The Synthesis, Structure, and Reactivity of a Di-rhenium Octacarbonyl μ-Carbene Complex; Molecular Structure of $[Re_2\{\mu-(\eta^1,\eta^3-CH\cdot CH\cdot CMe_2)\}(CO)_8]$

Michael Green, A. Guy Orpen, Colin J. Schaverien, and Ian D. Williams
Department of Inorganic Chemistry, The University, Bristol BS8 1TS, U.K.

Reaction of $[Re_2(\mu\text{-}H)(\mu\text{-}CH{=}CHEt)(CO)_8]$ with 3,3-dimethylcyclopropene leads to C–C bond cleavage and formation of the μ-carbene complex $[Re_2\{\mu-(\eta^1,\eta^3-CH\cdot CH\cdot CMe_2)\}(CO)_8]$; this reacts with CO to form $[Re_2\{\mu-(\eta^1,\eta^3-CH\cdot CH\cdot CMe_2)\}(CO)_9]$, which on u.v. irradiation undergoes C–H bond cleavage with formation of the η^1,η^2-butadienyl hydride $[Re_2(\mu\text{-}H)(\mu\text{-}CH{=}CH\cdot CMe{=}CH_2)(CO)_8]$.

Molecules which contain two transition metal centres bridged by carbene ligands have attracted attention because of their possible role in catalytic reactions and their potential for unusual chemical reactivity.[1] In seeking to understand the role of the metal to metal interaction in the reactions of such species we have begun to explore the chemistry of the Re(μ-carbene)Re system. We have gained access to such species by the reaction of 3,3-dimethylcyclopropene with the molecule $[Re_2(\mu\text{-}H)(\mu\text{-}CH{=}CHEt)(CO)_8]$ (**1**).[2]

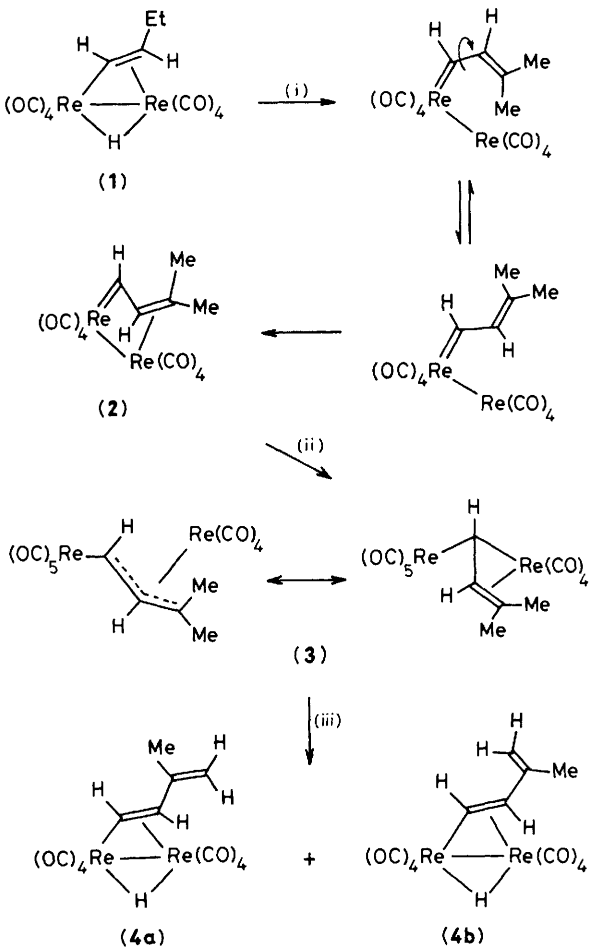
Treatment (room temperature) of a solution of (**1**) with an excess of 3,3-dimethylcyclopropene led to the formation (2 days, 80%) of the yellow crystalline di-rhenium complex (**2**), which was shown by i.r., mass, and n.m.r.† spectroscopy to be a 1 : 1 adduct of the cyclopropene and a $[Re_2(CO)_8]$ fragment, presumably generated by the reductive elimination of but-1-ene from (**1**). In contrast to the behaviour of unstrained olefins[2] on reaction with (**1**), this adduct is formed by oxidative addition of a ring C–C σ-bond to the di-rhenium unit rather than of a C–H bond. The molecular structure of (**2**) was established by single crystal *X*-ray crystallography.‡

The molecular structure of (**2**) is illustrated in Figure 1, which shows the atomic numbering scheme. Two $Re(CO)_4$

---

† Spectroscopic data for (**2**): ν_{CO} 2 097w, 2 059m, 2 000vs, 1 985s, 1 973m, 1 961m, and 1 941s cm^{-1} (hexane); n.m.r. ($CDCl_3$): ^1H, δ 7.65 [d, 1 H, CH, ^3J(HH) 11.45 Hz], 4.53 [d, 1 H, CH, ^3J(HH), 12.45 Hz], 2.09 (s, 3 H, Me), and 1.94 (s, 3 H, Me); ^{13}C-$\{^1H\}$, δ 195.1, 193.4, 191.9, 190.0, 188.9, 187.3, 186.9, 185.8 (8 × CO), 139.0 [CH, ^1J(CH) 138 Hz], 105.3 [CH, ^1J(CH) 156.3 Hz], 90.2 (CMe_2), 29.2 (Me), and 23.3 (Me) p.p.m.

‡ *Crystal data* for (**2**): $C_{13}H_8O_8Re_2$, M = 664.6, monoclinic, space group $P2_1/c$ (No. 14), a = 8.576(3), b = 9.682(7), c = 19.623(10) Å, β = 99.54(3)°, U = 1 607(2) Å^3, Z = 4, D_c = 2.75 g cm^{-3}, $F(000)$ = 1200, μ(Mo-K_α) 153 cm^{-1}. The structure was solved by heavy atom (Patterson and Fourier) methods and refined by a least-squares procedure. For 2314 unique observed intensities [$I > 2\sigma(I)$] measured at 293 K on a Nicolet P3m diffractometer in the range $3 \leqslant 2\theta \leqslant 50°$, the current residual R is 0.0415 (R_w 0.0422). Hydrogen atoms were given fixed geometries with the exception of H(9) and H(10) which were refined freely. The atomic co-ordinates for this structure 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 communcation.



Scheme 1. (i) Addition of 3,3-dimethylcyclopropene, loss of but-1-ene; (ii) addition of CO; (iii) u.v. irradiation.

units are bridged by a μ-allylidene ligand formed by ring-opening of the cyclopropene. The metal–metal distance [3.058(1) Å] is consistent[2–4] with a formal Re–Re single bond as required by the total of 34 valence electrons around the dimetal unit. The μ-CH·CH·CMe$_2$ moiety is η^1-bonded to Re(1) [Re(1)–C(9) 2.109(11) Å] and η^3-bonded to Re(2) [Re(2)–C(9) 2.353(11), Re(2)–C(10) 2.281(11), Re(2)–C(11) 2.494(13) Å]. Clearly the μ-carbenoid carbon, C(9), bridges the di-rhenium unit in a highly asymmetric fashion, the bond to Re(1) being of the same order, *i.e.* between one and two, as those found in rhenium formyl[5] and methoxy carbene complexes.[6] The relatively long Re(2)–C(9) distance presumably reflects the imbalance in the formal electron count at Re(1) and Re(2) if the binding of the allylidene is as in (A). In view of these geometric characteristics the bonding in (2) is perhaps more satisfactorily represented by (B) where the Re(1)(CO)$_4$·CH·CH·CMe$_2$ moiety binds as a 'metallabutadiene' to the Re(2)(CO)$_4$ unit. This 'metallabutadiene' is the *E* isomer, *i.e.* has the previously olefinic hydrogens H(9) and H(10) mutually *trans*. In contrast we have previously[7] observed ring opening of the 2,3 σ-bond of 3,3-dimethylcyclopropene to give a *cis* pattern of hydrogens in a dimolybdenum (μ-allylidene) complex. The formation of (2) implies rotation about the former 1,2 double bond of the cyclopropene, presumably after ring opening.

Reaction of (2) with carbon monoxide (100 atm, room temperature) leads to metal–metal bond cleavage and formation of (3) (75% yield), a di-rhenium complex characterised by i.r., n.m.r., and mass spectrometry§ (see Scheme 1). This complex is unusual in that it contains a μ-carbene system not supported by a metal–metal bond, a moiety observed before, in [Pt$_2$Cl$_2$(dppm)$_2$(μ-CH$_2$)][8] (dppm = Ph$_2$PCH$_2$PPh$_2$) and [Ru$_2$(μ-CH$_2$)(CO)$_4$(η-C$_5$H$_5$)$_2$].[9] In the latter the μ-CH$_2$ ^{13}C resonance occurs at −35 p.p.m. in marked contrast to the high frequency shifts observed[1] for $\overline{M(\mu\text{-}CH_2)M}$ systems. In (3) the μ-carbene ^{13}C resonance is likewise shifted to low frequency [21.7 p.p.m.; *cf.* 139.0 p.p.m. for (2)].

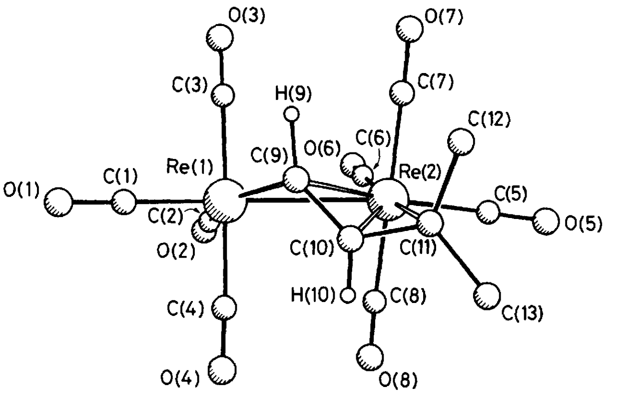
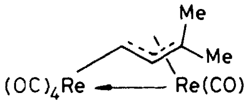
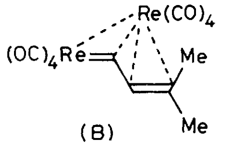


Figure 1. Molecular structure of [Re$_2${μ-(η^1,η^3-CH·CH·CMe$_2$)}(CO)$_8$] (2). Important molecular parameters are Re(1)–Re(2) 3.058(1), Re(1)–C(9) 2.109(11), Re(2)–C(9) 2.353(11), Re(2)–C(10) 2.281(11), Re(2)–C(11) 2.494(13), C(9)–C(10) 1.441(16), C(10)–C(11) 1.385(18) Å; bond angles Re(1)–C(9)–C(10) 123.1(7), C(9)–Re(2)–C(10) 36.2(4), C(9)–C(10)–C(11) 125.8(11)°; torsion angles C(3)–Re(1)–Re(2)–C(7) 18.6, C(4)–Re(1)–Re(2)–C(8) 26.7, C(2)–Re(1)–Re(2)–C(6) 26.7°.



(A)



(B)

The formation of (3) from (2) is in sharp contrast to the behaviour of other μ-allylidene complexes (*e.g.* see ref. 10) where dissociation of the vinyl group to form μ-η^1 carbene complexes has been observed on addition of CO.

Irradiation of (3) might be expected to result in loss of carbon monoxide and regeneration of (2). However, a more interesting reaction occurs on irradiation (u.v., 2 h, room temperature, hexane) resulting in the formation of the di-rhenium, η^1,η^2-butadienyl hydride (4),¶ which exists in solution as two rotameric species [(4a) and (4b), see Scheme 1].

---

§ Spectroscopic data for (3): ν_{CO} 2 069w, 2 021s, 2 017sh, 1 985m, 1 977m, 1 963m, and 1 941m cm^{-1} (hexane); n.m.r. (CDCl$_3$): ^{1}H, δ 4.83 [d, 1 H, CH, ^3J(HH) 14.65 Hz], 2.52 [d, 1 H, CH, ^3J(HH) 14.65 Hz], 2.08 (s, 3 H, Me), and 1.74 (s, 3 H, Me); ^{13}C-{^{1}H}, δ 195.06, 193.56, 192.76, 191.73 (4 × CO), 183.12(4 CO), 179.68 (CO), 111.73 [*C*H, ^1J(CH) 152.7 Hz], 67.77 (*C*Me$_2$), 32.3 (Me), 25.2 (Me), and 21.7 p.p.m. [*C*H, ^1J(CH) 138 Hz].

Note added in proof: we have determined the crystal structure of (3), which shows the expected geometric features with an Re···Re separation of 4.190(1) Å and Re–(μ-C)–Re angle 128.5(4)° [*cf.* 86.3(4)° in (2)].

¶ Spectroscopic data for (4): ν_{CO} 2 105vw, 2 079w, 2 009s, 1 989m, 1 975s, and 1 961m cm^{-1}; n.m.r. (CDCl$_3$): ^{1}H, major isomer (2:1), δ 7.50 (m, 2 H, CH$_2$), 6.68 [d, 1 H, CH, *J*(HH) 16.4 Hz], 6.00 [d, 1 H, CH, *J*(HH) 16.4 Hz], 1.67 (s, 3 H, Me), and −14.28 [s, 1 H, Re(μ-H)Re]; minor isomer, δ 7.50 (m, 2 H, CH$_2$), 6.70 [d, 1 H, CH, *J*(HH) 12.2 Hz], 5.28 [d, 1 H, CH, *J*(HH) 12.2 Hz], 1.07 (s, 3 H, Me), and −14.02 p.p.m. [s, 1 H, Re(μ-H)Re].

Reductive elimination of isoprene from (**4**) [as observed for but-l-ene in the formation of (**2**)] would allow the establishment of a cycle which isomerises 3,3-dimethylcyclopropene. Such isomerisation has been observed by us in a dimolybdenum system[11] but without identification of any intermediate species.

Finally we note that irradiation of (**2**) does not lead to formation of (**4**) implying a pathway from (**3**) to (**4**) that does not involve (**2**).

We thank the S.E.R.C. for support.

Received, 8th September 1983; Com. 1205

References

1 W. A. Herrmann, *Adv. Organomet. Chem.*, 1982, **20**, 160; *J. Organomet. Chem.*, 1983, **250**, 319; C. P. Casey, P. J. Fagan, and W. H. Miles, *J. Am. Chem. Soc.*, 1982, **104**, 1134, and references therein.

2 P. O. Nubel and T. L. Brown, *J. Am. Chem. Soc.*, 1982, **104**, 4955.

3 A. S. Foust, J. K. Hoyano, and W. A. G. Graham, *J. Organomet. Chem.*, 1971, **32**, C65.

4 M. R. Churchill, K. N. Amoh, and H. J. Wasserman, *Inorg. Chem.*, 1981, **20**, 1609.

5 W. K. Wang, W. Tan, C. E. Strouse, and J. A. Gladysz, *J. Chem. Soc., Chem. Commun.*, 1979, 530.

6 C. P. Casey, C. R. Cyr, R. L. Anderson, and D. F. Marten, *J. Am. Chem. Soc.*, 1975, **97**, 3053.

7 G. K. Barker, W. E. Carroll, M. Green, and A. J. Welch, *J. Chem. Soc., Chem. Commun.*, 1980, 1071.

8 M. P. Brown, J. R. Fischer, S. J. Franklin, R. J. Puddephatt, and K. R. Seddon, *Inorg. Chem.*, 1979, **18**, 2808.

9 Y. C. Lin, J. C. Calabrese, and S. S. Wreford, *J. Am. Chem. Soc.*, 1983, **105**, 1679.

10 A. F. Dyke, S. A. R. Knox, P. J. Naish, and G. E. Taylor, *J. Chem. Soc., Chem. Commun.*, 1980, 803.

11 M. Green, A. G. Orpen, C. J. Schaverien, and I. D. Williams, *J. Chem. Soc., Chem. Commun.*, 1983, 583.