

The Role of Metallacyclopropenes in the Formation of Alkylidyne Complexes; Evidence for a 1,2-Trimethylsilyl Shift and the X-Ray Crystal Structure of $[\text{Mo}=\text{C}(\text{SiMe}_3)\text{CH}_2\{\text{P}(\text{OMe})_3\}_2(\eta^5\text{-C}_9\text{H}_7)]$

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Reaction of $[\text{Mo}\{\text{P}(\text{OMe})_3\}_2(\text{Me}_3\text{SiC}_2\text{H})(\eta^5\text{-C}_9\text{H}_7)][\text{BF}_4]$ with $\text{K}[\text{BHBu}_3]$ affords the metallacyclopropene $[\text{Mo}=\text{C}(\text{SiMe}_3)\text{CH}_2\{\text{P}(\text{OMe})_3\}_2(\eta^5\text{-C}_9\text{H}_7)]$, structurally identified by X-ray crystallography, which rearranges quantitatively into the alkylidyne complex $[\text{Mo}=\text{C}.\text{CH}_2\text{SiMe}_3\{\text{P}(\text{OMe})_3\}_2(\eta^5\text{-C}_9\text{H}_7)]$.

There is at present considerable interest¹ in the formation and reactions of molecules containing metal-carbon multiple bonds, and as part of the general study of the reactions of nucleophilic reagents with cationic acetylene complexes of the type $[\text{Mo}\{\text{P}(\text{OMe})_3\}_2(\text{acetylene})(\eta\text{-C}_5\text{H}_5 \text{ or } \eta^5\text{-C}_9\text{H}_7)][\text{BF}_4]$,^{2,3}

we have observed the formation of a metallacyclopropene, and its novel rearrangement, *via* a 1,2-trimethylsilyl shift, into an alkylidyne complex.

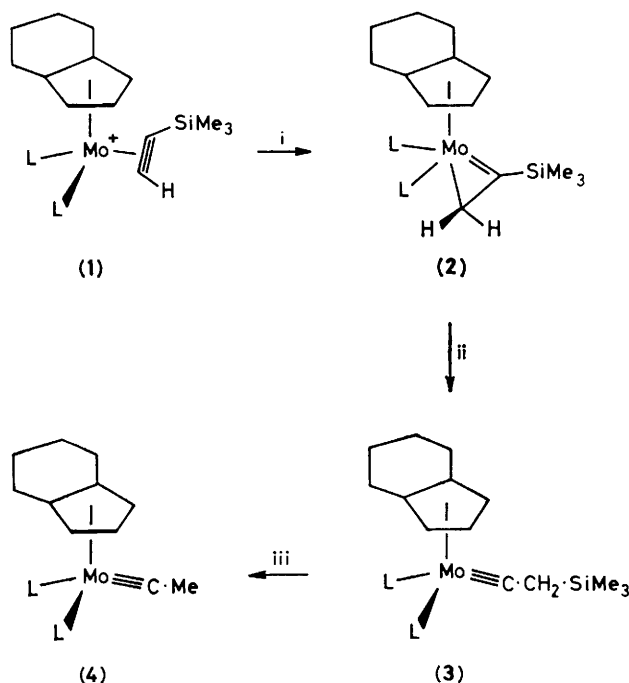
The addition of one molar equivalent of $\text{K}[\text{BHBu}_3]$ to a green, tetrahydrofuran suspension (-78°C) of

$[\text{Mo}\{\text{P}(\text{OMe})_3\}_2(\text{Me}_3\text{SiC}_2\text{H})(\eta^5\text{-C}_9\text{H}_7)][\text{BF}_4]$ (1),† produced, after low temperature work-up,‡ deep-blue, air-sensitive, hexane-soluble crystals of (2) (58% yield). Examination of the $^{13}\text{C}\{^1\text{H}\}$ n.m.r. spectrum§ revealed a low-field resonance at 276.5 p.p.m. typical of an alkylidene carbon and that of a methylene carbon at 23.9 p.p.m. suggesting³ the structure (2) illustrated in Scheme 1. Assignment of the Me_3Si group to the alkylidene carbon was deduced from an off-resonance, ^1H decoupled ^{13}C n.m.r. spectrum. These structural features were confirmed by a single-crystal X-ray diffraction study.¶

As shown in Figure 1 the molecule (2) contains a three-membered ring $\text{Mo}=\text{C}(\text{SiMe}_3)\text{CH}_2$ canted relative to the plane of the η^5 -indenyl ligand, in which the carbon atom C(8) carrying a trimethylsilyl substituent is doubly bonded to the molybdenum atom, where $\text{Mo}-\text{C}(8) = 1.957(3)$, $\text{Mo}-\text{C}(7) = 2.260(4)$, and $\text{C}(7)-\text{C}(8) = 1.436(5)$ Å. It is interesting that the resultant geometry around the molybdenum atom is somewhat distorted away from the usual four-legged piano-stool arrangement typical of the class of molecules $[\text{ML}_4(\eta\text{-C}_5\text{H}_5)]$.⁴ One leg of the stool is displaced below the plane of the other three, so that the observed geometry has elements of a capped trigonal bipyramid, in which C(7) and the indenyl ligand occupy the axial positions and C(8), P(1), and P(2) the equatorial sites. The $\text{C}(7)-\text{Mo}-\text{C}_9\text{H}_7$ (centroid of the 5-membered ring) angle of 150.4° is intermediate between that of 180° required by the trigonal bipyramid structure, and 120° characteristic of the piano-stool geometry.

In contrast to the solid-state structure, the time-averaged molecular structure of (2) in solution, as determined by n.m.r. spectroscopy, contains a plane of symmetry. This difference could be due to crystal packing effects, but it is more likely that the solid-state structure is the ground state of a low-energy fluxional process, that has the net effect of revolving the two-carbon unit with respect to the metal fragment, similar to the *exo-endo* isomerisation^{5,6} of the η^3 -allyl ligand in $[\text{Mo}(\text{CO})_2(\eta^3\text{-allyl})(\eta\text{-C}_5\text{H}_5)]$, and to the rotational behaviour of acetylenes in the cations $[\text{MoL}_2(\text{acetylene})(\eta\text{-C}_5\text{H}_5)]\text{[BF}_4\text{]}^2$.

In solution (toluene) over several hours [$t_{\frac{1}{2}}$ (303 K) ca. 45 min] the blue species (2) rearranges in quantitative yield



Scheme 1. L = $\text{P}(\text{OMe})_3$. Reagents and conditions: i, $\text{K}[\text{BHBu}_3]$, tetrahydrofuran (THF), -78°C ; ii, 25°C , toluene; iii, NaF, aqueous MeCN, 25°C .

into the yellow crystalline alkylidyne complex (3), characterised by analysis, mass spectrum, and n.m.r. spectroscopy.** Further confirmation of the structure of (3) was provided by the observation that reaction with a fluoride anion in aqueous solution led to a smooth desilylation reaction, and the formation of the ethylidyne complex (4).** Attack by the nucleophile F^- on the silicon centre of (3) would be expected to lead to carbon-silicon heterolysis^{7,8} and the formation of the stabilised vinyl alkylidene anion $[\text{Mo}(\text{C}=\text{CH}_2)\{\text{P}(\text{OMe})_3\}_2(\eta\text{-C}_9\text{H}_7)]^-$, which would then react rapidly with water to afford (4).

The rearrangement of (2) into (3) occurs under remarkably mild conditions, and involves an unusual 1,2-trimethylsilyl shift^{7,9} from an unsaturated alkylidene carbon on to a saturated carbon centre with probable concomitant formation of a metal-carbon triple bond. The isolobality concept,¹⁰ which relates the fragments CR and $\text{MoL}_2(\eta\text{-C}_5\text{H}_5)$ or $\eta^5\text{-C}_9\text{H}_7$, suggests an analogy between molecules like (2) and cyclopropenes, and it would be interesting to discover whether there is an analogous facile organic rearrangement of 1-trimethylsilyl substituted cyclopropenes to acetylenes, the high-temperature rearrangement of the corresponding unsubstituted species having been carefully studied. We have previously¹¹ observed that the vinyl complex $[\text{Mo}\{\eta^1\text{-CH}=\text{CHBu}^t\}\{\text{P}(\text{OMe})_3\}_2]$

† The cation $[\text{Mo}(\text{CO})(\text{Me}_3\text{SiC}_2\text{H})(\eta^5\text{-C}_9\text{H}_7)]\text{[BF}_4\text{]}$, prepared by an extension of the established procedure,² was treated with $\text{P}(\text{OMe})_3$ in CH_2Cl_2 to give (1).

‡ Removal of volatiles at -78°C *in vacuo*, extraction into cold (0°C) hexane, low-temperature (-40°C) column chromatography (alumina, eluting with 25% diethylether-hexane), followed by crystallisation (-78°C) from hexane.

§ N.m.r. spectra for (2) recorded in $[\text{C}_6\text{H}_6]$ /toluene: ^1H (223 K), δ 7.51 (m, 2H, C_9H_7), 6.72 (m, 2H, C_9H_7), 6.07 (m, 1H, C_9H_7), 5.72 (m, 2H, C_9H_7), 3.26 (m, 18H, POMe), 2.01 [t, 2H, CH_2 , $^3J(\text{HP})$ 7 Hz], and 0.54 (s, 9H, SiMe_3); $^{13}\text{C}\{^1\text{H}\}$ (203 K), δ 276.5 [t, $\text{Mo}=\text{C}$, $^2J(\text{CP})$ 6.4 Hz], 125.6 (s, C_9H_7), 122.5 (s, C_9H_7), 112.8 (s, C_9H_7), 97.2 (s, C_9H_7), 79.5 (s, C_9H_7), 51.4 (br.s, POCH_3), 23.9 (br. s, MoCH_2), and 1.2 p.p.m. (s, SiMe_3); $^{31}\text{P}\{^1\text{H}\}$ (203 K), δ 207.8 p.p.m. (s).

¶ Crystal data for (2): $\text{C}_{20}\text{H}_{36}\text{O}_6\text{P}_2\text{Si}$, $M = 558.1$, triclinic, space group $\overline{P}1$, $a = 10.145(2)$, $b = 10.446(3)$, $c = 15.384(6)$ Å, $\alpha = 101.85(3)$, $\beta = 97.66(3)$, $\gamma = 122.85(2)^\circ$, $U = 1279.7(7)$ Å³, $D_c = 1.45$ g cm⁻³, $Z = 2$, $F(000) = 580$ electrons, $\mu(\text{Mo-K}\alpha) = 6.99$ cm⁻¹. Current R 0.026 4 (R_w 0.026 5) for 2 830 unique, observed [$I > 2\sigma(I)$] reflections measured at 250 K on a Syntex P3m diffractometer in the range $3 < 2\theta < 45^\circ$. The structure was solved by the heavy-atom method (Patterson and Fourier) and refined by blocked-cascade least-squares. Non-hydrogen atoms were refined anisotropically, hydrogen atoms isotropically, with those in methyl and indenyl groups being constrained to idealised geometries. The atomic co-ordinates for this work 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.

** N.m.r. spectra for (3) in $[\text{C}_6\text{H}_6]$ /toluene: ^1H (303 K), δ 7.08 (m, 2H, C_9H_7), 6.54 (m, 2H, C_9H_7), 5.64 (d, 2H, C_9H_7), 5.37 (t, 1H, C_9H_7), 3.18 [t, 18H, POMe, $^3J(\text{HP}) + ^5J(\text{HP})$ 11.5 Hz], 1.85 [t, 2H, $\text{Mo}=\text{C}-\text{CH}_2$, $^4J(\text{HP})$ 5.5 Hz], and -0.04 (s, 9H, SiMe_3); $^{13}\text{C}\{^1\text{H}\}$ (303 K), δ 297.3 [t, $\text{Mo}=\text{C}$, $^2J(\text{CP})$ 30.8 Hz], 124.2 (s, C_9H_7), 122.7 (s, C_9H_7), 118.8 (s, C_9H_7), 93.6 (s, C_9H_7), 78.8 (s, C_9H_7), 51.3 (br.s, POCH_3), 45.7 ($\text{Mo}=\text{C}-\text{CH}_2$), and -0.2 p.p.m. (s, SiMe_3); $^{31}\text{P}\{^1\text{H}\}$ (303 K), δ 207.6 p.p.m. (s).

N.m.r. spectra for (4) in C_6D_6 : ^1H (303 K), δ 7.15 (m, 2H, C_9H_7), 6.65 (m, 2H, C_9H_7), 5.70 (d, 2H, C_9H_7), 5.42 (t, 1H, C_9H_7), 3.35 [t, 18H, POMe, $^3J(\text{HP}) + ^5J(\text{HP})$ 11.5 Hz], and 1.90 [t, 3H, $\text{Mo}=\text{C}-\text{Me}$, $^4J(\text{HP})$ 5.0 Hz]; $^{13}\text{C}\{^1\text{H}\}$ (303 K), δ 295.8 [t, $\text{Mo}=\text{C}$, $^2J(\text{CP})$ 29.5 Hz], 123.4 (s, C_9H_7), 122.1 (s, C_9H_7), 118.4 (s, C_9H_7), 92.5 (s, C_9H_7), 74.3 (s, C_9H_7), 50.7 (br.s, POCH_3), and 36.0 p.p.m. (s, $\text{Mo}=\text{C}-\text{CH}_3$); $^{31}\text{P}\{^1\text{H}\}$ (303 K), δ 207.7 p.p.m. (s).

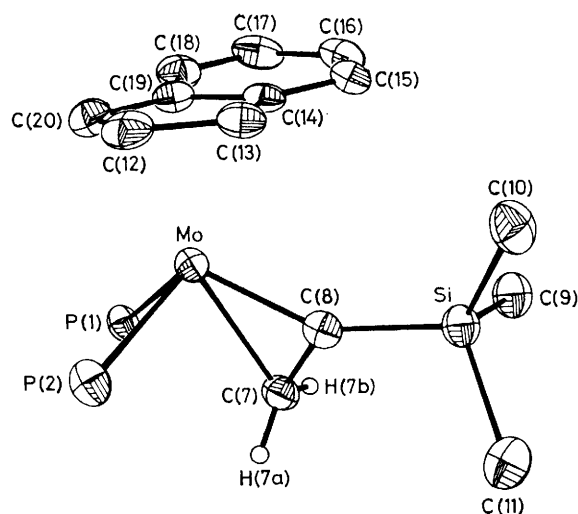


Figure 1. Molecular structure of $[\text{Mo}=\text{C}(\text{SiMe}_3)\text{CH}_2\{\text{P}(\text{OMe})_3\}_2-(\eta^5\text{-C}_9\text{H}_7)]$ (2). Important geometrical parameters: Mo-P(1) 2.351(1), Mo-P(2) 2.359(1), Mo-C(7) 2.260(4), Mo-C(8) 1.957(3), C(8)-Si 1.850(4), mean C(H₃)-Si 1.876(4), C(7)-C(8) 1.436(5) Å; C(7)-Mo-C(8) 39.0(1), Mo-C(7)-C(8) 59.0(2), Mo-C(8)-C(7) 82.0(2), P(1)-Mo-P(2) 91.8(1), P(2)-Mo-C(7) 89.0(1), P(2)-Mo-C(8) 96.3(1), C₉H₇-Mo-P(1) 121.4(1), C₉H₇-Mo-P(2) 114.5(1), C₉H₇-Mo-C(7) 150.4(2), C₉H₇-Mo-C(8) 116.5(2)°. C₉H₇ = centroid of indenyl five-membered ring.

($\eta\text{-C}_5\text{H}_5$) rearranges on heating with loss of one trimethyl phosphite molecule to form the alkylidyne $[\text{Mo}(\text{CCH}_2\text{Bu}^t)\text{-}\{\text{P}(\text{OMe})_3\}_2(\eta\text{-C}_5\text{H}_5)]$, and are examining the possibility that a related 1,2-H shift of a metallacyclopropene, $\text{Mo}=\text{CH}\text{-CHBu}^t$ into $\text{Mo}\equiv\text{CCH}_2\text{Bu}^t$, may be involved.

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