

Preliminary communication

Insertion of alkynes into molybdenum–phosphine
and molybdenum–carbon bonds. X-ray structure
of the phosphonium–alkylidene complex
[MoO{=C(Ph)CH=C(Ph)CH₂PMe₂Ph}(SC₆H₂ⁱPr_{3-2,4,6})₃]

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Received 12 July 1995

Abstract

Treatment of [MoH(SC₆H₂ⁱPr_{3-2,4,6})₃(PMe₂Ph)₂] with PhC≡CH in tetrahydrofuran (THF) followed by MeOH gives the phosphonium-alkylidene complex [MoO{=C(Ph)CH=C(Ph)CH₂PMe₂Ph}(SC₆H₂ⁱPr_{3-2,4,6})₃], whose X-ray crystal structure has been determined.

Keywords: Molybdenum; Alkyne; Alkylidene; Phosphonium; Thiolate; Ylide

We have recently described [1,2] the preparation of the highly reactive, electron-deficient complexes [MoH(SR)₃(PR¹Ph₂)] and [MoH(SR)₃(PR¹Ph)₂] (R = C₆H₂Me_{3-2,4,6} or C₆H₂Pr_{3-2,4,6}; R¹ = Me or Et) and their reactions with, for example: C₅H₅N to give [MoH(SR)₃(C₅H₅N)(PR¹Ph₂)] [2]; NC₅H₄SH-2 (pySH) to give [MoH(pyS)₂(SC₆H₂ⁱPr_{3-2,4,6})(PEtPh₂)] [2]; CO to give [Mo(SC₆H₂ⁱPr_{3-2,4,6})₂(CO)₃(PMePh₂)] [3]; and thermally to give S–C cleavage reactions [4]. Here we report an extension of these studies to reactions with PhC≡CH in the presence of methanol, where addition of oxide to the metal occurs, together with formal insertion of alkyne into an Mo–P bond to give the novel phosphonium–alkylidene complex described below.

Treatment of [MoH(SC₆H₂ⁱPr_{3-2,4,6})₃(PMe₂Ph)₂] with an excess of PhC≡CH in THF, followed by solvent removal and addition of MeOH, gave after stirring for 4 h, a good yield of red crystals of the novel diamagnetic phosphonium-alkylidene complex [MoO{=C(Ph)CH=C(Ph)CH₂PMe₂Ph}(SC₆H₂ⁱPr_{3-2,4,6})₃], **1**, whose X-ray crystal structure [5] is shown in Fig. 1, together with selected molecular dimensions [$\nu(\text{Mo}=\text{O})$ 920 cm⁻¹; $\delta(^{13}\text{C}_2)$ 30.5 ppm rel. SiMe₄; $\delta(^{31}\text{P})$ –108.2 ppm rel. P(OMe)₃].

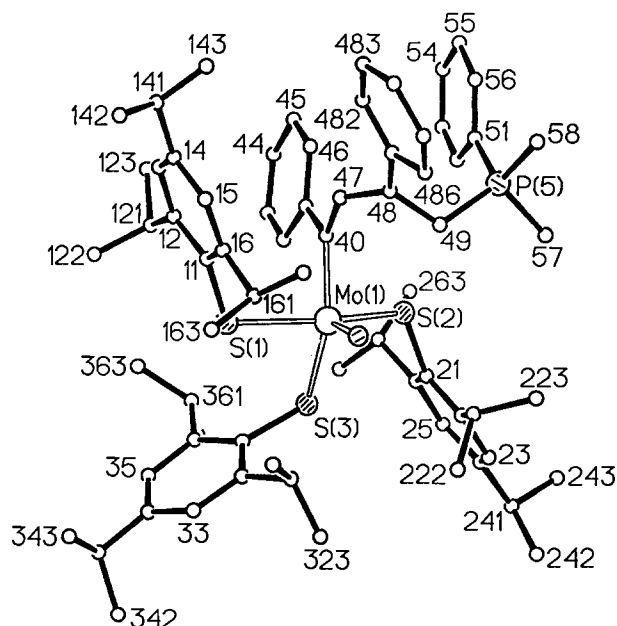
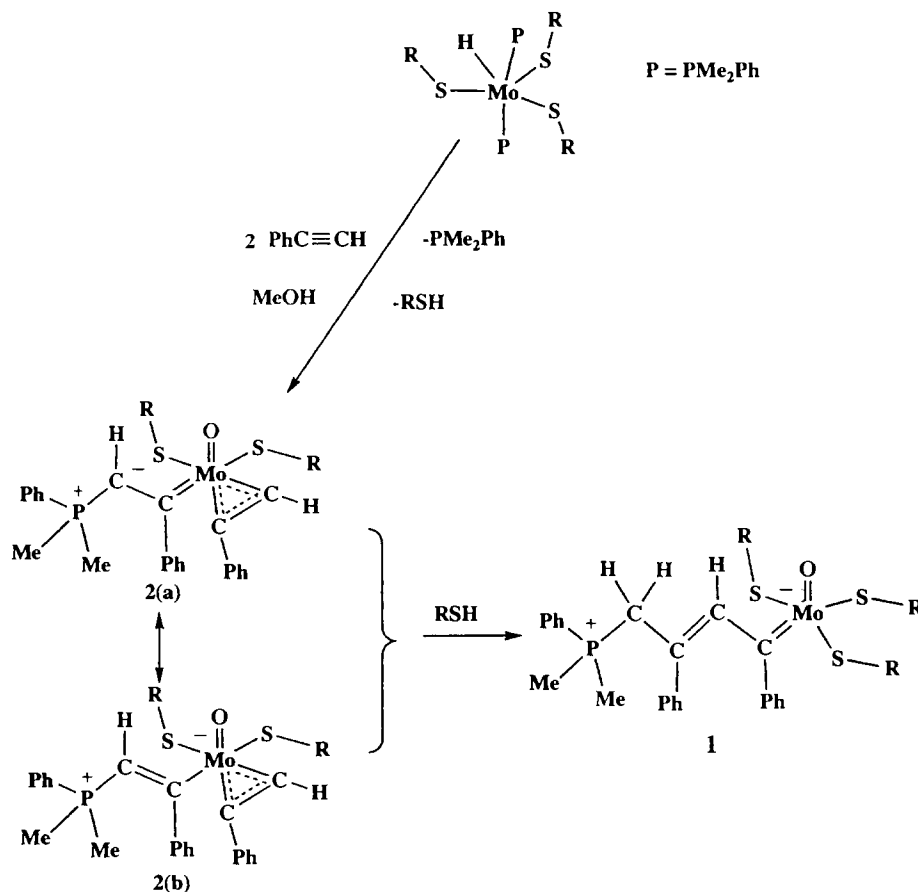


Fig. 1. A molecule of [MoO{C(Ph)CH=C(Ph)CH₂PMe₂Ph}(SC₆H₂ⁱPr_{3-2,4,6})₃], **1**. The atom numbering scheme is indicated; carbon atom names are shortened, e.g. C(323) is shown as 323. Selected bond lengths in the molecule: Mo(1)–S(1) 2.424(1), Mo(1)–S(2) 2.434(1), Mo(1)–S(3) 2.432(1), Mo(1)–C(40) 1.990(5), Mo(1)–O(6) 1.691(3), C(40)–C(47) 1.451(7), C(47)–C(48) 1.384(7), C(48)–C(49) 1.493(8), C(49)–P(5) 1.808(6) Å.

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Scheme 1. Proposed route to the formation of **1**; R = C₆H₂ⁱPr₃-2,4,6.

Obviously the process by which **1** is produced is complex. It involves generation of an Mo=O bond possibly by degradation of a pre-formed methoxide ligand [6], together with formal insertion of alkyne into an Mo–phosphine bond, then a second formal insertion of alkyne into the resulting Mo–C bond. Scheme 1 summarises the process, suggesting a probable alkyne–ylide complex intermediate, **2**, which is converted into **1**. Although we have not yet isolated an intermediate corresponding to **2** from reaction of PhC≡CH, we are prompted to suggest this final step, which involves the insertion of ligating alkyne into the Mo–C bond of **2**, because we have already isolated and structurally characterised the analogue of **2**, [MoO(η²-CHC(tol))(C(tol)CHPMePh₂)(SC₆H₂ⁱPr₃-2,4,6)₂] (tol = C₆H₄CH₃-4), **3**, from the reaction of [MoH(SC₆H₂ⁱPr₃-2,4,6)₃(PMePh₂)] and HC≡Ctol [7].

In Scheme 1, it is proposed that **1** is formed by the oxidative addition of HSC₆H₂ⁱPr₃ to **2**. Formally, the SC₆H₂ⁱPr₃ anion adds to the Mo and the proton adds to the nucleophilic ylide carbon of **2** to give the CH₂ group in **1**. Concomitantly, the alkyne in **2** inserts into the Mo–C bond to produce the novel alkylidene–phosphonium ylide ligand in **1**, whose charge separation appears to be as indicated in the Scheme, based on the following structural features.

First, the Mo–C distance in **1** [1.990(5) Å] is in the

region typical of molybdenum(VI)–alkylidene distances (e.g. 1.93(1) Å in [Mo(CH^tBu)(NC₆H₃ⁱPr₂-2,6)(OSO₂CF₃)₂(MeOCH₂CH₂OMe)] [8]), i.e. the Mo–C bond in **1** has essentially alkylidene character. Second, the P–CH₂ distance of 1.808(6) Å is, as expected, longer than the P–CR (R = H or organic substituent) distances of around 1.68–1.78 Å generally observed in ylide complexes [7,9,10]. Third, the C(49)–C(48) distance [1.493(8) Å] is significantly greater than the C(47)–C(48) distance [1.384(7) Å]. Compound **1** can therefore be regarded as a phosphonium–alkylidene complex of Mo^{VI} whereas **2** and **3** are ylide complexes and their bonding can be represented by resonance forms, as indicated in Scheme 1 for **2** where component **2(b)** predominates; they resemble the compounds [Re(O)R₃(CHCH(PMe₃))] (R = Me or CH₂SiMe₃) [10].

We are currently extending our studies to a wider range of alkynes and thiolate coligands to shed more light on the mechanism of formation of these novel complexes.

Acknowledgements

We thank the Ministry of Culture and Higher Education of the Islamic Republic of Iran for a maintenance grant to K.M.

References and notes

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- [5] Crystal data for **1**: $C_{69}H_{93}MoOPS_3 \cdot 2(CH_4O) \cdot C_7H_8$, $M = 1317.8$. Monoclinic, space group $P2_1/n$ (equiv. to no. 14), $a = 17.205(1)$, $b = 21.814(2)$, $c = 19.860(2)$ Å, $\beta = 92.121(8)^\circ$. Vol. = 7448.3 Å³. $Z = 4$, $D_c = 1.175$ g cm⁻³, $F(000) = 2824$, $\mu(Mo K\alpha) = 3.2$ cm⁻¹, $\lambda(Mo K\alpha) = 0.71069$ Å. Crystals are deep-red, diamond-shaped plates. One ca. $0.17 \times 0.43 \times 0.60$ mm mounted on glass fibre; photographic examination; then CAD4 diffractometer for accurate cell parameters and intensity measurements ($\theta_{max} = 23^\circ$). Intensity data corrected for Lorentz-polarisation effects, crystal deterioration (ca. 15%), absorption and to remove negative net intensities. 10240 Unique reflections (6528 with $I > 2\sigma_1$) entered into SHELX program system [11].
- Structure determination by heavy atom method. Refinement by large-block-matrix least-squares methods. In Mo-complex, all non-hydrogen atoms refined anisotropically; H atoms, in idealised positions, refined isotropically. Solvent molecules not fully resolved. Alternative site for the metal atom, Mo(2), identified and refined with occupancy of 0.064; alternative sites for other ligands, e.g. O(6) and alkylidene, not found. Final $R = 0.090$, $R_g = 0.069$ [11] for all 10240 reflections weighted $w = (\sigma_F^2 + 0.00027 F^2)^{-1}$. Only significant peak in difference map, 0.6 eÅ⁻³, close to Mo atom. Tables of atom coordinates, thermal parameters and bond angles and distances have been deposited at the Cambridge Crystallographic Data Centre.
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