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Preliminary communication

Formation of Metallacyclopent-2-enes from Alkene-Alkyne Rhodium Complexes. The reactions of pyridine and tetramethylallene with $[Rh(Me_3CCOCHCOCMe_3)(C_2H_4)(CF_3C{\equiv}CCF_3)]$ and the X-Ray Crystal Structures of (Pivaloylmethanato)-bis(pyridine)rhoda-2,3-bis(trifluoromethyl)cyclopent-2-ene and (Pivaloylmethanato)η-1,2,4,5{1,2-bis(trifluorimethyl)-4-methyl-3(prop-2'-ylidene)-penta-1,4-diene}rhodium(I).

By Christopher E. Dean, Raymond D. W. Kemmitt,* David R. Russell* and Michael D. Schilling.

Department of Chemistry, The University, Leicester LE1 7RH, (Great Britain)

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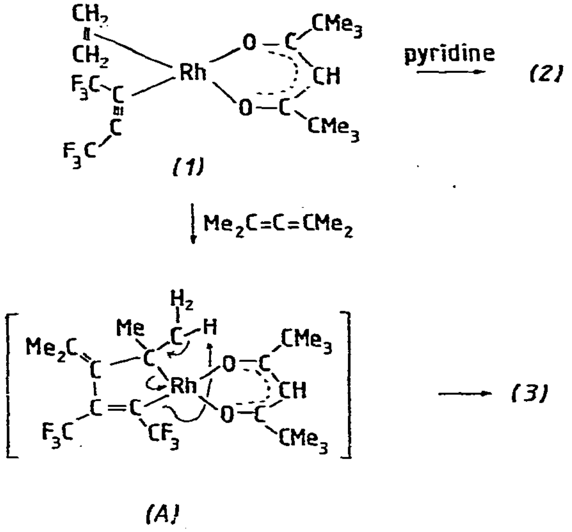
Summary. Pyridine and tetramethylallene react with $[Rh(Me_3CCOCHCOCMe_3)(C_2H_4)(CF_3C{\equiv}CCF_3)]$ (1) to give $[\overline{Rh\{CH_2CH_2C(CF_3)=C}(CF_3)\}(Me_3CCOCHCOCMe_3)py_2]$ (2) and $[Rh(Me_3CCOCHCOCMe_3)\{CH_2=C(Me)C(=CMe_2)C(CF_3)=CHCF_3\}]$ (3) respectively which have been characterised by single crystal X-ray studies; the formation of (2) provides evidence for the intermediacy of rhodacyclopent-2-enes in the rhodium assisted cyclotrimerisation of two alkynes and one alkene.

ALKYNES have been shown to react with bis(alkene) complexes of rhodium(I) to give cyclohexa-1,3-diene derivatives co-ordinated to rhodium(I).[1,2,3] We have shown[4] that an initial step in this cyclotrimerisation of two alkynes and one alkene is the formation of alkene-alkyne complexes[4] and it has been suggested[3] that a subsequent step involves metallacyclopent-2-ene intermediates. Recently some cobaltacyclopent-2-ene complexes have been shown to be of importance in the mechanism for cobalt assisted alkyne-alkene co-oligomerisation and kinetic studies have provided evidence for an intermediate in which alkene and alkyne are simultaneously co-ordinated to cobalt.[5] We now provide evidence for the collapse of an alkene-alkyne complex to metallacyclopent-2-ene complexes.

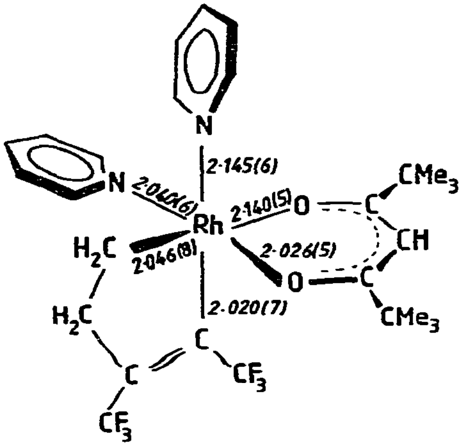
Pyridine reacts at room temperature with (1)[4] in diethyl ether to afford (40%) a pale green crystalline compound (2) [m.p. 48-49°C]. The ^{19}F n.m.r. spectrum ($CDCl_3$) of (2) between 20°C to 60°C showed signals at 52.8q, 54.7q [3F, J(FF) 14 Hz] and 57.9 p.p.m. [q, 3F, J(FF) 14 Hz] (rel. CCl_3F at 0.0 p.p.m.). In order to establish the molecular structure of (2) a single crystal X-ray diffraction study was carried out.



Scheme

<u>Crystal data</u>. $C_{27}H_{33}F_6N_2O_2Rh$, $\underline{M}$ = 634.5, monoclinic, $\underline{a}$ = 11.561(7), $\underline{b}$ = 16.686(10), $\underline{c}$ = 14.85(1)Å, β = 90.2(1)°, $\underline{U}$ = 2865.4Å^3, $\underline{Z}$ = 4, $\underline{F}(000)$ = 1296, $\underline{D}_m$ = 1.45, $\underline{D}_c$ = 1.47, Mo-K_α λ = 0.7107Å μ(Mo-K_α) = 5.81 cm^{-1}, space

group $P2_1/n$. 3557 reflections with $I \geqslant 3\sigma(I)$ measured by Stoe Weissenberg diffractometer gave $R = 0.077$ with anisotropic thermal parameters for Rh, F and methyl carbon atoms only. The molecular structure found for (2) is consistent with the formula shown on Figure 1. Bond lengths of co-ordinated atoms to rhodium show the large *trans* influence of σ-bonded carbon atoms.



(2)

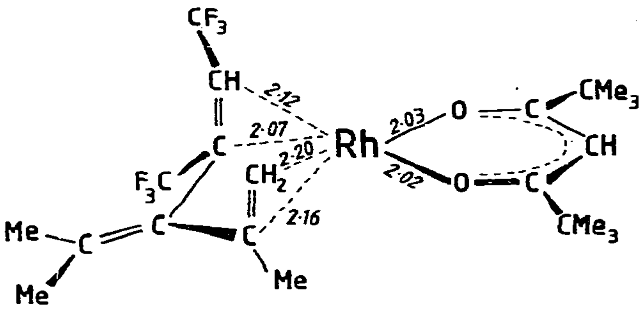
FIGURE 1 The molecular structure of $Rh(py)_2(dpm)(C_6H_4F_6)$.

The principal feature of interest in the structure of (2) is the presence of a rhodacyclopent-2-ene ring which provides further evidence for the intermediacy of metallacyclopent-2-enes[3,5] in the formation of cyclohexa-1,3-diene derivatives from two alkynes and one alkene. An alternative mechanism involving intermediate metallacyclopentadienes has also been reported.[6,7] The formation of (2) from an alkene-alkyne complex is relevant to recent studies on the equilibrium between metallacyclopentanes and bis(alkene)-metal complexes.[8] The complex (2) is also related to the rhodacyclopentane complex *cis*-[$\overline{\mathrm{Rh\{CH_2{-}C(=CH_2){-}C(=CH_2){-}CH_2}}\}$(acac)$\mathrm{py_2}$] derived from the reaction of allene with $[Rh(acac)(C_2H_4)_2]$.[9] Although crystals of (2) contain 2 *cis* pyridine ligands, the two ^{19}F n.m.r. resonances at 52.8 and 54.7 p.p.m. (total relative intensity three) are probably due to the presence of both cis- and trans- isomers of (2) in solution. Complexes analogous to (2) can also be obtained by the addition of 3-methylpyridine and 3,5-dimethylpyridine to (1). These reactions of (1) with nitrogen donor ligands contrast with the reactions of (1) with tertiary-phosphines, arsines, and stibines which result in displacement of ethylene to give the complexes $[Rh(Me_3CCOCHCOCMe_3)(C_4F_6)(MPh_3)_2]$ (M = P, As, and Sb).[4]

The reaction of tetramethylallene with (1) also results in displacement of ethylene to afford (70%) orange crystals of (3) [m.p. 113-114°C], characterised by a single crystal X-ray study.

Crystal Data. $C_{22}H_{31}F_6O_2Rh$, M = 544.4, monoclinic a = 11.50(1) b = 19.00(1) c = 23.32Å β = 99.7(1)°, U = 5022Å^3, Z = 8, D_m = 1.43 D_c = 1.440, Mo-K_α λ = 0.7107Å μ(Mo-K_α) = 6.53cm^{-1}, space group $P2_1/c$. 3316 reflections with $I \geq 3\sigma(I)$ gave R = 0.051 at the current stage of refinement.

The structure found for (3) is depicted in Figure 2, which shows that allene has reacted with the co-ordinated C_4F_6 to give a 1,4 diene ligand.



(3)

FIGURE 2 The molecular structure of $Rh(dpm)(C_{11}H_{12}F_6)$. Distances shown are the average of two independent molecules, and have e.s.d.'s of 0.01-0.015Å.

β-hydride elimination from a metallacyclopent-2-ene intermediate (A) provides an attractive route to (3), (Scheme) a reaction analogous to the formation of butenes from metallacyclopentanes.[10]

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