The Role of α-Hydrogen Elimination Reactions in the Formation of η³-Cyclopropenyl- and η⁴-Cyclopentadiene-molybdenum Complexes

Frank J. Feher, Michael Green, and A. Guy Orpen

Department of Inorganic Chemistry, University of Bristol, Bristol BS8 1TS, U.K.

Reaction of the Grignard reagents RMgX (R = Me or CH=CH₂) with [Mo(η²-PhC₂Ph){P(OMe)₃}₂(η-C₅H₅)][BF₄] leads to selective attack on molybdenum and formation of the complexes [MoR(η²-PhC₂Ph){P(OMe)₃}(η-C₅H₅)] which undergo thermally promoted α-hydrogen elimination reactions to give η³-cyclopropenyl and η⁴-cyclopentadiene complexes, the latter being identified by X-ray crystallography.

In exploring the chemistry of four-electron alkyne–molybdenum complexes[1] we have examined the reactivity of the cation [Mo(η²-PhC₂Ph){P(OMe)₃}₂(η-C₅H₅)][BF₄]² (**1**) towards Grignard reagents. Selective attack occurs on the metal centre leading to the formation of reactive molecules which undergo novel ring-forming reactions with alkynes.

Reaction (0 °C, 10 min) of a suspension of the violet complex (**1**) in tetrahydrofuran (thf) or Et₂O with MeMgI (2 equiv.) affords the green crystalline complex [Mo(CH₃){η²-PhC₂Ph}{P(OMe)₃}(η-C₅H₅)] (**2**) in 91% yield after column chromatography (Al₂O₃; 4:1 hexane–Et₂O). This molecule has previously[1] been obtained in lower yield by the reaction of the cation with LiCuMe₂; however, unlike the reaction with the magnesium reagent, competitive attack also occurs on the alkyne to form the η²-vinyl complex [Mo{=C(Ph)C(Me)Ph-{P(OMe)₃}₂(η-C₅H₅)] thus reducing the yield of the σ-methyl complex. The regioselective attack by the Grignard reagent on the molybdenum centre is a general reaction with a range of alkyl and aryl reagents and substituted alkynes thus providing synthetic access to a potentially interesting group of air-sensitive molecules. However, when the reaction of (**1**) with vinylmagnesium bromide was examined, an unusual rearrangement and ring-forming reaction was observed.

Addition (0 °C, 5 min) of CH₂=CHMgBr in thf to (**1**) leads to a transient green colour characteristic of a σ-organyl

complex, but on work-up† the colour changed to brown–yellow and column chromatography afforded a good yield of the bright yellow η³-cyclopropenyl complex (**3**)‡ (Scheme 1). Thus, the CH₂=CH group has apparently rearranged into a CH₃C fragment which then couples with the PhC₂Ph ligand to form the C₃ ring. This can be understood if it is assumed that the alkyne in the initially formed σ-vinyl complex switches its bonding mode [(η²)4e→(η²)2e] creating a co-ordination site for an α-hydrogen elimination reaction. The resultant hydrido (vinylidene) species can then rearrange *via* proton transfer[3] [assisted by P(OMe)₃] to a carbyne (alkylidyne) complex

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† The yield of (**3**) can be increased by the addition of several equivalents of P(OMe)₃ at 0 °C before work-up.

‡ Selected n.m.r. data (coupling constants in Hz), for (**3**): (C₆D₆), ¹H, δ 7.5—6.8 (m, 10 H, Ph), 4.662 (t, 5 H, C₅H₅, J 1.4), 3.241 [t, 18 H, P(OMe)₃, |J(HP) + J(HP')| 10.5], and 2.362 (s, 3 H, Me); ¹³C-{¹H}, δ 144.543, 129.903 (d, J 158.4), 128.000 (d, J 149.6), 123.0, 123.681 (d, J 159.5), 85.6 (d, J 176.0), 50.852 (q d, J 143.7, 3.3), 33.358 (t, J 12.4, CPh), 19.024 (t, J 3.3, CMe), and 11.764 (q, J 128.0, Me); for (**4**) ¹H (CD₂Cl₂), δ 7.3—6.71 (m, 20 H, Ph), 6.606 [dd, 1H, vinylic, J(HP) 9.4, J(HH) 1.2], 4.576 (d, 5 H, C₅H₅, J 1.3), 4.543 (br. s, 1 H, HCPh), 3.284 (d, 9 H, J 11.1), and −7.148 [d, 1 H, MoH, J(HP) 38.9]; for (**5**) ¹H (C₆D₆), δ 7.67—6.75 (m, 20 H, Ph), 5.294 (s, 1 H), 4.262 (s, 5 H, C₅H₅), and −6.532 (s, 2 H, MoH).
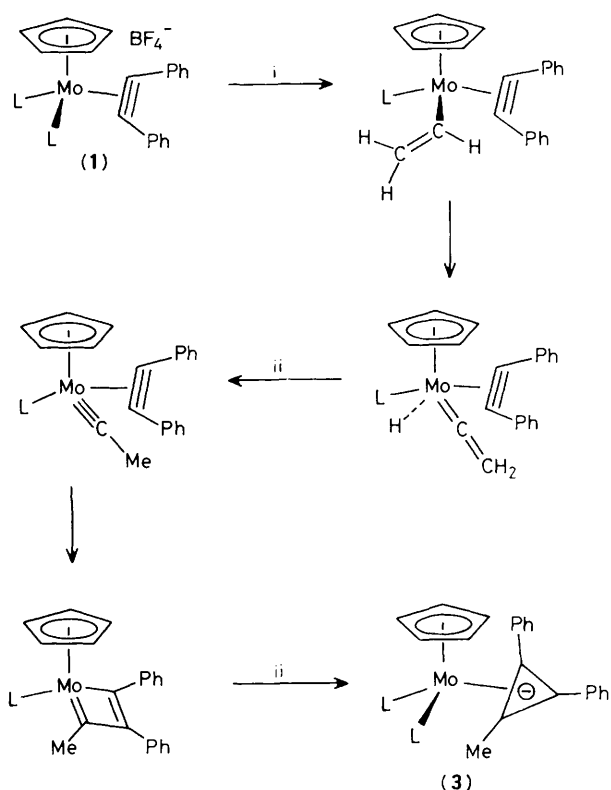
Scheme 1. L = P(OMe)$_3$. i, CH$_2$=CHMgBr, thf, −L; ii, + L.

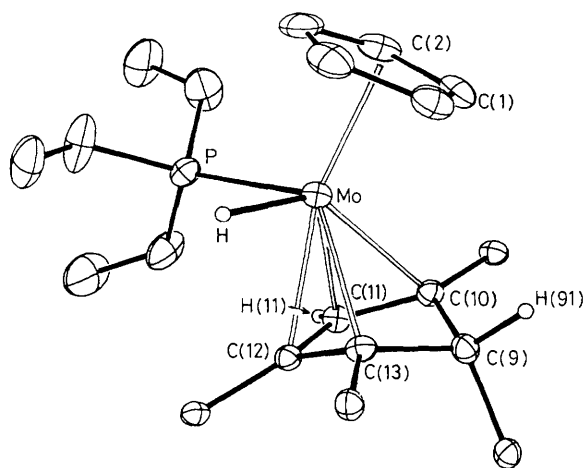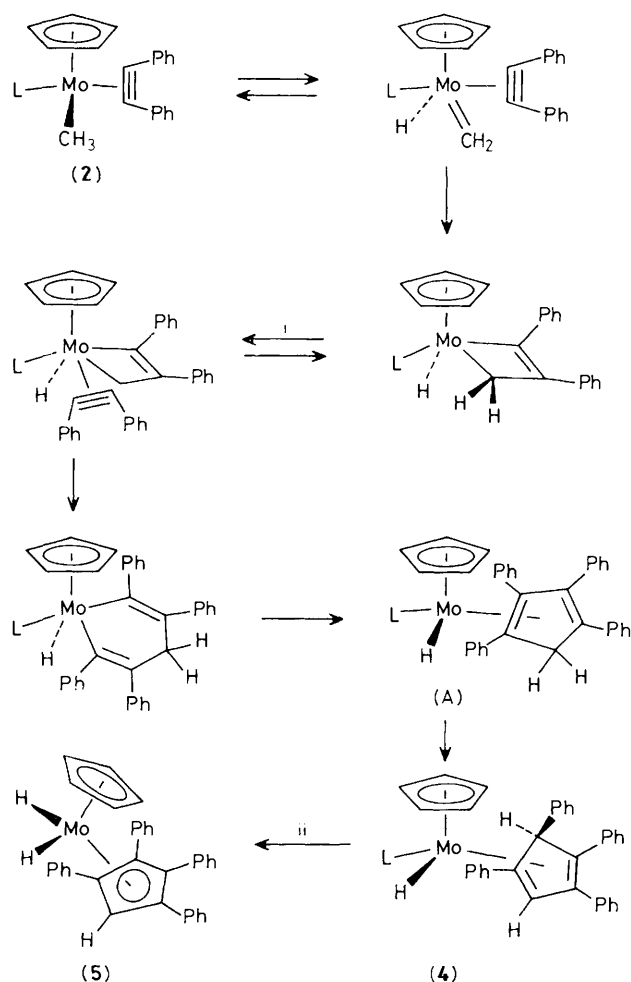**Scheme 2.** L = P(OMe)$_3$. i, PhC$_2$Ph; ii, −L.

Figure 1. Molecular structure of (**4**) with methyl, phenyl, and cyclopentadienyl group hydrogens and all but *ipso* carbons of phenyl groups omitted for clarity. Important geometric parameters include: bond lengths Mo–P 2.366(1), Mo–H 1.59(4), Mo–C(10) 2.377(3), Mo–C(11) 2.275(4), Mo–C(12) 2.248(4), Mo–C(13) 2.240(3), C(10)–C(11) 1.401(5), C(11)–C(12) 1.426(5), C(12)–C(13) 1.456(5) Å; torsion angle H–Mo–C(12)–C(13) −89(2)°.

carrying a co-ordinated PhC$_2$Ph, formation of a molybdena-cyclobutadiene followed by distortion to a metallatetrahedrane, *i.e.* a η^3-cyclopropenyl complex, completing the reaction sequence. It is particularly interesting that these last two steps have recently[4—7] been implicated in the reaction of tungsten(VI) alkylidyne complexes with alkynes which lead in some cases to alkyne metathesis.

Having developed an efficient synthesis of σ-organyl complexes such as (**2**), and being encouraged by the reaction shown in Scheme 1, we began to explore other possible reactions which might lead to carbon–carbon bond formation between the alkyne and σ-organyl ligands. The reaction (78 °C, 12 h) of (**2**) and PhC$_2$Ph (10 equiv.) in C$_6$H$_6$ affords a single orange-yellow crystalline complex (**4**) in high yield. N.m.r. data‡ suggested that the stoicheiometry of the complex was [MoH{P(OMe)$_3$}(η^4-tetraphenylcyclopentadiene)(η-C$_5$H$_5$)] but it was only after a single crystal *X*-ray diffraction study§ that this was confirmed and the regiochemistry of the

η^4-tetraphenylcyclopentadiene ring could be established. As shown in Figure 1 the complex adopts a pseudo-ML_2-(η-C_5H_5)$_2$ geometry. The angle between the centroid of the C_5H_5 ring, the Mo atom, and the centroid of the η^4-cyclopentadiene ring is 130°, while the P–Mo–H angle is 78.6(13)°; the four olefinic carbon atoms of the η^4-cyclopentadiene ring are essentially coplanar with C(9) deviating 0.585 Å from the least squares plane. All other angles are normal.[8]

The formation of (4) is particularly interesting in that the σ-bonded methyl group in (2) apparently loses two hydrogen atoms and the CH fragment is incorporated into the C_5 ring. It is possible that the first step in this reaction sequence is also an α-hydrogen elimination reaction with a concomitant 4e to 2e change in the degree of alkyne bonding (Scheme 2). Although the vacant co-ordination site presumed necessary for α-elimination could also be generated by phosphite dissociation, this apparently does not occur along the reaction pathway, since phosphite dissociation occurs only slowly (100 °C, C_6D_6, $t_{\frac{1}{2}}$ ~6 days) and then leads to the irreversible formation of the bis(η^5-cyclopentadienyl)molybdenumdihydride (5)‡ via carbon to molybdenum H-transfer. Thus, following reversible α-hydrogen elimination the resultant hydrido(methylene)-molybdenum species is captured by coupling with the co-ordinated PhC$_2$Ph leading to a 16e hydridomolybdenacyclobutene, which in turn is captured by a second molecule of PhC$_2$Ph. It is interesting that a reductive elimination reaction of the hydride and a Mo–C σ-bond does not compete with ring formation. The 1,3,4,5-tetraphenyl-η^4-cyclopenta-1,3-diene isomer (4) isolated is presumably formed under thermodynamic control from the intermediate (A) (Scheme 2) by a series of reversible β-hydride addition–elimination reactions from the Mo to the η^4-cyclopentadiene ring.

In summary these observations show that molecules of the type [MoR{η^2-R'C$_2$R'}{P(OMe)$_3$}(η-C$_5$H$_5$)](R = Me or CH$_2$=CH) do not undergo the expected 'insertion' reactions, but instead α-hydrogen elimination effectively competes. This is particularly interesting in the context of the Green–Rooney mechanism[9] for alkene[10,11] polymerisation, and its possible extension to alkyne[12] polymerisation.

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