Molybdenum(II)- and Tungsten(II)-Catalyzed Allylic Substitution

Andrei V. Malkov,[†] Ian R. Baxendale,[†,‡] Dalimil Dvořák,[†,§] Darren J. Mansfield,[∥] and Pavel Kočovský*,[†]

Department of Chemistry, University of Leicester, Leicester LE1 7RH, U.K., and AgrEvo UK Ltd., Chesterford Park, Saffron Walden, Essex, CB10 1XL, U.K.

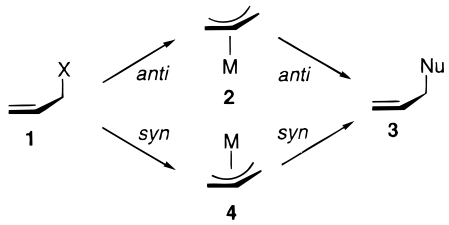
Received October 29, 1998

The molybdenum(II) complexes $Mo(CO)_5(OTf)_2$ (**7a**), $[Mo(CO)_4Br_2]_2$ (**8a**), their tungsten(II) congeners **7b** and **8b**, and bimetallic complex $Mo(CO)_3(MeCN)_2(SnCl_3)Cl$ (**9a**) have been found to catalyze the C−C bond-forming allylic substitution with silyl enol ethers derived from β-dicarbonyls (e.g., **16** + **30** → **46**) or from simple ketones (e.g., **16** + **32** → **50**), aldehydes, and esters as nucleophiles under mild conditions (room temperature, 1−2 h). Methanol, as a prototype oxygen nucleophile, reacts in a similar fashion (e.g., **16** + MeOH → **43**). Mechanistic and stereochemical experiments are indicative of Lewis-acid catalysis rather than a metal template-controlled process.

Introduction

The discovery of palladium(0) catalysis in allylic substitution[1] is one of the milestones in organic synthesis, partly because it helps solve an old problem of classical organic chemistry, namely the nonselectivity of the capricious S_N2' reaction.[2] The Pd(0)-catalyzed allylic substitution is stereospecific and occurs via the intermediate η^3-complex, arising from allylic esters in an *anti*-fashion (Scheme 1; **1** → **2**; M = Pd).[3,4] The subsequent reaction with stabilized C-nucleophiles (e.g., malonates) again proceeds with an *anti*-mechanism, giving **3**, which corresponds to an overall retention of configuration.[3]

Scheme 1



Several industrial processes are now using this chemistry either for the formation of a strategic C−C bond[5] or to facilitate selective deprotection of functional groups in molecules as sensitive as β-lactam antibiotics.[6]

Although the advent of Pd(0) catalysis has solved a number of industrial problems, the methodology suffers from two major limitations: (1) Whereas the η^3-Pd complexes readily react with enolates derived from β-dicarbonyls and their congeners as nucleophiles,[3] catalytic reactions with simple enolates often fail.[7] (2) When the catalytic turnover is low, the cost of Pd becomes prohibitive for industrial application. Hence, developing a less expensive catalyst for those cases where Pd is either ineffective or too costly would be of particular importance.

Aside from $(Ph_3P)_4Pd$ and related Pd(0) catalysts, group 6 complexes have also been shown to exhibit catalytic activity in allylic substitution and to give products of overall retention of configuration (**1** → **3**).[8,9]

* Correspondence author. E-mail: PK10@Le.ac.uk.
† University of Leicester.
‡ Current address: Department of Chemistry, University of Cambridge, Cambridge CB2 1EW, U.K.
§ On leave from the Department of Organic Chemistry, Prague Technical University, 16628 Prague 6, Czech Republic.
∥ AgrEvo UK Ltd.

(1) (a) Hata, H.; Takahashi, K.; Miyake, A. *J. Chem. Soc., Chem. Commun.* **1970**, 1392. (b) Hata, H.; Takahashi, K.; Miyake, A. *Bull. Chem. Soc. Jpn.* **1972**, *45*, 230. (c) Atkins, K. E.; Walker, W. E.; Maniyik, R. M. *Tetrahedron Lett.* **1970**, 3821. (d) Tsuji, J.; Takahashi, H.; Morikawa, M. *Tetrahedron Lett.* **1965**, 4387.

(2) (a) Magid, R. M. *Tetrahedron* **1980**, *36*, 1901. (b) Paquette, L. A.; Stirling, C. J. M. *Tetrahedron* **1992**, *48*, 7383.

(3) (a) Trost, B. M.; Strege, P. E. *J. Am. Chem. Soc.* **1975**, *97*, 2534. (b) Trost, B. M.; Verhoeven, T. R. *J. Org. Chem.* **1976**, *41*, 3215. (c) Hayashi, T.; Hagihara, T.; Konishi, M.; Kumada, M. *J. Am. Chem. Soc.* **1983**, *105*, 7767. For reviews, see: (d) Trost, B. M. *Tetrahedron* **1977**, *33*, 371. (e) Trost, B. M. *Acc. Chem. Res.* **1980**, *13*, 385. (f) Tsuji, J. *Tetrahedron* **1986**, *42*, 4361. (g) Frost, C. G.; Howarth, J.; Williams, J. M. J. *Tetrahedron: Asymmetry* **1992**, *3*, 1089. (h) Trost, B. M.; Van Vranken, D. L. *Chem. Rev.* **1996**, *96*, 395.

(4) The *syn*-mechanism (**1** → **4**) has been observed in two instances as a result of precoordination of Pd(0) to the leaving group (Ph_2PCH_2-CO_2 or Cl): (a) Starý, I.; Kočovský, P. *J. Am. Chem. Soc.* **1989**, *111*, 4981. (b) Starý, I.; Zajíček, J.; Kočovský, P. *Tetrahedron* **1992**, *48*, 7229. (c) Kurosawa, H.; Ogoshi, S.; Kawasaki, Y.; Murai, S.; Miyoshi, M.; Ikeda, I. *J. Am. Chem. Soc.* **1990**, *112*, 2813. (d) Kurosawa, H.; Kajimaru, H.; Ogoshi, S.; Yoneda, H.; Miki, K.; Kasai, N.; Murai, S.; Ikeda, I. *J. Am. Chem. Soc.* **1992**, *114*, 8417. Precoordination to a neighboring group can also enforce the *syn* mechanism: (e) Farthing, C. N.; Kočovský, P. *J. Am. Chem. Soc.* **1998**, *120*, 6661.

(5) (a) Hegedus, L. S. *Transition Metals in the Synthesis of Complex Organic Molecules*; University Science Books: Mill Valley, CA, 1994. (b) Harrington, P. J. *Transition Metals in Total Synthesis*; J. Wiley & Sons: New York, 1990. (c) Davies, S. G. *Organotransition Metal Chemistry. Applications to Organic Synthesis*; Pergamon: Oxford, U.K., 1982. For an overview of industrial applications of Pd, see: (d) Tsuji, J. *Synthesis* **1990**, 739.

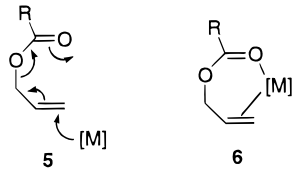
(6) Greene, T. W.; Wuts, P. G. M. *Protective Groups in Organic Synthesis*; J. Wiley & Sons: New York, 1991; pp 108 and 331−333.

(7) Attempts at developing the Pd(0)-catalyzed reaction of allylic esters with silyl enol ethers derived from simple ketones, as an extension of the established reactions with stabilized C-nucleophiles, have only met with modest success. In the examples reported to date, the more reactive carbonates (rather than acetates) have been employed and some of these reactions seem to work efficiently only as intramolecular processes: (a) Tsuji, J.; Minami, I.; Shimizu, I. *Chemistry Lett.* **1983**, 1325. (b) Tsuji, J.; Minami, I.; Shimizu, I. *Tetrahedron Lett.* **1983**, *24*, 1793. (c) Shimizu, I.; Minami, I.; Tsuji, J. *Tetrahedron Lett.* **1983**, *24*, 1797. (d) Tsuji, J.; Takahashi, K.; Minami, I.; Shimizu, I. *Tetrahedron Lett.* **1984**, *25*, 4783. For successful examples employing allylic acetates, see: (e) Fiaud, J.-C.; Malleron, J. *J. Chem. Soc., Chem. Commun.* **1981**, 1159. (f) Saitoh, A.; Achiwa, K.; Morimoto, T. *Tetrahedron Asymmetry* **1998**, *9*, 741.

(8) (a) Trost, B. M.; Lautens, M. *J. Am. Chem. Soc.* **1982**, *104*, 5543. (b) Trost, B. M.; Lautens, M. *J. Am. Chem. Soc.* **1983**, *105*, 3343. (c) Trost, B. M.; Lautens, M. *Organometallics* **1983**, *2*, 1687. (d) Trost, B. M.; Lautens, M.; Peterson, B. *Tetrahedron Lett.* **1983**, *24*, 4525. (e) Trost, B. M.; Lautens, M. *J. Am. Chem. Soc.* **1987**, *109*, 1469. (f) Trost, B. M.; Lautens, M. *Tetrahedron* **1987**, *43*, 4817. (g) Trost, B. M.; Merlic, C. A. *J. Am. Chem. Soc.* **1990**, *112*, 9590.

10.1021/jo9821776 CCC: $18.00
Published on Web 03/20/1999

Scheme 2



Interestingly, there is evidence that the mechanism for the reaction catalyzed by $Mo(CO)_6$ can differ from that for Pd:[10−12] instead of double inversion, we have recently demonstrated a double retention pathway for Mo (**1** → **4** → **3**).[11] In stoichiometric reactions, the first step has also been shown to occur with retention of configuration (**1** → **4**),[10,12] but the isolated η^3-complex **4** is known to react with stabilized nucleophiles via inversion.[10,12] Although this dichotomy may offer attractive synthetic applications, wider use of the group 6 catalysts is held back by their lower reactivity compared to Pd. Thus, Mo and W catalysts typically require refluxing in higher-boiling solvents (e.g., toluene) for several hours,[8,9,11] whereas reflux in THF or even ambient temperature is normally sufficient for Pd.[3,4] This striking difference can be attributed, in part, to the ease of ligand dissociation in the case of Pd catalysts, e.g., $(Ph_3P)_4Pd \rightarrow (Ph_3P)_3Pd + Ph_3P$, as opposed to the relative stability of $Mo(CO)_6$, $W(CO)_6$, and related complexes.[5a] In view of the relatively low cost of Mo and W complexes, increasing their reactivity would be highly desirable.[13]

The mechanism of formation of the η^3-Pd complex is generally accepted to involve a primary coordination of Pd(0) to the C=C bond followed by extrusion of the leaving group (**5**, Scheme 2) as a result of back-donation.[3] The different behavior of Mo(0) complexes can be understood if, instead of coordinating to the C=C bond, Mo is assumed to first associate with the Lewis-basic carbonyl oxygen of the acetate leaving group, followed by coordination to the C=C bond (**6**).[11,12] Hence, $Mo(CO)_6$ would act as a weak Lewis acid and this postulate appears to be compatible with the effect of altering the Lewis basicity of the carbonyl oxygen by varying the R in the leaving group: thus, an electron-donating nitrogen atom (**6**, R = Me_2N) accelerates the reaction, whereas an electron-withdrawing unit (**6**, R = CF_3) retards the process.[11,14] However, the increase of the reaction rate observed for carbamates is not dramatic, being in the range of 1 order of magnitude, so that synthetic benefits would not be as great as desired.

Alternatively, the above analysis suggests that enhancing the Lewis acidity of the Mo complex should also result in acceleration of the reaction. We reasoned that, by analogy with other transition metal complexes, the Lewis acidity of Mo could be increased by replacing some of the CO groups in the complex by weakly coordinating ligands, such as trifluoromethanesulfonate, and/or by increasing the oxidation state of the metal.[15−17]

Chart 1[a]

$M(CO)_5(OTf)_2$	$[M(CO)_4Br_2]_2$	$Mo(CO)_3(MeCN)_2(SnCl_3)Cl$
7a, M = Mo	**8a**, M = Mo	**9a**
7b, M = W	**8b**, M = W	

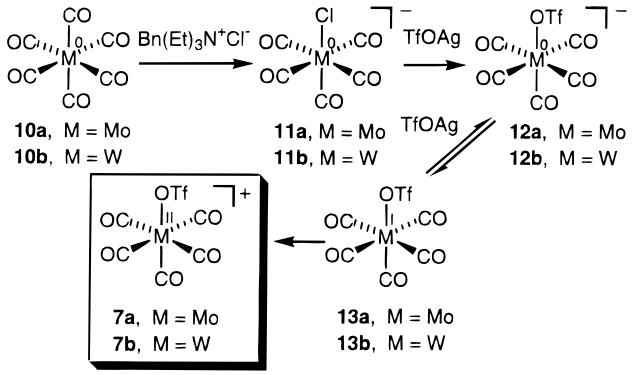
[a] TfO = CF_3SO_3.

Herein, we present a study of three variants of M(II) catalysts, namely complexes **7**−**9** (Chart 1); their preparation is discussed in appropriate paragraphs and illustrated in Schemes 3−5.

Results and Discussion

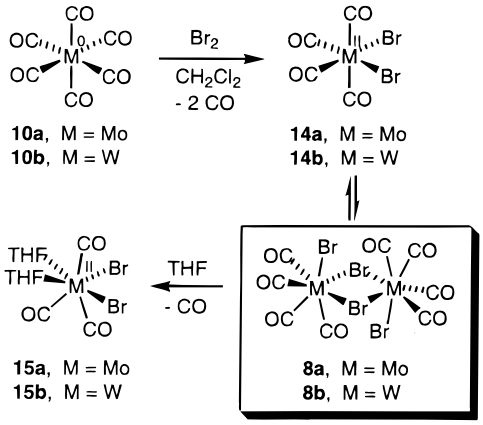
Preparation of Mo(II) and W(II) Complexes as Potential Catalysts. Group 6 complexes with a weakly coordinating ligand appeared to us to be promising candidates for catalysts in allylic substitution (vide supra). Therefore we first endeavored to prepare the corresponding triflates.

Scheme 3[a]



[a] Bn = $PhCH_2$, TfO = CF_3SO_3.

Scheme 4



(9) (a) Trost, B. M.; Hung, M.-H. *J. Am. Chem. Soc.* **1983**, *105*, 7757. (b) Trost, B. M.; Hung, M.-H. *J. Am. Chem. Soc.* **1984**, *106*, 6837. (c) Lloyd-Jones, G. C.; Pfaltz, A. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 462. (d) Lloyd-Jones, G. C.; Pfaltz, A. *Z. Naturforsch. B* **1995**, *50b*, 361. (e) Lehmann, J.; Lloyd-Jones, G. C. *Tetrahedron* **1995**, *51*, 8863. (f) Frisell, H.; Åkermark, B. *Organometallics*, **1995**, *14*, 561.

(10) Faller, J. W.; Linebarrier, D. *Organometallics* **1988**, *7*, 1670.

(11) Dvořák, D.; Starý, I.; Kočovský, P. *J. Am. Chem. Soc.* **1995**, *117*, 6130.

(12) Ward, Y. D.; Villanueva, L. A.; Allred, G. D.; Liebeskind, L. S. *J. Am. Chem. Soc.* **1996**, *118*, 897.

(13) Replacing some of the carbonyls in $Mo(CO)_6$ and $W(CO)_6$ by other ligands, such as MeCN, DMF, etc., has been shown to slightly accelerate the reaction.[8] See also: Pearson, A. J.; Schoffers, E. *Organometallics* **1997**, *16*, 5365.

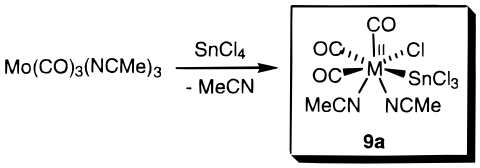
(14) Note that the opposite effect has been observed for the substrates in which the *syn*-mechanism is precluded by a steric bias so that the *anti*-mechanism (**5**) becomes the only possible pathway.[11]

(15) (a) Van Seggen, D. M.; Hurlburt, P. K.; Anderson, O. P.; Strauss, S. H. *Inorg. Chem.* **1995**, *34*, 3453 and references cited therein. (b) Marks, T. J. *Acc. Chem. Res.* **1992**, *25*, 57. (c) Strauss, S. H. *Chem. Rev.* **1993**, *93*, 927.

(16) Dvořáková, H.; Dvořák, D.; Šrogl, J.; Kočovský, P. *Tetrahedron Lett.* **1995**, *36*, 6351.

(17) (a) Malkov, A. V.; Baxendale, I. R.; Mansfield, D. J.; Kočovský, P. *Tetrahedron Lett.* **1997**, *38*, 4895. (b) Malkov, A. V.; Davis, S. L.; Mitchell, W. L.; Kočovský, P. *Tetrahedron Lett.* **1997**, *38*, 4899.

Scheme 5



(a) Triflate Complexes. To prepare triflate complexes of Mo, we examined the reaction of silver triflate with chloromolybdate **11a** which, in turn, can be readily obtained from $Mo(CO)_6$ on heating with a tetraalkylammonium chloride (Scheme 3).[18] Although replacement of the chloride with TfOAg is a standard technique in transition metal chemistry,[15] in the case of **11a** the reaction turned out to be more complex.[19] As expected, on treatment with TfOAg, the chloride in **11a** was, indeed, replaced by TfO^- (**11a** → **12a**). However, the reaction proceeded with concomitant oxidation of Mo(0) to Mo(I) (**12a** → **13a**). The latter species proved to be unstable and underwent disproportionation to give **12a** and Mo(II) complex **7a**. In practice, 3 equiv of TfOAg was required to drive the reaction to completion.[16,19] The resulting complex **7a** can be expected to behave like a weak Lewis acid in view of its oxidation state (+2) and the presence of a weakly coordinating TfO^- group. The corresponding tungsten complex **7b** was generated in situ from chlorotungstenate **11b** in a similar way.[19]

Preliminary investigations of the catalytic activity of complexes **7a**,**b** toward allylic substrates, employing both oxygen[16] and carbon nucleophiles,[17] were promising (vide infra). Control experiments demonstrated that neither Mo(0)/W(0) nor TfOAg was capable of catalyzing allylic substitution under the same conditions, suggesting that Mo(II) and/or W(II) are, indeed, responsible for the reactivity. However, the complexes themselves are not ideal catalysts as they have to be generated from chloromolybdates **10a**,**b** prior to each reaction and cannot be stored. The latter instability, in conjunction with the requirement for 3 equiv of TfOAg for the in situ generation of the active species, renders this method rather clumsy and expensive so that development of a simpler and less expensive alternative was desirable.

(b) $[Mo(CO)_4Br_2]_2$ and $[W(CO)_4Br_2]_2$ Complexes. In view of the disadvantages of **7a**,**b**, it was desirable to investigate related complexes that would be more stable and easier to handle. Since preliminary experiments suggested M(II) to be the reactive species, we endeavored to oxidize M(0) to M(II) by other means.

One of the methods for preparation of a potentially useful Mo(II) complex relies on titration of $Mo(CO)_6$ with 1 equiv of bromine (Scheme 4)[20] at low temperature in a noncoordinating solvent (e.g., CH_2Cl_2) under inert atmosphere; the resulting product **14a** (a 16 electron species) is stabilized as dimer **8a** (an 18 electron species).[20] The corresponding tungsten complex **8b** can be prepared from $W(CO)_6$ in the same way.[20] The dimeric complexes **8a**,**b** are orange powders and, when dry, can be handled in air. However, to retain their catalytic activity for >0.5 year (vide infra), they should be stored under nitrogen in a freezer (−20 °C). During our frequent preparations of **8a**,**b**, we obtained more active and pure complexes by removal of the solvent (CH_2Cl_2) at low temperature (−78 °C; see Experimental Section for details). By contrast, warming the mixture to ambient temperature prior to the solvent removal[20] often resulted in the formation of black-brown solid or tar. Although the latter substances still showed characteristic IR signals[20] of the desired product, additional impurities could also be detected; these products proved to be less stable and of low catalytic activity.

Interestingly, adding THF to either of the complexes **8a**,**b** is known to trigger a fast exchange of CO for THF, generating complexes **15a**,**b**, respectively.[20] The importance of the ease of the latter reaction for development of a catalytic process, though not recognized earlier, can easily be envisaged: if a ligand as weak as THF experiences no difficulty in entering the coordination sphere of the metal, then other eligible ligands, such as an allylic acetate and/or a nucleophile, should also be successful. This, indeed, proved to be the case, as shown below.

(c) Bimetallic Complex. Another suitable Mo(II) candidate was identified in the orange-red complex **9a**, which can be prepared by oxidative addition of $SnCl_4$ to $Mo(CO)_3(MeCN)_3$ (Scheme 5).[21−23] Pure **9a** is moderately stable and can be stored in the dark under nitrogen at room temperature; its solutions rapidly decompose when exposed to air. Although the crude product can be used directly in our catalytic reactions, recrystallization from acetonitrile is highly recommended as it gives more stable and more reactive species.

Model Substrates for Allylic Substitution. All the complexes **7**−**9** possess labile ligands (TfO^- in **7a**,**b**, CO in **8a**,**b**, and MeCN in **9a**) that can easily dissociate in solution, offering vacant coordination sites, potentially capable of accommodating an allylic substrate and/or a nucleophile.[24] To investigate their reactivity as catalysts for allylic substitution, we employed a set of allylic acetates (Chart 2) and two types of nucleophiles: methanol, as a prototype *O*-nucleophile, and enolate-type C-nucleophiles (Chart 3).

O-Nucleophiles. In a preliminary account,[16] we have shown that **7a** catalyzed substitution of an allylic acetoxy group with MeOH. Thus, **16** and **18** readily underwent the reaction at room temperature[25] to give methoxy derivatives **43** and **44**, respectively (Scheme 6; Table 1, entries 1, 6), accompanied by elimination products. By contrast, **23** (an allylic isomer of **22**) was found to react

(18) (a) Ganorkar, M. C.; Stiddard, M. H. B. *J. Chem. Soc.* **1965**, 3494. (b) Abel, E. W.; Butler, I. S.; Red, J. G. *J. Chem. Soc.* **1964**, 2068. (c) Šrogl, J.; Kočovský, P. *Tetrahedron Lett.* **1992**, *33*, 5991.

(19) Abbott, A. P.; Malkov, A. V.; Zimmermann, N.; Raynor, J. B.; Ahmed, G.; Steele, J.; Kočovský, P. *Organometallics* **1997**, *16*, 3690.

(20) (a) Bowden, J. A.; Colton, R. *Aust. J. Chem.* **1968**, *21*, 2657. (b) Cotton, F. A.; Falvello, L. R.; Meadows, J. H. *Inorg. Chem.* **1985**, *24*, 514. (c) Cotton, F. A.; Poli, R. *Inorg. Chem.* **1987**, *26*, 1514.

(21) (a) Baker, P. K.; Bury, A. *J. Organomet. Chem.* **1989**, *359*, 189. (b) Baker, P. K.; Quinlan, A. J. *Inorg. Chim. Acta* **1989**, *162*, 179.

(22) (a) Miguel, D.; Perez-Martinez, J. A.; Garcia-Granda, S. *Polyhedron* **1991**, *10*, 1717. (b) Barrado, G.; Miguel, D.; Perez-Martinez, J. A.; Riera, V. *J. Organomet. Chem.* **1993**, *463*, 127.

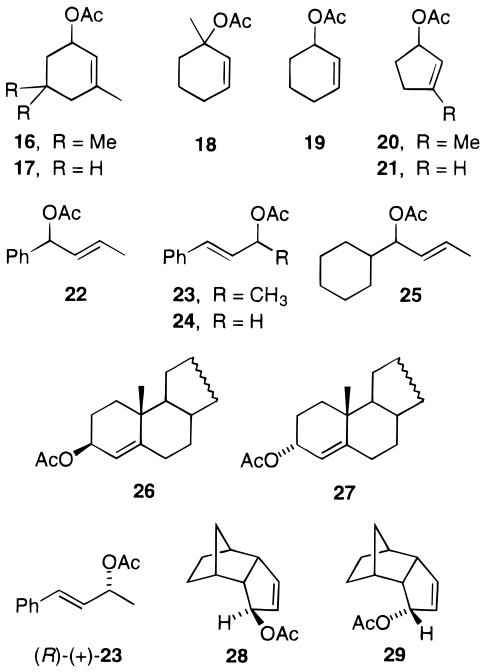
(23) Cano, M.; Panizo, M.; Campo, J. A.; Tornero, J.; Menendez, N. *J. Organomet. Chem.* **1993**, *463*, 121.

(24) Interestingly, when crystallized from acetone, **9a** undergoes a ligand exchange to produce $Mo(CO)_3(MeCN)(Me_2CO)(SnCl_3)Cl$, demonstrating the lability of the MeCN ligand.[22]

(25) The reactions were typically carried out in CH_2Cl_2 at room temperature with 2−5 mol % of the catalyst and a slight excess (1.1 equiv) of the nucleophile. The reaction times and yields are given in Tables 1−6. All yields refer to "isolated" yields rather than "GC yields".

(26) For a similar catalytic effect of Ce(IV) and/or Ce(III) on the transformation of allylic acetates or alcohols into the corresponding ethers on reaction with alcohols, see: (a) Iranpoor, N.; Mothaghineghad, E. *Tetrahedron* **1994**, *50*, 1859 and 7299. (b) Uzarewicz, A.; Dresler, R. *Pol. J. Chem.* **1997**, *71*, 181. The same effect has been reported for $(Ph_3P)_2PtCl_2-SnCl_2$ as catalyst: Sakamaki, H.; Kameda, N.; Iwadare, T.; Ichinohe, Y. *Bull. Chem. Soc. Jpn* **1995**, *68*, 3491.

Chart 2



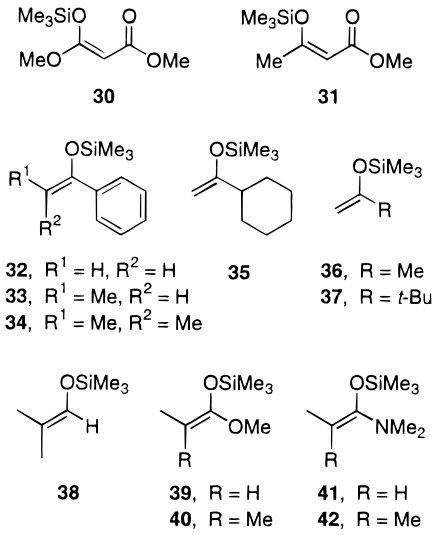
sluggishly (Table 1, entry 9), and **19** and **24** proved inert, suggesting a substantial S_N1 component in the initial ionization of the substrate. Analogous reactivity was observed for tungsten catalyst **7b** (Table 1, entry 2).[26]

Dibromo-catalyst **8a** proved to react in a similar way as documented by conversion of **16**, **17**, and **22** into the corresponding methoxy derivatives (Table 1, entries 3, 4, and 7). For acetate **23** (which reacted sluggishly in the presence of **7a**), this catalyst turned out to be clearly superior (compare entries 9 and 10 in Table 1).

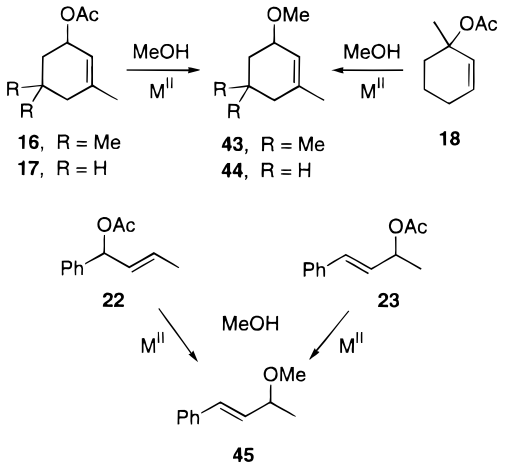
Bimetallic complex **9a** was also found to catalyze the reaction of **22** and of **23** with MeOH (Scheme 6) to give **45** in excellent yields (compare entries 8 and 11 with entries 7, 9, and 10 in Table 1). Note, in particular, the high conversion of **23** into **45**, which gave the best yield with **9a** (Table 1, entry 12). By contrast, conversion of **17** into **44** gave low yield (Table 1, entry 5), mainly due to predominant elimination.

C-Nucleophiles. Inspired by the successful and ready allylic substitution with O-nucleophiles, we endeavored to develop a C−C bond-forming reaction. However, initial attempts employing dimethyl lithiomalonate as the nucleophile failed under a range of conditions: the starting allylic acetates (Chart 2) either proved inert or underwent a slow elimination to give rise to the corresponding dienes and further decomposition products. This failure can be attributed to deactivation of the catalyst via a strong chelation of the metal by the β-dicarbonyl enolate,[27] suggesting that anionic nucleophiles should be avoided.

Chart 3



Scheme 6[a]



[a] For conditions and yields, see Table 1.

Table 1. Allylic Substitution[a] with MeOH as Nucleophile

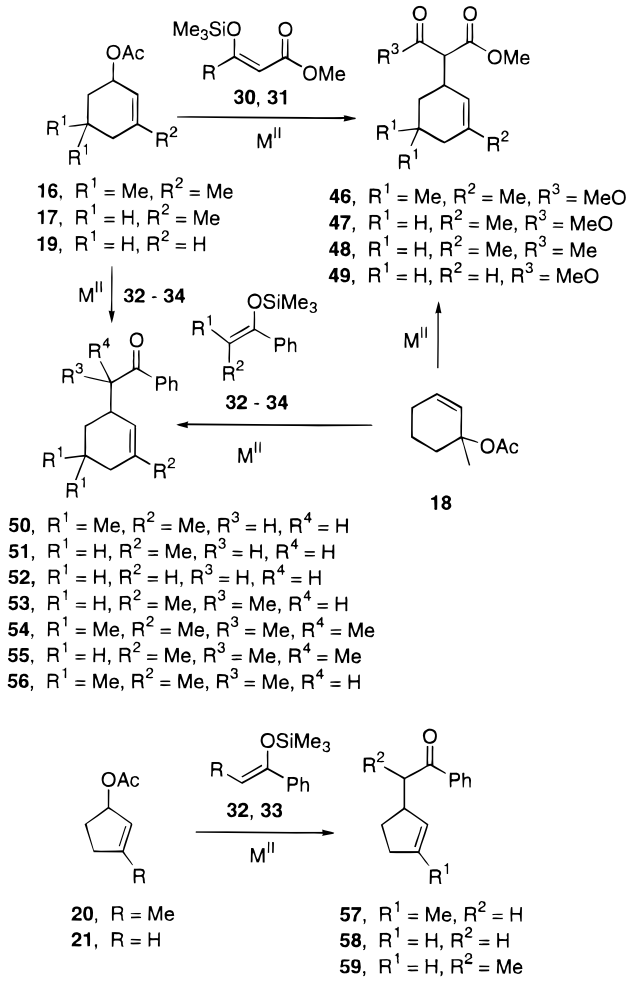
entry	allylic compd	catalyst (mol %)	time (h)	product	yield (%)[b]
1	**16**	**7a** (5)	4	**43**	20[c]
2	**16**	**7b** (5)	20	**43**	10
3	**16**	**8a** (5)	4	**43**	60
4	**17**	**8a** (5)	24	**44**	20
5	**17**	**9a** (5)	24	**44**	19
6	**18**	**7a** (5)	4	**44**	25[c]
7	**22**	**8a** (2)	4	**45**	55
8	**22**	**9a** (5)	2.5	**45**	92
9	**23**	**7a** (5)	4	**45**	12
10	**23**	**8a** (2)	4	**45**	63
11	**23**	**9a** (5)	2.5	**45**	94

[a] The reactions were carried out in CH_2Cl_2 at room temperature unless stated otherwise. [b] Isolated yield. [c] Conversion was quantitative.

(a) Silyl Enol Ethers Derived from β-Dicarbonyls. We reasoned that neutral silyl enol ethers might be less detrimental to the catalyst activity which, indeed, proved to be the case. Initial experimentation (Scheme 7) with acetate **16** and the malonate-derived silyl enol ether **30** met with modest success, affording the desired compound **46** accompanied by a substantial proportion of elimination products; under optimized conditions, **46** was obtained at ambient temperature in 48% isolated yield (Table 2, entry 1). The less reactive acetate **19** furnished the corresponding product **49** in only 16% yield (Table 2, entry 5). Finally, tertiary acetate **18** proved moderately reactive, affording **47** (55%) on reaction with **30** (Table 2, entry 4). In the presence of either **8a** or **9a**, silyl enol ether **31** (derived from methyl acetoacetate) produced **48** in high yields (Table 2, entries 2 and 3).

(27) Enolates of β-dicarbonyls are known to form relatively stable chelate complexes with Mo(II): Brower, D. C.; Winston, P. B.; Tonker, T. L.; Templeton, J. L. *Inorg. Chem.* **1986**, *25*, 2883. See also refs 8e,f.

Scheme 7[a]



[a] For conditions and yields, see Tables 2 and 3.

Table 2. Allylic Substitution[a] with β-Dicarbonyl-Derived Nucleophiles

entry	allylic compd	nucleophile	catalyst (mol %)	time	product	yield (%)[b]
1	**16**	**30**	**7a** (5)	1 h	**46**	48
2	**17**	**31**	**8a** (5)	45 min	**48**	86
3	**17**	**31**	**9a** (5)	30 min	**48**	80
4	**18**	**30**	**7a** (5)	1 h	**47**	55
5	**19**	**30**	**7a** (5)	20 h	**49**	16

[a] The reactions were carried out in CH_2Cl_2 at room temperature. [b] Isolated yield.

(b) Ketone-Derived Silyl Enol Ethers. Since the reaction of **16** with silylated malonate **30** proved reasonably efficient, being the first example of C−C bond formation catalyzed by Mo(II), it was of interest to establish whether simple silyl enol ethers, such as **32**, could also be used as nucleophiles (Chart 3).[28] If successful, these M(II) catalysts would present a substantial advantage over their Pd(0) counterparts by offering a broader scope of reactivity. In practice, **32** turned out to be more efficient than **30** on reaction with **16** (Scheme 7), giving the corresponding product **50** in 65% yield (Table 3, entry 1) with **7a** as catalyst. On the other hand, allylic acetate **19** with a disubstituted double bond reacted sluggishly again to afford **52** in mere 14% yield (Table 3, entry 35). The difference in the reactivity of **16** and **17** vs **19** further supports the notion that a substantial S_N1 component attends the transition state of the reaction. Increasing the steric bulk of the nucleophile turned out to have little effect on the reactivity, as demonstrated by the high yield of **53** from the reaction of **18** with **33** (Table 3, entry 34). Tungsten complex **7b** proved slightly less reactive (compare entries 1 and 2 in Table 3).

Complexes **8a**,**b** have proven to be superior to triflates **7a**,**b**. Thus, reactions of allylic acetates **16**−**18** with **32** (Scheme 7) proceeded to completion in 20−45 min at room temperature, giving excellent isolated yields (typically 80−90%) of the expected products (Table 3, entries 3, 4, 18, 19, 31, and 32). The yields were dramatically

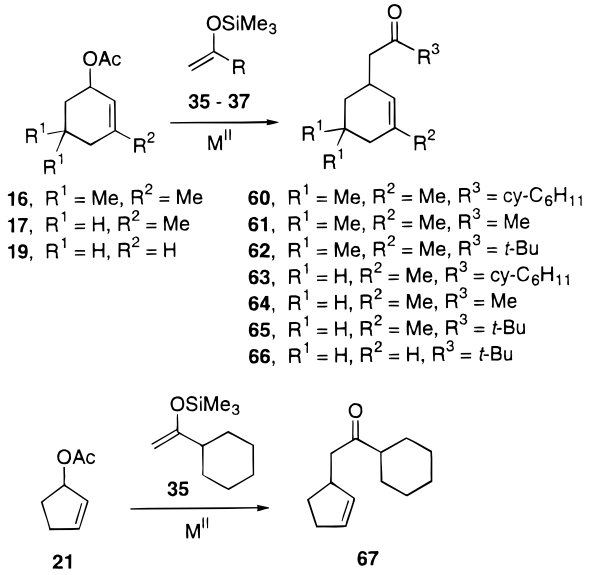
Table 3. Allylic Substitution[a] with Ketone- and Aldehyde-Derived Nucleophiles

entry	allylic compd	nucleophile	catalyst (mol %)	time	product	product ratio[b]	yield (%)[c]
1	**16**	**32**	**7a** (5)	1.5 h	**50**		65
2	**16**	**32**	**7b** (5)	2 h	**50**		59
3	**16**	**32**	**8a** (2)	20 min	**50**		89
4	**16**	**32**	**8b** (5)	45 min	**50**		86
5	**16**	**32**	**9a** (5)	25 min	**50**		80
6	**16**	**33**	**8a** (5)	20 min	**56**[d]		76
7	**16**	**33**	**9a** (5)	20 min	**56**[d]		81
8	**16**	**34**	**8a** (5)	30 min	**54**		79
9	**16**	**34**	**9a** (5)	30 min	**54**		82
10	**16**	**35**	**8a** (5)	25 min	**60**		73
11	**16**	**35**	**9a** (5)	25 min	**60**		80
12	**16**	**36**	**8a** (5)	10 min	**61**		72
13	**16**	**36**	**9a** (5)	10 min	**61**		80
14	**16**	**37**	**8a** (5)	20 min	**62**		74
15	**16**	**37**	**9a** (5)	15 min	**62**		91
16	**16**	**38**	**8a** (5)	15 min	**68**		92
17	**16**	**38**	**9a** (5)	15 min	**68**		83
18	**17**	**32**	**8a** (5)	30 min	**51**	96:4[e]	89
19	**17**	**32**	**8b** (5)	45 min	**51**	97:3[e]	80
20	**17**	**32**	**9a** (5)	25 min	**51**	94:6[e]	89
21	**17**	**34**	**8a** (5)	30 min	**55**		84
22	**17**	**34**	**9a** (5)	30 min	**55**		86
23	**17**	**35**	**8a** (5)	1.75 h	**63**		75
24	**17**	**35**	**9a** (5)	1.75 h	**63**		62
25	**17**	**36**	**8a** (5)	10 min	**64**		88
26	**17**	**36**	**9a** (5)	10 min	**64**		91
27	**17**	**37**	**8a** (5)	15 min	**65**		78
28	**17**	**37**	**9a** (5)	15 min	**65**		86
29	**17**	**38**	**8a** (5)	15 min	**69**		80
30	**17**	**38**	**9a** (5)	15 min	**69**		90
31	**18**	**32**	**8a** (2)	30 min	**51**		84
32	**18**	**32**	**8b** (5)	40 min	**51**		68
33	**18**	**32**	**9a** (5)	50 min	**51**		91
34	**18**	**33**	**7a** (5)	1.5 h	**53**		81
35	**19**	**32**	**7a** (5)	24 h	**52**		14
36	**19**	**32**	**8a** (2)	24 h	**52**		42
37	**19**	**32**	**8b** (5)	24 h	**52**		35
38	**19**	**32**	**9a** (5)	2 h	**52**		75
39	**19**	**37**	**8a** (5)	30 min	**66**		74
40	**19**	**37**	**9a** (5)	30 min	**66**		86
41	**20**	**32**	**8a** (5)	10 min	**57**		54
42	**20**	**32**	**9a** (5)	10 min	**57**		53
43	**21**	**32**	**8a** (5)	20 min	**58**		86
44	**21**	**32**	**9a** (5)	20 min	**58**		81
45	**21**	**33**	**8a** (5)	20 min	**59**		74
46	**21**	**33**	**9a** (5)	20 min	**59**		80
47	**21**	**35**	**8a** (5)	4 h	**67**		56
48	**21**	**35**	**9a** (5)	4 h	**67**		57

[a] The reactions were carried out in CH_2Cl_2 at room temperature. [b] The isomer ratios were determined by ^1H NMR. [c] Isolated yield. [d] A 60:40 mixture of diastereoisomer ratio was formed. [e] A regioisomer was formed as byproduct, as revealed by ^1H NMR spectroscopy.

(28) The silyl enol ethers were prepared from the corresponding ketones via deprotonation with LDA or LiHMDS in THF followed by quenching the intermediate enolate with Me_3SiCl.

Scheme 8[a]



[a] For conditions and yields, see Table 3.

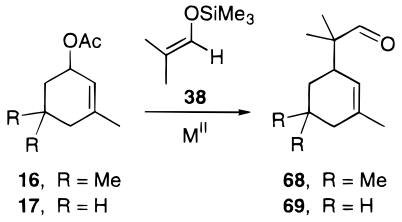
improved even in the case of acetate **19** (up to 42%), although this reaction required 24 h and considerable decomposition of the starting materials was detected (Table 3, entries 36 and 37). Again, the steric bulk of the nucleophile proved to have little effect, as revealed by the reaction of **16** or **17** with **34**, which furnished **54** and **55**, respectively (Table 3, entries 8 and 21). Reaction of **16** with **33** also proceeded readily, furnishing **56** (Table 3, entry 6).

The reactivity pattern for bimetallic complex **9a** turned out to be similar to that exhibited by other M(II) catalysts (vide supra). Thus, on reaction with **32**, acetates **16**−**19** afforded the respective products **50**−**52** in comparable or improved yields (Scheme 7) but often in a shorter period of time than the other M(II) catalysts (Table 3, entries 5, 20, 33, and 38). Sterically hindered enol ethers **33** and **34** gave essentially the same yields of **54**−**56**, respectively, on reaction with both **16** and **17**, as in the presence of **8a**,**b** (Table 3, compare entries 6 vs 7, 8 vs 9, and 21 vs 22).

The cyclopentene-derived allylic acetate **20** was readily converted into the expected ketone **57** on reaction with **32** in the presence of **8a** (Table 3, entry 41). Even **21**, lacking the additional methyl group, gave the corresponding product **58** in excellent yield (Table 3, entry 43), demonstrating the higher reactivity of the cyclopentene series. By analogy, **59** was readily produced on reaction of **21** with **33** (Table 3, entry 45). Similar reactivity was observed for complex **9a** (Scheme 7; Table 3, entries 42, 44, and 46).

To assess the effect of the aromatic ring (as in **32**−**34**) on the reactivity, nonaromatic silyl enol ethers **35**−**37** were screened as nucleophiles (Scheme 8). The cyclohexyl derivative **35**, lacking the stabilizing effect of the aromatic ring but having greater steric demand, gave rise, on reaction with **16** in the presence of **8a**, to the expected product **60** in high yield (Table 3, entry 10). The acetone-derived silyl enol ether **36** and even its *tert*-butyl analogue **37** reacted in the same way to furnish **61** and **62**, respectively, in excellent yields (Table 3, entries 12 and 14), showing that steric effects do not prevent the reaction from occurring. Acetate **17** exhibited the same reactivity

Scheme 9[a]



[a] For conditions and yields, see Table 3.

Table 4. Allylic Substitution[a] with Ester-Derived Nucleophiles

entry	allyllic compd	nucleophile	catalyst (mol %)	time	product	product ratio[b]	yield (%)[c]
1	**16**	**40**	**8a** (5)	20 min	**70**	87:13[d]	85
2	**16**	**40**	**8b** (5)	35 min	**70**	91:9[d]	89
3	**16**	**40**	**9a** (5)	15 min	**70**	86:14[d]	89
4	**17**	**39**	**8a** (5)	45 min	**71**		75
5	**17**	**39**	**9a** (5)	45 min	**71**		77
6	**17**	**40**	**8a** (5)	20 min	**72**	92:8[d]	77
7	**17**	**40**	**8b** (5)	25 min	**72**	87:13[d]	89
8	**17**	**40**	**9a** (2)	20 min	**72**	83:17[d]	93
9	**19**	**40**	**8a** (5)	2.5 h	**73**		83
10	**19**	**40**	**9a** (5)	2.5 h	**73**		89
11	**20**	**40**	**8a** (5)	15 min	**74**		46
12	**20**	**40**	**9a** (5)	15 min	**74**		50
13	**21**	**40**	**8a** (5)	30 min	**75**		82
14	**21**	**40**	**9a** (5)	30 min	**75**		83

[a] The reactions were carried out in CH_2Cl_2 at room temperature. [b] The isomer ratios were determined by ^1H NMR. [c] Isolated yield. [d] A regioisomer was formed as byproduct, as revealed by ^1H NMR spectroscopy.

toward **35**−**37**, producing **63**−**65**, respectively (Table 3, entries 23, 25, and 27). Even the least reactive allylic acetate **19** turned out to be a suitable substrate in the reaction with **37** (Table 3, entry 39). Cyclopentyl derivative **21** followed the trend, affording **67** on reaction with **35** (Table 3, entry 47). Similar yields of the respective products were attained with catalyst **9a** on reactions of **16**, **17**, **19**, and **21** (Table 3, entries 11, 13, 15, 24, 26, 28, 40, and 48). On the other hand, the silyl enol ethers derived from cyclohexanone or cyclopentanone proved inert. In this instance, rather than undergoing substitution, the starting allylic acetates were either recovered or found to be partly converted into elimination products and polymers; the silyl enol ethers slowly reverted into the corresponding carbonyl compounds.

(c) Aldehyde-Derived Silyl Enol Ether. In view of the successful reactions of allylic acetates with a number of ketone-derived silyl enol ethers, it was of interest to establish the suitability of other silyl enol ethers, such as those generated from aldehydes. Indeed, **38** was found to react with both **16** and **17** (Scheme 9) giving the corresponding products **68** and **69**, respectively, in the presence of either of the catalysts **8a** and **9a** (Table 3, entries 16, 17, 29, 30).

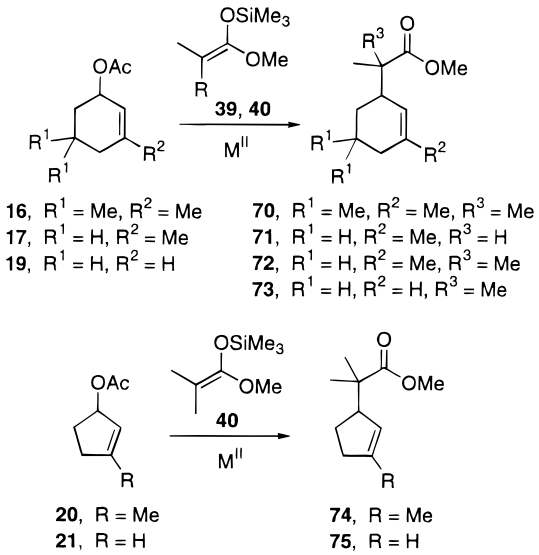
(d) Silyl Enol Ethers Derived from Esters and Amides. Ketene acetals **39** and **40** also proved reactive toward acetates **16** and **17** in the presence of **8a** (Scheme 10). Thus, **39** gave **71** as a single product on reaction with **17** (Table 4, entry 4), whereas formation of mixtures of regioisomers was observed with **40**, in which the major products **70** and **72**, respectively, originated from the attack on the less substituted carbon (6:1 to 10:1; Table entries 1, 2, 6, and 7). The usually less reactive allylic substrate **19** gave **73** in very good yield on reaction with

40 (Table 4, entry 9). The cyclopentane-derived allylic acetate **20** proved more regioselective than its cyclohexane congeners, affording **74** as a single isomer (Table 4, entry 11); its de-methyl analogue **21** gave the expected product **75** (Table 4, entry 13).

A practically identical pattern was observed for complex **9a**: whereas **39** afforded **71** as a single regioisomer on reaction with **17** (Table 4, entry 5), its analogue **40** reacted with **16** and **17** to give regioisomeric mixtures, in which **70** and **72** prevailed (Table 4, entries 3 and 8); under the same conditions, cyclohexenyl acetate **19** produced **73** in high yield (Table 4, entry 10). Cyclopentane derivatives **20** and **21** reacted with similar efficiency (Table 4, entries 12 and 14). In contrast to the reactivity of ketene acetals, attempts at introducing the related amide nucleophiles, namely **41** and **42**, failed even with the most reactive acetates **16** and **17**.

Regioselectivity. Methanol, as a representative O-nucleophile, exhibited excellent regioselectivity with the nonsymmetrically substituted allylic substrates **16**, **18**, **22**, and **23** (Scheme 6): the attack occurred exclusively at the less substituted carbon in the case of **16** and **18**. Remarkably, even the reaction of the allylic system flanked by Ph at one terminus and by Me at the other (**22** and **23**) gave the single methoxy derivative **45** (Table 1, entries 9−11). In all these instances, formation of the product was independent of the original position of the leaving group (compare **16** vs **18** and **22** vs **23**; Table 1, entry 3 vs 6 and 7, 8 vs 9−11).

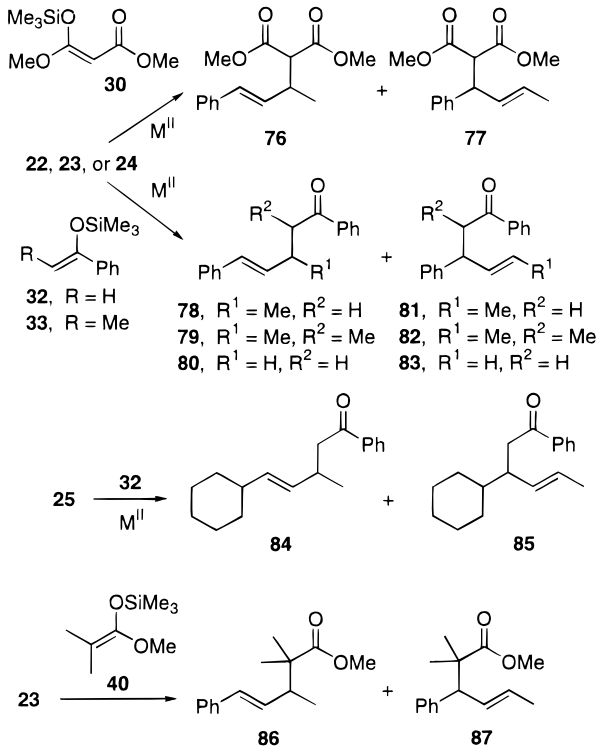
Scheme 10[a]



[a] For conditions and yields, see Table 4.

The reactivity of C-nucleophiles initially seemed to follow the same pattern. Thus, on reaction with the ketone-derived silyl enol ethers **32** or **33**, allylic acetates **16**−**18** afforded either exclusively or with high preference the products corresponding to the attack at the less substituted carbon of the allyl moiety (Scheme 7; Table 3, entries 1−5, 18−20, and 31−34). The reactions with ketene silyl acetal **40** (Scheme 10) were slightly less regioselective, but only minute amounts of the regioisomers were detected (Table 4, entries 1−3 and 6−8). By contrast, the reactivity of phenyl-substituted substrates **22** and **23** turned out to be dramatically different as there was little preference observed on reactions with **30**, **32**, **33**, or **40** (Scheme 11); the ratio of the isomeric products **76**/**77**, **78**/**81**, **79**/**82**, and **86**/**87** oscillated between 1:1 and 1:1.4 (Table 5, entries 1−11). Lowering the reaction temperature from 20 to −20 °C rendered the reaction of **23** with **32** slightly more selective in favor of the methyl terminus (Table 5, entry 9). For comparison, the Mo(0)-catalyzed reaction of **23** with $NaCH(CO_2Me)_2$ is known[8,11] to produce a ∼1:2 mixture of **76** and **77**, whereas the Pd(0)-catalyzed process affords **76** with excellent regioselectivity (up to 20:1).[29] On the other hand, employing more Lewis-acidic Pd(0) catalysts, i.e., those with TMEDA or $(PhO)_3P$ ligands, has been reported to result in

Scheme 11[a]



[a] For conditions and yields, see Table 5.

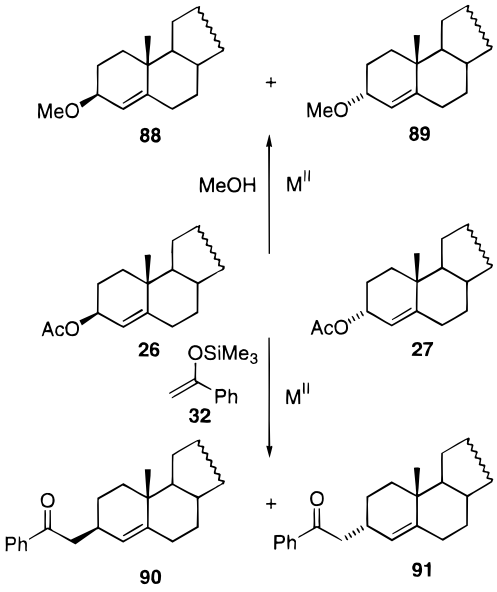
Table 5. Regioselectivity of Allylic Substitution[a] with C−Nucleophiles

entry	allylic compd	nucleophile	catalyst (mol %)	time	products	product ratio[b]	yield (%)[c]
1	**22**	**30**	**7a** (5)	1 h	**76** + **77**	43:57	59
2	**22**	**32**	**7a** (5)	1 h	**78** + **81**	40:60	54
3	**22**	**32**	**8a** (2)	30 min	**78** + **81**	50:50	65
4	**22**	**33**	**7a** (2)	30 min	**79** + **82**	42:58	80
5	**23**	**30**	**8a** (2)	1 h	**76** + **77**	43:57	92
6	**23**	**32**	**8a** (2)	30 min	**78** + **81**	43:57	65
7	**23**	**32**	**8b** (5)	30 min	**78** + **81**	50:50	87
8	**23**	**32**	**9a** (5)	20 min	**78** + **81**	50:50	97
9	**23**	**32**	**9a** (5)	2 h[d]	**78** + **81**	67:33	89
10	**23**	**32**	**9b** (25)	50 min	**78** + **81**	44:56	79
11	**23**	**40**	**9a** (5)	20 min	**86** + **87**	50:50	91
12	**24**	**32**	**8a** (5)	1 h	**80** + **83**	80:20	76
13	**24**	**32**	**9a** (5)	1 h	**80** + **83**	75:35	75
14	**25**	**32**	**8a** (5)	2 h	**84** + **85**	78:22	85
15	**25**	**32**	**8a** (5)	2 h	**84** + **85**	75:25	80

[a] The reactions were carried out in CH_2Cl_2 at room temperature unless stated otherwise. [b] The isomer ratios were determined by ^1H NMR spectra of the crude mixtures. [c] Isolated yield. [d] Carried out at −20 °C.

(29) Hayashi, T.; Yamamoto, A.; Hagihara, T. J. *J. Org. Chem.* **1986**, *51*, 723.

Scheme 12[a]



[a] For conditions and yields, see Table 6.

Table 6. Stereochemistry of Allylic Substitution

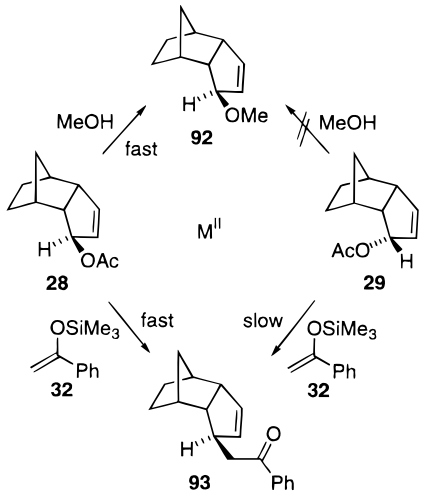
entry	allylic compd	nucleophile	catalyst (mol %)	time	products	product ratio[b]	yield (%)[c]
1	(*R*)-**23**	MeOH	**8a** (2)	4 h	(±)-**45**		65
2	(*R*)-**23**	**30**	**7a** (5)	2 h	(±) **76** + **77**	40:60	77
3	(*R*)-**23**	**30**	**8a** (2)	20 min	(±) **76** + **77**	42:58	95
4	**26**	MeOH	**7a** (5)	4 h	**88** + **89**	69:31	51
5	**26**	MeOH	**8a** (2)	4 h	**88** + **89**	55:45	25[d]
6	**26**	**32**	**8a** (2)	4 h	**90** + **91**	29:71	87
7	**27**	MeOH	**7a** (5)	2 h	**88** + **89**	19:81	46
8	**27**	MeOH	**8a** (2)	2 h	**88** + **89**	35:65	30[d]
9	**27**	**32**	**8a** (2)	30 min	**90** + **91**	22:78	99
10	**28**	MeOH	**8a** (2)	5 h	**92**		55
11	**29**	**32**	**8a** (2)	30 min	**93**		88
12	**29**	MeOH	**8a** (2)	24 h	no reaction		
13	**29**	**32**	**8a** (2)	14 h	**93**		88

[a] The reactions were carried out in CH_2Cl_2 at room temperature. [b] The isomer ratios were determined by ^1H NMR spectra of the crude mixtures. [c] Isolated yield. [d] The conversion was >90%, giving mainly elimination product.

less selective reaction.[3g,30] In contrast to the lack of regioselectivity in the case of **22** and **23**, cinnamyl acetate **24** gave ~4:1 to ~3:1 ratios of regioisomers **80** and **83** in the presence of catalysts **8a** and **9a**, respectively (Scheme 11; Table 5, entries 12 and 13). The nonaromatic analogue **25** produced a 3:1 mixture of **84** and **85** (Scheme 11; Table 5, entries 14 and 15).

Stereochemistry. The stereochemistry of the transition metal-catalyzed allylic substitution has recently been shown to be dependent on the metal used (Scheme 1).[11] It was therefore of interest to establish the stereochemistry of the present Mo(II)- and W(II)-catalyzed reactions. To this end, we first investigated the pair of epimeric acetates **26** and **27** (Scheme 12). With MeOH, the reaction catalyzed by **7a** turned out to proceed predominantly with retention of configuration, as documented by the ratios of the resulting methoxy derivatives **88** and **89** (Table 6, entries 4 and 7), but was substantially attended by competing elimination.[16] As expected, the axial epimer **27** reacted faster but gave a larger amount of the corresponding diene as byproduct. Complex **8a** exhibited essentially the same behavior though the isolated yields of the methoxy derivatives were even lower owing to the predominant elimination (Table 6, entries 5 and 8). By contrast, in the C−C bond-forming reaction with **32**, the axial ketone **91** was found to arise as the major product from both **26** and **27** (Table 6, entries 6 and 9), which is indicative of a common intermediate.

Scheme 13[a]



[a] For conditions and yields, see Table 6.

To further investigate the stereochemical course of these catalytic reactions, we employed another pair of epimeric allylic acetates, namely **28** and **29** (Scheme 13). Our previous experiments have demonstrated that *exo*-acetate **28** readily reacted with $LiCH(CO_2Me)_2$ in the presence of $Mo(CO)_6$, whereas its *endo*-epimer **29** was inert;[11] this behavior was used as an argument in favor of the *syn*,*syn*-mechanism of the Mo(0)-catalyzed allylic substitution (Scheme 1).[11] It is pertinent to note that the latter outcome is in sharp contrast to the reactivity of Pd(0), where *exo*-epimer **28** is inert (note that the required *anti*-approach by Pd is sterically hindered), while *endo*-acetate **29** readily forms the corresponding η^3-Pd complex.[4a,b,31] With **8a** as catalyst, *exo*-epimer **28** proved to react much faster: thus, with MeOH, **28** gave methoxy derivative **92** in 5 h (Table 6, entry 10), whereas **29** was practically inert (Table 6, entry 12). With **32** as nucleophile, *exo*-acetate **28** produced *exo*-ketone **93** in 30 min (Table 6, entry 11), while its *endo*-counterpart **29** required 14 h (Table 6, entry 13). Hence, M(II) catalysts seemed to follow the pattern previously observed[11] for Mo(0) catalysts.[32]

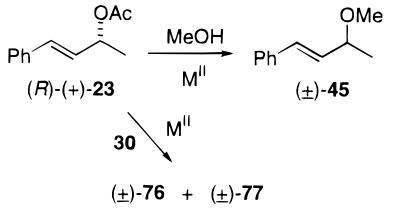
To eliminate any conformational effects associated with the nature of the six-membered ring (i.e., the axial/equatorial relationship) and the general steric effects, which attend the use of steroid derivatives **26** and **27** and tricyclic acetates **28** and **29**, the reactivity of O- and C-nucleophiles was further investigated with the aid of

(30) (a) Åkermark, B.; Hansson, S.; Krakenberger, B.; Vitagliano, A.; Zetterberg, K. *Organometallics* **1984**, *3*, 679. (b) Åkermark, B.; Krakenberger, B.; Hansson, S.; Vitagliano, A. *Organometallics* **1987**, *6*, 620.

(31) Fiaud, J.-C.; Legros, J.-Y. *J. Org. Chem.* **1987**, *52*, 1907.

(32) Whereas partial epimerization of the starting allylic substrate has occasionally been observed for Pd(0)-catalyzed reactions,[4a,e] this is not the case with our Mo(II) catalysts, as revealed by analysis of the reaction mixtures at ~50% conversion of **26** and **27** with MeOH and with **32**. Hence, our results are not distorted by isomerization prior to the substitution reaction.

Scheme 14

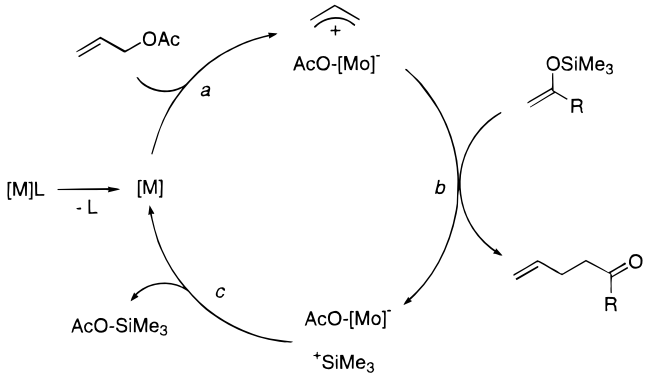


the enantiomerically pure allylic acetate (*R*)-(+)-**23** (≥99% ee).[4b] In the reaction catalyzed by **8a** (Scheme 14), methanol was found to produce racemic methoxy derivative **45**[33] (Table 6, entry 1) and, similarly, C-nucleophile **30** gave a mixture of racemic regioisomers **76** and **77** (Table 6, entries 2 and 3).

Mechanistic Considerations. The stereochemical experiments with **26**−**29** have demonstrated that a common intermediate is involved for each epimeric pair. Note that the steroidal intermediate preferentially reacts via axial attack and that, for the tricyclic system, only the *exo*-attack is sterically feasible. The difference in the reaction rates of **28** vs **29** is merely indicative of an easier ionization of **28** (as compared to **29**), presumably due to the better alignment of the C−OAc σ^*-orbital with the π-system of the C=C bond. This behavior is inconsistent with the template-directed reaction pathway (Scheme 1) and suggests an ionic, S_N1-like mechanism, which is further supported by complete racemization of (*R*)-(+)-**23** with both C- and O-nucleophiles (Scheme 14). In this respect, the reactivity of catalysts **7**−**9** parallels that of $LiClO_4$ (at high concentrations),[34] $LiCo(B_9C_2H_{11})_2$ (lithium cobalt bis(dicarbollide)),[35] trityl perchlorate,[36] and other Lewis acids.[37]

In such an ionic mechanism, the corresponding catalytic cycle (Scheme 15) can be assumed to involve dissociation of [M]L to generate its coordinatively unsaturated, Lewis-acidic[38] form [M],[39] followed by ionization of the allylic substrate, generating allylic cation and AcO−[M]$^-$ (step a); the allylic species should then react with silyl enol ether to give the final product (step b). The Me_3Si group is likely to be trapped by the AcO^- released from the complex, thereby regenerating the

Scheme 15



catalyst [M] for another cycle (step c). This scheme can be applied to all complexes **7**−**9** as they can dissociate prior to the reaction by losing a TfO^-, CO, or MeCN ligand, respectively. For MeOH as the nucleophile, the intermediate complex AcO−[M]$^-$ would undergo protonolysis, releasing AcOH (instead of $AcOSiMe_3$) and [M].

The regioselectivity of the methanol attack (e.g., **22** or **23** → **45** and **16** → **43** in Scheme 6) apparently results from thermodynamic control since, for instance, PhCH(OMe)CH=CHMe (allylic isomer of **45**) can be converted into **45** in the presence of the catalyst. By contrast, the products of the reaction with C-nucleophiles cannot be equilibrated so that the outcome should reflect the preferential site of attack. With the substrates possessing a trisubstituted double bond, e.g., **16**, the attack exclusively occurs at the less substituted terminus of the allylic system (e.g., **16** + **32** → **50**; Table 3, entries 1−5). Cinnamyl acetate **24** also preferentially yields products of reaction at the less substituted carbon, i.e., **80** (Table 5, entries 12 and 13). On the other hand, its homologue **23**, which generates an allylic cation flanked by a Ph substituent on one terminus and a Me on the other, is attacked by C-nucleophiles on both termini to give ∼1:1 mixtures (of, e.g., **78** and **81** on reaction with **32**; Table 5, entries 6−10). Interesting is the case of the reaction of **16** with **40**, where the expected product **70** is accompanied by 9−14% of its allylic isomer (Table 4, entries 1−3). Formation of a new C−C bond between two quaternary centers (a sterically most disfavored process) in the latter instance suggests participation of a competing single electron transfer (SET) mechanism.[40] According to this scenario, the electron-rich silyl enol ether **40** would transfer an electron (presumably via the metal catalyst), generating an allylic radical, whose subsequent reaction with the radical cation arising from **40** would afford the allylic byproduct.

Conclusions

Powerful, Lewis-acidic Mo(II) and W(II) catalysts **7**−**9** have been developed to promote C−C bond-forming allylic substitution under very mild conditions (typically, at ambient temperature over 1−2 h). Allylic acetates **16**−**29** have been found to react with a range of trimethylsilyl enol ethers, such as those derived from β-dicarbonyls (**30** and **31**), ketones (**32**−**37**), aldehyde (**38**), and esters (**39**,

(33) Initial experiments actually suggested retention of configuration since (*R*)-(+)-**23** produced (*R*)-(+)-**45** of ≥95% ee, as revealed by comparing the optical rotation of the latter product ($[\alpha]_D$ +36.5) with that of the compound obtained via methylation (Me_2SO_4, K_2CO_3, Me_2CO, room temperature, 6 h) of the enantiomerically pure[4b] (*R*)-(+)-4-phenyl-but-3-en-2-ol ($[\alpha]_D$ +36.9; ≥99% ee). However, this result could not be reproduced later. Painstaking analysis revealed that one batch of the starting ennatiomerically pure alcohol, used for the preparation of acetate (*R*)-(+)-**23**, was contaminated by ca. 5% of diisopropyl tartrate, originating from the Sharpless epoxidation (in kinetic resolution mode). Apparently, the tartrate, still present in the Mo(II)-catalyzed reaction, was the source of this error.

(34) (a) Pearson, W. H.; Schkeryantz, J. M. *J. Org. Chem.* **1992**, *57*, 2986. (b) Grieco, P. A.; Collins, J. L.; Henry, K. J., Jr. *Tetrahedron Lett.* **1992**, *33*, 4735. (c) Henry, K. J.; Grieco, P. A. *J. Chem. Soc., Chem. Commun.* **1993**, 510. (d) Smith, C. C.; Rothhaar, R. R.; Thobe, K. J.; Crago, C. M.; Pekelnicky, P. *Microchem. J.* **1997**, *56*, 65.

(35) Grieco, P. A.; DuBay, W. J.; Todd, L. J. *Tetrahedron Lett.* **1996**, *37*, 8707.

(36) Mukaiyama, T.; Nagaoka, H.; Oshima, M.; Murakami, M. *Chem. Lett.* **1986**, 1009.

(37) Yokozawa, T.; Furuhashi, K.; Natsume, H. *Tetrahedron Lett.* **1995**, *36*, 5243.

(38) For other examples of Lewis-acidic transition metal complexes, see, e.g.: Hollis, K.; Odenkirk, W.; Robinson, N. P.; Whelan, J.; Bosnich, B. *Tetrahedron* **1993**, *49*, 5415.

(39) Related Mo(II) and W(II) complexes $[M(NO)_2(MeCN)_4](BF_4)_2$ have also been shown to be Lewis-acidic and, as such, to polymerize and/or rearrange olefins: Sen, A.; Thomas, R. R. *Organometallics* **1982**, *1*, 1251.

(40) For a recent, detailed discussion of the competing ionic and SET mechanism in the Mukaiyama−Michael reaction, and its dependence on the Lewis acid employed and the steric bulk of the reaction partners, see: Otera, J.; Fujita, Y.; Sakuta, N.; Fujita, M.; Fukuzumi, S. *J. Org. Chem.* **1996**, *61*, 2951.

40); the amide-derived nucleophiles (**41**, **42**) and the Li and Na enolates proved inert. Methanol, as a prototype oxygen nucleophile, reacts in a fashion similar to give the corresponding methoxy derivatives. Both these C−C and C−O bond-forming reactions are believed to occur as Lewis acid-catalyzed (rather than metal template-directed[41,42]) processes, which can be stereoselective if carried out with stereochemically biased allylic substrates (e.g., **25**−**29**); on the other hand, racemization was observed with (*R*)-(+)-**23**. The catalytic cycle is summarized in Scheme 15. In the case of sterically hindered silyl enol ethers as nucleophiles, participation of a single electron-transfer pathway has been proposed as a competing process. Since these experiments reveal the Lewis acidic character of **7**−**9**, application of these complexes in the reactions prone to Lewis acid catalysis can be envisaged. To date, preliminary experiements, carried out in this laboratory in the areas of Diels−Alder and ene reactions, Michael addition, and aromatic electrophilic substitution, are particularly promising and will be reported in due course.[43]

Experimental Section

General Methods. The NMR spectra were recorded in $CDCl_3$, ^1H at 250 MHz and ^{13}C at 62.9 MHz with chloroform-d_1 (δ 7.26, ^1H; δ 77.0, ^{13}C) as internal standard; "a" and "b" are used to distinguish between the two diastereotopic protons. Various 2D-techniques and DEPT experiments were used to establish the structures 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 and/or CI) were measured on a dual sector mass spectrometer using direct inlet and the lowest temperature enabling evaporation. The GC-MS analysis was performed with RSL-150 column (25 m × 0.25 mm). All reactions were performed under an atmosphere of dry, oxygen-free nitrogen in oven-dried glassware twice evacuated and filled with the nitrogen. Solvents and solutions were transferred by syringe−septum and cannula techniques. All solvents for the reactions were of reagent grade and were dried and distilled immediately before use as follows: diethyl ether from lithium aluminum hydride; tetrahydrofuran (THF) from sodium/benzophenone; dichloromethane from calcium hydride. Standard workup of an ethereal solution means washing 3 × with 5% HCl (aqueous), water, and 3× with 5% $KHCO_3$ (aqueous) and drying with $MgSO_4$. Petroleum ether refers to the fraction boiling in the range 40−60 °C. The Mo and W complexes **7a**,**b** and **11a**,**b** were prepared as described in our earlier paper.[19] The allylic acetates **16**−**29** are known compounds[44] and were either prepared by acetylation of the corresponding allylic alcohols (Ac_2O, Et_3N, Et_2O, and 4-(dimethylamino)pyridine as catalyst) or purchased (**24**, **26**); the required allylic alcohols were either purchased or obtained by reduction of the corresponding ketones or, as in the case of **22** and **25**, by reaction of crotonaldehyde with the corresponding Grignard reagent. The enantiomerically pure alcohol (*R*)-(+)-4-phenylbut-3-en-2-ol,[4b] required for the synthesis of (*R*)-(+)-**23**, was obtained from the racemate by Sharpless epoxidation in kinetic resolution mode and had $[\alpha]_D$ +24.5 (*c* 2.5, $CHCl_3$). Since this sample was of ≥99% ee, as revealed by the ^1H NMR spectrum recorded in the presence of $Eu(tfc)_3$[4b] and by chromatography on Chiralcel OD-H with a 9:1 hexane−2-propanol mixture (retention times for the racemate: t_R = 15.2 min, t_S = 21.4 min; flow rate 0.5 mL/min), we conclude that the latter optical rotation represents the maximum, which is in agreement with an early report;[45a] another value, reported in the literature,[45b] namely $[\alpha]_D$ +34.9 (*c* 5.78, $CHCl_3$), seems to be too high. The silyl enol

(41) For the Mo- and W-template-controlled allylic substitution, see refs 8−13. For the formation of a stable π-allyl complex on reaction of allyl chloride with **11a**,**b**, see: Hull, C. G.; Stiddard, M. H. B. *J. Organomet. Chem.* **1967**, *9*, 519.

(42) For related Fe-template-controlled reactions, see, e.g.: (a) Xu, Y.; Zhou, B. *J. Org. Chem.* **1987**, *52*, 974. (b) Zhou, B.; Xu, Y. *J. Org. Chem.* **1988**, *53*, 4419. (d) Li, Z.; Nicholas, K. M. *J. Organomet. Chem.* **1991**, *402*, 105. (c) Green, J.; Carrol, M. K. *Tetrahedron Lett.* **1991**, *32*, 1141. (d) Johannsen, M.; Jörgensen, K.-A. *J. Org. Chem.* **1994**, *59*, 214. (e) Enders, D.; Jandeleit, B.; Raabe, G. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 1949.

(43) For catalytic activity of **8** in the Friedel−Crafts-type allylation of electron rich aromatics, and in the carbonyl ene-type cyclizations, see: (a) Malkov, A. V.; Davis, S. L.; Baxendale, I. B.; Mitchell, W. L.; Kočovský, P. *J. Org. Chem.* **1999**, *64*, 2751−2764. (b) Kočovský, P.; Ahmed, G.; Šrogl, J.; Malkov, A. V.; Steele, J. *J. Org. Chem.* **1999**, *64*, 2765−2775.

(44) Allylic acetates references, as follows: **16**: (a) Lessard, J.; Tan, P. V. M.; Martino, R.; Sanders, J. K. *Can. J. Chem.* **1977**, *55*, 1015. **17**: (b) Ishida, T.; Asakawa, Y.; Okano, M.; Aratani, T. *Tetrahedron Lett.* **1977**, *18*, 2437. **18**: (c) Mandrou, A.-M.; Potin, P.; Wylde-Lanchazette, R. *Bull. Chim. Soc. France* **1962**, 1546. **19**: ref 44a. **20**: (d) Masatoshi, A. *Bull. Chem. Soc. Jpn.* **1990**, *63*, 721. (e) Shono, T.; Ikeda, A.; *J. Am. Chem. Soc.* **1972**, *94*, 7892. **21**: (f) Hansson, S.; Heumann, A.; Rein, T.; Åkermark, B. *J. Org. Chem.* **1990**, *55*, 975. **22** and **23**: (g) Goering, H. L.; Seits, E. P., Jr.; Tseng, C.-C. *J. Org. Chem.* **1981**, *46*, 5304. **25**: (h) Grummitt, O.; Splitter, J. *J. Am. Chem. Soc.* **1952**, *74*, 3924. **27**: (i) Shopee, C. W.; Agashe, B. D.; Summers, G. H. R. *J. Chem. Soc.* **1957**, 3107. **28** and **29**: ref 31.

(45) (a) Kenyon, J.; Partridge, S. M.; Philips, H. *J. Chem. Soc.* **1936**, 85. (b) Goering, H. L.; Kantner, S. S.; Tseng, C. C. *J. Org. Chem.* **1983**, *48*, 715.

(46) General references for the silyl enol ether formation (including **32**, **35**, **39**, and **40**) include ref 21a and the following: (a) Rathke, M. W.; Sullivan, D. F. *Synth. Commun.* **1973**, *3*, 67. **33**: (b) Hnach, M.; Aycard, J. P.; Zineddine, H. *Bull. Soc. Chim. Fr.* **1991**, *3*, 393. **34**: (c) Hans Reich, J.; Carl, A.; Willis, W. W. *Tetrahedron* **1985**, *41*, 4771. (d) Tirpak, R. E.; Rathke, M. W. *J. Org. Chem.* **1987**, *52*, 1907. **41**: (e) Woodbury, R. P.; Rathke, M. W. *J. Org. Chem.* **1978**, *43*, 881. **42**: (f) McDaniel, R. S.; Peace, B. W.; Wulfman, D. S. *Tetrahedron* **1976**, *32*, 1241, 1251, and 1257. For the *E*/*Z* geometry, see: (g) Ireland, R. E.; Mueller, R. H.; Willard, A. K. *J. Am. Chem. Soc.* **1976**, *98*, 2868. (h) Evans, D. A. Stereoselective Alkylation Reactions of Chiral Metal Enolates. In *Asymmetric Synthesis*; Morrison, J. D., Ed.; Academic: New York, 1984; Vol. 3, p 1.

(47) Methoxy derivatives references are as follows. **43**: ref 26 and (a) House, H. O.; Kniloch, E. F. *J. Org. Chem.* **1974**, *39*, 1173. (b) Hutchins, R. O.; Kanasamy, D. *J. Org. Chem.* **1975**, *40*, 2530. (c) Grandi, R.; Marchesini, A.; Pagnoni, U. M.; Trave, R. *J. Org. Chem.* **1976**, *41*, 1755. **44**: ref 26 and (d) Zon, G.; Paquette, L. A. *J. Am. Chem. Soc.* **1984**, *96*, 215. (e) Zon, G.; Paquette, L. A. *J. Am. Chem. Soc.* **1974**, *96*, 215. (f) Chow, H.-F.; Fleming, I. *J. Chem. Soc., Perkin Trans. 1* **1984**, 1815. (g) Crabtree, R. H.; Davis, M. W. *J. Org. Chem.* **1986**, *51*, 2655. **45**: (h) Baldry, P. J. *J. Chem. Soc., Perkin Trans. 2*. **1980**, 809. **88** and **89**: ref 44i and (i) Henbest, H. B.; Eilson, R. A. L. *J. Chem. Soc.* **1957**, 1958. (j) Pusset, J.; Beugelmans, R. *Tetrahedron* **1976**, *32*, 797. **92**: ref 26a and (k) Wu, C.; Bartlett, P. D. *J. Org. Chem.* **1985**, *50*, 733.

(48) References for products of the C−C bond formation are the following. **47**: ref 46f. **49**: (a) Laidig, G. J.; Hegedus, L. S. *Synthesis* **1995**, 527. (b) Schaefer, J.; Al Azraka, H. *Chem. Ber.* **1972**, *105*, 2398. **52**: (c) Zhdankin, V. V.; Tykwinski, R.; Caple, R. *Tetrahedron. Lett.* **1988**, *29*, 3703. (d) Zhdankin V. V.; Tykwinski, R.; Caple, R.; Mullilin, M.; Berglund, B. *J. Org. Chem.* **1989**, *54*, 2605. (e) Snowden, R. L., Schulte-Elte, K.-H. *Helv. Chim. Acta* **1981**, *64*, 2193. **58**: (f) Morton, G. O.; Van Lear, G. E.; Fulmor, W. *J. Am. Chem. Soc.* **1972**, *92*, 5852. (g) Morton, G. O.; Van Lear, G. E.; Fulmor, W. *J. Am. Chem. Soc.* **1970**, *92*, 2590. (h) Padwa, A.; Eisenberg, W. *J. Am. Chem. Soc.* **1972**, *94*, 2590 and 5852. **59**: (i) Cagniant, Buu-Hoi; *C. R. Hebd. Seances Acad. Sci.* **1943**, *217*, 26. **64**: (j) Burgstahler, A. W.; Nordin, I. C. *J. Am. Chem. Soc.* **1961,** *83*, 198. (k) Grieco, P. A.; Clark, J. D.; Jagoe, C. T. *J. Am. Chem. Soc.* **1991**, *113*, 5488 and references therein. **66**: refs 48d,e. **67**: ref 48f. **72**: (l) Barabarich, T. J.; Handy, S. T.; Miller, S. M.; Anderson, O. P.; Grieco, P. A.; Strauss, S. H.; *Organometallics* **1996**, *15*, 3776. (m) Grieco, P. A.; DuBay, W. J.; Todd, L. J.; *Tetrahedron Lett.* **1996**, *37*, 8707. **73**: ref 48l. **74**: (n) Beereboom, J. J. *J. Org. Chem.* **1965**, *30*, 4230. (o) Erman, W. F.; Wenkert, E.; Jeffs, P. W. *J. Org. Chem.* **1969**, *34*, 2196. (p) Stevens, R. V.; Fitzpatrick, J. M.; Germeraad, P. B.; Harrison, B. L.; Lapalme, R. *J. Am. Chem. Soc* **1976**, *98*, 6313. **75**: (q) Patel, S. K.; Paterson, I. *Tetrahedron Lett.* **1983**, *24*, 1315. (r) Stevens, R. V.; Fitzpatrick, J. M.; Germeraad, P. B.; Harrison, B. L.; Lapalme, R. *J. Am. Chem. Soc.* **1976**, *98*, 8, 6313. **76** and **77**: (s) Hayashi, T.; Yamamoto, A.; Hagihara, T. *J. Org. Chem.* **1986**, *51*, 723. **78**: ref 36. **80**: (t) Itoh, I.; Hamaguchi, N.; Miura, M.; Nomura, M.; *J. Chem. Soc., Chem. Perkin Trans. 1* **1992**, 2833. (u) Ishikawa, N.; Tokuda, M.; Miyamoto, T.; Fujita, H.; Suginome, H. *Tetrahedron* **1991**, *47*, 747. (v) Mukaiyama, T.; Suzuki, K.; Yamada, T.; Tabusa, F. *Tetrahedron* **1990**, *46*, 265. (w) Kubota, T.; Miyashita, S.; Kitazume, T. *J. Org. Chem.* **1980**, *45*, 5052. **81**: ref 48r. **83**: (x) Takeda, T.; Torii, K.; Ogura, H. *Tetrahedron Lett.* **1990**, *31*, 265. **87**: ref 36.

ether reagents **31** and **36**−**38** were purchased from commercial suppliers and used without further purification; others were prepared from the corresponding ketone by means of LDA deprotonation (THF, −78 °C) followed by quenching with Me_3SiCl;[46] for details, see the Supporting Information. Some of the products, resulting from the allylic substitution, are known compounds.[36,47,48] Yields are given for isolated product showing one spot on a TLC plate and no impurities detectable in the NMR spectrum. The identity of the products prepared by different methods was checked by comparison of their NMR, IR, and MS data and by the TLC behavior.

Dibromomolybdenum Tetracarbonyl Dimer (8a). A solution of bromine (1.36 g; 8.5 mmol) in dichloromethane (10 mL) was added to a suspension of the finely ground molybdenum hexacarbonyl (2.24 g; 8.5 mmol) in deoxygenated dichloromethane (60 mL) at −78 °C; the mixture gradually evolved carbon monoxide, and the solid dissolved. The solution was maintained at −78 °C for 1 h, and the solvent was then evaporated under reduced pressure at −78 °C to yield **8a** as an orange, crystalline solid (3.03 g; 97%). Pure product, obtained by recrystallization from MeCN which could be stored in a freezer under nitrogen for several months: IR (CH_2Cl_2) ν(C≡O) 2100 (s), 2020 (m), 1980 (m), 1960 (m) cm^{-1} in accordance with the literature.[20]

Dibromotungsten Tetracarbonyl Dimer (8b). A solution of bromine (1.36 g; 8.5 mmol) in dichloromethane (10 mL) was added to a stirred suspension of the finely ground tungsten hexacarbonyl (3.0 g; 8.5 mmol) in deoxygenated dichloromethane (60 mL) at −78 °C; the mixture gradually evolved carbon monoxide, and the solid dissolved. After 1 h at −78 °C, the solution was allowed to warm slowly with stirring to room temperature to give a dark orange solution, which was concentrated to ca. 5 mL by evaporating under reduced pressure at −78 °C to afford an orange/brown, crystalline precipitate. The resulting green supernatant liquid was removed via cannula, and the precipitate was washed with dry hexane (20 mL). The residue was dried in a vacuum to furnish **8b** (2.41 g; 62%), which could be stored in a freezer under nitrogen for several months: IR (CH_2Cl_2) ν(C≡O) 2100 (s), 2020 (m), 1975 (m), 1940 (w) cm^{-1} in accordance with the literature.[20] A more stable and active complex was obtained by adopting the procedure described for **8a** (namely evaporation at low temperature).

Bis(acetonitrile)tricarbonylchloro(trichlorostannyl)-molybdenum (9a). A nitrogen-purged mixture of molybdenum hexacarbonyl (4.0 g; 15.4 mmol) and dry degassed acetonitrile (120 mL) was heated under reflux for 24 h to give a yellow/light brown solution. The solution was cooled to room temperature, tin(IV) chloride (3.18 g; 15.4 mmol) was added, the mixture was stirred for 10 min, and the solvent was removed in a vacuum to give a dark red solid. The latter solid was redissolved in dry acetonitrile (30 mL) and filtered through a sintered glass filter, which removed a black tar residue and gave an orange-red filtrate. Removal of the solvent by evaporation under reduced pressure at <40 °C gave **9a** as a red/orange solid (6.39 g; 79%): IR (CH_2Cl_2) ν(C≡O) 2027 (s), 1990 (s), 1953 (m), 1915 (w), ν(C≡N) 2320 (w), 2285 (w) cm^{-1}; IR (Nujol) ν(C≡O) 2030 (m), 1955 (m), 1920 (br), ν(C≡N) 2310 (w), 2295 (w) cm^{-1} in accordance with the literature.[21]

General Procedure A for the Allylic Substitution Reactions Catalyzed by Complexes 7a,b. To a stirred solution of the allylic substrate (1 mmol) and the silyl enol ether (1.4 mmol) or methanol (2 mmol) in CH_2Cl_2 (10 mL) at room temperature was added $PhCH_2(Et)_3N^+[M(CO)_5Cl]^-$ (M = Mo or W; 0.05 mmol) in one portion, followed by a solution of AgOTf (0.15 mmol) in DME (2 mL). The mixture was stirred under nitrogen at room temperature for 4 h and then diluted with ether (20 mL), and the ethereal solution was washed successively with 5% aqueous $NaHCO_3$ and water and dried with $MgSO_4$. The solvent was evaporated under reduced pressure to give a crude product, which was purified by flash chromatography on a silica gel column. For details and the yields see below and Tables 1−6.

General Procedure A for the Allylic Substitution Reactions Catalyzed by Complexes 8a,b and 9a. Catalyst (5 mol %) was added to a solution of the allylic substrate (1 mmol) and the silyl enol ether (1.1−1.4 mmol) or methanol (2 mmol) in dichloromethane (10 mL). The mixture was stirred at room temperature or at −5 °C until the TLC analysis indicated disappearance of the starting material or until no further reaction was observed after 24 h. Aqueous saturated hydrogen carbonate (15 mL) was then added, and the mixture was stirred for 15 min, then extracted with ether (2 × 15 mL), and dried ($MgSO_4$). The solvent was evaporated and the crude brown residue was purified by flash chromatography on a column of silica gel. Alternatively, acetic acid (0.5 mL) was added to the reaction mixture and stirred for 10 min; the mixture was then diluted with ether and adsorbed on silica gel (1.5 g), followed by flash chromatography. For details and the yields see below and Tables 1−6.

1-Methoxy-3,5,5-trimethyl-2-cyclohexene (43): ^{1}H NMR δ 5.48 (1 H, br s, 2-H), 3.80 (1 H, m, 1-H), 3.36 (3 H, s, MeO), 1.69 (3 H, s, 3-Me), 0.99 (3 H, s, 5-Me), 0.89 (3 H, s, 5-Me), in accordance with the literature.[26,47a−c]

1-Methoxy-3-methyl-2-cyclohexene (44): ^{1}H NMR δ 5.54 (1 H, br s, 2-H), 3.72 (1 H, m, 1-H), 3.36 (3 H, s, MeO), 1.69 (3 H, s, 3-Me), in accordance with the literature.[26,47a−c]

(*E*)-3-Methoxy-1-phenyl-1-butene (45): ^{1}H NMR δ 7.15 (m, 5 H, arom), 6.35 (1 H, d, J = 15 Hz, PhC*H*═C), 5.92 (1 H, dd, J = 15.0 and 7.5 Hz, *H*C═CHPh), 3.72 (1 H, d, J = 3.8 Hz, C*H*OCH$_3$), 3.18 (3 H, s, OC*H*$_3$), 1.20 (3 H, d, J = 3.8 Hz, Me); ^{13}C NMR δ 136.5 (s), 131.3 (d), 131.2 (d), 128.1 (2 × d), 127.8 (d), 126.3 (2 × d), 77.9 (d), 55.9 (q), 21.3 (q); MS (EI) *m*/*z* (%) 162 (74, M$^{\bullet+}$), 147 (100), in accordance with the literature.[47h]

Dimethyl (3,5,5-Trimethyl-2-cyclohexen-1-yl)malonate (46): ^{1}H NMR δ 5.10 (1 H, s, 2-H), 3.69 (3 H, s, OMe), 3.67 (3 H, s, OMe), 3.13 (1 H, d, J = 9.4 Hz, C*H*(CO$_2$Me)$_2$), 2.87 (1 H, m, 1-H), 1.78 (1 H, m, 6-H$_a$), 1.57 (3 H, s, 3-Me), 1.50 (1 H, m, 6-H$_b$), 1.27 (2 H, m, CH$_2$), 0.88 (3 H, s, 5-Me), 0.81 (3 H, s, 5-Me); ^{13}C NMR δ 168.7 (s), 168.7 (s), 135.2 (s), 119.8 (d), 56.9 (d), 52.1 (2 × q), 43.8 (t), 39.4 (t), 34.4 (d), 31.6 (q), 29.7 (s), 24.9 (q), 23.7 (q); IR (neat) ν 1758, 1735; MS (EI) *m*/*z* (%) 254 (45, M$^{\bullet+}$), 179 (100).

Dimethyl (3-Methyl-2-cyclohexen-1-yl)malonate (47): ^{1}H NMR δ 5.15 (1 H, s, 2-H), 3.68 (3 H, s, OMe), 3.66 (3 H, s, OMe), 3.17 (1 H, d, J = 10.1 Hz, C*H*(CO$_2$Me)$_2$), 2.80 (1 H, m, 1-H), 1.82 (2 H, m, CH$_2$), 1.65 (3 H, m, CH$_2$ and 6-H$_a$), 1.57 (3 H, s, 3-Me), 1.46 (1 H, m, 6-H$_b$); ^{13}C NMR δ 168.7 (s), 168.7 (s), 136.6 (s), 121.3 (d), 56.9 (d), 52.1 (2 × q), 35.5 (d), 29.7 (t), 26.2 (t), 23.7 (q), 21.0 (t); IR (neat) ν 1735, 1709 cm^{-1}; MS (EI) *m*/*z* (%) 226 (3, M$^{\bullet+}$), 95 (100), in accordance with the literature.[46f]

Methyl 1-(3′-Methyl-2′-cyclohexen-1′-yl)-3-oxobutanoate (48). Obtained as a 1:1 mixture of diastereoisomers: ^{1}H NMR δ 4.98 and 4.90 (1 H, s, C═CH), 3.50 and 3.49 (6 H, 2 × s, OMe), 3.15 and 3.10 (1 H, s, C*H*CO$_2$Me), 2.68 (1 H, m, CHC═C), 2.12 and 2.11 (3 H, s, CH$_3$CO), 1.75 (2 H, m, CH$_2$), 1.45 (2 H, m, CH$_2$), 1.40 (3 H, s, 3′-Me), 1.33 (1 H, m, 6′-H$_a$), 0.96 (1 H, m, 6′-H$_b$); ^{13}C NMR δ 203.0 (s) and 202.8 (s), 168.3 (s) and 168.3 (s), 137.1 (s) and 136.8 (s), 121.4 and 121.0, 65.4 and 65.3, 52.1 (2×), 35.5 and 35.4, 29.7 and 29.7 (t), 29.6 and 29.5, 26.3 (t) and 26.2 (t), 23.8, 21.5 (t); IR (neat) ν 1730 cm^{-1}; MS (EI) *m*/*z* (%) 210 (4, M$^{\bullet+}$), 143 (100).

Dimethyl (2-Cyclohexen-1-yl)malonate (49): ^{1}H NMR δ 5.76 (1 H, ddd, J = 10.1, 5.7, 3.5 Hz, 3-H), 5.52 (1 H, br d, J = 10.1 Hz, 2-H), 3.73 (3 H, s, OMe), 3.72 (3 H, s, OMe), 3.28 (1 H, dd, J = 9.4, 2.5 Hz, C*H*(CO$_2$Me)$_2$), 2.90 (1 H, m, 1-H), 1.98 (2 H, m, 4-CH$_2$), 1.70 (2 H, m, CH$_2$), 1.30 (2 H, m, CH$_2$); ^{13}C NMR δ 168.6 (2 × s), 129.3 (d), 127.2 (d), 56.6 (d), 52.0 (2 × q), 35.2 (d), 26.4 (t), 24.7 (t), 20.7 (t); IR (neat) ν 1728 cm^{-1}; MS (EI) *m*/*z* (%) 212 (12, M$^{\bullet+}$), 152 (100, M$^+$ − HCO$_2$Me), in accordance with the literature.[48a,b]

2-(3′,5′,5′-Trimethyl-2′-cyclohexen-1′-yl)-1-oxo-1-phenylethane (50): ^{1}H NMR δ 7.89 (2 H, m, arom), 7.30−7.48 (3 H, m, arom), 5.13 (1 H, s, 2′-H), 2.66 (2 H, m, CH$_2$CO), 2.73 (1 H, m, 1′-H), 1.75 (1 H, br d, J = 16.9 Hz, 6′-H$_a$), 1.55 (3 H, s, 3′-Me), 1.45 (1 H, br d, J = 16.9 Hz, 6′-H$_b$), 0.90 (2 H, m, CH$_2$), 0.88 (3 H, s, 5′-Me), 0.80 (3 H, s, 5′-Me); ^{13}C NMR δ 199.8 (s), 137.4 (s), 133.7 (s), 132.9 (d), 128.5 (d), 128.1 (2 × d), 123.3 (2 × d), 45.2 (t), 44.1 (t), 42.6 (t), 31.8 (d), 30.4 (t), 30.0 (s), 25.3

(q), 23.9 (q); IR (neat) ν 1670 cm^{-1}; MS (EI) *m*/*z* (%) 242 (7, M$^{\bullet+}$), 105 (100).

2-(3′-Methyl-2′-cyclohexen-1′-yl)-1-oxo-1-phenylethane (51): ^{1}H NMR δ 7.96 (2 H, m, arom), 7.55−7.40 (3 H, m, arom), 5.30 (1 H, d, J = 2.5 Hz, 2′-H), 2.89 (2 H, d, J = 7.5 Hz, CH_2COPh), 2.83−2.70 (1 H, m, 1′-H), 1.76 (2 H, m, CH_2), 1.65 (3H, s, 3′-Me), 1.54 (2 H, m, CH_2), 1.16 (2 H, m, CH_2); ^{13}C NMR δ 199.5 (s), 137.1 (s), 134.8 (s), 132.7 (d), 128.7 (2 × d), 128.1 (2 × d), 124.7 (d), 44.9 (t), 31.7 (d), 29.8 (t), 28.7 (t), 23.7 (q), 21.3 (t); IR (neat) ν 1680 cm^{-1}; MS (EI) *m*/*z* (%) 214 (6, M$^{\bullet+}$), 77 (100).

2-(2′-Cyclohexen-1′-yl)-1-oxo-1-phenylethane (52): ^{1}H NMR δ 7.95 (2 H, m, arom), 7.58−7.40 (3 H, m, arom), 5.72 (1 H, m, J = 10.1, 3.5 Hz, 3′-H), 5.58 (1 H, dd, J = 10.1 and 1.9 Hz, 2′-H), 2.94 (2 H, m, CH_2CO), 2.81 (1 H, m, 1′-H), 1.99 (2 H, m, CH_2), 1.86 (1 H, m, 6′-H$_a$), 1.78−1.48 (2 H, m, CH_2), 1.30 (1 H, m, 6′-H$_b$); ^{13}C NMR 199.6 (s), 137.4 (s), 132.9 (d), 130.8 (d), 128.6 (2 × d), 128.1 (2 × d), 127.9 (d), 44.8 (t), 31.6 (d), 29.1 (t), 25.1 (t), 21.1 (t); IR (neat) ν 1676 cm^{-1}; MS (EI) *m*/*z* (%) 200 (28, M$^{\bullet+}$), 105 (100, PhCO), in accordance with the literature.[48c−e]

2-(3′-Methyl-2′-cyclohexen-1′-yl)-1-oxo-1-phenylpropane (53). Obtained as a 1.7:1 mixture of diastereoisomers: ^{1}H NMR (diastereoisomer A): δ 7.93 (2 H, m, arom), 7.48 (3 H, m, arom), 5.34 (1 H, s, 2′-H), 3.41 (1 H, m, CHCO), 2.63 (1 H, m, 1′-H), 1.95 (2 H, m, CH_2), 1.93 (1 H, m, 6′-H$_a$), 1.79 (3 H, s, 3′-Me), 1.63 (1 H, m, 6′-H$_b$), 1.48 (2 H, m, CH_2), 1.28 (3 H, d, J = 6.9 Hz, 2-Me); ^{1}H NMR (diastereoisomer B) δ 7.93 (2 H, m, arom), 7.48 (3 H, m, arom), 5.17 (1 H, s, 2′-H), 3.41 (1 H, m, CHCO), 2.63 (1 H, m, 1′-H), 1.95 (2 H, m, CH_2), 1.93 (1 H, m, 6′-H$_a$), 1.72 (3 H, s, 3′-Me) 1.61 (1 H, m, 6′-H$_b$), 1.48 (2 H, m, CH_2), 1.23 (3 H, d, J = 6.9 Hz, 2-Me); ^{13}C NMR δ 204.4 (s), 204.3 (s), 137.1 (s), 137.0 (s), 136.0 (s), 135.4 (s), 132.7 (2 × d), 128.5 (2 × d), 128.2 (d), 128.1 (d), 124.3 (d), 121.9 (d), 45.5, 44.9, 38.3, 38.2, 29.9 (2 × t), 27.6 (t), 24.8 (t), 24.0, 23.8 (q), 21.9 (2 × q), 13.9 (q), 13.5 (q); IR (neat) ν 1674 cm^{-1}; MS (EI) *m*/*z* (%) 228 (22, M$^{\bullet+}$), 95 (100).

2-Methyl-2-(3′,5′,5′-trimethyl-2′-cyclohexen-1′-yl)-1-oxo-1-phenylpropane (54): ^{1}H NMR δ 7.66 (2 H, m, arom), 7.40 (3 H, m, arom), 5.21 (1 H, m, 2′-H), 2.86 (1 H, m, 1′-H), 1.80 (1 H, br d, J = 17.3 Hz, 6′-H$_a$), 1.64 (3 H, s, 3′-Me), 1.52 (1 H, d, J = 17.3 Hz, 6′-H$_b$), 1.30 (3 H, s, 2-Me), 1.18 (3 H, s, 2-Me), 1.05 (2 H, m, CH_2), 0.93 (3 H, s, 5′-Me), 0.80 (3 H, s, 5′-Me); ^{13}C NMR δ 209.5 (s), 139.5 (s), 134.8 (s), 130.5 (d), 127.9 (2 × d), 127.5 (2 × d), 119.9 (d), 50.5 (s), 44.0 (t), 40.4 (d), 36.8 (t), 32.0 (q), 29.8 (s), 25.1 (q), 24.1 (q), 22.8 (q), 22.3 (q); IR (neat) ν 1670 cm^{-1}; MS (EI) *m*/*z* 270 (3, M$^{\bullet+}$), 123 (100).

2-Methyl-2-(3′-methyl-2′-cyclohexen-1′-yl)-1-oxo-1-phenylpropane (55): ^{1}H NMR δ 7.66 (2 H, d, J = 1.6 Hz, arom), 7.39 (3 H, m, arom), 5.20 (1 H, d, J = 1.0 Hz, 2′-H), 2.82 (1 H, m, 1′-H), 1.84 (2 H, m, CH_2), 1.75 (1 H, m, 6′-H$_a$), 1.64 (3 H, s, 3′-Me), 1.45 (1 H, m, 6′-H$_b$), 1.25 (3 H, s, 2-Me), 1.21 (3 H, s, 2-Me), 1.18 (2 H, m, CH_2); ^{13}C NMR δ 209.7 (s), 139.6 (s), 136.3 (s), 130.6 (d), 128.0 (2 × d), 127.6 (2 × d), 121.7 (d), 51.0 (s), 42.6 (d), 30.0 (t), 24.1 (q), 23.9 (t), 22.7 (t), 22.6 (q), 22.4 (q); IR (neat) ν 1726 cm^{-1}; MS (EI) *m*/*z* (%) 242 (11, M$^{\bullet+}$), 95 (100).

2-(3′,5′,5′-Trimethyl-2′-cyclohexen-1′-yl)-1-oxo-1-phenylpropane (56). Obtained as a 15:1 mixture of diastereoisomers: ^{1}H NMR (diastereoisomer A) δ 7.94 (2 H, m, arom), 7.48 (3 H, m, arom), 5.32 (1 H, s, 2′-H), 3.36 (1 H, m, CHCO), 2.58 (1 H, m, 1′-H), 1.79 (1 H, m, 6′-H$_a$), 1.63 (3 H, s, 3′-Me), 1.51 (1 H, m, 6′-H$_b$), 1.27 (2 H, m, CH_2), 1.17 (3 H, d, J = 6.9 Hz, 2-Me), 0.90 (3 H, s, 5′-Me), 0.82 (3 H, s, 5′-Me); ^{1}H NMR (diastereoisomer B) δ 7.94 (2 H, m, arom), 7.48 (3 H, m, arom), 5.11 (1 H, s, 2′-H), 3.36 (1 H, m, CHCO), 2.58 (1 H, m, 1′-H), 1.79 (1 H, m, 6′-H$_a$), 1.58 (3 H, s, 3′-Me), 1.51 (1 H, m, 6′-H$_b$), 1.27 (2 H, m, CH_2), 1.11 (3 H, d, J = 6.9 Hz, 2-Me), 0.94 (3 H, s, 5′-Me), 0.79 (3 H, s, 5′-Me); ^{13}C NMR δ 204.5 (s), 204.2 (s), 137.2 (s), 134.8 (s), 134.2 (s), 132.8, 128.6, 128.3, 128.2, 122.7, 120.2, 45.7 (s), 44.8 (t), 44.2 (t), 44.1 (s), 40.9 (t), 38.3 (t), 36.4, 32.1, 31.9, 30.0, 29.9, 25.2 (2×), 24.1 (q), 23.9, 13.8, 13.7; IR (neat) ν 1725 cm^{-1}; MS (EI) *m*/*z* (%) 256 (13, M$^{\bullet+}$), 105 (100).

2-(3′-Methyl-2′-cyclopenten-1′-yl)-1-oxo-1-phenylethane (57): ^{1}H NMR δ 7.94 (2 H, m, arom), 7.57−7.38 (3 H, m, arom), 5.30 (1 H, dq, J = 1.6, 1.6 Hz, 2′-H), 3.23 (1 H, m, 1′-H), 3.02 (1 H, dd, J = 16.4, 6.6 Hz, H$_a$ of CH_2CO), 2.91 (1 H, dd, J = 16.4, 7.9 Hz, H$_b$ of CH_2CO), 2.25 (2 H, m, CH_2), 2.22 (1 H, m, 5′-H$_a$), 1.79 (3 H, s, 3′-Me), 1.50 (1 H, m, 5′-H$_b$); ^{13}C NMR δ 199.7 (s), 140.8 (s), 137.1 (s), 132.6 (d), 128.1 (d), 127.9 (d), 127.8 (d), 44.9 (t), 41.5 (d), 36.0 (t), 31.0 (t), 16.4 (q); IR (neat) ν 1715 cm^{-1}; MS (EI) *m*/*z* (%) 200 (20, M$^{\bullet+}$), 80 (100).

2-(2′-Cyclopenten-1′-yl)-1-oxo-1-phenylethane (58): ^{1}H NMR δ 7.94 (2 H, m, arom), 7.49 (3 H, m, arom), 5.76 (2 H, m, HC═CH), 3.31 (1 H, m, 1′-H), 3.09 (1 H, dd, J = 16.4, 6.7 Hz, H$_a$ of CH_2CO), 2.97 (1 H, dd, J = 16.4, 7.9 Hz, H$_b$ of CH_2CO), 2.40 (2 H, m, CH_2), 2.21 (1 H, m, 5′-H$_a$), 1.45 (1 H, m, 5′-H$_b$); ^{13}C NMR δ 199.6 (s), 137.1 (s), 134.1 (d), 132.4 (d), 131.1 (d), 128.4 (d), 128.0 (d), 44.7 (t), 47.3 (d), 31.7 (t), 29.9 (t); IR (neat) ν 1682 cm^{-1}; MS (EI) *m*/*z* (%) 186 (16, M$^{\bullet+}$), 105 (100), in accordance with the literature.[48f−l]

2-(2′-Cyclopenten-1′-yl)-1-oxo-1-phenylpropane (59). Obtained as a 1:1 mixture of diastereoisomers: ^{1}H NMR δ 7.95 (4 H, m, arom), 7.69−7.40 (6 H, m, arom), 5.85−5.70 (3 H, m, HC═CH), 5.55 (1 H, m, CH═C), 3.43 and 3.42 (1 H, m, CHCH$_3$), 3.14 and 3.13 (1 H, m, 1′-H), 2.31 and 2.30 (2 H, m, 4′-CH_2), 2.02 (1 H, m, 5′-H$_a$ for diastereoisomer A), 1.97 (1 H, m, 5′-H$_b$ for diastereoisomer A), 1.60 (1 H, m, 5′-H$_a$ for diastereoisomer B), 1.45 (1 H, m, 5′-H$_b$ for diastereoisomer B), 1.19 and 1.15 (3 H, d, J = 7.2 Hz, CH_3CH); ^{13}C NMR δ 204.2 (s), 204.1 (s), 136.9 (2 × s), 133.0 (d), 132.7 (2 × d), 132.2 (d), 131.9 (d), 131.5 (d), 128.5 (2 × d), 128.2 (2 × d), 48.7 (d), 48.2 (d), 45.5 (d), 45.2 (d), 32.0 (2 × t), 28.6 (t), 26.4 (t), 15.2 (q), 14.7 (q); IR (neat) ν 1678 cm^{-1}; MS (EI) *m*/*z* (%) 200 (8, M$^{\bullet+}$), 105 (100).

2-(3′,5′,5′-Trimethyl-2′-cyclohexen-1′-yl)-1-cyclohexyl-1-oxoethane (60): ^{1}H NMR δ 5.01 (1 H, s, 2′-H), 2.52 (1 H, m, 1′-H), 2.23 (3 H, m, CH_2CO, 1-H-cyclo), 1.80−1.52 (6 H, m, 3 × CH_2), 1.51 (3 H, s, 3′-Me), 1.46−1.00 (8 H, m, 4 × CH_2), 0.83 (3 H, s, 5′-Me), 0.75 (3 H, s, 5′-Me); ^{13}C NMR δ 213.5 (s), 133.4 (s), 123.5 (d), 51.2 (d), 47.4 (t), 44.1 (t), 42.5 (t), 31.8 (d), 29.9 (s), 29.7, 27.9 (2 × t), 26.0 (t), 25.9 (2 × t), 25.7 (q), 25.3 (q); IR (neat) ν 1705 cm^{-1}; MS (EI) *m*/*z* (%) 248 (15, M$^{\bullet+}$), 165 (100).

1-(3′,5′,5′-Trimethyl-2′-cyclohexen-1′-yl)propan-2-one (61): ^{1}H NMR δ 5.15 (1 H, br s, 2′-H), 2.63 (1 H, m, 1′-H), 2.41 (1 H, m, H$_a$ of CH_2CO), 2.31 (1 H, m, H$_b$ of CH_2CO), 2.14 (3 H, d, J = 1.9 Hz, CH_3CO), 1.79 (1 H, br d, J = 17.3 Hz, 6′-H$_a$), 1.62 (3 H, s, 3′-Me), 1.54 (1 H, br d, J = 17.3 Hz, 6′-H$_b$), 1.41 (1 H, m, 4′-H$_a$), 0.94 (3 H, s, 5′-Me), 0.88 (3 H, s, 5′-Me), 0.87 (1 H, m, 4′-H$_b$); ^{13}C NMR δ 208.4 (s), 133.7 (s), 129.9 (d), 50.4 (t), 44.0 (t), 42.3 (t), 31.7 (q), 30.4 (q), 29.9 (d), 29.8 (s), 25.2 (q), 23.8 (q); IR (neat) ν 1712 cm^{-1}; MS (EI) *m*/*z* (%) 180 (22, M$^{\bullet+}$), 107 (100).

1-(3′,5′,5′-Trimethyl-2′-cyclohexen-1′-yl)-3,3-dimethylbutan-2-one (62): ^{1}H NMR δ 5.05 (1 H, s, 2′-H), 2.64 (1 H, m, 1′-H), 2.37 (2 H, d, J = 12.5 Hz, CH_2CO), 1.74 (1 H, m, 6′-H$_a$), 1.58 (3 H, s, 3′-Me), 1.51 (1 H, m, 6′-H$_b$), 1.35 (2 H, m, 4′-CH_2), 1.09 (9 H, s, *t*-Bu), 0.90 (3 H, s, 5′-Me), 0.85 (3 H, s, 5′-Me); ^{13}C NMR δ 214.8 (s), 133.2 (s), 123.6 (d), 44.1 (t), 43.9 (s), 43.1 (t), 42.3 (t), 31.8 (d), 29.8 (s), 29.4, 26.2 (3 × q), 25.2 (q), 23.8 (q); IR (neat) ν 1732 cm^{-1}; MS (EI) *m*/*z* (%) 222 (9, M$^{\bullet+}$), 165 (100).

2-(3′-Methyl-2′-cyclohexen-1′-yl)-1-cyclohexyl-1-oxoethane (63): ^{1}H NMR δ 5.17 (1 H, m, 2′-H), 2.59 (1 H, m, 1′-H), 2.38 (2 H, m, CH_2CO), 2.30 (1 H, m, 1-H-cyclo), 1.93−1.65 (10 H, m, 5 × CH_2), 1.65 (3 H, s, 3′-Me), 1.55 (1 H, m, 6′-H$_a$), 1.40 (4 H, m, 2 × CH_2), 1.08 (1 H, m, 6′-H$_b$); ^{13}C NMR δ 213.6 (s), 134.8 (s), 125.0 (d), 51.2 (d), 47.3 (t), 31.2 (d), 30.0 (t), 28.4 (t), 28.3 (t), 25.9 (t), 25.7 (t), 23.8 (q), 21.5 (t); IR (neat) ν 1703 cm^{-1}; MS (EI) *m*/*z* (%) 220 (28, M$^{\bullet+}$), 137 (100).

1-(3′-Methyl-2′-cyclohexenyl)propan-2-one (64): ^{1}H NMR δ 5.29 (1 H, br s, 2′-H), 2.59 (1 H, m, 1′-H), 2.38 (2 H, d, J = 6.6 Hz, CH_2CO), 2.13 (3 H, s, CH_3CO), 1.87 (2 H, m, CH_2), 1.71 (2 H, m, CH_2), 1.63 (3 H, s, 3′-Me), 1.52 (1 H, m, 6′-H$_a$), 1.12 (1 H, m, 6′-H$_b$); ^{13}C NMR δ 208.3 (s), 134.9 (s), 124.4 (d), 50.2 (t), 31.3 (d), 30.2 (q), 29.8 (t), 28.6 (t), 23.6 (q), 21.3 (t); IR (neat) ν 1709 cm^{-1}; MS (EI) *m*/*z* (%) 152 (17, M$^{\bullet+}$), 94 (100), in accordance with the literature.[48j,k]

1-(3′-Methyl-2′-cyclohexen-1′-yl)-3,3-dimethylbutan-2-one (65): ^{1}H NMR δ 5.18 (1 H, s, 2′-H), 2.63 (1 H, m, 1′-H),

2.49 (1 H, m, H_a of CH_2CO), 2.37 (1 H, m, H_b of CH_2CO), 1.87 (2 H, m, CH_2), 1.75 (2 H, m, CH_2), 1.69 (1 H, m, 6′-H_a), 1.57 (3 H, s, 3′-Me), 1.50 (1 H, m, 6′-H_b), 1.14 (9 H, s, *t*-Bu); ^{13}C NMR δ 215.2 (s), 134.6 (s), 125.2 (d), 44.0 (s), 43.0 (t), 30.9 (d), 30.0 (t), 28.7 (t), 24.8 (3 × q), 23.8, 21.5 (t); IR (neat) ν 1705 cm^{-1}; MS EI *m*/*z* (%) 194 (15, M$^{\bullet+}$), 123 (100).

1-(2′-Cyclohexen-1′-yl)-3,3-dimethylbutan-2-one (66): ^{1}H NMR δ 5.61 (1 H, ddd, J = 10.1, 5.7, 2.2 Hz, 3′-H), 5.41 (1 H, dd, J = 10.1, 2.2 Hz, 2′-H), 2.64 (1 H, m, 1′-H), 2.43 (1 H, dd, J = 20.8, 7.2 Hz, H_a of CH_2CO), 2.36 (1 H, dd, J = 20.8, 6.9 Hz, H_b of CH_2CO), 1.92 (2 H, m, 4′-CH_2), 1.77−1.43 (4 H, m, 2 × CH_2), 1.07 (9 H, s, *t*-Bu); ^{13}C NMR δ 214.5 (s), 131.0 (d), 127.4 (d), 44.0 (s), 42.7 (t), 30.6 (d), 28.9 (t), 26.1 (3 × q), 25.0 (t), 21.0 (t); IR (neat) ν 1701 cm^{-1}; MS (EI) *m*/*z* (%) 180 (9, M$^{\bullet+}$), 81 (100), in accordance with the literature.[48f,g]

2-(2′-Cyclopenten-1′-yl)-1-cyclohexyl-1-oxoethane (67): ^{1}H NMR δ 5.73 (1 H, m, J = 5.7, 2.2 Hz, C=CH), 5.62 (1 H, m, J = 5.7, 2.2, 1.9 Hz, C=CH), 3.10 (1 H, m, 1′-H), 2.53 (1 H, dd, J = 16.7, 7.3 Hz, H_a of CH_2CO), 2.47 (1 H, dd, J = 16.7, 8.3 Hz, H_b of CH_2CO), 2.32 (2 H, m, CH_2), 2.11 (1 H, m, CHCO cyclohexyl), 1.80−1.63 (6 H, m, CH_2), 1.30−1.10 (7 H, m, cyclohexyl); ^{13}C NMR δ 213.5 (s), 134.2 (d), 130.9 (d), 50.9 (d), 46.8 (t), 40.8 (d), 31.7 (t), 29.9 (t), 28.3 (2 × t), 25.8 (t), 25.6 (2 × t); IR (neat) ν 1701 cm^{-1}; MS (EI) *m*/*z* (%) 192 (13, M$^{\bullet+}$), 109 (100), in accordance with the literature.[48h]

2-Methyl-2-(3′,5′,5′-trimethyl-2′-cyclohexen-1′-yl)propan-1-al (68): ^{1}H NMR δ 9.50 (1 H, s, CHO), 5.17 (1 H, s, 2′-H), 2.37 (1 H, m, 1′-H), 1.79 (1 H, br d, J = 17.1 Hz, 5′-H_a), 1.64 (3 H, s, 3′-Me), 1.54 (1 H, d, J = 17.1 Hz, 5′-H_b), 1.26 (1 H, m, 4′-H_a), 1.08 (1 H, m, 4′-H_b), 1.01 (6 H, s, CMe_2), 0.96 (3 H, s, 5′-Me), 0.87 (3 H, s, 5′-Me); ^{13}C NMR δ 206.7 (d), 135.4 (s), 119.1 (d), 48.2 (s), 43.9 (t), 38.9 (d), 36.5 (t), 32.0 (q), 29.8 (s), 25.0 (q), 24.0 (q), 18.9 (q), 18.4 (q); IR (neat) ν 1724 cm^{-1}; MS (EI) *m*/*z* (%) 194 (20, M$^{\bullet+}$), 123 (100).

2-Methyl-2-(3′-methyl-2′-cyclohexenen-1′-yl)propan-1-al (69): ^{1}H NMR δ 9.50 (1 H, s, CHO), 5.18 (1 H, s, 2′-H), 2.32 (1 H, m, 1′-H), 1.86 (2 H, m, CH_2), 1.79 (1 H, m), 1.72 (1 H, m), 1.65 (3 H, s, 3′-Me), 1.49 (1 H, m), 1.15 (1 H, m), 1.01 (6 H, s, CMe_2); ^{13}C NMR δ 206.8 (d), 136.7 (s), 120.7 (d), 48.6 (s), 40.9 (d), 29.8 (t), 23.9 (q), 23.6 (t), 22.5 (t), 18.8 (q), 18.3 (q); IR (neat) ν 1724 cm^{-1}; MS (EI) *m*/*z* (%) 166 (10, M$^{\bullet+}$), 95 (100).

Methyl 2,2-dimethyl-2-(3′,5′,5′-trimethyl-2′-cyclohexen-1′-yl)acetate (70): ^{1}H NMR δ 5.10 (1 H, s, 2′-H), 3.66 (3 H, s, OMe), 2.45 (1 H, m, 1′-H), 1.72 (1 H, d, J = 17.3 Hz, 6′-H_a), 1.69 (3 H, s, 3′-Me), 1.42 (1 H, d, J = 17.3 Hz, 6′-H_b), 1.10 (2 H, m, CH_2), 1.07 (3 H, s, 2-Me), 1.05 (2 H, m, CH_2), 1.01 (3 H, s, 2-Me), 0.89 (3 H, s, 5′-Me), 0.79 (3 H, s, 5′-Me); ^{13}C NMR δ 178.6 (s), 134.7 (s), 120.1 (d), 51.6 (q), 45.1 (s), 44.0 (t), 41.1 (d), 36.7 (t), 32.2 (q), 29.9 (s), 25.2 (q), 24.1 (q), 21.8 (q), 21.7 (q); MS (EI) *m*/*z* (%) 224 (13, M$^{\bullet+}$), 123 (100).

Methyl 2-(3′-Methyl-2′-cyclohexen-1′-yl)propionate (71). Obtained as a 1:1 mixture of diastereoisomers: ^{1}H NMR δ 5.35 and 5.15 (1 H, s, 2′-H), 3.68 and 3.66 (3 H, s, OMe), 2.45 and 2.45 (1 H, m, 1′-H), 2.05 and 2.05 (1 H, m, CHCO), 1.89−1.71 (10 H, m, CH_2), 1.68 and 1.68 (1 H, m, 6′-H_a), 1.64 and 1.64 (3 H, s, 3′-Me), 1.55 and 1.55 (1 H, m, 6′-H_b), 1.16 and 1.11 (3 H, d, J = 9 Hz, C*H*$_3$CHCO); ^{13}C NMR δ 176.7 (s), 176.6 (s), 136.0 (s), 135.7 (s), 123.5 (d), 122.0 (d), 51.3 (2 × q), 44.5, 44.3, 38.4, 29.9 (t), 29.9 (t), 27.0 (t), 25.0 (q), 23.9 (2 × q), 21.9 (t), 21.7 (t), 13.7 (q), 13.6 (q); IR (neat) ν 1728 cm^{-1}; MS (EI) *m*/*z* (%) 182 (9, M$^{\bullet+}$), 95 (100).

Methyl 2,2-dimethyl-2-(3′-methyl-2′-cyclohexen-1′-yl)acetate (72): ^{1}H NMR δ 5.10 (1 H, br d, J = 1 Hz, 2′-H), 3.65 (3 H, s, OMe), 2.45 (1 H, m, 1′-H), 1.81 (2 H, m, CH_2), 1.75 (1 H, m, 6′-H_a), 1.63 (3 H, s, 3′-Me), 1.30 (2 H, m, CH_2), 1.14 (3 H, s, 2-Me), 1.05 (3 H, s, 2-Me); ^{13}C NMR δ 178.3 (s), 135.9 (s), 121.6 (d), 51.4 (q), 45.3 (s), 43.1 (d), 29.9 (t), 23.9 (q), 23.8 (t), 22.5 (t), 21.5 (2 × t); IR (neat) ν 1728 cm^{-1}; MS EI *m*/*z* (%) 196 (26, M$^{\bullet+}$), 95 (100), in accordance with the literature.[48l,m]

Methyl 2,2-dimethyl-2-(2′-cyclohexen-1′-yl)acetate (73): ^{1}H NMR δ 5.72 (1 H, br. m, J = 10.1 Hz, C=CH), 5.42 (1 H, br m, J = 10.1 Hz, C=CH), 3.62 (3 H, s, OMe), 2.45 (1 H, m, 1′-H), 1.91 (2 H, m, CH_2), 1.75 (1 H, m), 1.60 (1 H, m), 1.47 (1 H, m), 1.23 (1 H, m), 1.10 (3 H, s, 2-Me), 1.06 (3 H, s, 2-Me); ^{13}C NMR δ 178.3 (s), 129.0 (d), 127.6 (d), 51.5 (q), 45.2 (s), 43.0 (d), 25.3 (t), 24.2 (t), 23.0 (t), 22.3 (q), 22.2 (q); IR (neat) ν 1728 cm^{-1}; MS EI *m*/*z* (%) 182 (8, M$^{\bullet+}$), 102 (100), in accordance with the literature.[48l]

Methyl 2,2-dimethyl-2-(3′-methyl-2′-cyclopenten-1′-yl)-acetate (74): ^{1}H NMR δ 5.17 (1 H, m, J = 1.9, 1.6 Hz, 2′-H), 3.65 (3 H, s, OMe), 2.98 (1 H, m, 1′-H), 2.19 (2 H, br t, J = 6 Hz, 4′-CH_2), 1.88 (1 H, m, 5′-H_a), 1.72 (3 H, s, 3′-Me), 1.56 (1 H, m, 5′-H_b), 1.11 (3 H, s, 2-Me), 1.07 (3 H, s, 2-Me′); ^{13}C NMR δ 178.4 (s), 142.2 (s), 124.7 (d), 53.9, 51.5, 45.4 (s), 36.6 (t), 25.9 (t), 22.6 (q), 21.6 (q), 16.6 (q); IR (neat) ν 1712 cm^{-1}; MS (EI) *m*/*z* (%) 182 (6, M$^{\bullet+}$), 81 (100), in accordance with the literature.[48m−p]

Methyl 2,2-dimethyl-2-(2′-cyclopenten-1′-yl)acetate (75): ^{1}H NMR δ 5.76 (1 H, m, J = 5.7, 4.4, 2.5 Hz, 2′-H), 5.55 (1 H, m, J = 5.7, 2.2, 2.2 Hz, 3′-H), 3.62 (3 H, s, OMe), 2.99 (1 H, m, J = 2.5, 1.6 Hz, 1′-H), 2.24 (2 H, m, J = 2.5, 1 Hz, 4′-CH_2), 1.86 (1 H, m, J = 13.5, 8.5, 6.6 Hz, 5′-H_a), (1 H, m, J = 13.5, 8.5, 6.6 Hz, 5′-H_b), 1.09 (3 H, s, 2-Me), 1.05 (3 H, s, 2-Me); ^{13}C NMR δ 176.2 (s), 132.4 (d), 131.0 (d), 53.7, 51.5, 45.1 (s), 32.3 (t), 25.0 (t), 22.7 (q), 21.7 (q); IR (neat) ν 1718 cm^{-1}; MS (EI) *m*/*z* (%) 168 (2, M$^{\bullet+}$), 102 (100), in accordance with the literature.[48q,r]

(*E*)-Dimethyl (4-Phenyl-3-buten-2-yl)malonate (76). Obtained as a 1:1.3 mixture with **80**; the spectrum was measured for the mixture: ^{1}H NMR δ 7.03−7.22 (5 H, m, arom), 6.32 (1 H, d, J = 15.7 Hz, 4-H), 5.99 (1 H, dd, J = 15.8, 8.3 Hz, 3-H), 3.61 (3 H, s, OMe), 3.53 (3 H, s, OMe), 3.27 (1 H, d, J = 9.1 Hz, 2′-H), 2.99 (1 H, m, 2-H), 1.06 (3 H, d, J = 6.6 Hz, Me), in accordance with the literature.[48s]

(*E*)-Dimethyl (1-Phenyl-2-buten-1-yl)malonate (77). Obtained as a 1.3:1 mixture with **79**; the spectrum was measured for the mixture: ^{1}H NMR δ 7.03−7.22 (5 H, m, arom), 5.46 (2 H, m, 2-H, 3-H), 3.91 (1 H, dd, J = 11.0, 6.9 Hz, 1-H), 3.69 (1 H, d, J = 11.0 Hz, 2′-H), 3.60 (3 H, s, OMe), 3.34 (3 H, s, OMe), 1.50 (3 H, d, J = 4.7 Hz, Me), in accordance with the literature.[48s]

(*E*)-1,5-Diphenyl-3-methyl-1-oxo-4-pentene (78). Obtained as a mixture with **81**, which was separated on a Dynamax 60 Å column (C18, 250 × 41.4 mm i.d.) using a 40:60 H_2O−MeCN mixture, flow rate 50 mL min^{-1}, detection UV at 210 nm; **78** was the less polar fraction (t = 18.18 min): ^{1}H NMR δ 7.94 (2 H, m, ArCO), 7.56−7.38 (3 H, m, ArCO), 7.35−7.12 (5 H, m, Ar), 6.41 (1 H, d, J = 16 Hz, Ph*H*C=C), 6.22 (1 H, dd, J = 16, 6.3 Hz, PhHC=C*H*), 3.34−2.90 (3 H, m, C*H*Me and CH_2), 1.18 (3 H, d, J = 6.3 Hz, HC*Me*); ^{13}C NMR δ 199.0 (s), 137.4 (s), 137.2 (s), 134.8 (d), 132.9 (d), 128.5 (d), 128.4 (d), 128.1 (d), 128.0 (d), 127.0 (d), 126.1 (d), 45.4 (t), 33.0 (d), 20.1 (q); IR (neat) ν 1686 cm^{-1}; MS (EI) *m*/*z* (%) 250 (20, M$^{\bullet+}$), 105 (100), in accordance with the literature.[36]

(*E*)-2,3-Dimethyl-1,5-diphenyl-1-oxo-4-pentene (79). Obtained from **22** and **33** as a 1:1.4 mixture of regioisomers with **82**; each regioisomer was represented by a 1:1 mixture of diastereoisomers. All spectra were recorded for the mixture of all isomers: ^{1}H NMR (**79**; ∼1:1 mixture of diastereoisomers) δ 0.85 and 0.98 (3 H, 2 × d, J = 7.7 Hz, CH=CHCH*Me*), 1.10 and 1.13 (3 H, 2 × d, J = 7.7 Hz, COCH*Me*), 2.68 (1 H, m, MeC*H*CO), 3.33 and 3.47 (1 H, 2 × m, CH=CHC*H*Me), 6.04 (1 H, m, CH=C*H*CH), 6.27 and 6.29 (1 H, 2 × d, J = 16.0 and 15.7 Hz, PhC*H*=CH), 7.01−7.88 (10 H, m, arom); IR ν 1682 cm^{-1}; MS (EI) *m*/*z* (%) 264 (4, M$^{\bullet+}$), 105 (100).

1,5-Diphenyl-1-oxo-4-pentene (80): ^{1}H NMR δ 8.05 (2 H, m, arom), 7.65−7.17 (8 H, m, arom), 6.51 (1 H, d, J = 16.1 Hz, PhC*H*), 6.32 (1 H, dt, J = 16.1, 6.7 Hz, PhCH=C*H*), 3.17 (2 H, t, J = 7.3 Hz, $COCH_2$), 2.69 (2 H, dt, J = 7.3, 6.7 Hz, =CCH_2); ^{13}C NMR δ 199.2 (s), 137.3 (s), 136.8 (s), 132.9 (d), 130.7 (d), 129.0 (d), 128.4 (d), 127.9 (d), 127.6 (d), 126.9 (d), 125.9 (d), 38.1 (t), 27.4 (t); IR (neat) ν 1693, 1640 cm^{-1}; MS (EI) *m*/*z* (%) 236 (9, M$^{\bullet+}$), 105 (100), in accordance with the literature.[48t−v]

(*E*)-1,3-Diphenyl-1-oxo-4-hexene (81). Obtained as a mixture with **78**, which was separated by HPLC (see above); **81** was eluted as the more polar fraction (t = 20.84 min): ^{1}H NMR δ 7.91 (2 H, m, ArCO), 7.57−7.38 (3 H, m, ArCO), 7.32−7.13 (5 H, m, Ar), 5.65 (1 H, ddq, J = 15.4, 7.1, 1.3 Hz, *H*C=CHMe), 5.45 (1 H, ddq, J = 15.4, 6.2, 1 Hz, HC=C*H*Me), 4.06

(1 H, m, PhC*H*), 3.49 (1 H, dd, J = 16.4, 7.6 Hz, Ha of CH_2-CO), 3.31 (1 H, dd, J = 16.4, 6.6 Hz, Hb of CH_2CO), 1.62 (3 H, d, J = 6.2 Hz, =CH*Me*); ^{13}C NMR δ 198.5 (s), 144.1 (s), 137.3 (s), 133.6 (d), 132.9 (d), 128.5 (2 × d), 128.4 (d) 128.1 (2 × d), 127.6 (2 × d), 126.4 (d), 125.5 (d), 44.7 (t), 43.9 (d), 17.9 (q); IR (Nujol) ν 1683 cm^{-1}; MS (EI) m/z (%) 250 (11, M$^{\bullet+}$), 105 (100), in accordance with the literature.[48s]

(*E*)-2-Methyl-1,3-diphenyl-1-oxo-4-hexene (82). Obtained from **22** and **33** as a 1.4:1 mixture of regioisomers with **79**; each regioisomer was represented by a 1:1 mixture of diastereoisomers. The spectra were recorded for the mixture of all isomers: ^{1}H NMR (**82**; ~1:1 mixture of diastereoisomers) δ 1.34 and 1.57 (3 H, 2 × d, J = 6.1 Hz, CH=CH*Me*), 1.05 and 1.08 (3 H, 2 × d, J = 7.8 Hz, CH*Me*), 3.60 (1 H, m, C*H*CO), 3.77 (1 H, m, PhC*H*), 5.48 (2 H, m, C*H*=C*H*), 7.01−7.88 (10 H, m, 2 × Ph).

1,3-Diphenyl-1-oxo-4-pentene (83): ^{1}H NMR δ 7.82 (2 H, m, arom), 7.49−7.26 (3 H, m, arom), 7.22 (5 H, m, arom), 5.94 (1 H, ddd, J_{trans} = 17.0, J_{cis} = 10.4, 6.8 Hz, CH=CH), 4.96 (1 H, ddd, J_{cis} = 10.4, J_{gem} = 1.25, $J_{allylic}$ = 1.25 Hz, H_{cis}), 4.92 (1 H, ddd, J_{trans} = 17.0, J_{gem} = 1.25, $J_{allylic}$ = 1.25 Hz, H_{trans}), 4.03 (1 H, ddd, J = 6.9, 6.8, 1.25 Hz, $H_{allylic}$), 3.32 (1 H, dd, J = 16.5, 6.9 Hz, H_a of CH_2CO), 3.26 (1 H, dd, J = 16.5, 7.0 Hz, H_b of CH_2CO); ^{13}C NMR δ 198.2 (s), 143.1 (s), 139.6 (d), 137.1 (s), 132.9 (d), 128.5 (2 × d), 128.0 (d), 127.6 (d), 126.5 (d), 114.6 (t), 44.5 (d), 44.0 (t); IR (neat) ν 1692 cm^{-1}; MS (EI) m/z (%) 236 (37, M$^{\bullet+}$), 105 (100), in accordance with the literature.[48x]

(*E*)-1-Phenyl-3-methyl-5-cyclohexyl-1-oxopent-4-ene (84). Obtained as a mixture with **85**, which was separated on a Dynamax 60 Å column (C18, 250 × 41.4 mm i.d.) using an 85:15 MeCN−H_2O mixture, flow rate 50 mL min^{-1}, detection by UV at 230 nm. Analysis of the mixture was performed on a HP 1050 Dynamax 60 Å column (C18, 250 × 4.6 mm 8 m i.d.) using an 80:20 MeCN−H_2O mixture, flow rate 1 mL min^{-1} at 2.30 kpsi; **84** was the more polar fraction (t = 28.47): ^{1}H NMR δ 7.92 (2 H, m, Ar), 7.60−7.37 (3 H, m, Ar), 5.35 (2 H, m, CH=CH), 3.02−2.74 (3 H, m, 2-CH_2 and CH of cyclohexyl), 1.85 (1 H, m, 3-H), 1.75−1.55 (5 H, m, CH_2-cyclohexyl), 1.30−0.90 (8 H, m), 1.06 (3 H, d, J = 6.2 Hz, Me); ^{13}C NMR 199.8 (s), 137.5 (s), 135.2 (d), 132.8 (d), 131.9 (d), 128.5 (2 × d), 128.1 (2 × d), 46.0 (t), 40.5 (d), 33.2 (d), 33.1 (t), 26.2 (t), 26.0 (2 × t), 20.6 (q); MS (EI) m/z (%) 256 (8, M$^{\bullet+}$), 105 (100).

(*E*)-1-Phenyl-3-cyclohexyl-1-oxo-hex-4-ene (85). Obtained as a mixture with **84**, which was separated by preparative HPLC (vide supra); **85** was the less polar fraction (t = 23.89 min): ^{1}H NMR δ 7.98 (2 H, m, Ar), 7.40−6.62 (3 H, m, Ar), 5.30 (2 H, m, CH=CH), 2.99 (2 H, m, 2-CH_2), 2.55 (1 H, m, 3-H), 1.90−1.60 (4 H, m), 1.62 (3 H, d, J = 5.0 Hz, Me), 1.40−0.80 (6 H, m, CH_2 of cyclohexyl); ^{13}C NMR δ 200.4 (s), 137.6 (s), 132.6 (d), 132.2 (d), 128.4 (2 × d), 128.1 (2 × d), 126.0 (d), 44.6 (d), 42.0 (d), 41.6 (t), 31.0 (t), 29.7 (t), 26.5 (3 × t), 17.8 (q); MS (EI) m/z (%) 256 (7, M$^{\bullet+}$), 105 (100).

Methyl 2,2-Dimethyl-2-(4′-phenyl-3′-buten-2′-yl)acetate (86). Obtained as a mixture with **87**, which was separated 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}, detection UV at 210 nm; **86** was the more polar fraction (t = 33.92 min): ^{1}H NMR δ 7.38−7.13 (5 H, m, Ar), 6.39 (1 H, d, J = 15.7 Hz, Ph*H*C=), 6.08 (1 H, dd, J = 15.7, 8.8 Hz, PhHC=C*H*), 3.67 (3 H, s, OMe), 2.64 (1 H, dq, J = 8.8, 6.9 Hz, MeC*H*), 1.17 (3 H, s, 2-Me), 1.15 (3 H, s, 2-Me), 1.03 (3 H, d, J = 6.9 Hz, CH*Me*); ^{13}C NMR δ 177.9 (s), 140.9 (s), 137.5 (d), 131.6 (d), 130.9 (2 × d), 128.4 (d), 127.0 (2 × d), 126.1 (d), 51.5 (s), 45.9 (s), 44.7 (d), 23.2 (q), 21.1 (q), 15.7 (q); IR (neat) ν 1728 cm^{-1}; MS (EI) m/z (%) 232 (4, M$^{\bullet+}$), 131 (100).

Methyl 2,2-Dimethyl-2-(1′-phenyl-2′-buten-1′-yl)acetate (87). Obtained as a mixture with **86**, which was separated by HPLC (see above); **87** was eluted as the less polar fraction (t = 27.44 min): ^{1}H NMR δ 7.3−7.13 (5 H, m, Ar), 5.85 (1 H, ddq, J = 15.1, 9.8, 1.6 Hz, 2-H), 5.57 (1 H, ddq, J = 15.1, 6.5, 1 Hz, 3′-H), 3.60 (3 H, s, OMe), 3.54 (1 H, d, J = 9.8 Hz, 1′-H), 1.67 (3 H, dd, J = 6.5, 1.6 Hz, 3′-H), 1.15 (3 H, s, 2-Me), 1.09 (3 H, s, 2-Me); ^{13}C NMR δ 177.6 (s), 141.1 (s), 129.4 (d), 129.3 (2 × d), 129.1 (d), 128.2 (2 × d), 127.9 (d), 126.6 (d), 56.7 (d), 51.3 (q), 47.1 (s), 23.1 (q), 22.3 (q), 18.1 (q); IR (neat) ν 1730 cm^{-1}; MS (EI) m/z (%) 232 (1, M$^{\bullet+}$), 131 (100), in accordance with the literature.[36]

3*β*-Methoxy-4-cholestene (88): ^{1}H NMR δ 5.34 (1 H, d, J = 1.4 Hz, 4-H), 3.73 (1 H, br m, 3α-H), 3.37 (3 H, s, MeO), 1.04 (3 H, s, 19-H), 0.67 (3 H, s, 18-H), in accordance with the literature.[44i,47i,j]

3α-Methoxy-4-cholestene (89): ^{1}H NMR δ 5.46 (1 H, br d, J = 4.8 Hz, 4-H), 3.56 (1 H, m, 3β-H), 3.34 (3 H, s, MeO), 1.02 (3 H, s, 19-H), 0.67 (3 H, s, 18-H), in accordance with the literature.[44i,47i,j]

3*β*-(Benzoylmethyl)-4-cholestene (90). Obtained along with **91** as a 1:3.5 mixture of diastereoisomers: ^{1}H NMR δ (recorded for a mixture with **91**) 7.89 (2 H, d, J = 6.9 Hz, 2′-H, 6′-H), 7.46 (1 H, t, J = 7.2 Hz, 4′-H), 7.38 (2 H, t, J = 7.2 Hz, 3′-H, 5′-H), 5.08 (1 H, br s, 4-H), 2.82 (2 H, dd, J = 7.2, 2.8 Hz, $COCH_2$), 2.67 (1 H, m, 3α-H).

3α-(Benzoylmethyl)-4-cholestene (91). Obtained along with **90** as a 3.5:1 mixture of diastereoisomers: ^{1}H NMR δ (recorded for a mixture with **90**) 7.89 (2 H, d, J = 6.9 Hz, 2′-H, 6′-H), 7.46 (1 H, t, J = 7.2 Hz, 4′-H), 7.38 (2 H, t, J = 7.2 Hz, 3′-H, 5′-H), 5.20 (1 H, br d, J = 4.1 Hz, 4-H), 2.88 (2 H, dd, J = 7.1, 2.3 Hz, $COCH_2$), 2.67 (1 H, m, 3β-H), 0.94 (3 H, s, 19-H), 0.61 (3 H, s 18-H); IR (thin film) ν 1690 cm^{-1}; MS (EI) m/z (%) 488 (20, M$^{\bullet+}$), 105 (100).

1-Methoxy-3a,4,5,6,7,7a-hexahydro-(1α,3aα,4α,7α,7aα)-4,7-methano-1*H*-indene (92): ^{1}H NMR δ 5.89 (1 H, dd, J = 5.7, 1.9 Hz, 2-H), 5.77 (1 H, dt, J = 5.7, 2.0 Hz, 3-H), 4.23 (1 H, br s, 1-H), 3.23 (3 H, s, OMe), 3.05 (1 H, m, 3a−H), 2.26 (3 H, m, 4-H, 7-H, 7a−H), 1.04−1.46 (6 H, m, 3 × CH_2); ^{13}C NMR δ 140.5 (d), 130.7 (d), 86.8 (q), 55.8 (d), 52.5 (d), 50.7 (d), 42.0 (t), 40.4 (d), 39.5 (d), 25.2 (t), 23.7 (t), identical with the known compound.[26a,47k]

1-(Benzoylmethyl)-3a,4,5,6,7,7a-hexahydro-(1α,3aα,4α,7α,7aα)-4,7-methano-1*H*-indene (93). Colorless oil: ^{1}H NMR δ 7.94 (2 H, d, J = 7.1 Hz, 2′-H, 6′-H), 7.54 (1 H, t, J = 6.9 Hz, 4′-H), 7.44 (2 H, t, J = 6.9 Hz, 3′-H, 5′-H), 5.63 (2 H, m, C*H*=C*H*), 3.13 (1 H, m, 1-H), 3.07 (1 H, dd, J = 16.5, 5.8 Hz; COCH*H*), 3.01 (1 H, m, 3a-H), 2.89 (1 H, dd, J = 16.5, 8.3 Hz, COC*H*H), 2.28 (2 H, m, 4,7-H), 2.09 (1 H, dt, J = 10.1, 3.1 Hz, 7a−H), 1.25 (6 H, m, 3 × CH_2); ^{13}C NMR δ 199.8 (CO), 137.3 (1′-C), 134.0 (4′-CH), 133.9 and 132.9 (2,3-CH), 128.5 and 128.0 (2′,3′,5′,6′-CH), 52.1 and 50.7 (1,3a-CH), 45.9 ($COCH_2$), 41.0 (8-CH_2), 40.9 and 39.4 (4,7,7a-CH), 25.0 and 22.9 (5,6-CH_2); IR (thin film) ν 1674 cm^{-1}; MS (EI) m/z (%) 252 (13, M$^{\bullet+}$), 105 (100).

Acknowledgment. We thank the EPSRC for Grants No. GR/H92067 and GR/K07140 and EPSRC and AgrEvo UK Ltd. for a CASE award to I.R.B.

Supporting Information Available: Detailed experimental procedures, including the preparation of silyl enol ethers and their spectral characterization, IR, MS, and HRMS spectral characteristics, and elemental analyses, and ^{1}H and ^{13}C NMR spectra for the new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

JO9821776