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Preliminary communication

THE FORMATION OF DIMETALLOCYCLES FROM REACTIONS OF ALKYNES WITH $(\eta\text{-}C_5Me_5)_2Rh_2(CO)_2$; X-RAY STRUCTURE OF $[(\eta\text{-}C_5Me_5)_2Rh_2(\mu\text{-}CO)\{\mu\text{-}\eta^2,\eta^2\text{-}C(O)C_2(CF_3)_2\}]$

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Summary

The complexes $(\eta\text{-}C_5Me_5)_2Rh_2(\mu\text{-}CO)\{\mu\text{-}\eta^2,\eta^2\text{-}C(O)CRCR\}$ are obtained from reactions between $(\eta\text{-}C_5Me_5)_2Rh_2(CO)_2$ and the alkynes RC≡CR (R = CF_3 , CO_2Me, or Ph) at 25°C. The molecular geometry of the complex with R = CF_3 has been established by X-ray diffraction; the bridging 'ene-one' unit adopts a $\mu\text{-}\eta^2,\eta^2$ conformation. Other complexes isolated from these reactions include $(\eta\text{-}C_5Me_5)Rh(C_6R_6)$ (R = CF_3 , CO_2Me), $(\eta\text{-}C_5Me_5)_2Rh_2(C_4R_4)$ (R = CO_2Me) and $(\eta\text{-}C_5Me_5)_2Rh_2(CO_2C_2R_2)$ (R = Ph). The reaction between $(\eta\text{-}C_5Me_5)_2Rh_2(CO)_2$ and $C_6F_5C{\equiv}CC_6F_5$ gives $(\eta\text{-}C_5Me_5)_2Rh_2(CO)_2(C_6F_5C_2C_6F_5)$. Mononuclear complexes such as $(\eta\text{-}C_5Me_5)Co(C_4R_4CO)$ are the major products isolated from reactions between $(\eta\text{-}C_5Me_5)_2Co_2(CO)_2$ and alkynes at 25°C.

Dimetallocycles can be formed by the condensation of unsaturated organic molecules (e.g. RC≡CR) with other substrates (e.g. RC≡CR, CO, CNR) on a dimetal centre. These ring systems have been implicated in a variety of catalytic processes [1, 2]. If the formation, rearrangement, and breaking of new C—X bonds in these systems could be achieved under mild conditions, then a better understanding of the precise role of particular dimetallocycles might be developed. There have been some successes [3—6] in this area recently, and we now report further progress that emanates from our investigations of reactions between $(\eta\text{-}C_5Me_5)_2Rh_2(CO)_2$ and alkynes at room temperature.

The major products isolated from the reactions between $(\eta\text{-}C_5Me_5)_2Rh_2(CO)_2$ and hexafluorobut-2-yne in acetone at 25°C are the *tetrahapto*-benzene complex $(\eta\text{-}C_5Me_5)Rh\{\eta^4\text{-}C_6(CF_3)_6\}$ (ca. 20% yield) and an orange-red solid, $(\eta\text{-}C_5Me_5)_2Rh_2(\mu\text{-}CO)\{C(O)C_2(CF_3)_2\}$ (ca. 50% yield) (Found: C, 45.0; H, 4.4;

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F, 16.1. $C_{26}H_{30}F_6O_2Rh_2$ calcd.: C, 45.0; H, 4.4; F, 16.4%). The infrared spectrum (CH_2Cl_2 soln.) of the latter complex reveals a bridging carbonyl (ν(CO) at 1819vs cm^{-1}) and a ketonic carbonyl (ν(CO) at 1717vs(sh) and 1698s cm^{-1}). The NMR spectra ($CDCl_3$ solutions) show inequivalent C_5Me_5 (δ(Me) at 1.88 and 1.81 ppm) and CF_3 groups (δ 54.8(q) and 59.3(qd) ppm). The precise geometry of this complex has been determined by single crystal X-ray diffraction data.

Crystal data: $C_{26}H_{30}F_6O_2Rh_2$, $M = 694.36$, monoclinic, space group $P2_1/n$, a 9.451(4), b 15.287(5), c 18.821(8) Å, β 98.66(5)°, U 2688.2 $Å^3$, D_m 1.72(3), D_c ($Z = 4$) 1.72 g cm^{-3}, $F(000) = 1384$, μ 11.6 cm^{-1} for Mo-K_α radiation (λ 0.7107 Å).

Single crystal X-ray diffraction data were collected out to a limit of θ 35° with a Philips PW1100 X-ray diffractometer. For 9282 unique reflections [$I \geqslant 3\sigma(I)$] R is 0.066*.

A representation of the structure and some important bond parameters are given in Fig. 1. It is interesting that the μ-η^2,η^2 conformation of the bridging unit —CR:CR·CO— is subtly different from that established for each of the related complexes (η-C_5H_5)$_2$Rh$_2$(CO)$_2${μ-η^1,η^1-C(O)C_2(CF_3)$_2$} [6], (η-C_5H_5)$_2$Ru$_2$(CO)(μ-CO){μ-η^1,η^3-C(O)C_2Ph_2} [4], (η-C_5H_5)$_2$W$_2$(CO)$_4${μ-η^2,η^2-C(O)C_2(CO_2Me)$_2$} [5].

An analogous complex (η-C_5Me_5)$_2$Rh$_2$(μ-CO){μ-η^2,η^2-C(O)C_2(CO_2Me)$_2$} is obtained in ca. 65% yield from the reaction between (η-C_5Me_5)$_2$Rh$_2$(CO)$_2$ and dimethyl acetylenedicarboxylate in acetone at 25°C (Found: C, 50.1; H, 5.5; mol. wt. (M^+, m/e, 674). $C_{28}H_{36}O_6Rh_2$ calcd.: C, 50.0; H, 5.4%; mol. wt. 674).

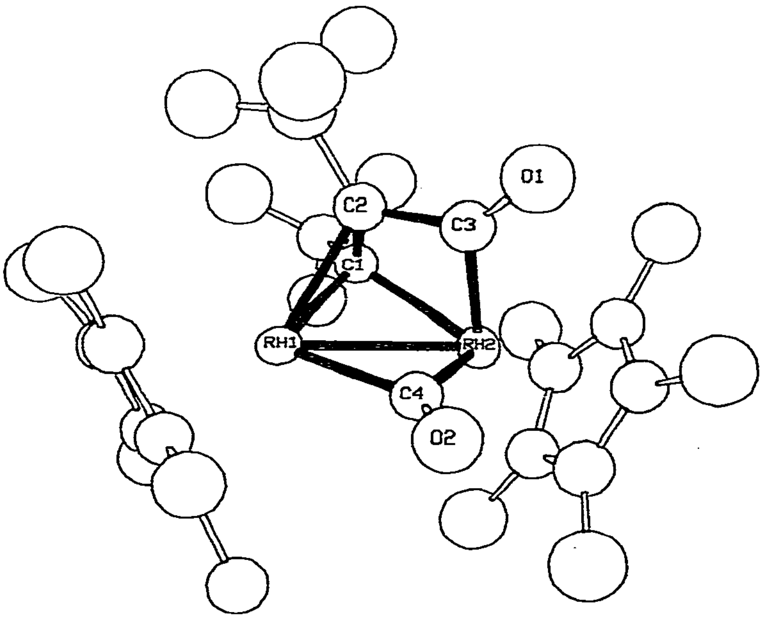

Fig. 1. Molecular structure of [(η-C_5Me_5)$_2$Rh$_2$(μ-CO){μ-η^2,η^2-C(O)C(CF_3)C(CF_3)}. Bond lengths: Rh(1)—Rh(2) 2.687(1), Rh(1)—C(1) 2.009(8), Rh(1)—C(2) 2.167(9), Rh(2)—C(1) 2.057(8), Rh(2) . . . C(2), Rh(2)—C(3) 2.049(10), C(1)—C(2) 1.456(12), C(2)—C(3) 1.415(13) Å.

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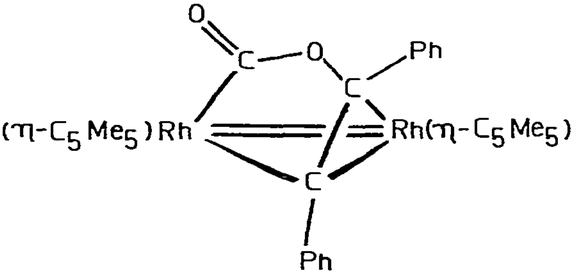
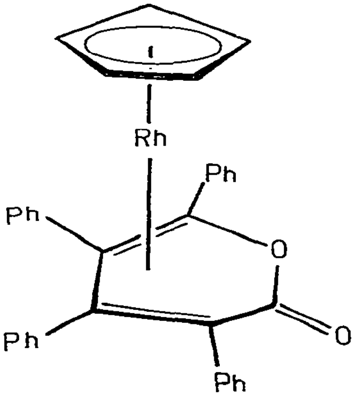
*Atomic coordinates for this work are available from the author.

In the infrared spectrum ($CHCl_3$ solution), $\nu(CO)$ are observed at 1813vs and 1700vs(br) cm^{-1}; the ^1H NMR spectrum shows resonances at δ 3.94 (s, 3H), 3.55 (s, 3H), 1.81 (s, 15H), and 1.75 (s, 15H) ppm. Upon heating solutions of the complex to ca. 100°C, there is considerable broadening of the pair of CO_2Me resonances at δ 3.94 and 3.55 ppm, and coalescence (at ca. 60°C) of the C_5Me_5 resonances at δ 1.81 and 1.75 ppm. This indicates that the molecule is fluxional. Exchange of the C_5Me_5 environments could occur either by rupture of the metal—carbon (ketonic) or the carbon—carbon (ketonic) bond (cf. ref. 4 and 5), and measurement of the ^{13}C NMR spectrum is planned to determine which mechanism is involved. Minor products isolated from this reaction are the *tetrahapto*-benzene complex $(\eta\text{-}C_5Me_5)Rh[\eta^4\text{-}C_6(CO_2Me)_6]$ (ca. 15% yield) and the binuclear metallodiene complex $(\eta\text{-}C_5Me_5)_2Rh_2[C_4(CO_2Me)_4]$ (ca. 6% yield).

Again, an analogous product is obtained from the reaction of $(\eta\text{-}C_5Me_5)_2Rh_2(CO)_2$ and diphenylacetylene. The dark red solid $(\eta\text{-}C_5Me_5)_2Rh_2(\mu\text{-}CO)\{\mu\text{-}\eta^2,\eta^2\text{-}C(O)C_2Ph_2\}$ is isolated in ca. 70% yield and has been characterized by elemental (Found: C, 60.9; H, 5.7. $C_{36}H_{40}O_2Rh_2$ calcd.: C, 60.9; H, 5.7%) and spectroscopic ($\nu(CO)$ at 1794vs and 1667vs cm^{-1} in the IR; δ(Me) at 1.52 and 1.48 in the ^1H NMR) analysis. Other products of different type are obtained also in this system. A dark red complex of formula $(\eta\text{-}C_5Me_5)_2Rh_2\{CO_2C_2Ph_2\}$ is isolated in ca. 12% yield (Found: C, 60.5; H, 6.0. $C_{35}H_{40}O_2Rh_2$ calcd.: C, 60.2; H, 5.8%). A parent ion at *m/e* 698 (3%) is observed in the mass spectrum of this complex, and there is a prominent peak at *m/e* 654 (68%) due to loss of CO_2 from the parent. This and the other spectroscopic properties (IR (CH_2Cl_2), $\nu(CO)$ at 1713m cm^{-1}; ^1H NMR (CD_2Cl_2), δ(Me) at 1.67 and 1.52 ppm) are consistent with a structure such as I.



(I)



(II)

A related mononuclear complex of formula $(\eta\text{-}C_5Me_5)Rh\{CO_2C_4Ph_4\}$ has been obtained in ca. 6% yield (Found: C, 73.3; H, 5.5. $C_{39}H_{35}O_2Rh$ calcd.: C, 73.3; H, 5.5%). In the mass spectrum, prominent peaks are observed at 638 (40%, *P*), 610 (100%, *P* — CO), and 594 (17%, *P* — CO_2). There is a single δ (Me) at 1.44 ppm in the NMR spectrum, and $\nu(CO)$ is observed at 1694s cm^{-1} in the infrared spectrum. These results are consistent with a structure II. The incorporation of [O] in structures I and II is unusual (cf. ref. 7), and further work is needed to establish the source of the oxygen.

The reaction between $(\eta\text{-}C_5Me_5)_2Rh_2(CO)_2$ and decafluorodiphenylacetylene in acetone at 25°C gives $(\eta\text{-}C_5Me_5)_2Rh_2(CO)_2(C_6F_5C_2C_6F_5)$ (75% yield) (Found: C, 49.0; H, 4.1; F, 21.1. $C_{36}H_{30}F_{10}O_2Rh_2$ calcd.: C, 48.6; H, 3.4; F, 21.3%). The spectroscopic properties (e.g. ν(CO) at 1970vs cm^{-1} in the IR and δ(Me) at 1.76(s) ppm in the NMR) are consistent with a $\mu\text{-}\eta^1$ attachment of the alkyne and a *trans*-arrangement of the terminal carbonyls as has been established [8] for $(\eta\text{-}C_5H_5)_2Rh_2(CO)_2(CF_3C_2CF_3)$.We have not been able to induce the complex to undergo transformation to $(\eta\text{-}C_5Me_5)_2Rh_2(\mu\text{-}CO)\{COC_2(C_6F_5)_2\}$.

Similar reactions between $(\eta\text{-}C_5Me_5)_2Co_2(CO)_2$ and alkynes generally give mononuclear complexes such as $(\eta\text{-}C_5Me_5)Co\{C_4(CF_3)_4CO\}$ (79% yield).

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