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Preliminary communication

PREPARATIONS, STRUCTURES AND REACTIONS OF MONO-ALKENE ALKYNE
COMPLEXES OF RHODIUM(I): THE CRYSTAL STRUCTURES OF ACETYL-
ACETONATO(ETHYLENE)(HEXAFLUOROBUT-2-YNE)RHODIUM(I) AND ACETYL-
ACETONATO(CYCLO-OCTENE)(HEXAFLUOROBUT-2-YNE)RHODIUM(I)

By John H. Barlow, George R. Clark, Matthew G. Curl, Martin E. Howden,
Raymond D. W. Kemmitt and David R. Russell

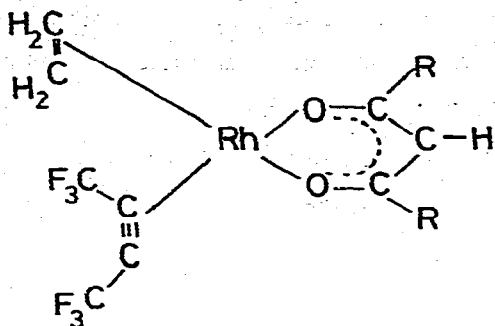
Chemistry Department, The University, Leicester LE1 7RH, United Kingdom
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SUMMARY

Mono-alkene alkyne complexes of rhodium(I) have been synthesised, and characterised by i.r., ^{19}F n.m.r., and crystallography. Their role as intermediates in the formation of cyclohexadienes is described.

The formation of cyclohexadienes by metal-catalysed cyclotrimerisations of two molecules of alkyne with one molecule of alkene proceed by both metallacyclopentene¹ and metallacyclopentadiene^{2,3} intermediates. The metallacyclopentene intermediate complex is presumably derived from a mono-alkene alkyne precursor which then reacts with a further molecule of alkyne, but whereas diene alkyne complexes are known,⁴⁻⁶ mono-alkene alkyne complexes have not hitherto been reported. We now describe the preparation, reactions, and structural characterisation of some mono-alkene alkyne complexes of rhodium(I).

Treatment of the bis-ethylene complexes $[\text{Rh}(\text{acac})(\text{C}_2\text{H}_4)_2]$ and $[\text{Rh}(\text{dpm})(\text{C}_2\text{H}_4)_2]$, ($\text{acac} = \text{MeCOCHCOMe}$; $\text{dpm} = \text{Me}_3\text{CCOCHCOMe}_3$) in diethyl ether with hexafluorobut-2-yne at 195 K affords the novel alkene-alkyne complexes (1a) and (1b).

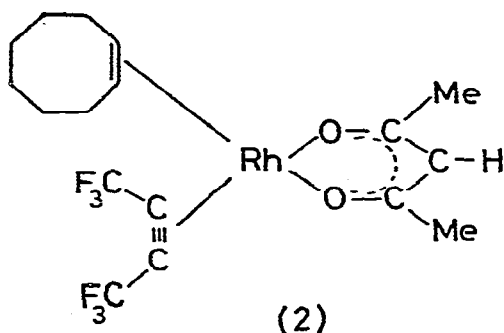


a; R = Me

b; R = CMe₃

(1)

The reaction of hexafluorobut-2-yne with $[\text{Rh}(\text{acac})(\text{cis-cyclo-octene})_2]$ at 195 K similarly yields the complex (2)



(2)

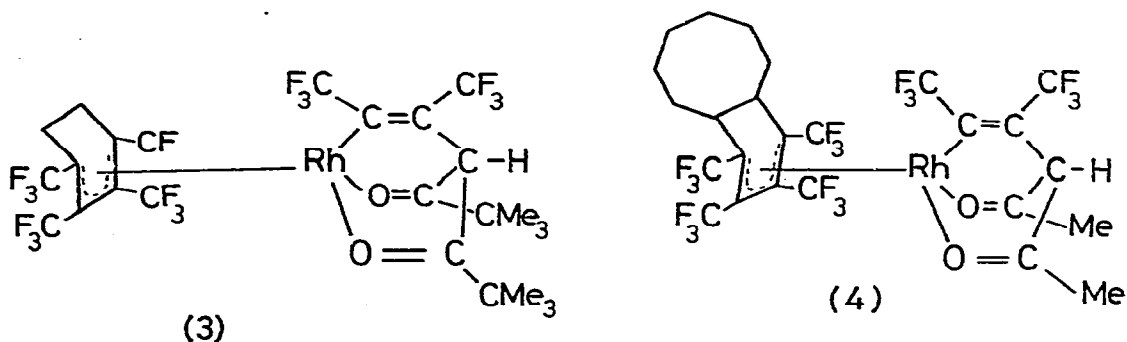
Each complex exhibits a strong band in its i.r. spectrum typical of an η^2 -coordinated acetylene [(1a) 1976 cm^{-1} ; (1b) 1976 cm^{-1} ; (2) 1958 cm^{-1}], and a single resonance in the room temperature ^{19}F n.m.r. spectrum [(1a) $\delta = -8.95$; (1b) $\delta = -8.68$ p.p.m. in $(\text{CD}_3)_2\text{CO}$; (2) $\delta = -9.91$ p.p.m. in CD_2Cl_2 , all relative to α,α,α -trifluorotoluene}.

The crystal structures of (1a) and (2) were determined using conventional methods with diffractometer data. (1a) Triclinic, $\bar{P}1$, $Z = 2$, $a = 7.89(2)$, $b = 12.64(3)$, $c = 8.57(2)\text{ \AA}$, $\alpha = 95.9(2)^\circ$, $\beta = 121.1(2)^\circ$,

$\delta = 94.8(2)^\circ$. Blocked full-matrix refinement gave $R = 0.053$ for 1228 observed reflections. (2) Monoclinic, $B2_1/c$, $Z = 8$, $a = 14.16(3)$, $b = 17.89(3)$, $c = 15.71(3)\text{\AA}$, $\beta = 97.5(2)^\circ$. Block-diagonal least-squares refinement gave $R = 0.048$ for 1296 observed reflections.

The structural analyses verify that both complexes are monomeric, and have structures corresponding to those drawn for (1a) and (2). Important distances are: (1a), Rh-O 2.015(6), 2.033(7); Rh-C(alkyne) 2.042(11), 2.016(10); Rh-C(alkene) 2.171(17), 2.142(14); C \equiv C 1.23(2); C=C 1.31(3)\AA: (2), Rh-O 2.038(7), 2.017(8); Rh-C(alkyne) 2.059(10), 2.034(10); Rh-C(alkene) 2.196(11), 2.163(13); C \equiv C 1.24(2); C=C 1.37(2)\AA. Thus the geometries within the coordination spheres of the two complexes are very similar. We can now compare the structures of (1a) and (2) with those of acetylacetonatobis(ethylene)rhodium(I) and acetylacetonato(ethylene)(tetrafluoroethylene)rhodium(I), where replacement of one C_2H_4 by C_2F_4 causes a considerable weakening in the bonding between Rh and the remaining C_2H_4 . The Rh-C(C_2H_4) distances in the bis(ethylene) complex are 2.117, 2.118(4)\AA whereas those in the mixed complex are 2.190, 2.174(12)\AA.⁷ In (1a) and (2) these distances are again long, showing that the $CF_3C\equiv CCF_3$ ligand has exerted a similar influence to $CF_2=CF_2$.

Treatment of the complexes (1b) and (2) with excess hexafluorobut-2-yne at room temperature gives the cyclohexadiene complexes (3)⁸ and (4) respectively. These reactions provide good evidence for the intermediacy



of mono-alkene alkyne complexes in the formation of cyclohexadiene complexes from bis-alkene rhodium(I) complexes and hexafluorobut-2-yne.^{8,9}

The passage of carbon monoxide gas through an ether solution of (Ib) results in the rapid displacement of both alkene and alkyne to give $[\text{Rh}(\text{dpm})(\text{CO})_2]$. However, the reactions of triphenyl-phosphine-, -arsine, and -stibine with (Ib) result in the displacement of ethylene only to give the complexes $[\text{Rh}(\text{dpm})(\text{C}_4\text{F}_6)_2]$, ($L = \text{PPh}_3, \text{AsPh}_3, \text{SbPh}_3$). This is consistent with the previously described weakening of the $\text{Rh}-\text{C}_2\text{H}_4$ bonds by hexafluorobut-2-yne. These rhodium complexes are structurally related to the osmium complexes $[\text{Os}(\text{CO})(\text{NO})(\text{RC}\equiv\text{CR})(\text{PPh}_3)_2][\text{PF}_6]$, ($\text{R} = \text{H}, \text{Ph}, \text{CO}_2\text{Me}$) for which there is evidence for rotation about the osmium-alkyne bond.¹⁰ The room temperature ^{19}F n.m.r. spectrum of the complex $[\text{Rh}(\text{dpm})(\text{C}_4\text{F}_6)(\text{PPh}_3)_2]$ exhibits one signal at -12.04 p.p.m. ($J_{\text{RhF}} = 2\text{Hz}$, relative to internal α, α, α -trifluorotoluene) which at 215 K splits into two signals at -12.08 p.p.m. (d, 3F, $J_{\text{PF}} = 16.8\text{Hz}$) and -11.29 p.p.m. (s, 3F). However, the absence of phosphorus-fluorine coupling in the room temperature ^{19}F n.m.r. spectrum of $[\text{Rh}(\text{dpm})(\text{C}_4\text{F}_6)(\text{PPh}_3)_2]$, together with the observation that addition of excess triphenylphosphine raises the coalescence point in the low temperature spectrum from 254 K to 263 K, suggests that the temperature dependent ^{19}F n.m.r. spectrum is a consequence of phosphine dissociation and not alkyne rotation in this complex.

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