The Rearrangement of Coordinated η^2-Vinyl Ligands into η^3-Allyl and Alkylidyne Species

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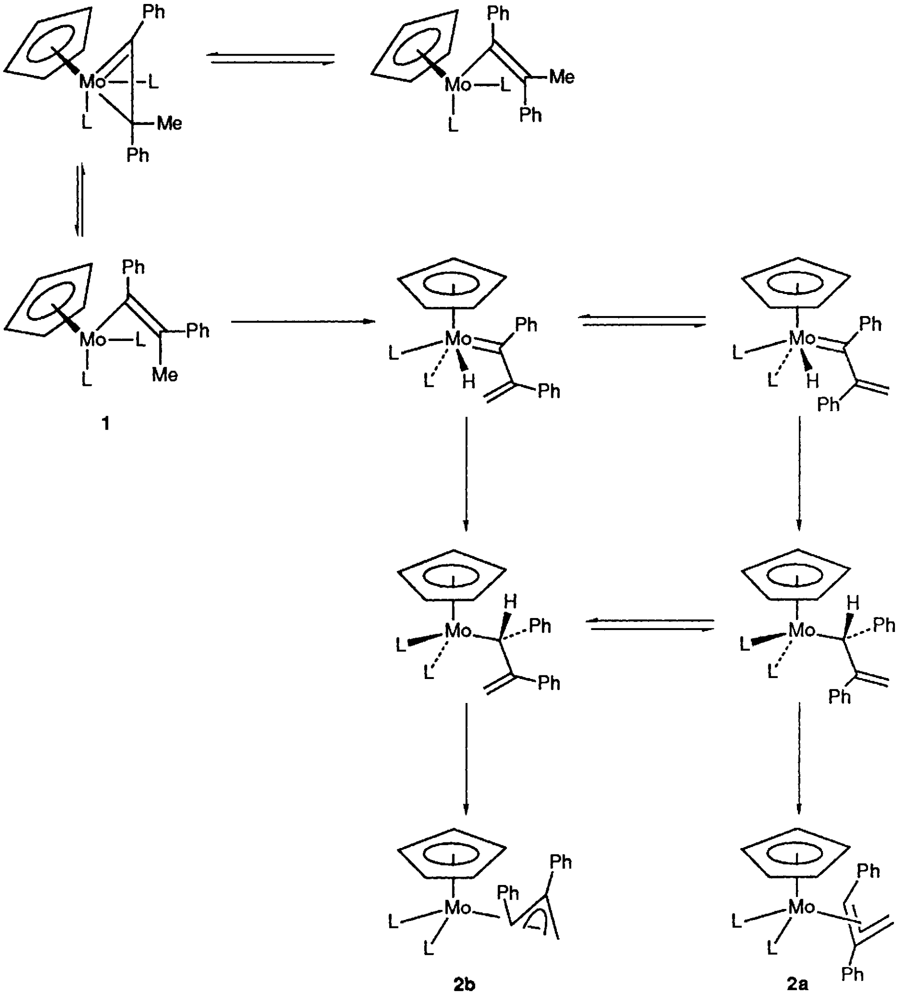
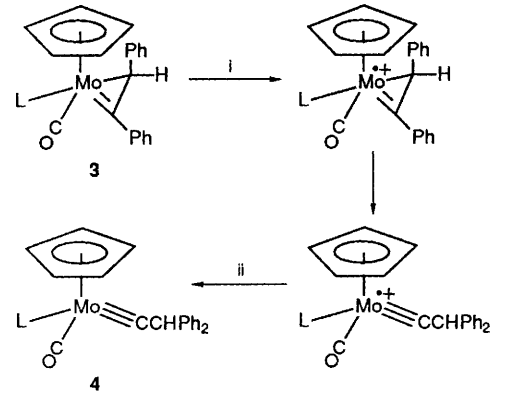
Details of the rearrangement of the η^2-vinyl complex [Mo{=C(Ph)CMe(Ph)}{P(OMe)$_3$}$_2$(η-C$_5$H$_5$)] **1** to the η^3-allyl species [Mo{η^3-CH$_2$C(Ph)CH(Ph)}{P(OMe)$_3$}$_2$(η-C$_5$H$_5$)] **2a**, **2b**, and of [Mo{=C(Ph)CH(Ph)}(CO)(PMe$_2$Ph)(η-C$_5$H$_5$)] **3** into [Mo{≡CCHPh$_2$}(CO)(PMe$_2$Ph)(η-C$_5$H$_5$)] **4**, are described together with a crystal structure determination of **2b** and possible mechanistic pathways.

Complexes containing η^2-vinyl ligands are now well established, particularly for molybdenum, and we have recently published a full report describing their synthesis and molecular and electronic structures.[1] However, studies dealing with the reactivity of these species are still at an early stage. In the particular case where the metal fragment to which the vinyl ligand is bonded is Mo{P(OMe)$_3$}$_2$(η-C$_5$H$_5$ or η-C$_9$H$_7$), two reactions have been observed. The first involves rearrangement to an alkylidyne complex, *i.e.* [Mo{=C(SiMe$_3$)CH$_2$}{P(OMe)$_3$}$_2$(η-C$_9$H$_7$)] to [Mo{≡CCH$_2$(SiMe$_3$)}{P(OMe)$_3$}$_2$(η-C$_9$H$_7$)],[2] whilst the second type results in the formation of an allyl ligand, *i.e.* [Mo{=C(CH$_3$)CPh$_2$}{P(OMe)$_3$}$_2$(η-C$_5$H$_5$)] to [Mo{η^3-CH$_2$CHCPh$_2$}{P(OMe)$_3$}$_2$(η-C$_5$H$_5$)].[1] The former reaction involves a migration of the SiMe$_3$ group attached to the α or alkylidene carbon of the η^2-vinyl ligand, whereas in the latter it is a β-hydrogen from the methyl group on the alkylidene carbon which is necessary for the subsequent rearrangement. In exploring further the reactivity of η^2-vinyl complexes we have discovered two novel molecular rearrangements, one involving an apparent γ-hydrogen abstraction reaction and the other, an alkylidyne forming reaction involving a phenyl migration which is initiated by a one-electron transfer process.

Solutions of [Mo{=C(Ph)CMe(Ph)}{P(OMe)$_3$}$_2$(η-C$_5$H$_5$)]



Scheme 1 L = P(OMe)$_3$



Scheme 2 L = PMe$_2$Ph. i, +PhIO, −PhIO$^{\bullet+}$; ii, +PhIO$^{\bullet+}$, −PhIO

1^1 in [^{2}H$_6$]benzene are dark green and ^{1}H, ^{13}C and ^{31}P NMR spectra obtained within 24 h were consistent with the expected η^2-vinyl structure (full details on the synthesis and spectroscopic characterisation of **1** can be found in ref. 1). However, over a period of one week a colour change from dark green to orange was observed and a ^{1}H NMR spectrum obtained after this time showed the formation of two new complexes in a *ca.* 2 : 1 ratio.† Purification by column chromatography (alumina; hexane–Et$_2$O, 20 : 1) gave a single dark yellow band containing both new complexes. Attempted separation by low temperature chromatography was unsuccessful but was achieved by fractional crystallisation from cooled (−30 °C) concentrated solutions (hexane–Et$_2$O, 20 : 1). This procedure initially yielded a crop of orange microcrystals **2a** (major product) and, after further concentration, well formed red blocks **2b** (minor product). Examination of the spectroscopic data‡ for these two compounds suggested that they were isomeric η^3-allyl complexes of the general formula [Mo{η^3-CH$_2$C(Ph)CH(Ph)}{P(OMe)$_3$}$_2$(η-C$_5$H$_5$)] **2a**, **2b**, implying that an unusual hydrogen shift process had occurred. In order to confirm this, a single crystal X-ray structure determination was carried out on the minor product **2b**, for which suitable crystals were available.§ As shown in Fig. 1, these data reveal a Mo{P(OMe)$_3$}$_2$(η-C$_5$H$_5$) fragment of normal geometry coordinated to a *syn*-1,2-diphenylallyl ligand which adopts an *exo*-conformation with regard to the Mo(η-C$_5$H$_5$) unit. Crystals of **2a** proved unsuitable for X-ray diffraction studies but ^{1}H and ^{13}C NMR data were consistent with an isomeric *anti*-1,2-diphenyl configuration for the allyl ligand. In order to explain this apparent 1,3-hydrogen shift it is necessary to postulate that the η^2(3e)-vinyl transforms into a η^1(1e)-vinyl complex. As is illustrated in Scheme 1 this ring-opening process can occur in either of two directions affording *E* and *Z* isomers respectively. Only one of these sixteen-electron isomers can transform *via* a γ-hydrogen abstraction into a hydrido η^2(2e)-vinylalkylidene complex which can in turn isomerise by rotation about a C–C bond. Hydrogen migration from the molybdenum centre to the alkylidene carbon would then afford the η^3-allyl complexes **2a** and **2b**. In agreement with this proposal, the trideuterio complex [Mo{=C(Ph)CCD$_3$(Ph)}{P(OMe)$_3$}$_2$(η-C$_5$H$_5$)] cleanly isomerises at approximately the same rate as **1** to form a mixture of isomeric complexes [Mo{η^3-CD$_2$C(Ph)CD(Ph)}{P(OMe)$_3$}$_2$(η-C$_5$H$_5$)]. The η^2-vinyl complexes [Mo{=C(Ph)CMe(Ph)}{P(OEt)$_3$}$_2$(η-C$_5$H$_5$)] and [Mo{=C(*p*-tolyl)CMe(*p*-tolyl)}{P(OMe)$_3$}$_2$(η-C$_5$H$_5$)] also rearrange at similar rates to analogous isomeric allyl compounds.

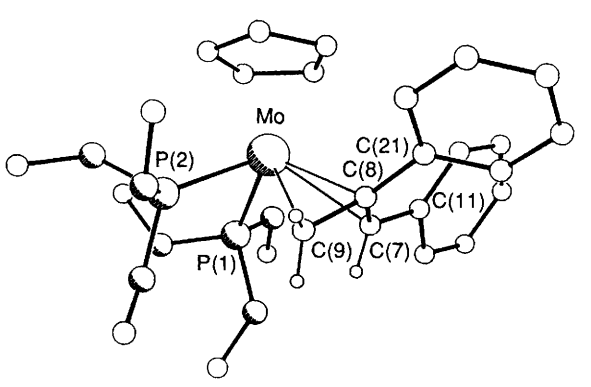


Fig. 1 A view of the molecular structure of **2b**, cyclopentadienyl, methyl and phenyl hydrogens omitted for clarity; important bond lengths (Å) and angles (°): Mo–C(7) 2.366(4), Mo–C(8) 2.205(4), Mo–C(9) 2.297(5), C(7)–C(8)–C(9) 111.4(4).

The second molecular rearrangement of a η^2-vinyl complex to be observed was discovered when an attempt was made to react the complex [Mo{=C(Ph)CH(Ph)}(CO)(PMe$_2$Ph)(η-

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† Solid **1** is also green as are solutions in CH$_2$Cl$_2$, THF and toluene. The rearrangement, as judged by the colour change, occurs in all the above solvents at a similar rate although all NMR experiments and preparative scale reactions were carried out in [^{2}H$_6$]benzene and toluene respectively.

‡ *Spectroscopic data* for **2a**: NMR (C$_6$D$_6$), ^{1}H, δ 7.87 (d, 2H, Ph), 7.44 (d, 2H, Ph), 7.16 (m, 4H, Ph), 6.95 (m, 2H, Ph), 5.27 [d, br, 1H, allyl CH, $|J(\mathrm{HP}) + J(\mathrm{HP'})| = 13.0$ Hz], 4.41 (s, 5H, C$_5$H$_5$), 3.18 [t, 18H, P(OMe)$_3$, $|J(\mathrm{HP}) + J(\mathrm{HP'})| = 10.1$ Hz], 2.83 [d, br, 1H, allyl CH, $|J(\mathrm{HP}) + J(\mathrm{HP'})| = 12.9$ Hz]; third allyl H resonance obscured by P(OMe)$_3$; ^{13}C-{^{1}H}, δ 153.5, 149.7 (*ipso*-Ph), 128.5, 128.1, 127.6, 125.1, 123.3 (Ph), 89.3 (C$_5$H$_5$), 86.4 (s, allyl *C*-Ph), 52.1 [d, P(OMe)$_3$, $|J(\mathrm{CP}) + J(\mathrm{CP'})| = 9.0$ Hz], 51.8 [d, P(OMe)$_3$, $|J(\mathrm{CP}) + J(\mathrm{CP'})| = 6.7$ Hz], 50.5 [d, allyl *C*HPh, $|J(\mathrm{CP}) + J(\mathrm{CP'})| = 9.4$ Hz], 33.8 [d, allyl CH$_2$, $|J(\mathrm{CP}) + J(\mathrm{CP'})| = 8.0$ Hz]; ^{31}P-{^{1}H}, δ 199.7, 195.9 [AB, P(OMe)$_3$, $J(\mathrm{PP}) = 79$ Hz]. **2b** NMR (C$_6$D$_6$), ^{1}H, δ 7.57 (d, 2H, Ph), 7.17 (m, 4H, Ph), 7.00 (m, 4H, Ph), 4.80 [d, 5H, C$_5$H$_5$, $|J(\mathrm{HP}) + J(\mathrm{HP'})| = 1.8$ Hz], 3.40 [d, 9H, P(OMe)$_3$, $|J(\mathrm{HP}) + J(\mathrm{HP'})| = 10.4$ Hz], 3.30 [d, 9H, P(OMe)$_3$, $|J(\mathrm{HP}) + J(\mathrm{HP'})| = 10.4$ Hz], 2.39 [d, 1H, *syn*-allyl CH, $|J(\mathrm{HP}) + J(\mathrm{HP'})| = 11.1$ Hz], 1.95 [d, 1H, *syn*-allyl CH, $|J(\mathrm{HP}) + J(\mathrm{HP'})| = 16.5$ Hz], 0.96 [dd, 1H, *anti*-allyl CH, $|J(\mathrm{HP}) + J(\mathrm{HP'})| = 2.9$ and 9.6 Hz]; ^{13}C-{^{1}H}, δ 148.8, 146.9 (*ipso*-Ph), 131.0, 130.5, 128.4, 127.6, 125.7, 123.8 (Ph), 92.2 (C$_5$H$_5$), 78.3 (s, allyl *C*-Ph), 53.0 [d, P(OMe)$_3$, $|J(\mathrm{CP}) + J(\mathrm{CP'})| = 7.5$ Hz], 52.4 [d, P(OMe)$_3$, $|J(\mathrm{CP}) + J(\mathrm{CP'})| = 6.6$ Hz], 48.4 [d, allyl *C*H$_2$ or *C*HPh, $|J(\mathrm{CP}) + J(\mathrm{CP'})| = 11.5$ Hz], 45.3 [d, allyl *C*H$_2$ or *C*HPh, $|J(\mathrm{CP}) + J(\mathrm{CP'})| = 22.7$ Hz]; ^{31}P-{^{1}H}, δ 196.6, 193.9 [AB, P(OMe)$_3$, $J(\mathrm{PP}) = 105$ Hz]. Satisfactory microanalytical data were obtained.

§ *Crystal data* for **2b**: C$_{26}$H$_{35}$MoO$_6$P$_2$, $M = 601.45$, monoclinic, $P2_1/n$, $a = 10.131(1)$, $b = 28.077(3)$, $c = 10.622(1)$ Å, $\beta = 113.224(6)°$, $U = 2776.8$ Å^3, $Z = 4$, $D_c = 1.439$ g cm^{-3}, λ(Mo-Kα) = 0.71073 Å, $\mu = 0.61$ mm^{-1}, $F(000) = 1244$, $T = 295$ K. The structure was determined by Patterson and difference syntheses and refined[3] to a minimum of $\Sigma w\Delta^2$ [$\Delta = |F_o| - |F_c|$, $w^{-1} = \sigma^2(F) = \sigma_c^2(F) + 5 + 23G - 12S + 9S^2 - 30GS$, $G = F_o/F_{max}$, $S = \sin\theta/\sin\theta_{max}$][4] from 3453 reflections with $2\theta < 50°$ and $F > 4\sigma_c(F)$ (σ_c from counting statistics only), measured with a Stoe–Siemens diffractometer and on-line profile fitting.[5] Anisotropic thermal parameters were refined for all non-hydrogen atoms. H atoms were constrained. Final $R = 0.036$, $R_w = (\Sigma w\Delta^2/\Delta wF_o^2)^{\frac{1}{2}} = 0.042$ for 343 parameters. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

$C_5H_5)]$ **3**[¶] with iodosobenzene, a reagent known to convert coordinated CO into uncoordinated CO_2 *via* oxygen transfer.[6] However, both in the presence and absence of coordinating ligands (PhC_2Ph or PMe_2Ph) the expected reactions did not take place. In dichloromethane, the reaction of **3** (room temp.; 16 h) with one equivalent of PhIO led to a gradual change in colour from green to orange. Column chromatography [Et_2O–tetrahydrofuran (THF), 12 : 1] afforded (20%) an orange crystalline product, **4**[‖] which elemental analysis and mass spectrometry showed to be isomeric with **3**. Examination of the IR and NMR spectra of **4** revealed that **4** was an alkylidyne complex $[Mo\{\equiv CCHPh_2\}(CO)(PMe_2Ph)(\eta\text{-}C_5H_5)]$. It is suggested (Scheme 2) that the relatively electron-rich η^2-vinyl complex **3** undergoes a one-electron transfer reaction on treatment with PhIO to give a radical cation which transforms *via* a 1,2-phenyl shift into an alkylidyne. In agreement with this proposal, the use of less than one equivalent of PhIO led to a similar yield of **4**.

In summary, two novel molecular rearrangements of η^2-vinyl complexes are reported which have interesting implications for the development of this area of chemistry.

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[¶] Treatment of $[Mo(\eta^2\text{-}PhC_2Ph)_2(CO)(\eta\text{-}C_5H_5)][BF_4]$[7] with PMe_2Ph affords $[Mo(\eta^2\text{-}PhC_2Ph)(CO)(PMe_2Ph)(\eta\text{-}C_5H_5)][BF_4]$ which on reaction (THF, −78 °C) with $K[BHBu^s_3]$ affords **3**.

Spectroscopic data for **3**: NMR (CD_2Cl_2), ^1H, δ 7.4–6.6 (m, br, 15H, Ph), 5.41 (s, 5H, C_5H_5), 3.68 [d, 1H, $CHPh$, $^3J(PH) = 3$ Hz], 1.56 [d, 6H, PMe_2Ph, $^2J(PH) = 9$ Hz]; $^{13}C\text{-}\{^1H\}$, δ 245.8 (=CPh), 152.6, 142.7, 130.1, 129.7, 129.2, 128.9, 128.7, 128.3, 127.6, 126.6, 123.8 (Ph), 93.8 (C_5H_5), 37.6 (CHPh), 19.2 [d, PMe_2Ph, $^1J(PC) = 29.7$ Hz], 19.0 [d, PMe_2Ph, $^1J(PC) = 29.7$ Hz]; $^{31}P\text{-}\{^1H\}$, δ 32.9; IR $\nu(C\equiv O)$ (CH_2Cl_2) 1840 cm^{-1}.

[‖] *Spectroscopic data* for **4**: NMR ^1H (C_6D_6), δ 7.6–6.8 (m, 20H, Ph), 4.35 [d, 5H, C_5H_5, $^3J(PH) = 0.5$ Hz], 3.55 [d, 1H, $CHPh_2$, $^4J(PH) = 8.5$ Hz], 1.24 [d, 3H, PMe_2Ph, $^3J(PH) = 8.5$ Hz], 1.00 [d, 3H, PMe_2Ph, $^3J(PH) = 8.3$ Hz]; $^{13}C\text{-}\{^1H\}$, (CD_2Cl_2), δ 282.2 [d, $Mo\equiv C$, $^2J(CP) = 22.1$ Hz], 248.9 [d, CO, $^2J(CP) = 17.2$ Hz], 159.3, 149.5, 144.7, 127–119 (Ph), 93.9 (C_5H_5), 70.2 [d, $CHPh_2$, $^3J(PC) = 4.9$ Hz], 16.5 [d, PMe_2Ph, $^1J(PC) = 36.8$ Hz], 16.1 [d, PMe_2Ph, $^1J(PC) = 36.8$ Hz]; $^{31}P\text{-}\{^1H\}$ (CD_2Cl_2), δ 17.0. An unidentified minor product (~2%) is also formed.