Interconversion of $\mu(\eta^2)$- and $\mu(\eta^1)$-Alkynyldirhodium Complexes

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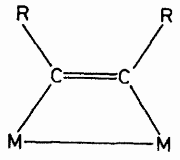
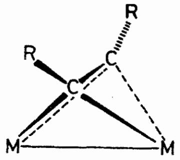
Summary Treatment of $[(\eta^5\text{-}C_5H_5)_2Rh_2(CO)_2\{\mu(\eta^1\text{-}CF_3C_2CF_3)\}]$ (**1**) with Me_3NO produces $[(\eta^5\text{-}C_5H_5)_2Rh_2(\mu\text{-}CO)\{\mu(\eta^2\text{-}CF_3C_2CF_3)\}]$ (**2**) which forms adducts with CO, $AsPh_3$, $P(OMe)_3$, $PMePh_2$, $Ph_2PCH_2CH_2PPh_2$, SO_2, Me_2SO, and Bu^tNC; reaction of (**2**) with alkynes gives binuclear metallodiene and metallodienone complexes and with H_2 under mild conditions yields $CF_3CH_2CH_2CF_3$.

In alkyne–dimetal complexes, the alkyne can adopt either the $\mu(\eta^1)$ (**A**) or the $\mu(\eta^2)$ (**B**) arrangement. Recently, it has been suggested[1,2] that interconversion of these two bonding modes might be an important process in catalysis and cluster chemistry. We have observed such interconversions in our studies of some binuclear hexafluorobut-2-yne-rhodium complexes.

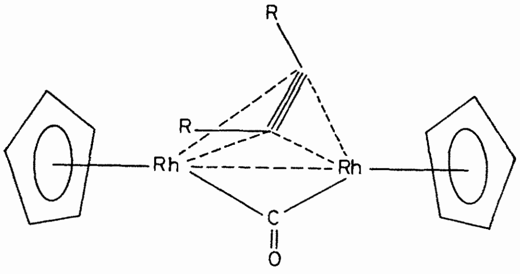
Treatment of *trans*-$[(\eta^5\text{-}C_5H_5)_2Rh_2(CO)_2\{\mu(\eta^1\text{-}CF_3C_2CF_3)\}]$[3] (**1**) with trimethylamine oxide, Me_3NO, in acetone at room temperature yields the green complex $[(\eta^5\text{-}C_5H_5)_2Rh_2(\mu\text{-}CO)\{\mu(\eta^2\text{-}CF_3C_2CF_3)\}]$ (**2**), m.p. 136 °C [i.r.: ν(CO) 1841 (^{13}C, 1800) and ν(C=C) 1592 cm^{-1}; n.m.r.: ^1H ($CDCl_3$, 28 °C) δ 5·79 (s, C_5H_5); ^{19}F ($CDCl_3$, 28 °C) δ 52·16 (dd, CF_3, J_{Rh-F} 2·0 and 1·9 Hz) p.p.m.; ^{13}C ($CDCl_3$, 39 °C) δ 205·1 (t, CO, J_{Rh-C} 41·5 Hz) and 90·4 (s, C_5H_5) p.p.m.; ^{13}C (CD_2Cl_2–CH_2Cl_2, −90 °C) δ 207·6 (t, CO, J_{Rh-C} 40·8 Hz) and 90·1 (s,



(A)



(B)



(2)

C_5H_5) p.p.m.]. The spectroscopic data indicate that (**2**) possesses a bridging carbonyl group and a $\mu(\eta^2)$ alkyne group. The multiplicity observed in the ^{19}F n.m.r. spectrum indicates a twist of the alkyne group from the perpendicular, as has been observed in some $M_2(CO)_6(RC_2R)$ complexes (M = Fe or Co).[4]

Treatment of solutions of (**2**) with CO (1 atm, 20 °C) yields *cis*- and *trans*-(**1**). With Bu^tNC, spontaneous reaction gives the fluxional species $[(\eta^5\text{-}C_5H_5)_2Rh_2(CO)(Bu^tNC)\{\mu(\eta^1\text{-}CF_3C_2CF_3)\}]$ (**3**), m.p. 110 °C [i.r.: ν(CO) 1975, ν(C≡N) 2154, and ν(C=C) 1631 cm^{-1}; n.m.r.: ^1H (CD_2Cl_2, 28 °C) δ 5·40 (s, C_5H_5) and 1·41 (s, Bu^t); ^1H (CD_2Cl_2, −88 °C) δ 5·49 (s, C_5H_5), 5·37 (s, C_5H_5), (coalescence at −18 °C), and 1·41 (s, Bu^t); ^{19}F ($CDCl_3$–$CFCl_3$, 28 °C) δ 54·9 (br, s, CF_3) p.p.m.; ^{19}F ($CDCl_3$–$CFCl_3$, −65 °C) 54·6 (br m, CF_3) p.p.m.; ^{13}C (CD_2Cl_2, 57 °C) δ 191·8 (t, CO, J_{Rh-C} 41·2 Hz), 88·5 (s, C_5H_5), and 31·1 (s, Bu^t) p.p.m.; ^{13}C (CD_2Cl_2, −63 °C) δ 192·0 (d, CO, J_{Rh-C} 82·4 Hz), 89·4 (s, C_5H_5), 87·1 (s, C_5H_5), and 31·3 (s, Bu^t) p.p.m.]. At room temperature, the carbonyl and isonitrile ligands of (**3**) are scrambling over the two rhodium atoms, presumably by the pairwise bridge closing and opening mechanism that has been proposed for (**1**).[5]

The compounds $[(\eta^5\text{-}C_5H_5)_2Rh_2(CO)(L)\{\mu(\eta^1\text{-}CF_3C_2CF_3)\}]$, (**4**)—(**8**), are obtained by treatment of (**2**) with L (L = $AsPh_3$, $P(OMe)_3$, $PMePh_2$, SO_2, or Me_2SO, respectively). With $Ph_2PCH_2CH_2PPh_2$ (dppe), two compounds are isolated depending on the molar ratio of reactants. With equimolar amounts of (**2**) and dppe, the major product is $[(\eta^5\text{-}C_5H_5)_2Rh_2(CO)(dppe)\{\mu(\eta^1\text{-}CF_3C_2CF_3)\}]$ (**9**). With an excess of (**2**), a second product $[(\eta^5\text{-}C_5H_5)_2Rh_2(CO)\{\mu(\eta^1\text{-}CF_3C_2CF_3)\}]_2(dppe)$ (**10**) is obtained. Compounds (**4**)—(**10**) are orange-red, air stable, solids each exhibiting a single terminal carbonyl peak in the i.r. spectrum together with a peak near 1630 cm^{-1} which is assigned to the $\mu(\eta^1)$ alkyne group. The SO_2 complex (**7**) decomposes on heating to regenerate (**2**), and the Me_2SO complex (**8**) is converted into (**2**) by extraction of its chloroform solution with water. Oxidation of (**4**) in chloroform slowly yields (**2**) and Ph_3AsO.

Major products obtained from the reactions of (**2**) with RC≡CR (R = CH_3, CF_3, or Ph) are the bridging metallodiene complexes $[(\eta^5\text{-}C_5H_5)_2Rh_2\{C_4(CF_3)_2R_2\}]$, and the bridging pentadienone complexes $[(\eta^5\text{-}C_5H_5)_2Rh_2\{C_4(CF_3)_2R_2CO\}]$.

In contrast to some co-ordinatively saturated μ–η^2 alkyne–dimetal complexes studied by Muetterties *et al.*,[6] (**2**) reacts readily with H_2 (1 atm, 20 °C) to give a variety of products including $CF_3CH_2CH_2CF_3$, $(\eta^5\text{-}C_5H_5)_3Rh_3(CO)(CF_3C_2CF_3)$, $(\eta^5\text{-}C_5H_5)_3Rh_3(CO)_3$, $(\eta^5\text{-}C_5H_5)_4Rh_4(CO)_2$, and multinuclear hydrido-rhodium species.

We thank the Australian Research Grants Committee for financial support (R. S. D.), and the Australian Government for a Post-graduate Award (G. N. P.). We thank J. Weigold and M. Hughes for the n.m.r. spectra.

(*Received*, 4*th December* 1978; *Com.* 1292.)

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