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Preliminary communication

FORMATION OF A FULVENE BY TRIMERISATION OF AN ALKYNE AT A RHODIUM CENTRE; CRYSTAL STRUCTURE OF CYCLOOCTA-1,5-DIENE(η^5-1,3,6-TRI-t-BUTYLFULVENE)RHODIUM HEXAFLUOROPHOSPHATE

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Summary

Reaction of $[RhCl(1,5\text{-}C_8H_{12})]_2$ with silver hexafluorophosphate in the presence of an excess of 3,3-dimethylbut-1-yne gives cycloocta-1,5-diene(η^5-1,3,6-tri-t-butylfulvene)rhodium hexafluorophosphate, which was identified by X-ray crystallography.

Although metal complexes containing coordinated fulvenes [1,2] have been synthesised from preformed fulvenes, and complexes containing fulvenyl fragments have been observed or implicated in the reaction of alkynes with palladium(II) and rhodium(III) species [3—6], it is interesting that with the exception of Hubel's fulvenediiron complex [7], there are no reports of simple fulvene complexes being formed directly from alkynes. In exploring the reaction of alkynes with cationic rhodium(I) complexes we have observed such a reaction.

Reaction (0°C, CH_2Cl_2) of $[RhCl(1,5\text{-}C_8H_{12})]_2$ with silver hexafluorophosphate and an excess of 3,3-dimethylbut-1-yne affords (83% yield) the red crystalline (from CH_2Cl_2/Et_2O) complex I (^{1}H NMR ($CDCl_3$), δ 1.3 (s, 9 H, Bu^t exocyclic), 1.38 (s. 18 H, Bu^t ring), 2.2—2.35 (m, 4 H, CH_2), 2.4—2.6 (m, 4 H, CH_2), 5.2—5.7 (m, 6 H, CH=C), 6.58 (s, 1 H, fulvene exocyclic); ^{13}C-{^{1}H} NMR (CD_2Cl_2), δ 152.26 (s), 138.84 (d, J(RhC) 4.4 Hz), 119.7 (d, J(RhC) 5.9 Hz), 113.66 (d, J(RhC) 2.9 Hz), 103.39 (d, J(RhC) 2.9 Hz), 90.1 (d, J(RhC) 10.2 Hz), 88.32 (d, J(RhC) 10.2 Hz), 86.85 (d, J(RhC) 10.2 Hz), 86.66 (d, J(RhC) 10.2 Hz), 78.52 (d, J(RhC) 4.4 Hz), 34.9 (s), 34.64 (s), 34.12 (s), 32.69 (s), 30.93 (s), 30.61 (s), 29.76 (s) and 28.79 (s) ppm]. Whilst the spectroscopic and analytical data clearly established that I contained a hexafluorophosphate anion, a cyclooctadiene ligand, and an organic ligand derived

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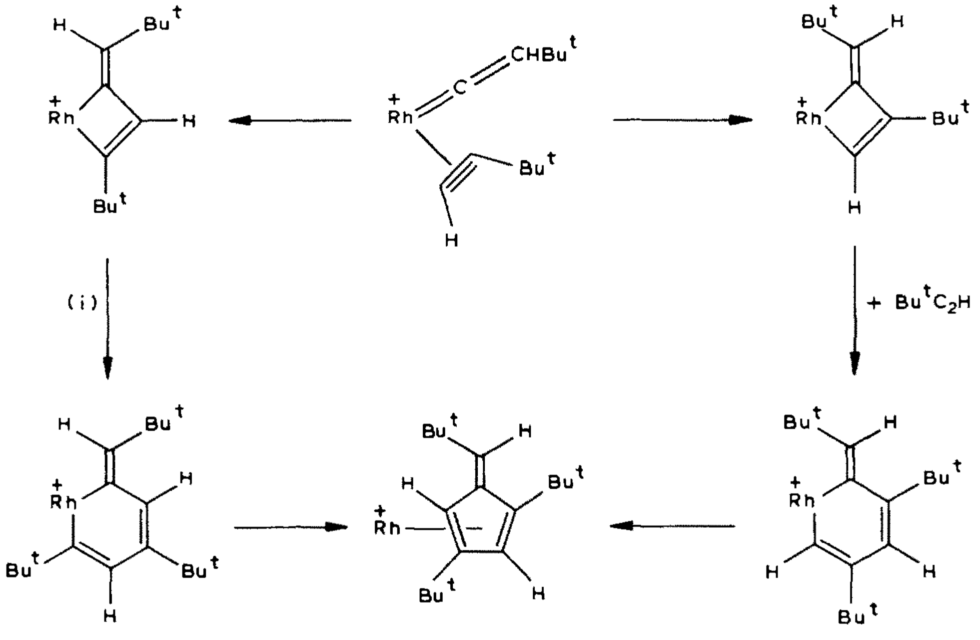
from three alkynes it was not possible to define the structure, and therefore a single crystal X-ray diffraction study was undertaken.

Crystal data: $C_{26}H_{42}F_6PRh$, $M = 563.9$, monoclinic, space group $P2_1/n$, a 10.456(4), b 18.781(9), c 14.728(6) Å, β 102.93(3)°, $U = 2818(2)$ Å^3, $Z = 4$, D_c 1.29 g cm^{-3}, $F(000)$ 1248 electrons, Mo-K_α X-radiation, graphite monochromator, $\lambda = 0.71069$ Å, μ(Mo-K_α) 7.02 cm^{-1}.

The structure was solved and refined by conventional Fourier and least squares methods. The structure was disordered with the entire cation occupying two alternative orientations each showing the stereochemistry illustrated in the Scheme, in the same region of the unit cell, the anion was ordered. The relative occupancies of the two cationic orientations were refined to 0.66/0.34. For 3133 independent observed ($I > 2\sigma(I)$) reflections collected at room temperature on a Nicolet P3m diffractometer in the range $3° < 2\theta < 50°$, the current R is 0.082 (R_w 0.082)*.



(I)

SCHEME 1. Cycloocta-1,5-diene ligand omitted for clarity.

The structure of the cation is given in Fig. 1. It shows that rhodium is coordinated to a 1,3,6-tri-t-butylfulvene ligand formed formally by the linking of three 3,3-dimethylbut-1-yne molecules. The cycloocta-1,5-diene ligand is bonded in the normal manner. The interesting feature of the structure is the mode of coordination of the fulvene. The five ring carbons are within bonding distance of the rhodium. The exocyclic double bond C(11)—C(14) is bent towards the

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*The atomic coordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW (Great Britain). Any request should be accompanied by the full literature citation for this communication.

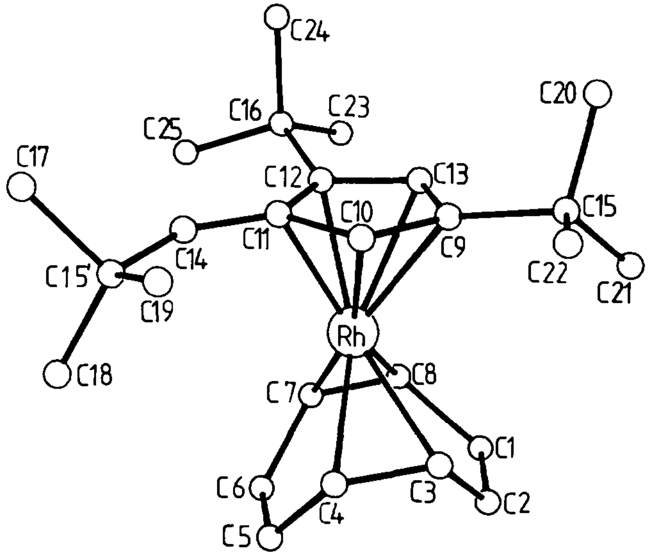
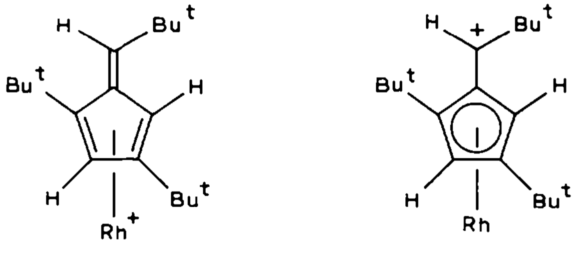


Fig. 1. Molecular structure of I (major orientation 66%). Important bond lengths include: Rh—C(3) 2.226(13), Rh—C(4) 2.174(12), Rh—C(7) 2.166(15), Rh—C(8) 2.231(14), Rh—C(9) 2.252(9), Rh—C(10) 2.224(12), Rh—C(11) 2.119(13), Rh—C(12) 2.197(8), Rh—C(13) 2.303(12), Rh....C(14) 2.88(1), C(9)—C(10) 1.455(15), C(10)—C(11) 1.44(2), C(11)—C(12) 1.52(2), C(12)—C(13) 1.40(2), C(9)—C(13) 1.34(2), C(11)—C(14) 1.29(2) Å.

metal atom by 5.5°, with a Rh—C(14) distance of 2.88 Å. This angle is less than that found [1] in [Cr(CO)$_3$(η^6-fulvene)] (θ 35°), while in [Ni(1,5-C$_8$H$_{12}$)(η^4-fulvene)] [2] the *exo*-cyclic bond bends away from the nickel by 6°. This suggests that the coordination of the fulvene in I may best be described by two resonance forms (a) and (b), Fig. 2. Support for this description is found in the ^{13}C spectrum, which shows ^{103}Rh—^{13}C coupling for all five ring carbons but not for C(14).



(a) (b)

Fig. 2.

The formation of I contrasts with the reaction of the cation [Rh(norbornadiene)]$^+$ (generated from [RhCl(norbornadiene)]$_2$ and AgPF$_6$) with but-2-yne to give [Rh(norbornadiene)(hexamethylbenzene)]$^+$, but in a sense parallels the formation of cyclopentadienone complexes from alkynes and coordinated carbon monoxide. We suggest that a vinylidene complex is involved which is formed by

TABLE 1

ATOMIC POSITIONAL (FRACTIONAL COORDINATES) AND THERMAL PARAMETERS WITH ESTIMATED STANDARD DEVIATIONS IN PARENTHESES FOR CYCLOOCTA-1,5-DIENE-(η^5-1,3,6-t-BUTYLFULVENE)RHODIUM HEXAFLUOROPHOSPHATE

Atom[a]	x	y	z	U
F(1)	−0.059 6(10)	0.079 6(5)	0.779 2(6)	19.2(6)*
F(2)	0.115 5(8)	0.151 3(5)	0.771 9(8)	19.9(6)*
F(3)	−0.005 7(9)	0.093 0(5)	0.648 2(6)	18.2(5)*
F(4)	−0.179 9(8)	0.148 1(5)	0.670 2(7)	18.0(5)*
F(5)	−0.066 9(9)	0.200 5(5)	0.790 8(7)	19.6(6)*
F(6)	−0.005 3(9)	0.209 5(4)	0.658 0(7)	18.2(5)*
P	−0.029 6(4)	0.147 04(15)	0.723 8(3)	10.35(14)*
Rh(C)	0.144 85(12)	0.152 45(6)	0.355 47(9)	5.90(5)*
C(1)	0.311(2)	0.012 3(11)	0.414(3)	19.3(14)*
C(2)	0.405 5(14)	0.067 2(10)	0.395 3(12)	10.5(8)*
C(3)	0.358 0(13)	0.137 3(9)	0.362 6(12)	9.7(7)*
C(4)	0.336 2(13)	0.191 5(9)	0.428 2(10)	9.2(7)*
C(5)	0.355(2)	0.183 2(10)	0.535 1(11)	12.4(8)*
C(6)	0.265(3)	0.137 1(14)	0.562 2(12)	16.7(12)*
C(7)	0.159 2(15)	0.097 4(9)	0.486 6(10)	9.7(7)*
C(8)	0.173 5(14)	0.046 4(8)	0.425 2(11)	8.6(7)*
C(9)	0.077 7(10)	0.152 4(6)	0.199 1(6)	6.6(4)
C(10)	0.089 0(12)	0.225 2(7)	0.233 9(9)	6.5(4)
C(11)	−0.001 0(13)	0.227 4(8)	0.294 9(10)	7.7(4)
C(12)	−0.066 7(8)	0.155 2(6)	0.293 4(9)	8.5(5)
C(13)	−0.014 6(13)	0.116 0(8)	0.229 6(10)	7.8(4)
C(14)	−0.017 6(12)	0.276 7(6)	0.351 6(9)	8.9(5)
C(15)	0.141 1(6)	0.129 6(3)	0.110 8(5)	8.2(3)
C(16)	−0.196 4(11)	0.130 2(6)	0.317 9(6)	7.2(4)
C(17)	0.119(3)	0.359 1(9)	0.473 8(10)	21.0(14)*
C(18)	−0.073 6(15)	0.407 5(7)	0.354(2)	17.0(13)*
C(19)	0.112(3)	0.381 0(9)	0.301(2)	22(2)*
C(20)	0.021 8(13)	0.117 2(12)	0.027 5(8)	12.1(10)*
C(21)	0.207(2)	0.057 1(7)	0.131 9(12)	12.8(10)*
C(22)	0.218(3)	0.194 4(9)	0.087 3(12)	15.6(12)*
C(23)	−0.202(2)	0.048 6(7)	0.326(2)	17.1(13)*
C(24)	−0.315 0(9)	0.151 2(11)	0.240 2(13)	14.3(10)*
C(25)	−0.219(2)	0.163 2(12)	0.408 4(12)	18.1(13)*
Rh(D)	−0.021 4(3)	0.162 9(11)	0.316 4(2)	5.44(9)
D(1)	−0.228(3)	0.151 8(15)	0.438(2)	8.8(8)
D(2)	−0.305(4)	0.182(2)	0.340(3)	10.2(11)
D(3)	−0.225(3)	0.202(2)	0.274(2)	8.3(8)
D(4)	−0.198(3)	0.157 2(13)	0.207(2)	6.9(7)
D(5)	−0.246(4)	0.086(2)	0.191(3)	10.6(10)
D(6)	−0.218(4)	0.047(3)	0.265(3)	13.2(13)
D(7)	−0.105(3)	0.061 1(15)	0.355(2)	8.1(8)
D(8)	−0.107(3)	0.110 3(13)	0.421(2)	6.4(7)
D(9)	0.081(2)	0.268 4(8)	0.350 3(13)	6.5(7)
D(10)	0.099(2)	0.246 0(11)	0.264 7(14)	5.1(6)
D(11)	0.140(3)	0.168 9(12)	0.273(2)	6.1(6)
D(12)	0.186(3)	0.152 5(13)	0.390(2)	9(2)
D(13)	0.140(3)	0.217 4(15)	0.422(2)	8.0(8)
D(14)	0.154 7(14)	0.131 7(7)	0.216 6(5)	10.3(10)
D(15)	0.040 6(7)	0.350 9(4)	0.372 9(5)	8.2(3)
D(16)	0.295(2)	0.100 3(10)	0.445 0(13)	8.4(8)
D(17)	0.277(2)	0.119(3)	0.086 5(13)	14.1(14)
D(18)	0.057(4)	0.067 0(15)	0.063 6(12)	11.8(12)
D(19)	0.093(3)	0.199 6(9)	0.061 1(11)	9.7(9)
D(20)	−0.013(3)	0.387 6(11)	0.280 1(11)	7.5(7)
D(21)	0.173(2)	0.386 9(12)	0.420(2)	10.2(10)
D(22)	−0.052(3)	0.345 1(13)	0.440(2)	9.4(9)
D(23)	0.431(2)	0.123 0(15)	0.429(2)	14.2(14)
D(24)	0.296(3)	0.105 5(14)	0.551 2(12)	11.1(11)
D(25)	0.263(3)	0.022 7(10)	0.411(2)	9.3(9)

[a] D denotes atoms in the minor orientation (34%), and C those atoms in the major orientation (66%).

TABLE 2

BOND LENGTHS (Å) WITH ESTIMATED STANDARD DEVIATIONS IN PARENTHESES FOR CYCLOOCTA-1,5-DIENE(η^5-1,3,6-t-BUTYLFULVENE)RHODIUM HEXAFLUOROPHOSPHATE

F(1)—P	1.576(9)	P—F(2)	1.526(8)	D(3)—D(2)	1.45(5)
P—F(3)	1.567(9)	P—F(4)	1.594(8)	D(4)—D(5)	1.42(4)
P—F(5)	1.518(10)	P—F(6)	1.578(9)	D(7)—D(6)	1.60(5)
Rh(C)—C(3)	2.226(13)	Rh(C)—C(4)	2.174(12)	D(8)—D(1)	1.55(4)
Rh(C)—C(7)	2.166(15)	Rh(C)—C(8)	2.231(14)	D(9)—D(13)	1.46(3)
Rh(C)—C(9)	2.252(9)	Rh(C)—C(10)	2.224(12)	D(12)—Rh(D)	2.21(3)
Rh(C)—C(11)	2.119(13)	Rh(C)—C(12)	2.197(8)	D(12)—D(13)	1.43(4)
Rh(C)—C(13)	2.303(12)	C(1)—C(2)	1.50(3)	D(14)—D(11)	1.12(3)
C(3)—C(2)	1.45(3)	C(3)—C(4)	1.46(3)	D(15)—C(18)	1.58(2)
C(3)—D(12)[a]	1.95(4)	C(4)—C(5)	1.55(3)	D(15)—D(9)	1.66(2)
C(5)—C(6)	1.40(3)	C(7)—C(6)	1.57(3)	D(15)—D(21)	1.56(2)
C(7)—C(8)	1.35(3)	C(8)—C(1)	1.61(3)	D(16)—D(23)	1.56(3)
C(9)—C(10)	1.455(15)	C(9)—C(13)	1.34(2)	D(16)—D(25)	1.55(3)
C(9)—C(15)	1.644(12)	C(10)—C(11)	1.44(2)	D(1)—D(2)	1.60(5)
C(11)—C(12)	1.52(2)	C(11)—C(14)	1.29(2)	D(3)—D(4)	1.37(4)
C(12)—C(13)	1.40(2)	C(12)—C(16)	1.553(15)	D(5)—D(6)	1.28(5)
C(14)—D(15)	1.524(12)	C(15)—C(20)	1.559(13)	D(7)—D(8)	1.34(4)
C(15)—C(21)	1.528(15)	C(15)—C(22)	1.54(2)	D(9)—D(10)	1.38(3)
C(15)—D(14)	1.533(10)	C(15)—D(17)	1.55(2)	D(10)—D(11)	1.51(3)
C(15)—D(18)	1.54(3)	C(15)—D(19)	1.53(2)	D(12)—D(11)	1.71(4)
C(16)—C(23)	1.540(15)	C(16)—C(24)	1.54(2)	D(12)—D(16)	1.58(3)
C(16)—C(25)	1.54(3)	Rh(D)—D(3)	2.20(3)	D(15)—C(17)	1.54(2)
Rh(D)—D(4)	2.16(3)	Rh(D)—D(7)	2.23(3)	D(15)—C(19)	1.53(3)
Rh(D)—D(8)	2.18(3)	Rh(D)—D(9)	2.254(15)	D(15)—D(20)	1.52(2)
Rh(D)—D(10)	2.24(3)	Rh(D)—D(11)	1.94(3)	D(15)—D(22)	1.54(3)
		Rh(D)—D(13)	2.27(3)	D(16)—D(24)	1.56(3)

[a] D denotes atoms in the minor orientation (34%), and C those in the major orientation (66%).

the oxidative addition of the terminal alkyne to the rhodium(I) centre to afford a hydrido(acetylide) species, which rearranges via proton transfer. Such a reaction would provide access to an alkyne(vinylidene) complex (Scheme), which would be expected to form a metallacyclobutene. "Insertion" of a second molecule of Bu^tC_2H followed by a reductive elimination reaction would then result in the formation of the fulvene complex.

Reaction (room temperature, 4 h) of I with acetonitrile led to a quantitative yield of 1,3,6-tri-t-butylfulvene* and $[Rh(NCMe)_2(1,5\text{-}C_8H_{12})][PF_6]$, whereas, $[KBHBu^s{}_3]$ in THF (−78°C) selectively attacks C(6) of the coordinated fulvene to give (74% yield) II $[Rh(1,5\text{-}C_8H_{12})(\eta^5\text{-}1,3,4\text{-}Bu^t{}_2(Bu^tCH_2)(C_5H_2)]$** in agreement with a contribution from the canonical form (b) in Fig. 2.

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*Spectroscopic data for 1,3,6-tri-t-butylfulvene, ^1H NMR (C_6D_6), δ 1.1 (s, 9 H, Bu^t), 1.21 (s, 18 H, Bu^t), 6.08 (s, 2 H, CH=C) and 6.6 (s, 1 H, CH=C exocyclic) ppm.

**Spectroscopic data for II, ^1H NMR (C_6D_6), δ 0.97 (s, 9 H, Bu^t), 1.28 (s, 9 H, Bu^t), 1.42 (s, 9 H, Bu^t), 1.68—2.68 (m, 10 H, CH_2, CH_2Bu^t), 4.62 (d, 1 H, J(RhH) 2.6 Hz), 4.88 (d, 1 H, J(RhH) 2.6 Hz), 5.44—5.68 (m, 2 H, CH=CH) and 5.8—6.0 (m, 2 H, CH=CH) ppm.

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