Molybdenum(0) and tungsten(0) catalysts with enhanced reactivity for allylic substitution: regioselectivity and solvent effects †

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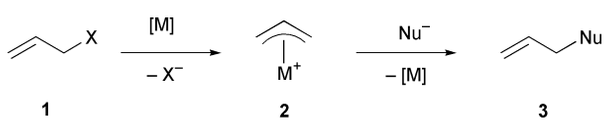
Received (in Cambridge, UK) 24th January 2001, Accepted 19th March 2001
First published as an Advance Article on the web 26th April 2001

The binuclear Mo(II) and W(II) complexes **28a**,**b** and **29a**,**b** have been developed as pre-catalysts for allylic substitution with β-dicarbonyl nucleophiles. These complexes are reduced *in situ* to Mo(0) and W(0) catalytic species **30a**,**b** and **31a**,**b** by excess of NaH, employed to generate sodiomalonate nucleophiles, or by DIBAL-H. 1,3-Dioxolane and 1,4-dioxane, when used as solvents, substantially accelerate the reaction. These new catalysts exhibit "traditional" Mo regiochemistry, *i.e.*, the nucleophilic attack occurring preferentially at the more substituted carbon (**5** ⟶ **9**; **37** ⟶ **38**), unless an additional factor, such as further coordination to another moiety of the allylic electrophile takes part (**41**), as in the case of the geranyl-type substrates (**32** or **33** ⟶ **36**).

Introduction

Palladium(0)-catalysed allylic substitution is a well established synthetic method with numerous applications both in academia and industry (Scheme 1).[1] As a potential replacement for the



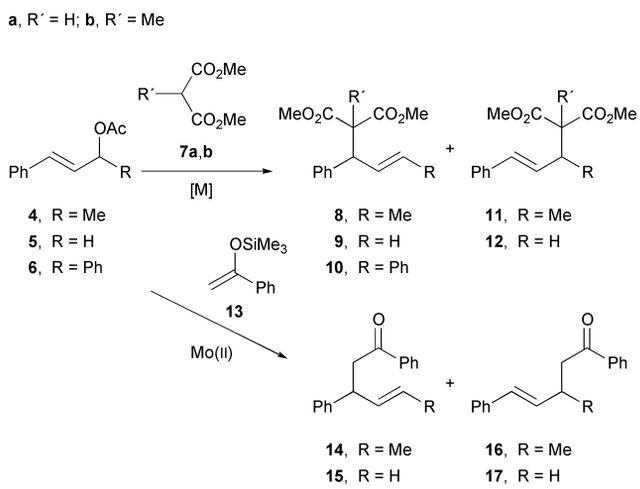
Scheme 1

expensive palladium, Group 6 metals (Mo and W) have also been shown to effectively catalyse this reaction,[2,3] although their mode of action may differ from that of Pd.[4,5] However, in spite of the suitable cost, Mo and W are stained with generally lower reactivity than Pd. Thus, while the Pd(0)-catalysed reactions occur in THF at reflux or even at ambient temperature,[1] Mo and W catalysts typically require reflux in higher-boiling solvents (*e.g.*, toluene) for several hours.[2–4] This striking difference can be attributed, in part, to the ease of ligand dissociation in the case of Pd catalysts that creates vacancy in the coordination sphere, *e.g.*, $(Ph_3P)_4Pd \rightleftharpoons (Ph_3P)_3Pd + Ph_3P$. By contrast, $Mo(CO)_6$, $W(CO)_6$, and their congeners are relatively stable, so that heating at higher temperature is required.[6] Hence, increasing the reactivity of Mo and W complexes would be highly desirable.[7]

The latter goal may seem to have been met by Mo(II) and W(II) complexes with weakly coordinating ligands (TfO^-, labile CO, or MeCN), for which we have demonstrated catalytic allylic substitution at room temperature and a broader spectrum of nucleophiles than that for Pd(0)-catalysts, including simple silyl enol ethers derived from ketones, aldehydes and esters, and the electron-rich aromatics and heteroaromatics.[8] However, in all these reactions Mo(II) and W(II) proved to behave purely as mild Lewis acids rather than serving as metal templates, so that the original stereochemical information present in the substrate was usually lost and asymmetric induction would hardly be feasible.[8e,f] Therefore, we turned our attention back to Mo(0) complexes and, herein, we report on our endeavour to enhance their reactivity.

Results and discussion

The main difference between Pd(0)- and Mo(0)-catalysed allylic substitution reactions is their regioselectivity toward the β-dicarbonyl-derived nucleophiles, such as $NaCH(CO_2Me)_2$:[1,2] while Pd(0) mainly gives the products of substitution at the less substituted terminus of the intermediate η^3-complex **2**,[1,9] $Mo(CO)_6$ and other Mo(0) and W(0) complexes preferentially afford their more substituted isomers, unless the nucleophile is too bulky.[2,3] Thus, cinnamyl acetate **5** is converted into the "linear" product **12a** in the Pd(0)-catalysed reaction (Scheme 2; Table 1, entry 1),[1g] whereas W(0) preferentially gives the



Scheme 2

† Electronic supplementary information (ESI) available: experimental procedures for compounds not covered in the Experimental. See http://www.rsc.org/suppdata/p1/b1/b100903f/

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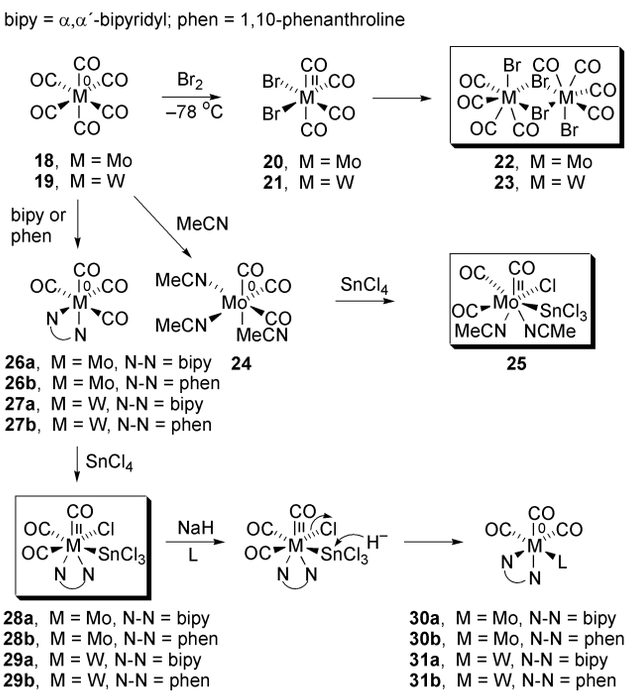
 DOI: 10.1039/b100903f

Table 1 Allylic substitution of **5** with **7a**,**b** and **13** catalysed by Pd(0), Mo(0) or W(0), and Mo(II) complexes (Scheme 2)

Entry	Allylic substrate	Nucleophile	Catalyst	Solvent	Products	Ratio
1	**5**	**7a**	$(dba)_3Pd_2$	THF	**9a** + **12a**[a]	≤1 : 99
2	**5**	**7a**	$(bipy)W(CO)_3(MeCN)$	Toluene	**9a** + **12a**[b]	98 : 2
3	**5**	**7b**	$(bipy)W(CO)_3(MeCN)$	Toluene	**9b** + **12b**[b]	98 : 2
4	**5**	**13**	**22**	CH_2Cl_2	**15** + **17**[c]	20 : 80
5	**5**	**13**	**25**	CH_2Cl_2	**15** + **17**[c]	25 : 75
6	**5**	**7a**	**28b**[d]	Dioxane	**9a** + **12a**	92 : 8
7	**5**	**7b**	**28b**[d]	Dioxane	**9b** + **12b**	80 : 20

[a] Ref. 1*g*. [b] Ref. 3*a*. [c] Ref. 8*e*. [d] With NaH employed as the base.

"branched" isomer **9a** (Table 1, entries 2 and 3).[2]‖ On the other hand, we have recently shown that the Lewis-acidic Mo(II) and W(II) complexes, such as **22** and **25**, whose preparation from $Mo(CO)_6$ is outlined in Scheme 3, tend to exhibit reactivity similar to that of Pd(0) in most cases (Table 1, entries 4 and 5).[8]



Scheme 3

Development of more reactive Mo(0) and W(0) catalysts

We have previously shown that the Lewis-acidic Mo(II) complexes are deactivated by enolate-type nucleophiles.[8] Thus, while **22** and **23** readily facilitate the reaction of a variety of silyl enol ethers with allylic substrates, no reaction occurred with the corresponding enolates. The binuclear complex **25**, prepared in two steps from the commercially available $Mo(CO)_6$ *via* ligand exchange with MeCN (**18** ⟶ **24**), followed by an oxidative addition of $SnCl_4$ (**24** ⟶ **25**),[8,10] behaved in the same way (Table 1, entries 4, 5).[8e]

In order to further explore the reactivity of binuclear catalysts, Mo and W bipyridyl and phenanthroline complexes **28a**,**b** and **29a**,**b** were prepared by the oxidative addition of $SnCl_4$ to **26a**,**b** and **27a**,**b**, respectively, which in turn were obtained by heating $M(CO)_6$ (**18** and **19**, respectively) with the respective heterocycles. With complexes **28a**,**b** and **29a**,**b**, enolates could be expected to have the same deactivating effect which, initially, seemed to be the case as no reaction of **4** or **5** with $NaCH(CO_2Me)_2$ was observed in the presence of **25**. However, with **28b** in toluene and the temperature being raised to reflux, the reaction did slowly occur on some occasions.

The latter observation was intriguing and certainly worth further investigation. After much experimentation, it turned out that the reaction did occur only when $NaCH(CO_2Me)_2$ was generated (from dimethyl malonate) with a slight excess of NaH; with larger excess or less then an equivalent of NaH, the reaction did not occur. Moreover, the regiochemistry of the substitution switched to that typical for Mo(0), *i.e.*, the "branched" isomer **9** became the major product when cinnamyl acetate **5** was employed as the electrophilic partner (Table 1, entries 6, 7). This behaviour clearly suggests that the initial Mo(II) complex **28b** was reduced *in situ* by the excess of NaH to a reactive Mo(0) species, whose structure can be tentatively formulated as **30b** (L = ligand, such as the solvent). Since **28b** is present in a catalytic amount, only a small quantity of NaH (presumably equivalent to the amount of **28b**) is required to generate the active species. On the other hand, if a substoichiometric amount of NaH is used to generate $NaCH(CO_2Me)_2$, there is none left to reduce **28b**, whereas its excess apparently decomposes the catalyst, presumably by further reduction of the CO groups. In view of a difficult accurate dosage of very small quantities of NaH, we turned to DIBAL-H as a substitute and, indeed, were also able to generate the active species from the precatalyst **28b** as reflected by the successful reaction of **5** with $NaCH(CO_2Me)_2$ and $NaCMe(CO_2Me)_2$. However, this issue had not been pursued further since the practicality of handling NaH in the amounts of 50–100 mg was acceptable. The remaining complexes **28a**, **29a**, and **29b** were then found to exhibit behaviour similar to that of **28b**. **

Reactivity of the Mo and W complexes

With the initial results at hand, we set out to probe the catalytic efficiency of the new Mo and W complexes and their regioselectivity in allylic substitution. To this end, we employed the monoterpene-derived allylic acetates **32** and **33** and the malonate-type nucleophiles **7a** and **7b** of different steric bulk. The reactions were carried out by adding the catalyst (typically 10–20 mol%) and allylic substrate to a preformed solution of dimethyl sodiomalonate (generated from dimethyl malonate and NaH) in toluene, followed by a reflux for 24 h. The results are summarized in Scheme 4 and Table 2. It is pertinent to note that while the reaction of **33** with **7a**, carried out in the presence of Pd(0), is known to preferentially afford the terminal isomer **36** (Table 2, entry 1),[2] $Mo(CO)_6$-catalysed reactions produce its isomer **34**, regardless of whether linalyl or geranyl acetate (**32** or **33**) is used as starting material (Table 2, entries 2 and 3).[2] Interestingly, complex $(bipy)Mo(CO)_3(MeCN)$ has been reported to resemble Pd(0), giving mainly the terminal product **36** (Table 2, entry 4).[2g]

Our bipyridyl Mo and W complexes **28a** and **29a** turned out to give almost identical results to those reported for **26a** (Table 2, entries 5–8). The regioselectivity in favour of terminal substitution was further increased for the sterically more hindered methylmalonate **7b**, with barely any internal product detected (Table 2, entries 9–12). However, in contrast to Pd(0), the Mo-

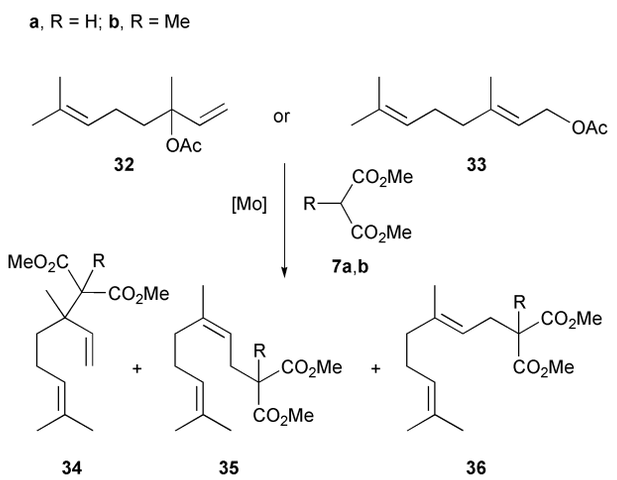
‖ By contrast, with the bulkier $NaC(Me)(CO_2Me)_2$, the Mo(0)-catalysed reaction preferentially gives the "linear" product **11b**.

** Attempted isolation of the reactive complexes **30a**,**b** and **31a**,**b**, generated *in situ* from the precatalysts **28a**,**b** and **29a**,**b**, was unsuccessful.

Table 2 Reactions of linalyl and geranyl acetates **32** and **33** with malonates **7a**,**b** (Scheme 4)[a]

Entry	Allylic substrate	Nucleophile	Catalyst	**34**[b]	**35**[b]	**36**[b]	Yield (%)[c]
1	**33**	**7a**	Pd[d]	13	0	87	84[g]
2	**32**	**7a**	**18**[e]	85	3	12	80[h]
3	**33**	**7a**	**18**[e]	85	3	12	65[h]
4	**33**	**7a**	[Mo][f]	16	22	62	45[h]
5	**32**	**7a**	**28a**	16	23	61	59
6	**32**	**7a**	**29a**	15	22	63	59
7	**33**	**7a**	**28a**	18	23	59	58
8	**33**	**7a**	**29a**	17	23	60	56
9	**32**	**7b**	**28a**	1	22	77	76
10	**32**	**7b**	**29a**	—	23	77	68
11	**33**	**7b**	**28a**	1	16	83	25
12	**33**	**7b**	**29a**	1	17	82	25

[a] The reactions were carried out in toluene at reflux for 24 h with 20 mol% of the catalyst unless stated otherwise. [b] The isomer ratios were determined by GC of the crude mixtures. [c] Isolated yield of the mixture. [d] $(Ph_3P)_4Pd$ (5 mol%). [e] 10 mol%. [f] (bipy)$Mo(CO)_3$(MeCN), 24 h. [g] Ref. 1. [h] Ref. 2.



Scheme 4

and W-catalysed reactions exhibited a higher proportion of the (*Z*)-isomer **35** (Table 2, entries 4–12), with the exception of $Mo(CO)_6$ (Table 2, entries 2 and 3). While the reactivity of **32** and **33** toward **7a** did not dramatically differ, substantial differences were experienced with the more bulky nucleophile **7b**. In this case, good yields were obtained with the tertiary acetate **32** (Table 2, entries 9 and 10), whereas poor conversions were attained with the inherently less reactive primary acetate **33** (Table 2, entries 11 and 12).

Solvent effects

In his early studies, Trost and Lautens demonstrated the sensitivity of Mo(0)-catalysed reactions to solvents.[2e] Thus, DMF and diglyme poisoned the catalyst, presumably *via* coordination, whereas toluene seemed to be the reasonable compromise. A standard procedure using the latter solvent requires that the nucleophile be added to a suspension of NaH, followed by a period of reflux, which generates a gelatinous mixture of the solvent and the salt, to which the other ingredients are added. This protocol was later superseded by the utilization of enolates derived from the reaction of malonate with *N,O*-bis(trimethylsilyl)acetamide (BSA),[11] although this protocol has been shown to give somewhat different product ratios and stereochemistry to those of the corresponding enolates.[2,11]

Clearly, the problems associated with the sodiomalonate-type nucleophiles are those of the non-homogeneity and viscosity of the reaction mixture. To address this issue, we conducted a series of experiments in toluene containing 20–25% of THF (Table 3, entries 1–4).†† This modification resulted in a three-fold acceleration as shown by quantitative conversions of **32** with either **7a** or **7b** within 8 h (*vs.* 24 h in pure toluene). The product ratios have been slightly altered in favour of the terminal nucleophilic attack, which can be attributed to the change in the solvation (compare entries 5–8 in Table 2 with entries 1–4 in Table 3).‡‡ Increasing the content of THF in toluene to >30% had a detrimental effect on the reactivity. Thus, with a 2 : 1 toluene–THF mixture, only 12% conversion was observed under otherwise identical conditions (reflux for 8 h), which may be, in part, attributed to the lowering of the boiling point.§§

After the modest success with toluene–THF mixtures, we searched for solvents with similar relative permittivities (ε) and boiling points; suitable candidates were identified in 1,3-dioxolane (**C**) and 1,4-dioxane (**D**).¶¶ Using our standard probe (Scheme 4), we found that these solvents brought about a substantial acceleration of the reaction (Table 3, entries 5–13). Thus, with the more reactive **32** and the less hindered malonate **7a**, the reaction times could be shortened to 6 or even 3 hours, and the regioselectivity was substantially improved in favour of the "terminal" attack (Table 3, entries 5–11). The catalyst load could be decreased from 20 to 10 mol% without any effect on the reactivity (compare entries 5 *vs.* 6 and 8 in Table 3) and the reaction proceeded acceptably well even with as little as 5 mol% of the catalyst (Table 3, entries 7, 9–11). While **32** produced ~2 : 1 *E*–*Z* mixtures (**35**–**36**), its allylic isomer **33** was much more selective in favour of **36**, demonstrating the conservation of the original information present in the substrate (Table 3, entries 10 and 11).[12] Similar trends were observed for the less reactive nucleophile **7b** (Table 3, entries 12 and 13). Interestingly, comparison of 1,3-dioxolane (**C**) with 1,4-dioxane (**D**) shows that, with these coordinating solvents, the reaction temperature plays a minor role: the difference in boiling point here is 27 °C ¶¶ and yet the reactions were essentially unaffected. By contrast, a switch from toluene to benzene (a difference of 30 °C in bp) as the solvent results in stopping the reaction almost completely.[2e]

Regioselectivity

To further address the regioselectivity issue (*vide supra*), we employed cinnamyl-type substrates **4** and **5** (Scheme 2, Table 4). In all cases, **4** exhibited a strong preference for attack at the allylic terminus proximal to the phenyl ring, regardless of whether malonate **7a** (Table 4, entries 1–9) or the bulkier methylmalonate **7b** (entries 10–17) was employed as the nucleophile.

†† Other combinations of the two solvents proved inferior, often resulting in very little reaction or extended reaction times.

‡‡ For computation of solvation effects in Pd(0)-catalysed allylic substitution, see ref. 9.

§§ Using a larger excess of the nucleophile had little effect on the overall conversion.

¶¶ Toluene: bp 110 °C, ε = 2.379; THF: bp 66 °C, ε = 7.58; 1,4-dioxane: bp 102–103 °C, ε = 2.209; 1,3-dioxolane, bp 74–75 °C. The value for ε of the latter solvent can be approximated by the value for $CH_3CH(OEt)_2$ (ε = 3.80). The data have been taken from ref. 20.

Table 3 Solvent effects in the reactions of linalyl and geranyl acetates **32** and **33** with malonates **7a**,**b** (Scheme 4)[a]

Entry	Allylic substrate	Nucleophile	Catalyst (mol%)	Solvent[b]	Time/h	**34**[c]	**35**[c]	**36**[c]	Yield (%)[d]
1	**32**	**7a**	**28a** (20)	**A**	8	5	30	65	60
2	**32**	**7a**	**29a** (20)	**A**	8	5	31	64	60
3	**32**	**7b**	**28a** (20)	**B**	8	9	17	74	62
4	**32**	**7b**	**29a** (20)	**B**	8	11	16	73	62
5	**32**	**7a**	**28a** (20)	**C**	6	3	24	73	75
6	**32**	**7a**	**28a** (10)	**C**	6	2	24	73	75
7	**32**	**7a**	**28a** (5)	**C**	4[e]	2	29	69	47
8	**32**	**7a**	**28a** (10)	**D**	3	4	27	69	70
9	**32**	**7a**	**28a** (5)	**D**	3[e]	3	30	67	50
10	**33**	**7a**	**28a** (5)	**C**	4[e]	—	1	99	51
11	**33**	**7a**	**28a** (5)	**D**	3[e]	1	9	90	50
12	**32**	**7b**	**28a** (20)	**C**	5	9	11	80	92
13	**32**	**7b**	**28a** (20)	**D**	5	11	14	75	88

[a] The reactions were carried out at reflux (see the General procedure). [b] **A** = toluene–THF (3 : 1); **B** = toluene–THF (4 : 1); **C** = 1,3-dioxolane; **D** = 1,4-dioxane. [c] The isomer ratios were determined by GC of the crude mixtures. [d] Isolated yield of the mixture. [e] No further reaction was observed on prolonged time.

Table 4 The reactions of acyclic acetates **4**–**6** with malonates **7a**,**b** (Scheme 2)[a]

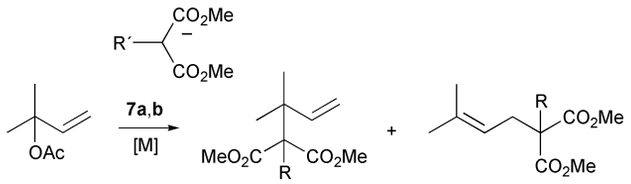
Entry	Allylic substrate	Nucleophile	Catalyst (mol%)	Solvent[b]	Time/h	Products	Ratio[c]	Yield (%)[d]
1	**4**	**7a**	**28a** (20)	**C**	24	**8a** + **11a**	83 : 17	81
2	**4**	**7a**	**28a** (20)[e]	**C**	4	**8a** + **11a**	84 : 16	84
3	**4**	**7a**	**28a** (20)	**D**	1.5	**8a** + **11a**	82 : 18	82
4	**4**	**7a**	**28b** (20)	**C**	1.5	**8a** + **11a**	89 : 11	89
5	**4**	**7a**	**28b** (20)	**D**	1.5	**8a** + **11a**	90 : 10	94
6	**4**	**7a**	**29a** (20)	**C**	24	**8a** + **11a**	83 : 17	89
7	**4**	**7a**	**29a** (20)	**D**	1.5	**8a** + **11a**	90 : 10	81
8	**4**	**7a**	**29b** (20)	**C**	1.5	**8a** + **11a**	89 : 11	80
9	**4**	**7a**	**29b** (20)	**D**	1.5	**8a** + **11a**	90 : 10	84
10	**4**	**7b**	**28a** (20)[e]	**C**	4	**8b** + **11b**	88 : 12	89
11	**4**	**7b**	**28a** (20)	**D**	1.5	**8b** + **11b**	88 : 12	85
12	**4**	**7b**	**28b** (20)	**C**	1.5	**8b** + **11b**	94 : 6	90
13	**4**	**7b**	**28b** (20)	**D**	1.5	**8b** + **11b**	93 : 7	98
14	**4**	**7b**	**29a** (20)	**C**	1.5	**8b** + **11b**	88 : 12	87
15	**4**	**7b**	**29a** (20)[e]	**D**	4	**8b** + **11b**	89 : 11	88
16	**4**	**7b**	**29b** (20)	**C**	1.5	**8b** + **11b**	93 : 7	85
17	**4**	**7b**	**29b** (20)	**D**	1.5	**8b** + **11b**	93 : 7	87
18	(*R*)-**4**	**7a**	**28a** (20)	**D**	1.5	**8a** + **11a**[f]	83 : 17	78
19	**5**	**7a**	**28b** (10)	**C**	7	**9a** + **12a**	93 : 7	68
20	**5**	**7a**	**28b** (10)	**D**	7	**9a** + **12a**	92 : 8	74
21	**5**	**7a**	**29b** (10)	**C**	7	**9a** + **12a**	95 : 5	79
22	**5**	**7b**	**28a** (10)	**D**	7	**9b** + **12b**	76 : 24	75
23	**5**	**7b**	**28b** (10)	**C**	7	**9b** + **12b**	80 : 20	87
24	**5**	**7b**	**28b** (10)	**D**	7	**9b** + **12b**	80 : 20	88
25	**5**	**7b**	**29a** (10)	**D**	7	**9b** + **12b**	76 : 24	61
26	**6**	**7a**	**28a** (10)	**C**	0.5	**10**	—	95
27	**6**	**7a**	**28b** (10)	**C**	0.5	**10**	—	94
28	**6**	**7a**	**29a** (10)	**C**	0.5	**10**	—	93
29	**6**	**7a**	**29b** (10)	**C**	0.5	**10**	—	91

[a] The reactions were carried out at reflux (see the General procedure). [b] **C** = 1,3-dioxolane; **D** = 1,4-dioxane. [c] The isomer ratios were determined by GC of the crude mixtures. [d] Isolated yield of the mixture. [e] The catalyst recrystallised prior to use. [f] Both products were racemic.

Cinnamyl acetate **5** followed essentially the same trend but was slightly more discriminating between **7a** and **7b** (compare entries 19–21 with 22–25 in Table 4). All the complexes **28a**,**b** and **29a**,**b** exhibited similar reactivity; differences in the reaction times required for completion were, apparently, mainly associated with the reaction temperature (*i.e.*, with the boiling point of the solvent—*vide supra*). However, the purity of the pre-catalyst proved to be crucial. Thus, recrystallised **28a** was much more reactive than its crude counterpart (compare entries 1 *vs.* 2 and 6 *vs.* 7 in Table 4). The bisphenyl substrate **6** proved more reactive than the other cinnamyl derivatives, being almost quantitatively converted into **10** in 30 min (Table 4, entries 26–29).

The striking difference in regioselectivity observed between the monoterpenes **32** or **33** (attack at the less substituted terminus) and the cinnamyl model **5** (attack at the more substituted terminus of the allylic system) is intriguing. While Trost has shown that attack at the more substituted terminus is characteristic for Mo(0) catalysts[2] (as in the case of **5**), our monoterpene models seem to be out of line, raising the following questions. (1) Is it the steric hindrance exercised by the additional methyl group in **32** and **33** that swings the reaction toward the primary (*vs.* tertiary) terminus, or is it the electronic effect that plays the decisive role in the cinnamyl model **5**? (2) Does the additional double bond at the far end of the molecule of the terpenes **32** and **33** play any role, *e.g.*, by chelating the metal?[13] To address these issues, we employed the truncated prenyl-type acetate **37** as a mimic of linalyl acetate **32** lacking the additional double bond (Scheme 5). On reaction with $NaCH(CO_2Me)_2$, carried out in the presence of **28a**, acetate **37** produced a 50 : 50 mixture of the regioisomers **38** and **39** (55%), which represents a dramatic enhancement of the internal product as compared to the geranyl system (Tables 2 and 3). Similarly, $NaC(Me)(CO_2Me)_2$ also produced

a, R = H; **b**, R = Me

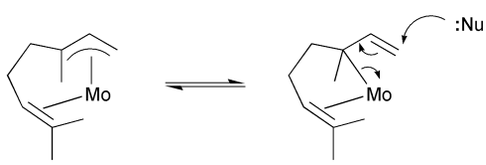


37 **38** **39**

Scheme 5

substantially more of the internal isomer (**38**–**39** = 34 : 66; 75%) than its linalyl congener, although this shift was not as strong as in the latter case, presumably owing to the inherent bias of the more bulky nucleophile to seek the less hindered site of attack.

Thus, the above results strongly indicate that the marked preference for terminal attack in the case of the geranyl system is, indeed, associated with the chelation of the transient species by the double bond.[13] Since the η^3–η^1 (**40** $\rightleftharpoons$ **41**) equilibrium can be expected for the latter chelate (Scheme 6), the preferential attack on the terminal carbon can be understood in terms of the η^1-species **41**.



40 **41**

Scheme 6

Conclusions

In conclusion, we have demonstrated that the binuclear Mo(II) and W(II) complexes **28a**,**b** and **29a**,**b** can serve as pre-catalysts in allylic substitution. These complexes are reduced *in situ* to Mo(0) and W(0) species by a slight excess of NaH (equivalent to the amount of the catalyst), employed to deprotonate malonate nucleophiles. 1,3-Dioxolane and 1,4-dioxane have been shown to be the solvents of choice as they substantially accelerate the reaction and render it homogeneous (in contrast to toluene, the traditional solvent in this area). These complexes exhibit "traditional" Mo regiochemistry, *i.e.*, the nucleophilic attack occurring preferentially at the more substituted carbon. The exception to this rule, observed for the geranyl system, has been rationalized *via* coordination of the metal to the distal C=C bond in the substrates which leads to a distortion of the complex geometry and, consequently, to the change of the regiochemical outcome (**41**).

Experimental

General

Melting points were determined on a Kofler block and remain uncorrected. Optical rotations were measured at 20 °C. The NMR spectra were recorded in $CDCl_3$ or DMSO-d_6, ^{1}H at 250 MHz and ^{13}C at 62.9 MHz with reference to the solvent signals of chloroform-d_1 (δ 7.27, ^{1}H; δ 77.0, ^{13}C) and dimethyl sulfoxide-d_6 (δ 2.62, ^{1}H; δ 39.7, ^{13}C) as internal standards; the suffixes "a" and "b" are used to distinguish between two diastereotopic protons or equivalent groups. Coupling constants were determined by first order approximation. Various 2D-techniques and DEPT experiments were used to establish a compound's structure and to assign the signals. The IR spectra were recorded for a thin film between KBr plates or using the "Golden-Gate" technique. The mass spectra (EI, ES or CI) were measured on a dual sector mass spectrometer using direct inlet and the lowest temperature enabling evaporation. All products were dried under high vacuum before the recording the yield; the term yield refers to isolated product(s) showing a single spot on TLC. The identity of the known compounds prepared by different methods was checked by comparison of their NMR, IR, and MS and by their TLC behaviour. All solvents for the reactions were of reagent grade and were dried and distilled under nitrogen immediately prior to use as follows: tetrahydrofuran (THF) from sodium–benzophenone; dichloromethane from calcium hydride (40 Mesh); diethyl ether was provisionally dried over sodium wire followed by distillation from lithium aluminium hydride; acetonitrile was dried by stirring over phosphorus pentaoxide (10% by weight) for 24 h followed by distillation onto potassium carbonate and a second distillation to remove acidic impurities.

General procedure for the allylic substitution reactions catalysed by complexes 28a–29b

To a stirred suspension of sodium hydride (4 mmol) in 1,3-dioxolane or 1,4-dioxane (6 mL) was added dropwise a solution of the nucleophile (4 mmol) in the appropriate solvent (2 mL). To the resulting clear solution was added catalyst (10–20 mol%) followed by a solution of the allylic substrate (2 mmol) in the corresponding solvent (2 mL). The reaction was heated at reflux until TLC analysis indicated disappearance of the starting material or until no further reaction was detected after 24 h. The reaction mixture was diluted with ether (10 mL), absorbed onto silica (~2.5 g) and the product was purified by flash chromatography. The amount of silica, the polarity of the eluent, and the size of the column used for each separation were varied with respect to the number and relative polarities of the products. For details and yields see Tables 2–4.

Dimethyl (1-phenylbut-2-en-1-yl)malonate 8a. Obtained as a mixture with **11a**; for experimental details see General procedure and Table 4: ^{1}H NMR δ 7.21–7.03 (5 H, m, arom), 5.5–5.3 (2 H, m, CH=CH), 3.91 (1 H, dd, J = 11, 7 Hz, 1-H), 3.63 (1 H, d, J = 11 Hz, C*H*($CO_2Me)_2$), 3.58 (3 H, s, OMe), 3.34 (3 H, s, OMe), 1.53 (3 H, d, J = 6 Hz, 3-Me); ^{13}C NMR δ 168.1 (C), 167.7 (C), 140.6 (C), 139.3 (CH), 128.3 (2 × CH), 127.6 (2 × CH), 127.4 (CH), 126.7 (CH), 57.7 (CH), 52.2 (CH_3), 52.0 (CH_3), 48.8 (CH), 17.7 (CH_3), in accordance with the literature.[2,3,14]

Dimethyl methyl(1-phenylbut-2-en-1-yl)malonate 8b. Obtained as a mixture with **11b**; for experimental details see General procedure and Table 4: ^{1}H NMR δ 7.38–7.15 (5 H, m, arom), 5.95 (1 H, dd, J = 15.8, 8 Hz, 2-H), 5.55 (1 H, dq, J = 15.8, 6 Hz, 3-H), 4.09 (1 H, d, J = 8 Hz, 1-H), 3.68 (3 H, s, OMe), 3.58 (3 H, s, OMe), 1.67 (3 H, d, J = 6 Hz, 3-Me), 1.43 (3 H, s, Me); ^{13}C NMR δ 171.4 (C), 171.2 (C), 139.8 (C), 129.4 (2 × CH), 129.2 (CH), 128.6 (CH), 128.0 (2 × CH), 126.8 (CH), 59.0 (C), 53.5 (CH), 52.2 (CH_3), 52.1 (CH_3), 18.1 (CH_3), 18.0 (CH_3), in accordance with the literature.[2,3,14]

Dimethyl (1-phenylprop-2-en-1-yl)malonate 9a. Obtained as a mixture with **12a**; for experimental details see General procedure and Table 4: ^{1}H NMR δ 7.21–7.03 (5 H, m, arom), 5.90 (1 H, m, 2-H), 5.01 (1 H, d, J_{trans} = 14 Hz, 3-H_a), 4.96 (1 H, d, J_{cis} = 6 Hz, 3-H_b), 4.01 (1 H, dd, J = 11, 6 Hz, 1-H), 3.74 (1 H, d, J = 11 Hz, C*H*($CO_2Me)_2$), 3.60 (3 H, s, OMe), 3.35 (3 H, s, OMe); ^{13}C NMR δ 167.9 (C), 167.6 (C), 139.8 (C), 137.6 (CH), 128.4 (2 × CH), 127.9 (2 × CH), 126.9 (CH), 116.3 (CH_2), 57.1 (CH), 52.3 (CH_3), 52.1 (CH_3), 49.5 (CH), in accordance with the literature.[2,3,14,15]

Dimethyl methyl(1-phenylprop-2-en-1-yl)malonate 9b. Obtained as a mixture with **12b**; for experimental details see General procedure and Table 4: ^{1}H NMR δ 7.36–7.15 (5 H, m, arom),

6.32 (1 H, m, 2-H), 5.17 (1 H, m, 3-H_a), 5.06 (1 H, m, 3-H_b), 4.13 (1 H, d, J = 9 Hz, 1-H), 3.70 (3 H, s, OMe), 3.60 (3 H, s, OMe), 1.46 (3 H, s, Me); ^{13}C NMR δ 171.3 (C), 171.2 (C), 139.0 (C), 137.0 (CH), 129.4 (2 × CH), 128.1 (2 × CH), 127.0 (CH), 117.6 (CH_2), 58.8 (C), 54.5 (CH), 52.4 (CH_3), 52.3 (CH_3), 18.3 (CH_3), in accordance with the literature.[15]

Dimethyl (1,3-diphenylprop-2-en-1-yl)malonate 10a. ^{1}H NMR δ 7.35–7.13 (10 H, m, 2 × arom), 6.48 (1 H, d, J = 15.7 Hz, PhC*H*=), 6.32 (1 H, dd, J = 15.7, 8.5 Hz, PhCH=C*H*), 4.27 (1 H, dd, J = 11.0, 8.5 Hz, PhC*H*), 3.96 (1 H, d, J = 11.0 Hz, C*H*($CO_2Me)_2$), 3.69 (3 H, s, OMe), 3.50 (3 H, s, OMe); ^{13}C NMR δ 168.1 (C), 167.7 (C), 140.1 (C), 136.8 (C), 131.8 (CH), 129.1 (CH), 128.6 (CH), 128.4 (CH), 127.8 (CH), 127.5 (CH), 127.1 (CH), 126.3 (CH), 57.6, 52.4 (CH_3), 52.3 (CH_3), 49.1; IR (neat) ν 2951, 1747, 1601, 1493, 1431, 1319, 1261, 1173, 1142, 968, 744 cm^{-1}; MS (EI) m/z (%) 324 (29, $M^{\bullet+}$), 264 (11), 232 (17), 205 (87), 193 (100), 178 (20), 128 (10), 115 (73), 91 (30), 77 (9); HRMS (EI) 324.13616 ($C_{20}H_{20}O_4$ requires 324.13623), in accordance with the literature.[16]

Dimethyl (4-phenylbut-3-en-2-yl)malonate 11a. Obtained as a mixture with **8a**; for experimental details see General procedure and Table 4: ^{1}H NMR δ 7.25–7.00 (5 H, m, arom), 6.30 (1 H, d, J = 16 Hz, 4-H), 6.01 (1 H, dd, J = 16, 8 Hz, 3-H), 3.60 (3 H, s, OMe), 3.52 (3 H, s, OMe), 3.28 (1 H, d, J = 8 Hz, C*H*($CO_2Me)_2$), 2.98 (1 H, m, 1-H), 1.06 (3 H, d, J = 7.4 Hz, Me), in accordance with the literature.[2,3,14,18]

Dimethyl methyl(4-phenylbut-3-en-2-yl)malonate 11b. Obtained as a mixture with **8b**; for experimental details see General procedure and Table 4: ^{1}H NMR δ 7.25–7.00 (5 H, m, arom), 6.45 (1 H, d, J = 15 Hz, 4-H), 6.13 (1 H, dd, J = 15, 8 Hz, 3-H), 3.72 (6 H, s, 2 × OMe), 3.47 (1 H, m, 1-H), 1.44 (3 H, s, Me), 1.16 (3 H, d, J = 8 Hz, 1-Me), in accordance with the literature.[2,3,14,18]

Dimethyl (3-phenylprop-2-en-1-yl)malonate 12a. Obtained as a mixture with **9a**; for experimental details see General procedure and Table 4: ^{1}H NMR δ 7.35–7.20 (5 H, m, Ar), 6.48 (1 H, d, J = 16 Hz, PhCH=), 6.15 (1 H, dt, J = 16, 6 Hz, CH=), 3.55 (1 H, d, J = 7 Hz, C*H*($CO_2Me)_2$), 3.51 (6 H, s, 2 × OMe), 2.82 (2 H, dd, J = 7, 6 Hz, CH_2); ^{13}C NMR δ 169.0 (2 × C), 140.3 (CH), 134.1 (C), 132.7 (CH), 128.3 (2 × CH), 127.2 (CH), 126.0 (2 × CH), 125.2 (CH), 52.1 (CH), 51.5 (2 × CH_3), 32.1 (CH_2), in accordance with the literature.[15]

Dimethyl methyl(3-phenylprop-2-en-1-yl)malonate 12b. Obtained as a mixture with **9b**; for experimental details see General procedure and Table 4: ^{1}H NMR δ 7.36–7.18 (5 H, m, arom), 6.42 (1 H, d, J = 16 Hz, 3-H), 6.09 (1 H, dq, J = 16, 8 Hz, 2-H), 3.73 (6 H, s, 2 × OMe), 2.78 (2 H, d, J = 8 Hz, 1-CH_2), 1.48 (3 H, s, Me); ^{13}C NMR δ 172.2 (2 × C), 136.9 (C), 134.0 (CH), 128.4 (2 × CH), 127.3 (2 × CH), 126.1 (CH), 124.1 (CH), 53.9 (C), 52.2 (2 × CH_3), 39.4 (CH_2), 20.0 (CH_3), in accordance with the literature.[15]

Methyl 2-methoxycarbonyl-3,7-dimethyl-3-vinyloct-6-enoate 34a. Prepared according to General procedure and Tables 2 and 3, separation from the regioisomers **35a** and **36a** was accomplished by preparative HPLC on a Dynamax 60 Å column (C18, 250 × 41.4 mm id) using a 40 : 60 H_2O–MeCN mixture, flow rate 50 mL min^{-1} at 1.59 kpsi, detection by UV at 230 nm. Analysis of the mixture was performed on a Dynamax 60 Å column (C18, 250 × 4.6 mm, 8 μm id) using a 45 : 55 H_2O–MeCN mixture, flow rate 1 mL min^{-1} at 2.30 kpsi, detection by UV at 230 nm (R_t = 31.37 min): ^{1}H NMR δ 6.01 (1 H, dd, J = 17, 11 Hz, C*H*=CH_2), 5.15–5.00 (3 H, m, Me_2C=C*H*, C=CH_2), 3.73 (6 H, s, 2 × OMe), 3.46 (1 H, s, C*H*($CO_2Me)_2$), 1.70–1.56 (4 H, m, 2 × CH_2), 1.62 (3 H, s, Me), 1.58 (3 H, s, Me), 1.21 (3 H, s, Me); ^{13}C NMR δ 168.2 (2 × C), 131.5 (C), 124.0 (CH), 120.1 (CH), 113.8 (CH_2), 59.9 (CH), 52.0 (2 × CH_3), 42.1 (C), 39.0 (CH_2), 31.8 (CH_2), 25.6 (CH_3), 23.3 (CH_3), 19.6 (CH_3), in accordance with the literature.[2,13,19]

Methyl 2-methoxycarbonyl-2,3,7-trimethyl-3-vinyloct-6-enoate 34b. We were unable to obtain a pure sample of **34b** from the reaction of **32** with **7b** (General procedure and Tables 2 and 3) due to its low concentration, although the ^{1}H NMR spectrum of the crude product mixture showed characteristic signals compatible with the structure of **34b**: ^{1}H NMR 5.96 (2 H, m, CH_2=C), 3.32 (6 H, s, 2 × OMe).

Methyl (*Z*)-2-methoxycarbonyl-5,9-dimethyldeca-4,8-dienoate 35a. Prepared according to General procedure and Tables 2 and 3; separation from its isomers **34a** and **36a** was accomplished by preparative HPLC as above (R_t = 30.29 min): ^{1}H NMR δ 5.05 (2 H, m, 2 × C=CH), 3.72 (6 H, s, 2 × OMe), 3.35 (1 H, t, J = 7 Hz, 2-CH), 2.60 (2 H, m, 3-CH_2), 2.05 (4 H, m, 6- and 7-CH_2), 1.66 (3 H, s, Me), 1.64 (3 H, s, Me), 1.60 (3 H, s, Me); ^{13}C NMR δ 169.5 (2 × C), 138.7 (C), 131.8 (C), 124.0 (CH), 120.1 (CH), 52.3 (2 × CH_3), 52.1 (CH), 31.8 (CH_2), 27.3 (CH_2), 26.4 (CH_2), 25.6 (CH_3), 23.4 (CH_3), 17.6 (CH_3), in accordance with the literature.[2,13,19]

Methyl (*Z*)-2-methoxycarbonyl-2,5,9-trimethyldeca-4,8-dienoate 35b. Prepared according to General procedure and Tables 2 and 3; separation from its isomer **36b** was accomplished by preparative HPLC on a Dynamax 60 Å column (C18, 250 × 41.4 mm id) using a 30 : 70 H_2O–MeCN mixture, flow rate 50 mL min^{-1} at 1.58 kpsi, detection by UV at 230 nm. Analysis of the mixture was performed on a Dynamax 60 Å column (C18, 250 × 4.6 mm 8 μm id) using a 40 : 60 H_2O–MeCN mixture, flow rate 1 mL min^{-1} at 2.02 kpsi, detection by UV at 230 nm; **35b** was the most polar fraction (R_t = 29.51 min): ^{1}H NMR δ 5.10 (2 H, m, 2 × C=C*H*), 3.71 (6 H, s, 2 × OMe), 2.60 (2 H, d, J = 7.6 Hz, 3-CH_2), 2.04 (4 H, m, 6- and 7-CH_2), 1.68 (3 H, s, Me), 1.61 (3 H, s, Me), 1.59 (3 H, s, Me), 1.38 (3 H, s, Me); ^{13}C NMR δ 172.6 (2 × C), 139.2 (C), 131.3 (C), 123.9 (CH), 117.9 (CH), 53.8 (C), 52.2 (2 × CH_3), 39.8 (CH_2), 33.9 (CH_2), 26.4 (CH_2), 25.5 (CH_3), 19.5 (CH_3), 17.5 (CH_3), 16.0 (CH_3); IR (neat) ν 2975, 2940, 1725, 1464, 1452, 1435, 1380, 1250, 1170, 1110, 938, 809 cm^{-1}.

Methyl (*E*)-2-methoxycarbonyl-5,9-dimethyldeca-4,8-dienoate 36a. Prepared according to General procedure and Tables 2 and 3 as a mixture with **34a** and **35a**, which were separated by preparative HPLC as above, (R_t = 29.66 min): ^{1}H NMR δ 5.05 (2 H, m, 2 × C=CH), 3.72 (6 H, s, 2 × OMe), 3.35 (1 H, t, J = 7 Hz, C*H*($CO_2Me)_2$), 2.61 (2 H, m, 3-CH_2), 1.96 (4 H, m, 6- and 7-CH_2), 1.67 (3 H, s, Me), 1.63 (3 H, s, Me), 1.58 (3 H, s, Me); ^{13}C NMR δ 169.5 (2 × C), 138.6 (C), 131.4 (C), 124.0 (CH), 119.4 (CH), 52.3 (2 × CH_3), 51.9 (CH), 39.6 (CH_2), 27.5 (CH_2), 26.5 (CH_2), 25.6 (CH_3), 17.6 (CH_3), 16.0 (CH_3), in accordance with the literature.[2,13,19]

Methyl (*E*)-2-methoxycarbonyl-2,5,9-trimethyldeca-4,8-dienoate 36b. Prepared according to General procedure and Tables 2 and 3 as a mixture with **35b**, which was separated by preparative HPLC; **36b** was the least polar fraction (R_t = 28.32 min): ^{1}H NMR δ 5.10 (1 H, m, 8-H), 4.98 (1 H, t, J = 7.3 Hz, 4-H), 3.73 (6 H, s, 2 × OMe), 2.60 (2 H, d, J = 7.3 Hz, 3-CH_2), 2.05 (4 H, m, 6- and 7-CH_2), 1.70 (3 H, s, Me), 1.68 (3 H, s, Me), 1.61 (3 H, s, Me), 1.38 (3 H, s, Me); ^{13}C NMR δ 172.6 (2 × C), 139.3 (C), 131.6 (C), 124.0 (CH), 118.4 (CH), 53.7 (C), 52.3 (2 × CH_3), 33.8 (CH_2), 31.9 (CH_2), 26.5 (CH_2), 25.6 (CH_3), 23.5 (CH_3), 19.8 (CH_3), 17.6 (CH_3); IR (neat) ν 2979, 2960, 1728, 1465, 1460, 1435, 1409, 1380, 1280, 1195, 1120, 942 cm^{-1}.

Acknowledgements

We thank the EPSRC for grants No. GR/H 92067, GR/K07140 and GR/L41448 and EPSRC and Aventis CropScience UK Ltd for a CASE award to I. R. B.

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