Carbon–Carbon Bond Formation mediated by Molybdenum in an Intermediate η^4-s-*trans*-Diene Cation

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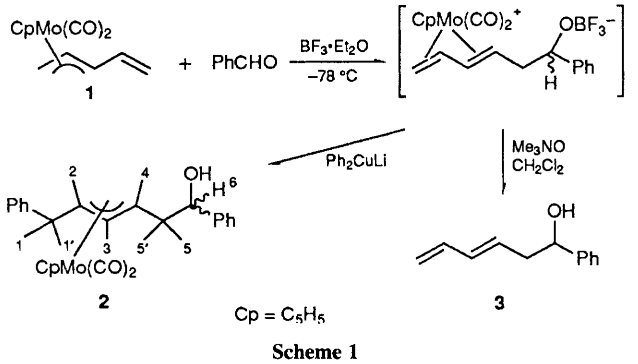
The η^3-allylmolybdenum complexes [Mo(C_5H_5)(CO)$_2$(*syn*-1-C_3H_4R)] (R = vinyl or buta-1,3-dienyl) undergo BF_3 catalysed carbon–carbon bond formation with aldehydes, ketones and α,β-unsaturated ketones; applications to the synthesis of functionalized 1,3-dienes and 1,3,5-trienes are reported, and evidence for formation of an s-*trans*-diene as an intermediate is presented.

An s-*trans*-diene cation was first prepared by Green *et al.*[1] by protonation of a molybdenum-η^3-pentadienyl ligand. It was shown later that the s-*trans-cis*-pentadiene can be generated by treatment of (*RR*)- or (*SS*)-[Mo(C_5H_5)(CO)$_2${η^3-1-C_3H_4CH(OH)Me}] with (CF_3SO_2)$_2$O by an intramolecular S_N2 mechanism.[2] In the latter, the cation is highly reactive and readily forms various C–X bonds (X = O, S, N, C, H, or halides) with diverse nucleophiles to produce α-functionalised allyl compounds.[3] Although the reactivity of an η^4-s-*trans*-diene[4,5] is considerably greater than that of η^4-s-*cis*-diene, we report here the possibility of carbon–carbon bond formation involving the s-*trans*-form as the intermediate.

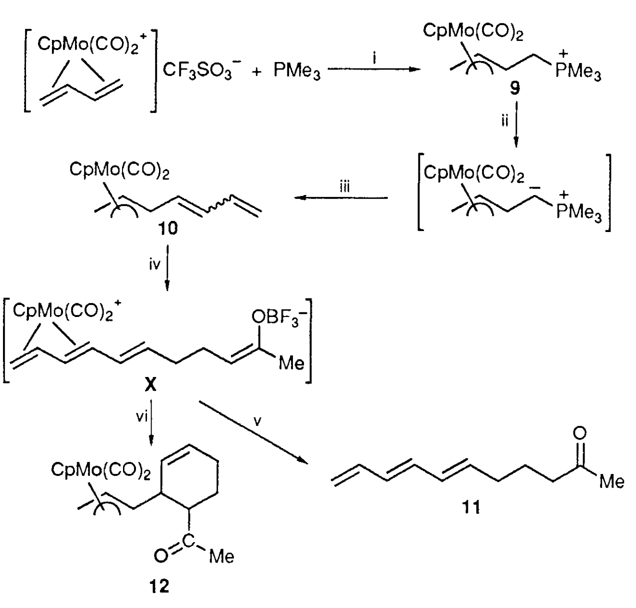
The reaction of [Mo(C_5H_5)(CO)$_2$(*syn*-η^3-pentadienyl)][6][†] **1** with PhCHO (2.0 mol equiv., −78 °C, toluene) in the presence of $BF_3{\cdot}Et_2O$ (1.0 mol equiv.) slowly deposits a red precipitate which is very sensitive to air. Its IR spectrum (Nujol) exhibited terminal ν(Mo–CO) stretching at 2050vs and 2005vs cm^{-1}, indicative of an η^4-diene cation.[3] Although its low-temperature ^{1}H NMR spectrum (CD_3COCD_3, −60 °C) was ill defined, the s-*trans*-diene structure can be deduced from the structure of **2** which was obtained from the reaction of the unstable used compound with Ph_2CuLi [tetrahydrofuran (thf), −78 °C]. Two diastereoisomers in equal amounts were obtained, separable on a preparative silica TLC plate (73%).[‡] The *syn,syn*-η^3-allyl configurations of the two diastereoisomers of **2** are indicated by the



Scheme 1

[†] *syn* refers to the relative positions of $PhCH_2$ and PhCH(OH)CH_2.

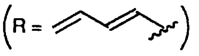
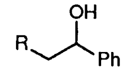
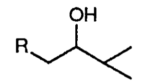
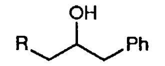
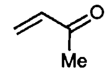
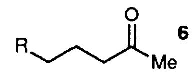
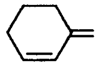
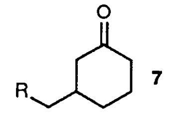
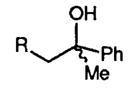
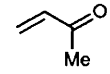
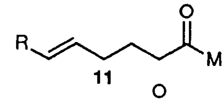
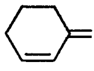
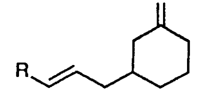
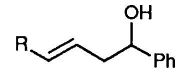
[‡] Satisfactory elemental analyses and mass spectral data were obtained for **2–14**.



Scheme 2 *Reagents and conditions*: i, CH_2Cl_2, 23 °C; ii, BuLi (1.1 mol equiv., −78 °C, THF); iii, $CH_2{=}CHCHO$ (1.2 mol equiv., −78 °C, THF); iv, $CH_2{=}CHCOMe$ (1.1 mol equiv.), $BF_3{\cdot}OEt_2$ (1.0 mol equiv., toluene −78 °C); v, CH_2Cl_2, Me_3NO (10.0 mol equiv., 23 °C); vi, H_2O–MeCN (1 : 1), −78 to 23 °C (THF = tetrahydrofuran)

magnitude of the coupling constants $J_{2,3} = J_{3,4} = 9.8$ Hz.§ Redissolution of the red precipitate¶ in CH_2Cl_2 (23 °C, 1 h stirring) followed by demetallation with excess of anhydrous Me_3NO afforded (*E*)-1-phenylhexa-3,5-dien-1-ol **3** (Table 1, entry 1) in 68% yield after work-up. We have also synthesised (*E*)-2-methylocta-5,7-diene-3-ol **4** and 1-phenylhepta-4,6-dien-2-ol **5** in yields > 50% when Me_2CHCHO and $PhCH_2CHO$ were employed. Complex **1** undergoes BF_3-catalysed Michael reaction with methyl vinyl ketone and cyclohex-2-enone to give more useful functionalized (*E*)-1,3-dienes; the yields were 40–42% (entry 4, 5). Its reaction with acetophenone occurred in only a low yield (10%, entry 6).

Table 1 Reactions of the allyl complexes **1** and **10** with electrophiles[a]

Entry	Complex	+ Electrophile[b]	Product 	Yield (%)[c]
1	**1**	PhCHO	 **3**	68
2	**1**	Me_2CHCHO	 **4**	55
3	**1**	$PhCH_2CHO$	 **5**	53
4	**1**		 **6**	42
5	**1**		 **7**	40
6	**1**	PhCOMe	 **8**	10
7	**10**[d]		 **11**	38
8	**10**		 **13**	38
9	**10**	PhCHO	 **14**	50

[a] *Reagents and conditions*: $BF_3{\cdot}OEt_2$ (1.0 mol equiv., toluene, −78 °C), then excess of Me_3NO (10 mol equiv., CH_2Cl_2, 23 °C). [b] 2.0–2.5 mol equiv. [c] All organic products were purified by preparative TLC on silica. [d] Mixture of (*Z*)- and (*E*)-isomers (3 : 2).

More interestingly, a molybdenum η^3-allyl complex bearing a buta-1,3-dienyl group is also reactive with electrophiles in carbon–carbon formation to give useful functionalized (*E*,*E*)-hexa-1,3,5-trienes. As outlined in Scheme 2, treatment of $[Mo(C_5H_5)(CO_2)(\eta^4\text{-s-}trans\text{-pentadiene})]CF_3SO_3$[3] with PMe_3 (1.5 mol equiv., 23 °C, CH_2Cl_2, 2.5 h) produced the salt **9** (95%). Deprotonation of **9** with BuLi (1.2 mol. equiv., thf, −78 °C) generated the ylide which then reacted with acrolein to give **10** as a mixture of (*Z*)- and (*E*)-forms (*Z* : *E* 3 : 2) in 51% yield. The reaction of **10** with methyl vinyl ketone (1.2 mol. equiv., −78 °C, toluene, 6 h) in the presence of $BF_3{\cdot}Et_2O$ (1.1 mol. equiv.) likewise produced a red precipitate (**X**) which then liberated methyl (*E*,*E*)-nona-4,6,8-trienyl ketone **11** upon demetallation with Me_3NO in CH_2Cl_2. Slow addition of H_2O–MeCN (1 : 1 v/v) to the suspension of **X** at −78 °C, then warming to 23 °C, led to its dissolution. A [4 + 2] cyclized allyl-molybdenum complex **12** was isolated as a single diastereisomer (*exo* : *endo* 6 : 4) in 42% yield, again indicating that the s-*trans*-diene cation (**X**) was an intermediate. Reactions of **10** with cyclohexenone and benzaldehyde proceed reasonably well to afford **13** and **14** in 36 and 50% yields respectively.

In their synthetic utility **1** and **10** are essentially equivalent to the pentadienyl[7] and heptatrienyl anions[8] respectively. The resulting η^4-s-*trans*-diene is of particular interest owing to its

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§ *Selected ¹H NMR data* ($CDCl_3$, 300 MHz, 298 K, coupling constants in Hz) for **2**, diastereoisomer A, δ 1.35 (ddd, 1H, H^4), 1.47 (ddd, 1H, H^2), 1.86 (ddd, 1H, H^5), 2.60–2.68 (complex m, 2H, H^1 + $H^{5'}$), 3.33 (dd, 1H, H^1), 3.70 (t, 1H, H^3), 4.74 (dd, 1H, H^6), 5.22 (s, 5H, C_5H_5), 7.08–7.35 (10H, $2C_6H_5$); $J_{1,1'} = 13.1$, $J_{1',2} = 3.6$, $J_{1,2} = 9.7$, $J_{2,3} = J_{3,4} = 9.8$, $J_{4,5} = 10.2$, $J_{4,5'} = 3.9$, $J_{5,5'} = 10.2$, $J_{5,6} = 6.9$, $J_{5,6'} = 6.4$; diastereoisomer B, 1.42 (ddd, 1H, H^4), 1.60 (ddd, 1H, H^2), 1.97 (ddd, 1H, H^5), 2.39 (ddd, 1H, $H^{5'}$), 2.82 (dd, 1H, H^1), 3.41 (dd, 1H, $H^{1'}$), 4.11 (t, 1H, H^3), 4.76 (dd, 1H, H^6), 5.24 (s, 5H, C_5H_5), 7.26–7.35 (10H, $2C_6H_5$); $J_{1,1'} = 14.6$, $J_{1,2} = 9.8$, $J_{1',2} = 3.9$, $J_{2,3} = J_{3,4} = 9.8$, $J_{4,5'} = 4.6$, $J_{4,5} = 9.3$, $J_{5,5'} = 14.0$, $J_{5,6} = 8.2$, $J_{5',6} = 3.9$.

3: ($CDCl_3$, 400 MHz, 298 K), δ 2.50–2.54 (complex m, CH_2CHOH), 4.71 (dd, 1H, *J* 7.1, 5.8), 5.01 (d, 1H, *J* 9.7), 5.13 (d, 1H, *J* 16.8), 5.67 (dt, 1H, *J* 15.1, 7.4), 6.15 (dd, 1H, *J* 15.1, 10.1), 6.30 (ddd, *J* = 16.8, 10.1, 9.7).

10a: (*Z*), δ 1.0 (dd, 1H, *J* 1.92, 8.52), 2.70 (dd, 1H, *J* 1.92, 5.04), 2.85 (t, 1H, *J* 10.6, 11.12), 4.22 (m, 1H), 5.10 (d, 1H, *J* 9.72), 5.23 (dd, 1H, *J* 15.56, 5.36), 5.28 (s, 5H, C_5H_5), 5.36 (t, 1H, *J* 11.12, 11.0), 5.90 (t, 1H, *J* 11.0, 10.52), 6.93 (ddd, 1H, *J* 10.52, 9.72, 15.56).

10b: (*E*), δ 0.92 (dd, 1H, *J* 2.08, 8.2), 2.32 (t, 1H, *J* 10.4, 11.0), δ 2.65 (dd, 1H, *J* 2.08, 4.92), 5.01 (dd, 1H, *J* 4.68, 8.04), 5.18 (dd, 1H, *J* 4.68, 12.68), 5.27 (s, 5H, C_5H_5), 5.65 (dd, 1H, *J* 10.8, 11.0), 6.21–6.33 (complex m, 2H).

11: δ 1.52 (m, 2H), 1.60 (s, 3H, Me), 1.85 (m, 4H), 4.98 (dd, 1H, *J* 1.64, 10.12), 5.12 (dd, 1H, *J* 1.64, 16.96), 5.46 (dt, 1H, *J* 7.36, 7.48, 7.56), 5.96 (dd, 1H, *J* 7.36, 8.72), 6.0 (dd, 1H, *J* 8.72, 9.92), 6.11 (dd, 1H, *J* 9.84, 9.92), 6.33 (m, 1H).

¶ It is well-established that molybdenum-s-*trans*-η^4-diene undergoes rapid isomerization to its more stable s-*cis*-diene isomer in CH_2Cl_2 at 23 °C.

remarkable reactivity[3] towards nucleophiles to afford η^3-allyl complexes.[9] Further exploration of this cationic intermediate in organic synthesis is in progress.

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References

1 S. A. Benyunes, M. Green and M. J. Grimshire, *Organometallics*, 1989, **8**, 2268.
2 W. J. Vong, S. M. Peng and R. S. Liu, *Organometallics*, 1990, **9**, 2187.
3 W. J. Vong, S. M. Peng, S. H. Lin, W. J. Lin and R. S. Liu, *J. Am. Chem. Soc.*, 1991, **113**, 573.
4 G. Erker, J. Wicher, K. Engel, F. Rosenfeldt, W. Dietrich and C. Kruger, *J. Am. Chem. Soc.*, 1980, **102**, 6433; A. Nakamara and H. Yasuda, *Angew. Chem., Int. Ed. Engl.*, 1987, **26**, 723.
5 A. D. Hunter, P. Legzdins, C. Nurse, F. W. B. Einstein and A. C. Willis, *J. Am. Chem. Soc.*, 1985, **107**, 1971.
6 T. W. Lee and R. S. Liu, *Organometallics*, 1988, **7**, 878.
7 H. Yasuda, K. Nagasuma, M. Akita, K. Lee and A. Nakamura, *Organometallics,* 1984, **3**, 1470; H. Yasuda and A. Nakamura, *J. Organomet. Chem.*, 1986, **285**, 15.
8 R. B. Bates, W. H. Deines, D. A. McCombs and D. E. Potter, *J. Am. Chem. Soc.*, 1969, **91**, 4608; E. A. Zuech, D. C. Craig and R. F. Kleinschmidt, *J. Org. Chem.*, 1968, **33**, 771.
9 For application of allyl-molybdenum complexes in organic reactions, see A. J. Pearson, *Synlett*, 1990, 10; J.W. Faller and D. L. Linebarriers, *J. Am. Chem. Soc.*, 1989, **111**, 1937.