# Carbon–Hydrogen Activation in a 1,3-Diene Coordinated onto a Molybdenum(II) Centre

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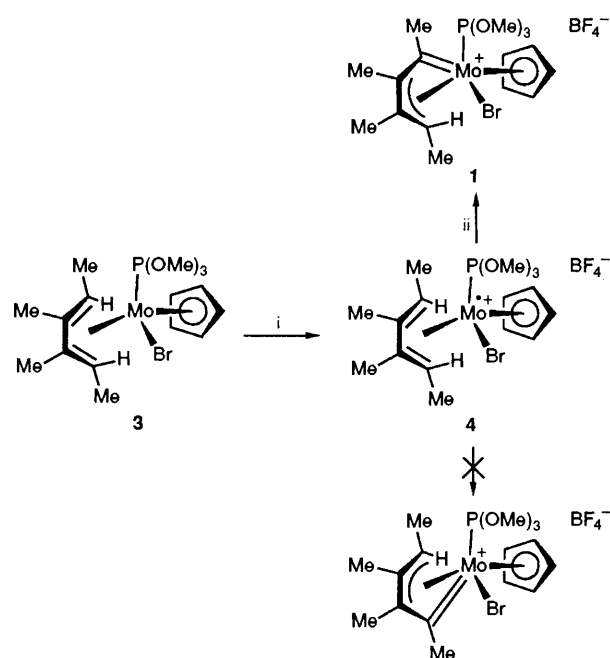
Trimethyl phosphite reacts selectively with [BrMo=C(Me)CHMe(η^2-MeC$_2$Me)(η^5-C$_5$H$_5$)][BF$_4$] to form the X-ray crystallographically identified η^4(5e)-butadienyl cation [BrMo=C(Me)-η^3-{C(Me)C(Me)CHMe}{P(OMe)$_3$}(η^5-C$_5$H$_5$)][BF$_4$], which in turn reacts with Bu$^s_2$AlH to form the 1,3-diene complex [BrMo{η^4-CH(Me)=C(Me)C(Me)=C(H)Me}{P(OMe)$_3$}(η^5-C$_5$H$_5$)]; this unexpectedly reacts regioselectively with [Ph$_3$C][BF$_4$] to regenerate the parent η^4(5e)-butadienyl cation with significant implications for alkenic C–H activation.

In developing the chemistry of organic molecules coordinated onto transition metal centres the reactions of 1,3-dienes have played an important role.[1] Despite these developments and also a considerable general concern with alkenic C–H activation,[2] it is interesting to note that there are no reports of reactions involving the activation of the terminal alkenic carbon–hydrogen bonds of coordinated 1,3-dienes. In exploring the reaction chemistry of cationic molybdenum η^4(5e)-butadienyl complexes we have discovered the first example of such an unusual reaction.

We have previously[3] shown that protonation of the complexes [MoX(η^2-MeC$_2$Me)$_2$(η^5-C$_5$H$_5$ or η^5-C$_9$H$_7$)] (X=Cl, Br, I) affords the cations [XMo=C(Me)CHMe(η^2-MeC$_2$Me)-(η^5-C$_5$H$_5$ or η^5-C$_9$H$_7$)][BF$_4$], which on treatment with PR$_3$ (R=Me, or OMe) undergo C–C coupling reactions to form η^4(5e)-butadienyl complexes of the type [XMo=C(Me)-η^3-{C(Me)C(Me)CHMe}(PR$_3$)(η^5-C$_5$H$_5$ or η^5-C$_9$H$_7$)][BF$_4$]. In developing the chemistry of these species it was clearly of interest to attempt to transform the C$_4$ butadienyl fragment into a 1,3-diene by delivering a nucleophile to the α or carbenoid carbon atom.† However, reaction [0°C, thf (tetrahydrofuran)] of, for example, [BrMo=C(Me)-η^3-{C(Me)C(Me)CHMe}{P(OMe)$_3$}(η^5-C$_5$H$_5$)][BF$_4$] **1** with K[BHBu$^s_3$] afforded a mixture of two products (**2** and **3**, see Scheme 1) in a ratio of 1:3. Examination of the ^{1}H and ^{13}C-{H} NMR spectra‡ showed that the major product was the required 1,3-diene substituted complex [MoBr{η^4-CH(Me)=C(Me)C(Me)=C(H)Me}{P(OMe)$_3$}(η^5-C$_5$H$_5$)] **3**, the minor product being the σ,η^3-(4e)-bonded vinylallene substituted molecule [MoBr{σ,η^3-CH(Me)C(Me)C(Me)-CCH$_2$}{P(OMe)$_3$}(η^5-C$_5$H$_5$)] **2**. In order to improve the regioselectivity of this reaction a less proton basic source of 'H$^-$' was sought. This was provided by diisobutylaluminium hydride. Reaction (thf, −78 to 25°C) of [BrMo=C(Me)-η^3-{C(Me)C(Me)CHMe}{P(OMe)$_3$}(η^5-C$_5$H$_5$)][BF$_4$] **1** with a molar equivalent of Bu$^s_2$AlH afforded selectively, and in good
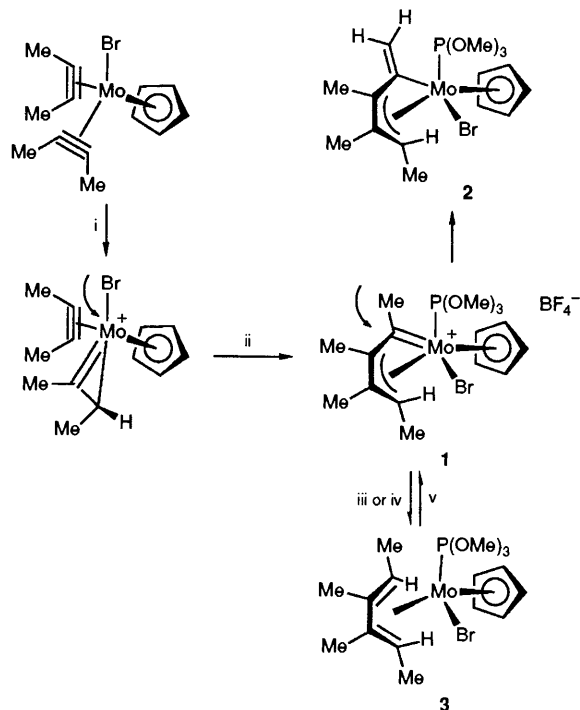
Scheme 1 *Reagents*: i, HBF$_4$·Et$_2$O, CH$_2$Cl$_2$; ii, P(OMe)$_3$, CH$_2$Cl$_2$; iii, K[BHBu$^s_3$], thf; iv, Bu$^s_2$AlH, thf; v, [Ph$_3$C][BF$_4$], CH$_2$Cl$_2$

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† It is interesting that EHMO calculations (R. Deeth and C. B. M. Nation) suggest that such a reaction should occur on C$_\alpha$ under frontier orbital control.

‡ *Selected spectroscopic data* for **1**: NMR ^{1}H(CD$_3$NO$_2$), δ 5.86 [d, 5H, C$_5$H$_5$, ^{3}J(Ph) 1.6 Hz], 3.89 [d, 9H, POMe, ^{3}J(Ph) 10.4 Hz], 2.70 [d, 3H, Mo=C(*Me*), ^{4}J(Ph) 7.0 Hz], 2.65 [m, 1H, C*H*Me, ^{3}J(MeH) 5.9 Hz], 2.35 (s, 3H, *Me*C), 2.23 (s, 3H, *Me*C), 2.17 [d, 3H, *Me*CH, ^{3}J(MeH) 5.9 Hz]; ^{13}C-{^{1}H} (CD$_3$NO$_2$), δ 305.5 [d, Mo=C, ^{2}J(PC) 23.5 Hz], 132.5 (*C*Me), 108.4 (*C*Me), 101.3 (*C*$_5$H$_5$), 73.4 (*C*HMe), 57.2 [d, PO*Me*, ^{2}J(PC) 10.5 Hz], 29.5 [d, Mo=C*Me*, ^{3}J(PC) 2.7 Hz] 18.0 (*C*Me), 16.0 (*C*Me), 15.1 [d, C*H*Me, ^{3}J(PC) 1.9 Hz]; ^{31}P{^{1}H} (CD$_2$Cl$_2$), δ 119.0 (POMe).

Compound **3**: NMR ^{1}H(C$_6$D$_6$), δ 4.54 [d, 5H, C$_5$H$_5$, ^{3}J(PH) 1.3 Hz], 3.37 [d, 9H, POMe, ^{3}J(PH) 9.6 Hz], 2.35 [d, 3H, C(Me), ^{4}J(PH) 2.0 Hz], 2.24 (s, 3H, C(Me)], 1.89 [d, 3H, CH(*Me*), ^{3}J(MeH) 6.1 Hz], 1.29 [d, 3H, CH(*Me*), ^{3}J(MeH) 6.1 Hz], 1.25 [apparent quintet, 1H, C*H*(Me), ^{3}J(MeH) $\approx$ ^{3}J(PH) 6.2 Hz], 0.43 [apparent quintet, [1H, C*H*(Me)], ^{3}J(MeH) $\approx$ ^{3}J(PH) 6.3 Hz]; ^{13}C-{^{1}H} (C$_6$D$_6$), δ 116.3 (*C*Me), 112.2 (*C*Me), 89.9 (C$_5$H$_5$), 60.6 (*C*HMe), 57.6 (*C*HMe), 53.6 [d, PO*Me*, ^{2}J(PC) 9.0 Hz], 17.0 (*C*Me), 16.8 (CH*Me*), 16.1 (*C*Me), 15.4 (CH*Me*); ^{31}P-{^{1}H}(CD$_2$Cl$_2$), δ 143.8 (POMe).

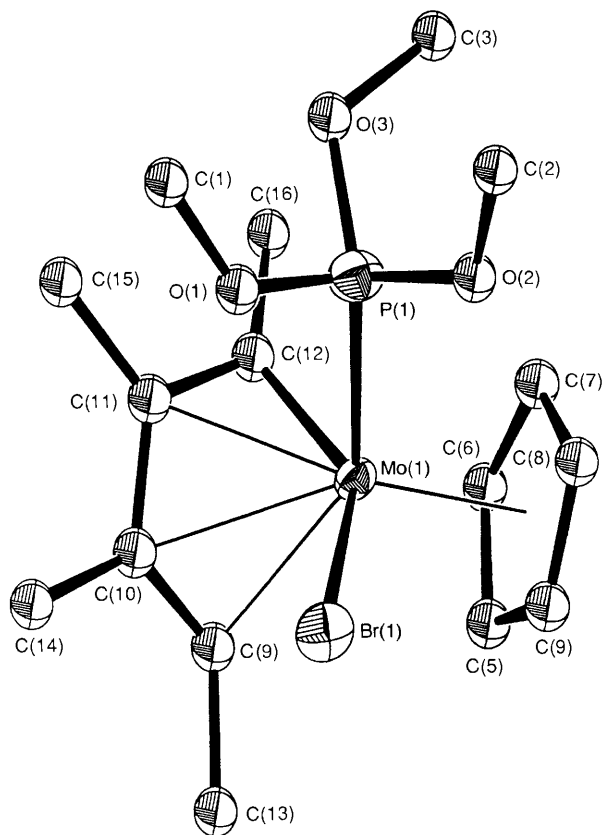Scheme 2 *Reagents*: i, + [Ph$_3$C][BF$_4$], −Ph$_3$C·; ii, + Ph$_3$C·, −Ph$_3$CH

Fig. 1 Molecular structure of the cation part of **1** showing the labelling scheme used in the text. All hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (°): Mo(1)–Br(1) 2.648(3), Mo(1)–P(1) 2.496(6), Mo(1)–C(9) 2.34(2), Mo(1)–C(10) 2.44(2), Mo(1)–C(11) 2.35(2), Mo(1)–C(12) 1.94(2), C(9)–C(10) 1.34(3), C(10)–C(11) 1.40(3), C(11)–C(12) 1.40(3); C(12)–Mo(1)– Br(1) 136.9(7), C(12)–Mo(1)–C(9) 76.8(8), C(9)–C(10)–C(11) 122(2), C(10)–C(11)–C(12) 114(2), Mo(1)–C(9)–C(10) 78(1), Mo(1)– C(12)–C(11) 88(1).

yield (75%), the purple crystalline air-sensitive *endo*-η^4-*cis*-2,3-dimethylhexa-2,4-diene complex **3**,‡ which was structurally characterised by NMR spectroscopy. The relative position of the two 1,3-diene hydrogen substituents was determined by nuclear Overhauser enhancement (NOE) difference spectroscopy, the presence of a strong interaction indicating that both hydrogens occupy 'inside' positions as illustrated.§

When a solution of the 1,3-diene complex **3** in dichloromethane was treated at room temperature with a molar equivalent of trityl tetrafluoroborate there was a rapid change in colour from purple to orange and addition of diethyl ether resulted in the precipitation in good yield of the parent orange crystalline η^4(5e)-butadienyl complex **1**.

This last reaction is most unusual and involves an unprecedented formal hydride abstraction by the trityl cation from one of the terminal diene C–H bonds. In order to clarify

the regiochemistry of this reaction a single crystal X-ray diffraction study¶ was undertaken on the parent η^4(5e)-butadienyl cation **1**. The molecular geometry of the cation is shown in Fig. 1. This shows that the butadienyl ligand adopts an *endo*-type geometry where the hydrogen substituent attached to C(9) points towards the η^5-C_5H_5 ligand, *i.e.* is in an 'inside' position. The bromine substituent is *trans* to the carbon atom C(12), which is clearly double bonded [Mo(1)– C(12) 1.94(2) Å] to the metal centre, the other three butadienyl carbons showing longer Mo–C distances [Mo(1)– C(11) 2.35(2), Mo(1)–C(10) 2.44(2), Mo(1)–C(9) 2.34(2) Å] more compatable with a η^3-allylic bonding mode.

This clearly shows that in the reaction of **1** with Bu^s_2AlH, 'H⁻' selectively adds to the carbenoid carbon C(12) to give a 1,3-diene with both hydrogens in the 'inside' position, and that significantly the formal hydride abstraction reaction is also regioselective, the C–H bond of the 1,3-diene *trans* to the bromine ligand being preferentially activated and abstracted. We suggest (see Scheme 2) that hydride is not actually directly abstracted and the trityl cation is acting initially as a one-electron oxidant transforming **3** into the radical cation **4**. It is this odd electron (17e) species **4** which then undergoes C–H bond cleavage. This could occur either by direct attack by the radical $Ph_3C\cdot$ on an alkenic C–H *trans* to bromine, or, more likely, by the alkenic C–H bond of the 1,3-diene adding oxidatively to the molybdenum centre followed by H· abstraction from the metal.

The suggestion that alkenic C–H activation can be facilitated by an initial one-electron oxidation[4] has interesting implications, while the ability to transform a η^4-*cis*-1,3-diene ligand into a reactive η^4(5e)-butadienyl is also potentially important from a synthetic standpoint.

References

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2 P. O. Stoutland and R. G. Bergman, *J. Am. Chem. Soc.*, 1988, **110**, 5732, and references cited therein.
3 G. C. Conole, M. Green, M. McPartlin, C. Reeve and C. M. Woolhouse, *J. Chem. Soc., Chem. Commun.*, 1988, 1310.
4 Although there are now several known examples of C–H bond cleavage induced by oxidation (see, N. G. Connelly, *Chem. Soc. Rev.*, 1989, 153; and references cited therein) there are no reported cases of such reactions with alkenic or 1,3-diene C–H bonds. It is possible that the transformations **3** → **4** → **1** are facilitated by spin delocalisation *via* the developing metal to carbon double bond.

§ This structural assignment is supported by the observation that reaction of Bu^s_2AlH with the mixture (1:6) of isomeric cations [BrMo=C(Me)-η^3-{C(Me)C(Me)CHMe}(PMe₃)(η^5-C_9H_7)]- [BF₄] (differing only with respect to the relative positions of the PMe₃ ligand and Mo=C bond) affords only *one* 1,3-diene complex [BrMo-{η^4-CH(Me)=C(Me)C(Me)=C(Me)H}(PMe₃)(η^5-C_9H_7)], in which the C*H*Me ¹H resonances exhibit a significant upfield shift relative to the η^5-C_5H_5 complex.