

Alkene Fragmentation at a Dimetal Centre; X-Ray Crystal Structure and Protonation of the Bridged Carbene Complex $[\text{Rh}_2(\mu\text{-CO})\{\mu,\mu\text{-}(\text{CHCMe}_2\text{CHCO})\}(\eta\text{-C}_5\text{Me}_5)_2]$

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Reaction of $[\text{Rh}_2(\mu\text{-CO})_2(\eta\text{-C}_5\text{Me}_5)_2]$ with 3,3-dimethylcyclopropene results in the cleavage of the carbon-carbon double bond, and the formation of the bridged carbene complex $[\text{Rh}_2(\mu\text{-CO})\{\mu,\mu\text{-}(\text{CHCMe}_2\text{CHCO})\}(\eta\text{-C}_5\text{Me}_5)_2]$, which was structurally identified by X-ray crystallography, and shown to undergo selective carbon-rhodium bond cleavage on treatment with $\text{CF}_3\text{CO}_2\text{H}$.

The cleavage of carbon-carbon bonds in cyclopropenium cations and cyclopropenones by transition metal species is well established,¹ and has been the subject of a theoretical study.² In contrast, cyclopropenes have received less attention, and it is interesting that in the reactions that have been reported to date, either the three-membered ring remains intact³ or the 2,3-carbon-carbon single bond is broken,⁴ there being no examples of reactions involving the fragmentation of the carbon-carbon double bond, a process which could in principle² generate a dicarbene ligand. We wish to report an example of such a reaction at a dimetal centre.

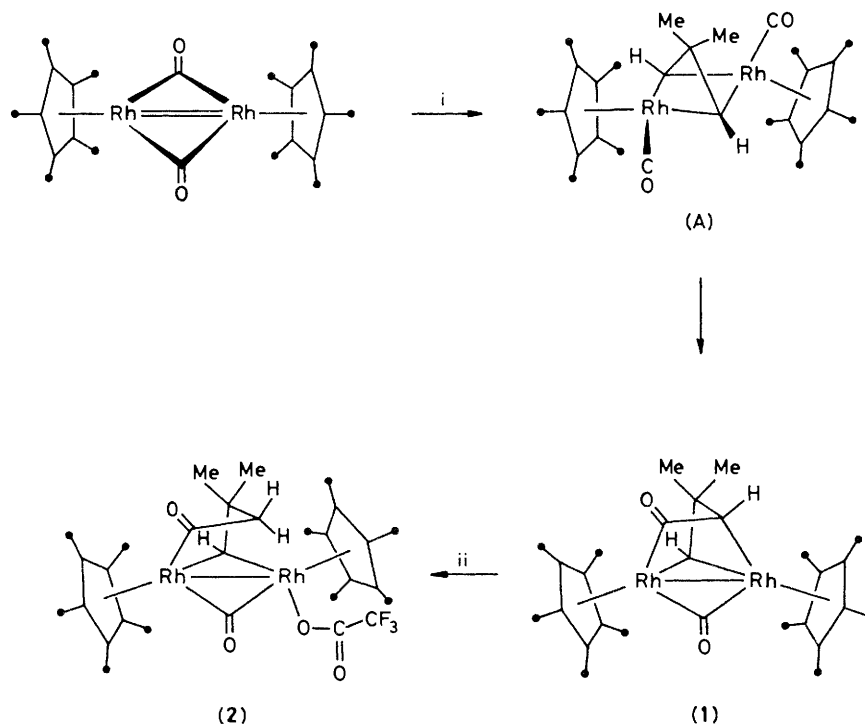
3,3-Dimethylcyclopropene rapidly reacts at 0 °C with $[\text{Rh}_2(\mu\text{-CO})_2(\eta\text{-C}_5\text{Me}_5)_2]$ (ref. 5) in methylene chloride or hexane as solvent to give in quantitative yield the red crystalline complex (**1**) (i.r. ν_{CO} 1 809 s, 1 683 m cm^{-1} (hexane). N.m.r.: ¹H (C_6D_6), δ 1.12 (3H, s, Me), 1.55 (3H, s, Me), 1.62 [15H, d, ³J(RhH) 0.48 Hz, C_5Me_5], 1.79 [15H, d, ³J(RhH) 0.48 Hz, C_5Me_5], 2.55 [1H, t, ²J(Rh¹H) 2.5, ⁴J(HH) 2.8 Hz, CH], 9.46 [1H, dt, ²J(Rh¹H) 2, ²J(Rh²H) 2, ⁴J(HH) 2.8 Hz, CH]; ¹³C {¹H} (C_6D_6), δ 216.32 [d, ¹J(Rh²C) 23 Hz, CO], 178.50 [dd, ¹J(RhC) 31.74, ¹J(RhC) 19.53 Hz, CH], 101.38 [d, ¹J(RhC) 3.91 Hz, C_5Me_5], 101.22 [d, ¹J(RhC) 3.91 Hz, C_5Me_5], 55.84 [d, ¹J(RhC) 4.88 Hz, CMe_2], 53.58 [d, ¹J(Rh¹C) 17.09 Hz, CH], 35.75 (s, Me), 28.99 (s, Me), 10.02 (s, C_5Me_5), and 9.39 p.p.m. (s, C_5Me_5). Whilst the spectroscopic data indicated that (**1**) was a 1 : 1 adduct of the reactants, and that a carbonyl insertion reaction had occurred, there was an apparent ambi-

guity in that ¹H-¹H coupling of 2.8 Hz was observed between the two CH groups originating in the 3,3-dimethylcyclopropene, suggesting that the 3-membered ring might still be intact. An X-ray crystal structure† clarified the problem.

Crystal data for (1): $\text{C}_{27}\text{H}_{38}\text{O}_2\text{Rh}_2$, $M = 600.1$, monoclinic, space group $P2_1/c$, $a = 14.544(7)$, $b = 9.280(5)$, $c = 19.258(8)$ Å, $\beta = 102.28(4)^\circ$, $U = 2\ 540(2)$ Å³, $Z = 4$, $D_c = 1.57$ g cm^{-3} , $F(000) = 1\ 224$, $\mu(\text{Mo-K}\alpha) = 12.99$ cm^{-1} , $\lambda = 0.71069$. Current R 0.050 (R_w 0.051) for 3 201 unique observed [$I > 2\sigma(I)$] reflections measured in the range $3 \leq 2\theta \leq 50^\circ$ at 250 K on a Nicolet $P2_1$ diffractometer. The structure was refined by blocked-cascade least squares with all non-hydrogen atoms anisotropic; hydrogen atoms being ascribed idealised geometries and refined isotropically.

The structure of (**1**) is shown in Figure 1, and consists of two $\text{Rh}(\eta\text{-C}_5\text{Me}_5)$ units linked by a metal-metal single bond of 2.624(2) Å, a length typical^{6,7} in bridged dirhodium structures. In this case the rhodium atoms are bridged by one carbonyl ligand, and an unusual ligand containing a four carbon chain and derived presumably from a carbonyl 'insertion' into one of the four rhodium-carbon σ -bonds of

† The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.



Scheme 1. Reagents and conditions: i, 3,3-dimethylcyclopropene; ii, $\text{CF}_3\text{CO}_2\text{H-Et}_2\text{O}$, -78°C .

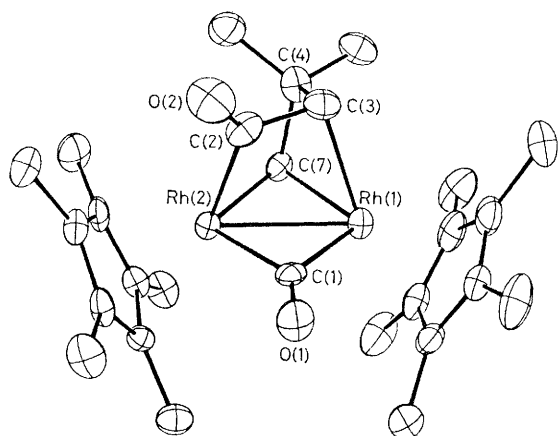


Figure 1. Molecular structure of $[\text{Rh}_2(\mu\text{-CO})\{\mu, \mu\text{-}(\text{CHCMe}_2\text{-CHCO})\}(\eta\text{-C}_5\text{Me}_5)_2]$. Dimensions: Rh(1)–Rh(2) 2.624(2), Rh(1)–C(7) 2.059(8), Rh(2)–C(7) 2.050(8), Rh(1)–C(3) 2.191(9), Rh(2)–C(2) 2.065(8), Rh(1)–C(1), 1.988(8), Rh(2)–C(1) 2.010(7), C(2)–O(2) 1.215(10), and C(1)–O(1) 1.189(8) Å.

the doubly bridged dicarbene intermediate (A) (see Scheme 1), which we believe is formed upon interaction of the cyclopropene with the unsaturated dirhodium species $[\text{Rh}_2(\mu\text{-CO})_2(\eta\text{-C}_5\text{Me}_5)_2]$. This ligand still possesses one bridging carbene, in which the carbene carbon atom C(7) is symmetrically disposed between the rhodium atoms [Rh(1)–C(7) 2.059(8), Rh(2)–C(7) 2.050(8) Å]. As a result of the carbonyl 'insertion' the other carbene moiety has become singly bonded to just one of the metal atoms [Rh(1)–C(3) 2.191(9) Å], which is considerably longer than most Rh–C σ -bonds. The metal-acyl bond [Rh(2)–C(2) 2.065(8) Å] is similar to other rhodium-acyl bond distances.^{10,11}

Studies of the thermal decomposition of bridged dicarbene complexes in di- and tri-metal complexes have been shown^{12,13} to lead to the formation of olefins, and it has been suggested¹⁴ that such reactions are important in Fischer–Tropsch chem-

istry. The fragmentation¹⁵ of the double bond of 3,3-dimethylcyclopropene may be viewed as the reverse of this reaction, and as such is particularly interesting. It is suggested that this facile reaction takes place at a dimetal centre, and consideration of the frontier orbitals^{16,17} of $[\text{Rh}_2(\text{CO})_2(\eta\text{-C}_5\text{H}_5)_2]$ (either doubly carbonyl bridged or with two terminal carbonyl ligands) indicates that there are frontier acceptor and donor molecular orbitals of appropriate symmetry to interact with the cyclopropene π and π^* orbitals when orientated transversely above the Rh–Rh vector as in Scheme 1. Further in the unbridged form of $[\text{Rh}_2(\text{CO})_2(\eta\text{-C}_5\text{H}_5)_2]$ there is a filled d-block donor orbital (π_x in Hofmann's notation) of suitable symmetry to combine with the σ^* orbital of the C=C unit, thus additionally weakening this bond. Preliminary studies have shown that 3,3-dimethylcyclopropene also undergoes facile reactions with $[\text{Co}_2(\mu\text{-CO})_2(\eta\text{-C}_5\text{Me}_5)_2]$ and $[\text{CoRh}(\mu\text{CO})_2(\eta\text{-C}_5\text{Me}_5)_2]$ (ref. 18) to form the Co_2 and CoRh analogues of (1), the reactivity sequence $\text{CoRh} > \text{Rh}_2 > \text{Co}_2$ being observed.

In an initial study of the chemistry of the molecule (1), which contains four different rhodium–carbon bonds in a tricyclic system containing a bridging keten, the reaction with protons was examined. In diethyl ether as solvent trifluoroacetic acid reacts with (1) to afford in quantitative yield the red-purple complex (2). Examination of the i.r. and n.m.r. spectra \ddagger of (2) showed that a regioselective reaction had

\ddagger Spectral data for complex (2): ν_{CO} 1 853 m, 1 681 br. cm^{-1} (CH_2Cl_2). N.m.r. (CDCl_3): ^1H , δ 10.93 [1H, dt, $^4J(\text{HH})$ 1.46, $^2J(\text{RhH})$ 2.2 Hz, CH], 2.38 [1H, AB quartet, $^2J(\text{HH})$ 18.5, $^4J(\text{HH})$ 1.46 Hz, CH_2], 2.73 [1H, AB quartet, $^2J(\text{HH})$ 18.5 Hz, CH_2], 1.82 (15H, s, C_5Me_5), 1.65 (15H, s, C_5Me_5), 1.55 (3H, s, Me), 1.47 (3H, s, Me); ^{13}C { ^1H }, δ 237.36 [d, CO(acyl)] $^1J(\text{RhC})$ 31.74 Hz], 222.06 [dd, $^1J(\text{RhC})$ 36.62, $^1J(\text{RhC})$ 51.27 Hz, $\mu\text{-CO}$], 215.5 [dd, $^1J(\text{RhC})$ 27.34, $^1J(\text{RhC})$ 31.25 Hz, CH], 161.0 [q, $^2J(\text{FC})$ 31.74 Hz, CF_3CO_2], 114.48 [q, $^1J(\text{FC})$ 290.5 Hz, CF_3], 104.92 [d, $^1J(\text{RhC})$ 3.9 Hz, C_5Me_5], 102.1 [d, $^1J(\text{RhC})$ 5.86 Hz, C_5Me_5], 69.56 (s, CH_2), 49.71 (s, CMe_2), 36.04 (s, Me), 25.58 (s, Me), 9.77 (s, C_5Me_5), and 9.33 p.p.m. (s, C_5Me_5); ^{19}F , δ -75.03 p.p.m. (s, CF_3CO_2). In acetone as solvent the complex showed zero conductivity.

occurred leading to protolytic cleavage of the longest Rh–C σ -bond, which is part of the μ -keten system. It is interesting that attack does not occur at the electron rich dirhodiacyclopropane¹⁷ centre as has been observed¹⁹ with the simple μ -methylene complex $[\text{Rh}_2(\mu\text{-CH}_2)(\text{CO})_2(\eta\text{-C}_5\text{H}_5)_2]$.

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