Olefin Metathesis: Preparation of a Carbene–Olefin–Metal Complex

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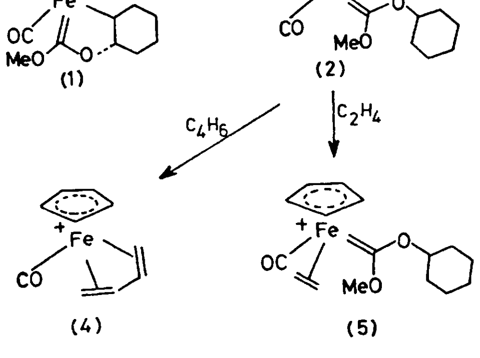
Summary Protonation of the chelated carbene–iron complex (**1**) in the presence of ethylene yields the complex (**5**) in which the metal is co-ordinated to separate olefin and carbene ligands.

The mechanism of olefin metathesis in the presence of transition metal complexes has been a subject of considerable interest and speculation.[1] Recent experiments have strongly implicated a chain process involving interconversions of a carbene–olefin–metal complex with a metallocyclobutane.[2] We report here the preparation of the first example of a stable complex in which the metal is bonded to separate olefin and carbene ligands.[3]



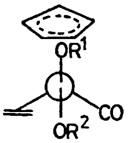
Protonation of the metallocycle carbene complex (**1**) in the presence of CO at −78 °C has been shown to yield (**3**).[4] When protonation of (**1**) with HBF_4 etherate is carried out in the presence of butadiene, cleavage of both σ-carbon and carbene–metal bonds takes place and complex (**4**) is isolated in moderate yield: δ (CD_3NO_2) 6·7 (m, 2H, H-2 and H-3), 5·5 (s, 5H, cyclopentadienyl H), 3·55 (d, 2H, *J* 7 Hz, *syn*-H-1 and H-4), and 0·75 (d, 2H, *J* 10 Hz, *anti*-H-1 and H-4); ν ($MeNO_2$) 2055 cm^{-1}.

In the absence of an external donor, protonation of (**1**) in CH_2Cl_2 solution at −78 °C yields an unstable cationic species, ν_{CO} 2030 cm^{-1}, which is formulated as the 16-electron complex (**2**).[5] The complex may be generated in an argon atmosphere as well as under nitrogen and is therefore not a nitrogen complex.[6] In CH_2Cl_2 solutions at −20 °C, (**2**) slowly disproportionates into (**3**), while addition of CO to these solutions affords (**3**) in high yield.

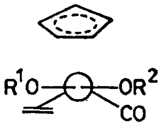
When CH_2Cl_2 solutions of (**2**) are treated at −20 °C with ethylene, or when (**1**) is protonated under 40 lbs of ethylene pressure, a yellow, moderately air stable crystalline complex is obtained in high yield. This substance, m.p. 72—73 °C, is formulated as the carbene–olefin complex (**5**): δ (CD_2Cl_2, 0 °C) 5·20 (s, 5H, cyclopentadienyl H), 4·83 (m, 1H, cyclohexyl 1-H), 4·18 (s, 3H, OMe), 3·55 (m, 2H, CH_2=), 3·21 (m, 2H, CH_2=), and 1·9—1·2 (m, 10H, CH and CH_2); ν (CH_2Cl_2) 2035 and 2020 cm^{-1}. Satisfactory C and H analyses were obtained for (**5**).

The olefin ligand in (**5**) is easily displaced by co-ordinating solvents. Displacement by nitromethane at 60 °C is slow ($t_{\frac{1}{2}}$, 1 h), but acetone or acetonitrile replace ethylene in (**5**) within 1 min at 35 °C.

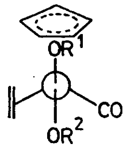
The presence of two closely spaced CO absorptions of nearly equal intensities in the i.r. spectrum of (**5**) suggests that two conformers exist in solution. These are not due to restricted rotation about the carbene carbon–oxygen bond since such isomerism, while well characterized for a number of heteroatom substituted carbene–metal com-



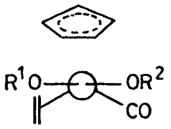
(5a)



(5b)



(5c)



(5d)

plexes,[7] has not been observed to give rise to splitting of carbonyl absorptions. It seems likely that conformational isomers, associated with restricted rotation about the carbene–metal bond are responsible for carbonyl doubling. Similar effects have been observed in $ArCr(CO)_2C(OMe)Ph$,[8] $ArCr(CO)_2C(NR_2)Ph$,[9] and $(C_5H_5)Mn(CO)_2C(OMe)Ph$.[9] Such isomers may be tentatively identified with structures (**5a**) and (**5b**), but the possibility of additional conformational isomerism associated with restricted rotation about the olefin–metal bond [*e.g.*, (**5c**) and (**5d**)], cannot be excluded.

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[6] See for example $[(C_5H_5)Fe(PMe_2CH_2CH_2PMe_2)]_2N_2^+$, W. E. Silverthorn, *Chem. Comm.*, 1971, 1310.

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