Synthesis of μ-Carbene Complexes of Rhodium from Substituted Diazirines

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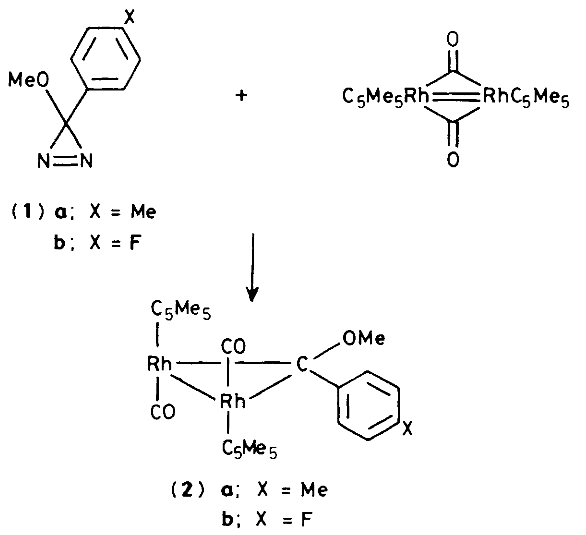
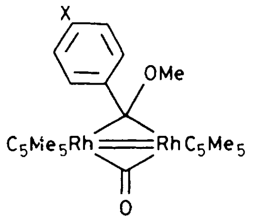
The reaction of aryl(methoxy)diazirines with $[(\eta^5\text{-}C_5Me_5)_2Rh_2(\mu\text{-}CO)_2]$ yields $[(\eta^5\text{-}C_5Me_5)_2Rh_2(CO)_2\{\mu\text{-}C(OMe)Ar\}]$ in near quantitative yield; the complex with Ar = $4\text{-}FC_6H_4$ has been characterised by *X*-ray diffraction.

There has been considerable interest in the synthesis of μ-carbene complexes[1] because of their significance in catalytic reactions and as models for carbene species bonded to metal surfaces. We now report a new approach to the synthesis of such species, which should be adaptable to the preparation of a wide range of complexes with varying substituion. Dropwise addition of a cooled (−30 °C) solution in pentane of an aryl(methoxy)diazirine (**1**)[2] to $[(\eta^5\text{-}C_5Me_5)_2Rh_2(\mu\text{-}CO)_2]$[3] in dichloromethane at room temperature over 3—4 h resulted in a colour change to deep red, and on evaporation of the solvent a reddish-brown solid was obtained. Spectroscopic data indicated quantitative conversion into the μ-carbene complex (**2**), but this was difficult to isolate from the decomposition products of the diazirine owing to its very high solubility. Crystallisation (CH_2Cl_2/EtOH, −78 °C) gave (**2**) as a deep reddish-purple crystalline solid in about 65% isolated yield. I.r. data (KBr) for (**2a**) and (**2b**) clearly indicate that the carbonyl groups are terminal [(**2a**) ν 1961 and 1942 cm^{-1}; (**2b**) 1967 and 1938 cm^{-1}]. This is supported by a variable temperature ^{13}C n.m.r. study of (**2a**), which allows us to

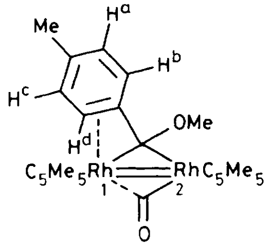


(**1**) **a**; X = Me
b; X = F

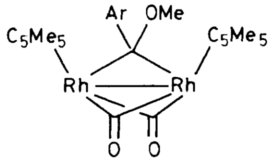
(**2**) **a**; X = Me
b; X = F



(3) a; X = Me
b; X = F



(4)



(5)

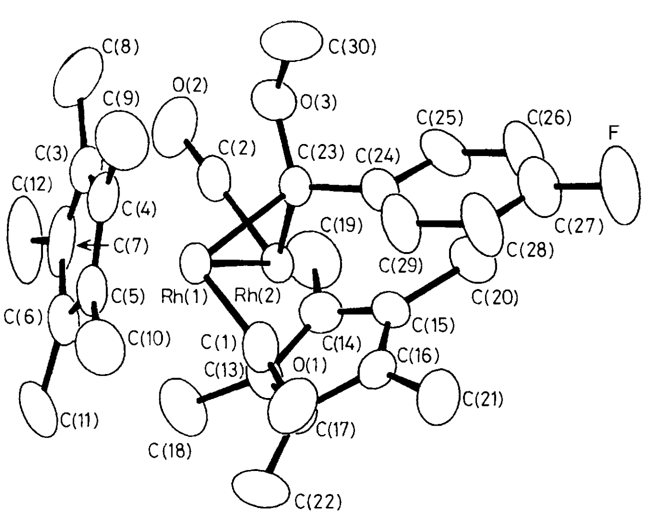


Figure 1. Molecular structure of $[(\eta^5\text{-}C_5Me_5)_2Rh_2\{\mu\text{-}C(OMe)C_6H_4\text{-}4\text{-}F\}(CO)_2]$ (**2b**): dimensions Rh(1)–Rh(2) 2.639(1), Rh(1)–C(1) 1.785(11), Rh(1)–C(23) 2.081(10), Rh(2)–C(23) 2.079(10), Rh(2)–C(2) 1.777(11), O(1)–C(1) 1.152(14), O(2)–C(2) 1.164(14), C(23)–O(3) 1.394(13) Å; Rh(2)–Rh(1)–C(1) 91.7(4), Rh(2)–Rh(1)–C(23) 50.6(3), C(1)–Rh(1)–C(23) 93.4(4), Rh(1)–Rh(2)–C(2) 91.7(3), Rh(1)–Rh(2)–C(23) 50.7(3), Rh(1)–C(1)–O(1) 171(1), Rh(2)–C(2)–O(2) 173(1), Rh(1)–C(23)–Rh(2) 78.8(4)°.

postulate that two dynamic processes involving the carbonyl ligands occur. At ambient temperature a broad signal is observed (δ 198.5) due to both carbonyl groups. On cooling to 252 K two distinct carbonyl resonances may be observed (δ 198.2 and 196.5, both typical of terminal carbonyl groups). Both are triplets (*J* 45 Hz) due to rhodium coupling, and this spectrum remains unchanged at 193 K. There are two possible explanations for the appearance of the carbonyl signals as triplets. It is possible that we are observing direct coupling to one rhodium nucleus and virtual coupling to the other. Alternatively, the carbonyls may migrate from one rhodium atom to the other, this process still being rapid at 193 K. The work of Stone[4] on related compounds suggests that the latter explanation is correct; in $[(\eta^5\text{-}C_5Me_5)_2Rh_2(\mu\text{-}CHR)(CO)_2]$ (R = H or CO_2Et) the dynamic exchange was slowed sufficiently at 233 K that the carbonyl signals were observed as rhodium-coupled doublets, implying that virtual coupling is not observed in such systems. It is noteworthy that despite migration between the rhodium nuclei, the carbonyl groups remain stereochemically distinct at 253 K. It is likely that the dynamic process observed at room temperature involves migration between the two faces of the three-membered ring.†

Careful crystallisation of (**2b**) from ethanol yielded dark red prisms suitable for an *X*-ray diffraction study.‡ The structure (Figure 1) confirms that the carbonyl groups are terminal, with no semi-bridging character. The carbene moiety is bridging with no apparent interaction between the methoxy group and either metal atom.[5] The metal–metal bond is similar in length with those in related structures[6,7] and there are no unexpectedly short non-bonding distances.

Thermolysis of (**2**) (refluxing toluene, purging with N_2, 5 h) yielded a deep blue–green solution. Removal of the solvent and recrystallisation (pentane, −78 °C) gave the complex (**3**) in 60% yield as moderately air-sensitive blue–black microcrystals [(**3a**) m.p. 208 °C (decomp.) in N_2]. I.r. data show that the carbonyl is now bridging [(**3a**) ν 1762 cm^{-1}]. Mass spectrometry (fast atom bombardment; 3-nitrophenylmethanol) allowed the observation of a molecular ion, *m/z* 638. Whilst a significant M^+ peak could be observed for (**2a**) (by electron impact; by chemical ionisation, MH^+ was observed) the largest peak in the spectrum was that corresponding to (**3a**), indicating that CO loss takes place readily. At room temperature the ^1H n.m.r. spectrum of (**3a**) (CD_2Cl_2) showed only a broad featureless signal for the hydrogen atoms attached to the aryl ring. On cooling (C_7D_8) this was readily resolved into four distinct signals, indicating restricted rotation about the C–aryl bond. Which pairs of signals were exchanging was established both by warming the solution and by a saturation transfer experiment at 293 K, and the signals due to H_a and H_c were identified by the observation of a nuclear Overhauser effect from the CH_3 group. Corresponding observations were made in the ^{13}C n.m.r. spectrum. We suggest that the restricted rotation arises from a weak interaction of the aryl ring with one of the rhodium atoms, as in (**4**), resulting in the non-equivalence of the two 'sides' of the aryl moiety.§ There have been a number of precedents for such interactions in homometallic[8] and heterometallic[9] complexes of this type. The additional electron density at Rh(1)

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† The signal for the carbenic carbon [δ 192.0, *J*(CRh) 37 Hz] was unchanged over the temperature range studied.

‡ *Crystal data:* (**2b**) $C_{30}H_{37}FO_3Rh_2$, M = 670.4, monoclinic, space group $P2_1/n$, a = 9.693(2), b = 16.883(2), c = 17.484(2) Å, β = 98.65(2)°, U = 2828.5 Å^3, Z = 4, D_c = 1.57 g cm^{-3}, monochromated Mo-K_α radiation, λ = 0.71069 Å, μ = 11.8 cm^{-1}. Data were collected with an Enraf-Nonius CAD4 diffractometer. A total of 5719 reflections were measured in the range $2 < \theta < 25°$ and $+h + k \pm l$, and 2565 unique reflections with $|F^2| > \sigma(F^2)$ were used in the refinement. There was no crystal decay and no absorption correction was made. The structure was solved by routine heavy atom methods and refined by full-matrix least-squares techniques with non-hydrogen atoms anisotropic. Hydrogen atoms were omitted. The weighting scheme was $w = 1/\sigma^2(F)$ and the final residuals were R = 0.045, R' = 0.053. Atomic co-ordinates, bond lengths and angles, and temperature factors have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

§ The ^1H n.m.r. signals may be tentatively assigned as δ 6.92 (H_c), 7.11 (H_a), 8.08 (H_b), and 6.40 (H_d).

provided by the arene may be partially offset by some semibridging character in the Rh(1)–CO bond.[10]

Although the mechanism of the reaction between the diazirine and $[(\eta^5\text{-}C_5Me_5)_2Rh_2(\mu\text{-}CO)_2]$ has not been fully established, it is worthy of note that no reaction occurs below the temperature at which the diazirine decomposes to give the aryl(methoxy)carbene.[2] This is in contrast to the previously reported carbene synthesis from $W(CO)_5$.[11] Optimal yields and minimum amounts of carbene and azine dimers were obtained with slow addition of the diazirine to the rhodium precursor. This strongly suggests that the synthesis represents an unprecedented capture of a free carbene by a transition metal complex. The species initially formed is probably (**5**), which isomerises under the reaction conditions to (**2**).[7]

We thank the S.E.R.C. for financial support (to S.A.B.), Johnson Matthey plc for the loan of rhodium salts, and ICI Pharmaceuticals for two mass spectrometric determinations.

Received, 2nd April 1987; Com. 427

References

1 W. A. Herrmann, *Adv. Organomet. Chem.*, 1982, **20**, 160.
2 J. Włostowska, R. A. Moss, W. Guo, and M. J. Chang, *J. Chem. Soc., Chem. Commun.*, 1982, 432.
3 A. Nutton and P. M. Maitlis, *J. Organomet. Chem.*, 1979, **167**, C21.
4 M. Green, R. M. Mills, G. N. Pain, F. G. A. Stone, and P. Woodward, *J. Chem. Soc., Dalton Trans.*, 1982, 1309.
5 E. O. Fischer, E. Winkler, G. Huttner, and D. Regler, *Angew. Chem., Int. Ed. Engl.*, 1972, **11**, 238.
6 W. A. Herrmann, C. Bauer, G. Kriechbaum, H. Kunkeley, M. L. Ziegler, D. Speth, and E. Guggolz, *Chem. Ber.*, 1982, **115**, 878.
7 W. A. Herrmann, C. Bauer, J. Plank, W. Kalcher, D. Speth, and M. L. Ziegler, *Angew. Chem., Int. Ed. Engl.*, 1981, **20**, 193.
8 D. L. Davies, A. F. Dyke, S. A. R. Knox, and M. J. Morris, *J. Organomet. Chem.*, 1981, **215**, C30.
9 J. C. Jeffery, J. C. V. Laurie, I. Moore, H. Razay, and F. G. A. Stone, *J. Chem. Soc., Dalton Trans.*, 1984, 1563.
10 L. Messerle and M. D. Curtis, *J. Am. Chem. Soc.*, 1980, **102**, 7789.
11 P. A. Chaloner, G. D. Glick, and R. A. Moss, *J. Chem. Soc., Chem. Commun.*, 1983, 880.