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Preliminary communication

MIGRATION OF A PHENYL GROUP FROM SULPHUR TO A CARBON ATOM OF A RING-OPENED CYCLOPROPENE; CRYSTAL STRUCTURE OF $[Mo(\eta^3\text{-}syn\text{-}1\text{-}Ph\text{-}3,3\text{-}Me_2C_3H_2)(1,2\text{-}C_6H_4S_2)(\eta\text{-}C_5H_5)]$

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Summary

Reaction of $[Mo(\eta\text{-}MeC_2Me)(SC_6H_4\text{-}o\text{-}SC_6H_5)(\eta\text{-}C_5H_5)]$ with 3,3-dimethylcyclopropene leads to displacement of the acetylene and a novel migration of the phenyl group from sulphur to a carbon atom of the ring-opened cyclopropene with formation of the η^3-allylic complex $[Mo(\eta^3\text{-}syn\text{-}1\text{-}Ph\text{-}3,3\text{-}Me_2\text{-}C_3H_2)(1,2\text{-}C_6H_4S_2)(\eta\text{-}C_5H_5)]$, which was identified by X-ray crystallography.

There is continuing interest in the ability of transition metals to promote ring opening reactions of cyclopropenium cations [1], cyclopropenone [1] and cyclopropene [2,3]. In exploring the reaction of 3,3-dimethylcyclopropene with the molybdenum complex (I) [4,5,6] $[Mo(\eta\text{-}MeC_2Me)(SC_6H_4\text{-}o\text{-}SC_6H_5)(\eta\text{-}C_5H_5)]$ we have observed an unusual molecular rearrangement.

Treatment (40°C, 3 *d*, toluene) of I with an excess of the alkene affords (60% yield) the red crystalline complex II (^1H NMR (C_6D_6): 1.52 (m, 2 H), 2.25 (d, 2 H), 2.80 (m, 5 H), 4.93 (d, 1 H, CH, ^3J(HH) 13.5 Hz), 6.24 (s, 5 H, C_5H_5), 6.74 (d, 1 H, CH, ^3J(HH) 13.5 Hz), 7.85 (s, 3 H, Me), 9.31 (s, 3 H, Me); $^{13}C\{^1H\}$ NMR (C_6D_6): δ (ppm), 144.3, 129.8, 129.1, 126.9, 125.7, 124.8, 123.1, 122.5 (aromatic carbons), 92.7 (C_5H_5), 79.1 (*C*H), 77.8 (*C*Me$_2$), 66.6 (*C*H), 30.3, 28.8 (Me)). In agreement with the NMR data the mass spectrum (f.d.) and elemental analysis of II indicated that 3,3-dimethylcyclopropene had displaced the but-2-yne leading to the observed stoichiometry. In order to differentiate between the various possible structures for II a single-crystal X-ray diffraction study was undertaken.

Crystal data: $C_{22}H_{22}S_2Mo$, $M = 446.5$, monoclinic, space group $P2_1/n$, a 12.729(5), b 14.071(6), c 11.048(4) Å, β 102.78(3)°, $U = 1\,929.8(1.3)$ Å^3,

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$Z = 4$, $F(000) = 912$, D_c 1.537 g cm^{-3}, Mo-K_α X-radiation, graphite monochromator, $\bar{\lambda} = 0.71069$ Å, μ(Mo-K_α) 8.7 cm^{-1}.

The structure was solved and refined by conventional heavy-atom, Fourier and least-squares methods. For 2040 independent observed ($I > 2\sigma(I)$) reflections collected at room temperature on a Syntex R3m diffractometer in the range $3° < 2\theta < 55°$, the current R is 0.067*.

As is shown by the structure illustrated in Fig. 1 complex II is a benzene-1,2-dithiolate [7] complex carrying an η^3-bonded 1-phenyl-3,3-dimethyl-substituted allyl ligand in an *exo*-configuration, the phenyl group adopting a *syn*-position. There is considerable puckering of the C_2S_2Mo ring about an axis through the sulphur atoms as shown by the dihedral angle of 23.1° between the planar units S(1)—C(12)—C(13)—S(2) and S(1)—Mo—S(2). The cyclopentadienyl and allylic fragments adopt typical bonding modes [8].

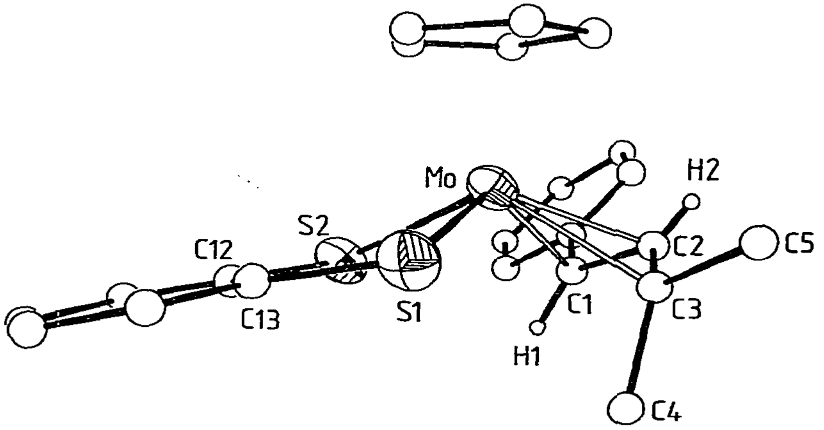

Fig. 1. Molecular structure of [Mo(η^3-*syn*-1-Ph-3,3-Me$_2$C$_3$H$_2$)(1,2-C$_6$H$_4$S$_2$)(η-C$_5$H$_5$)] (II). Important bond lengths include: Mo—S(1) 2.357(3), Mo—S(2) 2.328(3), Mo—C(1) 2.305(10), Mo—C(2) 2.231(9), Mo—C(3) 2.310(10), S(1)—C(12) 1.745(11), S(2)—C(13) 1.775(10) Å: Angles Mo—S(1)—C(12) 105.8(4), Mo—S(2)—C(13) 106.1(4)°.

Thus, a delocalised benzene-1,2-dithiolate ligand has been formed by phenyl migration from a 3*e* chelating SC_6H_4—SC_6H_5 ligand, a type of reaction which has not previously been observed. The phenyl group originating on a sulphur atom ends up on an olefinic carbon atom of 3,3-dimethylcyclopropene with cleavage of one of the ring 2,3-carbon—carbon bonds. It is an interesting possibility that coordination of the cyclopropene and loss of but-2-yne lead to an intermediate A (see Scheme 1) which then undergoes a ring opening to give a vinyl carbene [2,9] (B) with subsequent phenyl migration via the metal to the carbene carbon to afford the η^3-allyl (II). Although this last step is without precedent, we note that both migration of hydrogen from transition metal to carbene carbon [10] and phenyl transfer from coordinated phosphorus to metal [11] have been observed.

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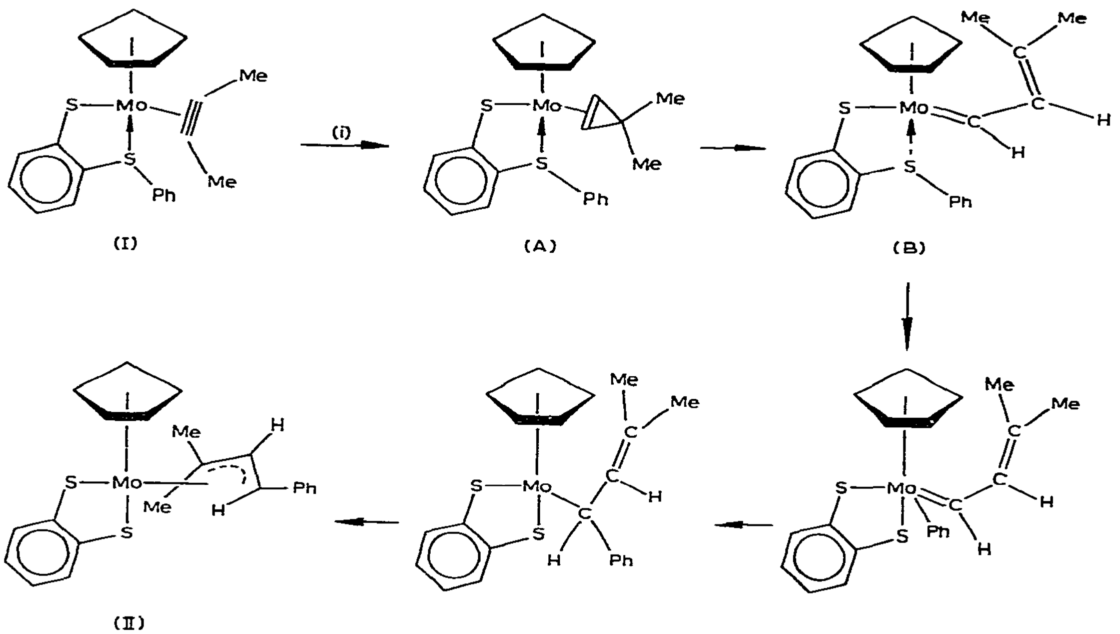
*The atomic coordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.



Scheme 1. (i) + 3,3-dimethylcyclopropene and —but-2-yne.

The ease with which I reacts with 2*e* donors is apparent from the observation that reaction with CO (room temperature, 1 atm, 15 minutes) affords $[Mo(\eta^2\text{-}MeC_2Me)(CO)(SC_6H_4\text{-}o\text{-}SC_6H_5)(\eta\text{-}C_5H_5)]$ (III)**.

Preliminary X-ray diffraction results [12] show not only coordinated CO but also that the ligand $SC_6H_4\text{-}o\text{-}SC_6H_5$, although monodentate, is unchanged, thereby making phenyl migration peculiar to the reaction with 3,3-dimethylcyclopropene.

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**Selected spectroscopic data for I (green crystals). ^1H NMR (C_6D_6): τ 2.05 (d, 2 H, aromatichydrogens), 2.86 (m, 7 H, aromatic hydrogens), 5.40 (s, 5 H, C_5H_5), 7.24 (s, 6 H, C*Me*); $^{13}C\{^1H\}$ NMR (acetone-d_6): δ (ppm) 208.7 ($C\equiv CMe$), 95.2 (C_5H_5) and 18.9 (C*Me*). III (purple crystals) ν(CO)(toluene) 1925 cm^{-1}. ^1H NMR (C_6D_6): τ 2.9 (m, 9 H, aromatic hydrogens), 5.03 (s, 5 H, C_5H_5), 7.26 (s, 3 H, Me), 7.33 (s, 3 H, Me); $^{13}C\{^1H\}$NMR (C_6D_6): δ (ppm) 234.5 (CO), 181.0 ($C\equiv CMe$), 178.9 ($C\equiv CMe$), 96.4 (C_5H_5), 20.5 (C*Me*), and 17.2 (C*Me*).

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