(48) 1.625(10), C(47)—C(48) 1.445(13), C(48)—C(41) 1.505(11), P(1)—Ru—P(2) 91.8(1), P(1)—Ru—P(3) 97.8(1), P(2)—Ru—P(3) 99.5(1), C(48)—C(41)—C(42) 126.8(6), C(41)—C(42)—C(43) 125.5(6), C(42)—C(43)—C(44) 122.6(5), C(43)—C(44)—C(45) 126.6(5), C(44)—C(45)—C(46) 126.4(5), C(45)—C(46)—C(47) 123.4(6), C(45)—C(46)—C(48) 114.3(5), C(47)—C(46)—C(48) 55.3(5), C(46)—C(47)—C(48) 67.6(6), C(41)—C(48)—C(46) 114.3(6), C(41)—(C48)—C(47) 121.6(7), C(46)—C(48)—C(47) 57.2(5).

to cases where the C(8) carbon has substituents. The ^{13}C spectrum establishes the symmetry of the η^5-system [12] and the large ^1J(CH) coupling shown by the aliphatic carbons conform with the values expected for a cyclopropyl ring [11,12]. The complexity of the ^{1}H spectrum of the minor species and the coalescence processes observed on cooling suggest a structure containing either a 1—5-η-C_8H_9 or a 1—3:6—7-η-C_8H_9 ligand.

In view of our detection of minor species ($\leqslant$ 5%) in solution together with III, and of Bennett's report of the isomerization of 1—5-η-C_8H_9 into 1—3,6—7-η-C_8H_9 ligands when coordinated to an areneruthenium moiety we were interested to know whether III would isomerize on heating. On heating, the pale yellow solution of III in acetone rapidly turns dark red out but the only detectable species (^{13}C NMR) was III in concentration close to the initial concentration. This suggests conversion of the minor species to new products which are both fluxional and in low concentration. Attempts to characterize these minor species using complexes analogous to II but with other phosphorus donor ligands are underway.

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