The Formation of Vinylidene Molybdenum Complexes and their Transformation into Mononuclear Carbyne Complexes; *X*-Ray Crystal Structure of $[\mathrm{Mo\{C{=}CHPh\}Br\{P(OMe)_3\}_2(\eta\text{-}C_5H_5)}]$

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Reaction of $[\mathrm{Mo(PhC_2Br)\{P(OMe)_3\}_2(\eta\text{-}C_5H_5)}][\mathrm{BF_4}]$ with $\mathrm{K[BHBu^s_3]}$ or $\mathrm{Li_2Cu_2Me_4}$ gives respectively $[\mathrm{Mo\{C{=}CHPh\}Br\{P(OMe)_3\}_2(\eta\text{-}C_5H_5)}]$ and $[\mathrm{Mo{\equiv}C{\cdot}CMe_2Ph\{P(OMe)_3\}_2(\eta\text{-}C_5H_5)}]$; the bromovinylidene reacts with $\mathrm{K[BHBu^s_3]}$ to give $[\mathrm{Mo{\equiv}C{\cdot}CH_2Ph\{P(OMe)_3\}_2(\eta\text{-}C_5H_5)}]$ in good yield and with $\mathrm{HBF_4{-}Et_2O}$ to give $[\mathrm{BrMo{\equiv}C{\cdot}CH_2Ph\{P(OMe)_3\}_2(\eta\text{-}C_5H_5)}][\mathrm{BF_4}]$, which is reduced by Na–Hg to $[\mathrm{Mo{\equiv}C{\cdot}CH_2Ph\{P(OMe)_3\}_2(\eta\text{-}C_5H_5)}]$.

The chemistry of carbyne (alkylidyne) transition metal complexes[1] continues to attract attention from many viewpoints including their use as building blocks for the synthesis of clusters.[2] However, the realisation of the full potential of these reactive molecules depends to a degree on the development of new synthetic methods.[3,4] In the study[5] of the reactions of nucleophiles with cationic alkyne complexes[6] we have discovered new relationships between vinylidene and carbyne complexes.

Reaction (−78 °C, 1 h) of the blue bromophenylethyne complex $[\mathrm{Mo(PhC_2Br)\{P(OMe)_3\}_2(\eta\text{-}C_5H_5)}][\mathrm{BF_4}]$ (**1**)† with

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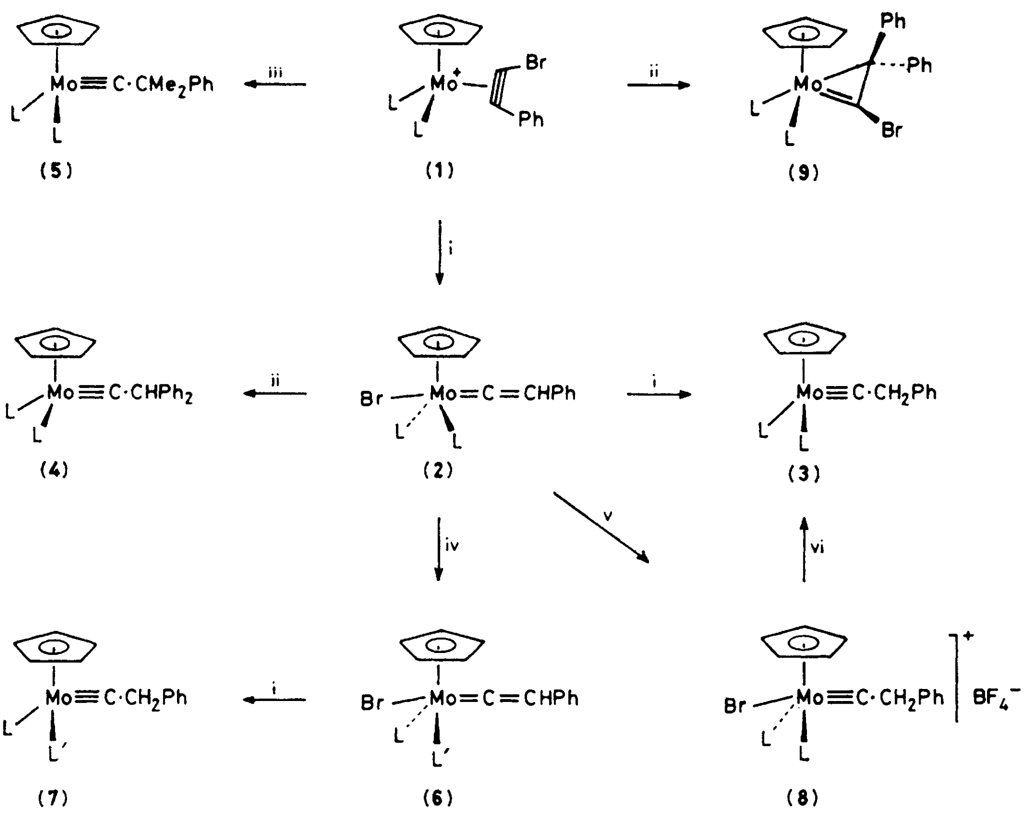
† Prepared by reaction of $[\mathrm{Mo(CO)(PhC_2Br)_2(\eta\text{-}C_5H_5)}][\mathrm{BF_4}]$ with an excess of $\mathrm{P(OMe)_3}$ (ref. 6).



Scheme 1. L = $P(OMe)_3$, L′ = PEt_3; i, $K[BHBu^s_3]$, thf; ii, $LiCuPh_2$, thf; iii, $Li_2Cu_2Me_4$, thf; iv, + PEt_3, $-P(OMe)_3$; v, HBF_4–Et_2O; vi, Na–Hg, thf.

$K[BHBu^s_3]$ in tetrahydrofuran (thf) afforded the orange-brown crystalline complex (**2**), which was identified by n.m.r. spectroscopy‡ and *X*-ray crystallography§ as the bromo-vinylidene complex shown in Figure 1 and Scheme 1. The complex has a four-legged piano-stool geometry[7] with the two phosphite ligands *trans* to each other and *cis* to the bromine and vinylidene moieties. The molybdenum-carbon bond length Mo–C(7) of 1.917(5) Å is short for a Mo=C double bond reflecting the relatively greater π-acceptor properties of the vinylidene ligand compared with CR_2 ligands. The bond distance C(7)–C(8) of 1.327(7) Å is typical for a C=C double bond with ∠C(7)–C(8)–C(9) 127.2(5)°. The orientation of the vinylidene fragment relative to the cyclopentadienyl ligand is also of interest in that the angle between the least-squares planes of C(15) to C(19) and C(7)–C(8)–C(9) is 90.4° in contrast to the parallel arrangement expected[8] from E.H.M.O. calculations.

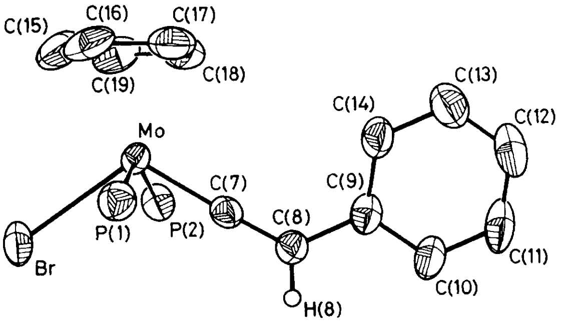


Figure 1. Molecular structure of $[Mo\{C=CHPh\}Br\{P(OMe)_3\}_2(\eta\text{-}C_5H_5)]$. Important dimensions: Mo–Br 2.651(1), Mo–P(1) 2.462(2), Mo–P(2) 2.463(2), Mo–C(7) 1.917(5), C(7)–C(8) 1.327(7), and C(8)–C(9) 1.465(8) Å; Br–Mo–C(7) 113.9(2), P(1)–Mo–P(2) 142.7(1), Br–Mo–P(1) 82.0(1), Br–Mo–P(2) 79.7(1), C(7)–Mo–P(1) 79.1(2), and C(7)–Mo–P(2) 79.2(2)°.

Careful examination of the reaction mixture from which (**2**) was isolated revealed the presence of a second minor (5%) product (**3**), which was identified by n.m.r. spectroscopy‡ as $[Mo{\equiv}C{\cdot}CH_2Ph\{P(OMe)_3\}_2(\eta\text{-}C_5H_5)]$. It was then observed that reaction (25 °C, 2 h) of (**2**) over a longer period of time gave the benzylcarbyne (**3**) in good yield (52%) as a yellow crystalline material.

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‡ Selected n.m.r. spectroscopic data measured in C_6D_6 at room temperature, with coupling constants in Hz. Compound (**2**): ^1H, δ 7.42—6.89 (m, 5 H, Ph), 5.18 [t, 5 H, C_5H_5, *J*(HP) 1.75], 3.64 [app. t, 18 H, POMe, |*J*(PH) + *J*(P′H) |10.5], 3.34 [t, 1 H, C=C*H*Ph, *J*(HP) 5.7]; $^{13}C\{^1H\}$, δ 336.5 [t, Mo=C, *J*(CP) 48.8], 142.4 [t, Mo=C=*C*, *J*(CP) 7.3], 130.2—122.3 (Ph), 92.1 (C_5H_5), 54.0 p.p.m. (PO*Me*); $^{31}P\{^1H\}$, δ 154.9 p.p.m. (s). Compound (**3**): ^1H, δ 7.35—7.04 (m, 5 H, Ph), 5.21 [t, 5 H, C_5H_5, *J*(HP) 0.73], 3.55 [t, 2 H, CH_2Ph, *J*(HP) 4.6], 3.46 [app. t, 18 H, POMe, |*J*(PH) + *J*(P′H)| 11.7]; $^{13}C\{^1H\}$ δ 292.7 [t, Mo≡*C*, *J*(CP) 29.3], 139.2 (Ph), 131.8—124.6 (Ph), 89.2 (C_5H_5), 55.3 (CH_2), 50.9 p.p.m. (PO*Me*); $^{31}P\{^1H\}$, δ 213.3 p.p.m. (s). Compound (**4**): ^1H, δ 7.54—6.56 (m, 10 H, Ph), 5.08 (s, 5 H, C_5H_5), 3.94 [t, 1 H, C*H*Ph_2, *J*(HP) 4.0], 3.35 [app. t, 18 H, PO*Me*, |*J*(PH) + *J*(P′H)| 11.3]; $^{31}P\{^1H\}$, δ 195.9 p.p.m. (s). Compound (**5**): $^{13}C\{^1H\}$, δ 311.3 p.p.m. [t, Mo≡*C*, *J*(CP) 36.1]; $^{31}P\{^1H\}$, δ 213.7 p.p.m. (s). Compound (**6**): $^{13}C\{^1H\}$, δ 325.6 [t, Mo=C, *J*(CP) 45.4], 143.0 p.p.m. [t, Mo=C=*C*, *J*(CP) 23.0]; $^{31}P\{^1H\}$, δ 160.5 [d, *J*(PP′) 83.0] and 19.7 p.p.m. [d, *J*(PP′) 83.0]. Compound (**7**): $^{13}C\{^1H\}$, δ 254.1 p.p.m. (Mo≡*C*); $^{31}P\{^1H\}$, δ 212.2 [d, *J*(PP′) 40.3] and 59.4 p.p.m. [d, *J*(PP′) 40.3]. Compound (**8**): $^{13}C\{^1H\}$ ($CDCl_3$), δ 384.7 p.p.m. [t, Mo≡*C*, *J*(CP) 43.95]; $^{31}P\{^1H\}$, δ 130.9 p.p.m. (s). Compound (**9**): $^{13}C\{^1H\}$, δ 230.5 p.p.m. [t, Mo=C, *J*(CP) 25.5]; $^{31}P\{^1H\}$, δ 195.5 p.p.m. (s).

An explanation for this observation is that (**2**) undergoes an S_N2' type reaction, in which hydride anion delivered by $[BHBu^s_3]^-$ attacks the olefinic carbon C(8) with concomitant heterolysis of the Mo–Br bond (see Scheme 1). The availability of an S_N2' reaction pathway was also implied by two further observations. Treatment of (**2**) with lithium diphenylcuprate in thf afforded $[Mo{\equiv}C{\cdot}CHPh_2\{P(OMe)_3\}_2(\eta\text{-}C_5H_5)]$ (**4**).‡ Secondly, reaction of (**1**) with lithium dimethylcuprate gave $[Mo{\equiv}C{\cdot}CMe_2Ph\{P(OMe)_3\}_2(\eta\text{-}C_5H_5)]$ (**5**).‡ If in the reaction of (**2**) with 'Ph⁻' the complex $[Mo\{C{=}CHPh\}Ph\{P(OMe)_3\}_2(\eta\text{-}C_5H_5)]$ was an intermediate, then although migration of the phenyl group from the molybdenum onto the α-carbene carbon can be readily envisaged, further rearrangement to (**4**) would not be expected to occur; instead the known[9] complex $[\overline{Mo{=}C(Ph)C}HPh\{P(OMe)_3\}_2(\eta\text{-}C_5H_5)]$ would be formed. Since this was not observed we favour S_N2' attack by 'Ph⁻' on C(8) of (**2**) as the pathway to the carbyne (**4**). Similarly, the formation of the dimethylphenyl substituted carbyne (**5**) probably involves S_N2' attack by 'Me⁻' on an intermediate $[Mo\{C{=}CMePh\}Br\{P(OMe)_3\}_2(\eta\text{-}C_5H_5)]$, which we have so far not isolated.

Reaction (55 °C, 24 h) of (**2**) with triethylphosphine led to replacement of one of the trimethyl phosphite ligands and formation of $[Mo\{C{=}CHPh\}Br(PEt_3)\{P(OMe)_3\}(\eta\text{-}C_5H_5)]$ (**6**),‡ an observation which has consequences for carbyne synthesis for, although the phosphite ligands of (**3**) as in the case of the neopentyl carbyne $[Mo{\equiv}C{\cdot}CH_2Bu^t\{P(OMe)_3\}_2(\eta\text{-}C_5H_5)]$[10] are not labile, the unsymmetrically substituted carbyne $[Mo{\equiv}C{\cdot}CH_2Ph(PEt_3)\{P(OMe)_3\}(\eta\text{-}C_5H_5)]$ (**7**)‡ is readily formed on reaction of (**6**) with $K[BHBu^s_3]$ in thf.

The bromovinylidene complex (**2**) is also reactive towards electrophiles. Thus, treatment with HBF_4–Et_2O in diethyl ether led to an immediate reaction and the precipitation of the pale yellow cationic carbyne complex $[BrMo{\equiv}C{\cdot}CH_2Ph\{P(OMe)_3\}_2(\eta\text{-}C_5H_5)][BF_4]$ (**8**)‡ isostructural with $[HMo{\equiv}C{\cdot}CH_2Bu^t\{P(OMe)_3\}_2(\eta\text{-}C_5H_5)][BF_4]$, which has been previously[11] structurally characterised by *X*-ray crystallography. Although it is possible that protonaton occurs on the α-carbon of the vinylidene followed by a hydrogen shift process to give the cationic carbyne (**8**), we believe that (**8**) is more likely formed by direct electrophilic attack on the β-carbon atom.[12] Reduction of (**8**) with sodium amalgam in thf affords the carbyne complex (**3**) thus establishing an alternative route to substituted carbynes from halogenovinylidenes *via* electrophilic attack and reduction.

The formation of (**2**) from a bromophenylethyne complex is also of importance mechanistically, and it is interesting that when (**1**) is treated with lithium diphenylcuprate in thf the metallacyclopropene[13] $[\overline{Mo{=}C(Br)C}Ph_2\{P(OMe)_3\}_2(\eta\text{-}C_5H_5)]$ (**9**) is formed carrying a potentially replaceable bromine substituent on the carbene carbon. However, we defer discussion of the mechanistic implications of these observations to a full paper.

We thank the S.E.R.C. for support and for studentships (to R. G. B. and I. D. W.).

Received, 7th March 1983; Com. 305

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§ *Crystal data for* (**2**): $C_{19}H_{29}BrMoO_6P_2$, $M = 591.0$, monoclinic, $a = 9.749(7)$, $b = 14.773(9)$, $c = 16.834(9)$ Å, $\beta = 101.34(5)°$, $U = 2\,377(3)$ Å^3, $Z = 4$, $D_c = 1.65$ g cm^{-3}, $F(000) = 1\,192$. Space group $P2_1/c$, Mo-K_α *X*-radiation (graphite monochromator) $\bar{\lambda} = 0.710\,69$ Å, μ(Mo-K_α) = 23.7 cm^{-1}. Intensities [3 078 with $I > 2\sigma(I)$] were measured on a Syntex *R*3*m* four-circle diffractometer at 293 K in the range $3 < 2\theta < 50°$ and corrected for Lorentz, polarisation, and absorption effects. The structure was refined to *R* 0.0463 (R_w 0.0468) by blocked-cascade least-squares.

The atomic co-ordinates 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 communication.

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