Molybdenum(IV) Complexes as Efficient, Lewis Acidic Catalysts for Allylic Substitution. Formation of C−C and C−N Bonds

Andrei V. Malkov,† Paul Spoor,† Victoria Vinader,‡ and Pavel Kočovský*,†

Department of Chemistry, University of Leicester, Leicester LE1 7RH, U.K., and GlaxoWellcome, Research and Development, Medicines Research Centre, Stevenage, Herts. SG1 2NY, U.K.

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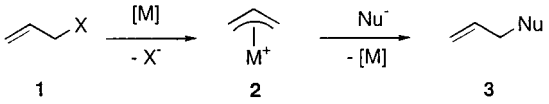
Introduction

In transition-metal-catalyzed allylic substitution (Scheme 1), allylic acetates and carbonates play a prime role as electrophilic substrates. Numerous studies and applications using Pd(0),[1] Mo(0),[2] and W(0)[3] complexes and a variety of reacting partners show how general this reaction is. Although the literature in this area is dominated by C−C bond-forming processes, examples of C−N, C−O, C−Cl, and C−S bond construction have also been reported.[1] In contrast to the wide use of allylic esters and related derivatives, direct application of the parent allylic alcohols in these reactions is rare.[4]

As part of a program aimed at designing new, more reactive molybdenum and tungsten complexes as replacement for the more expensive Pd(0) catalysts, we have recently shown that the Lewis-acidic Mo(II) complexes $Mo(CO)_5(OTf)_2$, $[Mo(CO)_4Br_2]_2$, and $Mo(CO)_3(MeCN)_2(SnCl_3)Cl$ and their W(II) counterparts are capable of catalyzing allylic substitution at ambient temperature. Using a series of allylic acetates, we have demonstrated efficient C−C bond-forming reactions not only with the usual malonate-type nucleophiles but also with silyl enol ethers and electron-rich aromatics and heteroaromatics.[5] Herein, we report on novel Mo(IV) complexes, which catalyze the C−C and C−N bond-forming allylic substitution of allylic alcohols (rather than acetates) with

Scheme 1

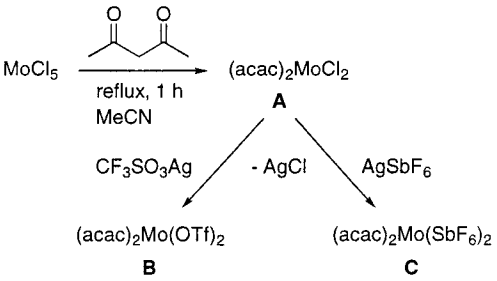


electron-rich aromatics and trimethylsilyl azide, respectively.

Results and Discussion

Preparation of Mo(IV) Catalysts. In a redox reaction with 2,4-pentanedione, molybdenum(V) chloride is known to produce the corresponding Mo(IV) bisacac complex **A** as a relatively stable solid (Scheme 2).[6,7] According to one original procedure,[6a] the reaction is simply carried out by heating $MoCl_5$ in 2,4-pentanedione so that the latter serves as a reagent, reducing agent, and solvent. An alternative procedure[6b] employs acetonitrile as the solvent and reducing agent; a mixture $MoCl_5$ and MeCN is first refluxed to reduce $MoCl_5$ to $MoCl_4$, followed by addition of 2,4-pentanedione. Of the two procedures, we found the latter to be more practicable as it exhibited better reproducibility and gave a cleaner product, which could be easily isolated as a precipitate. Of course, complex **A** can also be prepared directly[6a] from 2,4-pentanone and $MoCl_4$, which, however, is considerably more expensive than $MoCl_5$.

Scheme 2



While complex **A** proved to be practically inert under the conditions previously employed by us for Mo(II) complexes (vide supra), we envisaged that replacing its chlorides by weakly coordinating ligands, such as $CF_3SO_3^-$ or SbF_6^-, could provide a reactive catalyst.[8] Indeed, the two complexes **B** and **C**, generated in situ from **A** on reaction with stoichiometric amounts of TfOAg and

* To whom correspondence should be addressed. E-mail: PK10@Le.ac.uk.

† University of Leicester.

‡ GlaxoWellcome.

(1) For overviews of Pd(0)-catalyzed allylic substitution, see: (a) Trost, B. M. *Acc. Chem. Res.* **1980**, *13*, 385. (b) Tsuji, J. *Tetrahedron* **1986**, *42*, 4361. (c) Frost, C. G.; Howarth, J.; Williams, J. M. J. *Tetrahedron: Asymmetry* **1992**, *3*, 1089. (d) Trost, B. M.; Van Vranken, D. L. *Chem. Rev.* **1996**, *96*, 395. (e) Trost, B. M. *Acc. Chem. Res.* **1996**, *29*, 355. (f) Bäckvall, J.-E. *Acta Chem. Scand.* **1996**, *50*, 661. See also the reference section in: (g) Starý, I.; Zajíček, J.; Kočovský, P. *Tetrahedron* **1992**, *48*, 7229.

(2) Trost, B. M.; Lautens, M. *J. Am. Chem. Soc.* **1982**, *104*, 5543. (b) Trost, B. M.; Merlic, C. A. *J. Am. Chem. Soc.* **1990**, *112*, 9590. (c) Dvořák, D.; Starý, I.; Kočovský, P. *J. Am. Chem. Soc.* **1995**, *117*, 6130. (d) Trost, B. M.; Hachiya, I. *J. Am. Chem. Soc.* **1998**, *120*, 1104.

(3) (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.

(4) (a) Bergbreiter, D. E.; Weatherford, D. A. *J. Chem. Soc., Chem. Commun.* **1989**, 833. (b) Starý, I.; Stará, I. G.; Kočovský, P. *Tetrahedron* **1994**, *50*, 529. For a recent discussion of stoichiometric substitution of rhenium complexes of allylic alcohols, see: (c) Legoupy, S.; Crévisy, C.; Guillemin, J.-C.; Grée, R.; Toupet, L. *Chem.—Eur. J.* **1998**, *4*, 2162 and refs cited therein.

(5) (a) Dvořáková, H.; Dvořák, D.; Šrogl, J.; Kočovský, P. *Tetrahedron Lett.* **1995**, *36*, 6351. (b) Abbott, A. P.; Malkov, A. V.; Zimmermann, N.; Raynor, J. B.; Ahmed, G.; Steele, J.; Kočovský, P. *Organometallics* **1997**, *16*, 3690. (c) Malkov, A. V.; Baxendale, I. R.; Mansfield, D. J.; Kočovský, P. *Tetrahedron Lett.* **1997**, *38*, 4895. (d) Malkov, A. V.; Davis, S. L.; Mitchell, W. L.; Kočovský, P. *Tetrahedron Lett.* **1997**, *38*, 4899. (e) Malkov, A. V.; Baxendale, I. R.; Mansfield, D. J.; Kočovský, P. *J. Org. Chem.* **1999**, *64*, 2737. (f) Malkov, A. V.; Davis, S. L.; Baxendale, I. R.; Mitchell, W. L.; Kočovský, P. *J. Org. Chem.* **1999**, *64*, 2751. (g) Kočovský, P.; Ahmed, G.; Šrogl, J.; Malkov, A. V.; Steele, J. *J. Org. Chem.* **1999**, *64*, 2765.

(6) (a) Doyle, G. *Inorg. Chem.* **1971**, *10*, 2348. (b) van den Bergen, A.; Murray, K. S.; West, B. O. *Aust. J. Chem.* **1972**, *25*, 705.

(7) This redox reaction is not unusual. Thus, for instance, $(acac)_2VO$ is prepared from V_2O_5 in a similar manner: Rowe, R. A.; Jones, M. M. *Inorg. Chem.* **1966**, *5*, 114.

(8) For weakly coordinating ligands, see, e.g.: (a) Van Seggen, D. M.; Hurlburt, P. K.; Anderson, O. P.; Strauss, S. H. *Inorg. Chem.* **1995**, *34*, 3453 and refs cited therein. (b) Marks, T. J. *Acc. Chem. Res.* **1992**, *25*, 57. (c) Strauss, S. H. *Chem. Rev.* **1993**, *93*, 927.

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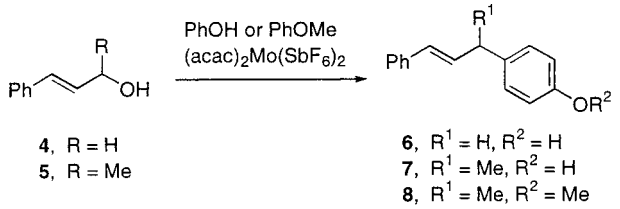
Scheme 3

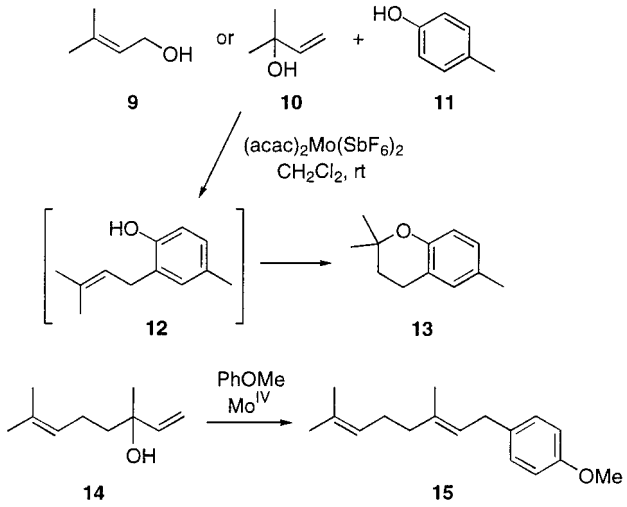


$AgSbF_6$, respectively, proved to react with allylic acetates though the main products corresponded to elimination.[9] Therefore, we focused on allylic alcohols as substrates.

Carbon Nucleophiles. Initially, no reaction was observed between cinnamyl alcohol **4** and the silyl enol ether derived from acetophenone in the presence of either **B** or **C**. In this case, the failure was mainly due to the preferential decomposition of the silyl enol ether to the parent ketone, which is faster than the desired reaction.[10] By contrast, the reaction of **4** with phenol occurred at room temperature (with 2 mol % of **C**), affording *p*-cinnamyl phenol (**6**; 58%) as the main product in 15 min (Scheme 3). Similarly, the homologous alcohol **5** gave the expected para-substituted products **7** (79%) and **8** (90%) on reaction with phenol and anisole, respectively, which parallels the results obtained[5] with Mo(II) catalysts.[11]

With Mo(II) catalysts, we have previously observed that allylations of phenol and anisole with acyclic allylic acetates (e.g., cinnamyl acetate) tend to preferentially occur in the para position;[5] when the para position was blocked, as in the case of *p*-cresol **11**, ortho-substituted products were formed exclusively.[5] Moreover, after prolonged reaction times, electrophilic cyclization of the resulting olefinic phenol was observed in those cases where protonation of the allylic bond could generate a tertiary carbocation. Therefore, it was desirable to compare the reactivity of Mo(II) catalysts with that of the new Mo(IV) complexes. To this end, a mixture of prenyl alcohol **9** and *p*-cresol was treated with complex **C** (2 mol %) at room temperature (Scheme 4). Monitoring of the reaction indicated the disappearance of the starting materials and a gradual conversion of the initially formed product (presumably **12**) to the chromane derivative **13**; after 24 h at ambient temperature, **13** was isolated in 28% yield.[12] The tertiary alcohol **10** proved to be a better choice as it gave a much cleaner reaction, producing **13** in 46% yield, contaminated by the "open" *o*-allyl intermediate **12** (~5%). Hence, the present Mo(IV) catalyst followed the same reaction course as, and proved to be superior to, its Mo(II) counterpart as it is giving higher conversion and a cleaner product.

Scheme 4



The reaction of linalool (**14**) with anisole was found to be less efficient, giving the expected[5] para-substituted product **15** in 30% yield (Scheme 4). On the other hand, geraniol and nerol (*trans*- and *cis*-allylic isomers of linalool) gave mainly elimination/polymerization products. In contrast to Mo(II) complexes,[5] other allylic substrates, such as isophorol, also turned out to undergo elimination. As catalysts for C−C bond formations, therefore, these Mo(IV) complexes appear to be in part complementary to their Mo(II) congeners.[5]

Nitrogen Nucleophiles. To investigate further the reactivity and scope of the new Mo(IV) catalysts, we have focused on C−N bond formation, where Mo(0) and Mo(II) complexes proved inefficient.[5] However, numerous initial experiments with a variety of allylic alcohols and acetates and primary or secondary amines and sodium azide were unsuccessful.[13] Finally, we found trimethylsilyl azide[14] to react with cinnamyl alcohol (**4**) in the presence of complex **B** (5 mol %) at ambient temperature in 10 min, affording cinnamyl azide **16** in 65% isolated yield (Scheme 5). Under the same conditions, homologous alcohol **5** produced azide **17** (30%).

Cinnamyl azide **16** was also formed from isocinnamyl alcohol **18** (57%), indicating that a common intermediate was generated from both **4** and **18**. Similarly, allylic alcohol **10** gave prenyl azide **19** (20%),[15] demonstrating that the intermediate is trapped by azide selectively at the less substituted terminus, a regioselectivity analogous to attack of oxygen nucleophiles in the presence of Mo(II) catalysts.[5,16] In contrast to the ready reaction of **10**, prenyl alcohol **9** reacted sluggishly, demonstrating the importance of the first ionizing step. The alicylic alcohols **20**, **21**, and **24** also produced the respective azides **22** (61%), **23** (89%), and **25** (54%).

To investigate the stereochemistry of this C−N bond-forming reaction, epimeric steroidal alcohols **26** and **27** were employed as probes (Scheme 6). Both these alcohols

(9) The only notable exception in several unsuccessful attempts was the reaction of 2-cyclohexen-1-yl acetate with phenol in the presence of **C** (2 mol %) in CH_2Cl_2, which gave a 1:1 mixture of *o*- and *p*-(2-cyclohexen-1-yl)phenols (75%) at ambient temperature in 30 min.

(10) Note that in the presence of Mo(II) catalysts, such as $[Mo(CO)_4Br_2]_2$, the analogous reaction with cinnamyl acetate is straightforward, giving the corresponding product at room temperature.[5e]

(11) Interestingly, while practically inert in other reactions, complex **A** (5 mol %) was found to catalyze the reaction of **5** with PhOH in CH_2Cl_2 (at rt, 24 h) to give products of O-allylation (rather than C-allylation), namely 1-phenyl-3-phenoxy-1-butene (33%) and di(1-phenyl-1-buten-3-yl) ether (30%). With 5 mol % of $(acac)_2Mo(O_2CCF_3)_2$, generated in situ from **A** and CF_3CO_2Ag (2 equiv), the same mixture (~1:1) was obtained in 70% yield. Another C−O bond-forming reaction was observed between (*R*)-(+)-1-phenyl-1-buten-3-yl acetate and MeOH in the presence of **C** (5 mol %) in CH_2Cl_2 (rt, 1 h), which gave (±)-3-methoxy-1-phenyl-1-butene.

(12) The yield is based on **9** and is rather low in this case owing to the competing elimination and polymerization. More than 60% of the unreacted **11** has been detected in the crude reaction mixture.

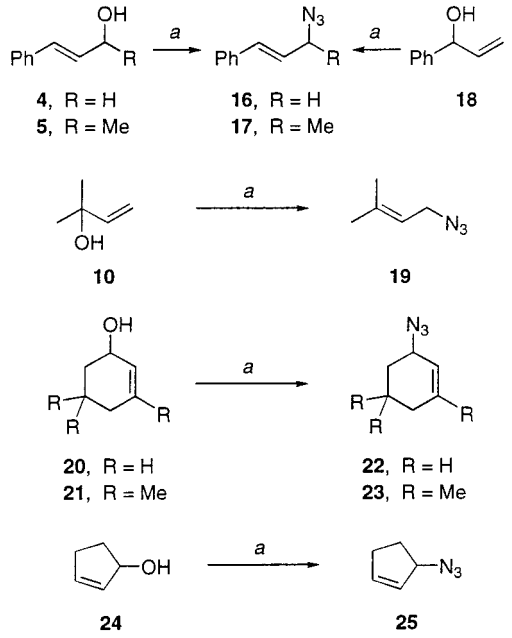
(13) The failure in these cases is apparently due to the preferential coordination of the catalyst to the amine or N_3^-, which renders Mo(IV) unreactive.

(14) For the use of Me_3SiNe_3 in the Pd(0)-catalyzed allylic substitution, see: Trost, B. M.; Cook, G. R. *Tetrahedron Lett.* **1996**, *37*, 7485.

(15) In this case, the relatively low isolated yield is due to the high volatility of the product.

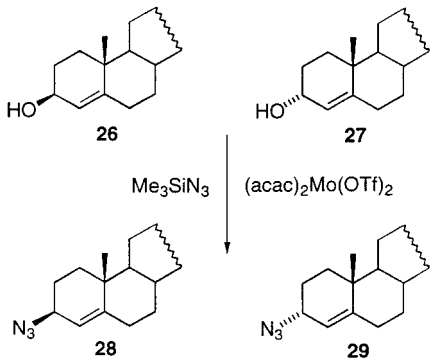
(16) Note that treatment of **10** with HBr is a preparative method to make prenyl bromide: Tietze, L.-F.; Eicher, T. *Reaktionen und Synthesen im organisch-chemischen Praktikum*; G. Thieme: Stuttgart, 1981; p 42.

Scheme 5



[a] Key: (a) Me_3SiN_3, $(acac)_2Mo(OTf)_2$ (5 mol %), CH_2Cl_2, rt, 10 min.

Scheme 6



turned out to produce a mixture of 3β- and 3α-azides **28** and **29** (rt, 10 min), in which the 3α-azide **29** predominated. Thus, starting from **26**, a 15:85 mixture of **28** and **29** was obtained (80%), whereas **27** afforded a 30:70 mixture (75%). This behavior again demonstrates the existence of a common intermediate that is preferentially attacked from the axial side, presumably owing to the stereoelectronic effect that dictates an axial attack;[17] the slight imbalance in the product distribution indicates a nonideal S_N1 mechanism.

The latter results parallel those obtained with Mo(II) catalysts for C−C bond formation;[5] all the data accumulated to date clearly indicate that, rather than generating η^3-complexes, both Mo(II)[5] and Mo(IV) catalysts act as mild Lewis acids with noncoordinated allylic cations as intermediates. This behavior is in sharp contrast to Mo(0)[2] catalysts that are known to react via intermediate η^3 complexes (Scheme 1).

(17) The configuration at the 3-position of **28** and **29** was determined from the signal of 4-H in the ^{1}H NMR spectra: while 3β-substituted derivatives consistently exhibit this signal as a broad singlet, the 3α epimers are characterized by a broad doublet with $J \approx 5$ Hz. The **28**:**29** ratio was determined by integration of the 4-H signals in the ^{1}H NMR spectrum of the crude mixture. For further details, see: Ortar, G.; Paradisi, M. P.; Morera, E.; Romeo, A. *J. Chem. Soc., Perkin Trans. 1* **1978**, 4.

Conclusions

We have designed novel Mo(IV) complexes **B** and **C** that catalyze C−C bond-forming reactions of allylic alcohols with electron-rich aromatics (e.g., **4** → **6**) and C−N bond-forming reactions with Me_3SiN_3 (e.g., **4** → **16** ← **18**) under mild conditions. Since the Mo(II) complexes, described by us earlier (vide supra),[5] failed to form C−N bonds, it can be concluded that the new Mo(IV) catalysts **B** and **C** are complementary to Mo(II). All these catalysts act as mild and selective Lewis acids. Ongoing preliminary experiments suggest that both Mo(II) and Mo(IV) complexes could become very useful in carbonyl ene cyclizations[5g] and other Lewis acid-catalyzed reactions and introduce new, interesting features to this area.

Experimental Section

General Methods. Melting points were determined on a Kofler block and are uncorrected. The NMR spectra were recorded in $CDCl_3$, ^{1}H at 250 MHz and ^{13}C at 62.9 MHz with chloroform-d_1 (δ 7.26, ^{1}H; δ 77.0, ^{13}C) as internal standard; 2D-techniques were used to establish the structures and to assign the signals. The IR spectra were recorded for a thin film between KBr plates unless otherwise stated. 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 an RSL-150 column (25m × 0.25 mm). All reactions were performed under an atmosphere of dry, oxygen-free nitrogen in oven-dried glassware. Solvents and solutions were transferred by syringe-septum and cannula techniques. All reagents were purchased at highest commercial quality and used without further purification, unless otherwise stated. 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. Most of the products are known compounds.[18,19] Complex **A** was prepared following the procedure reported in ref 6b.

General Procedure for the Allylic Substitution Reactions Catalyzed by Complex C and with Electron-Rich

(18) **6**: (a) Wenkert, E.; Fernandes, J. B.; Michelott, E. L.; Swindell, C. S. *Synthesis* **1983**, 701. (b) Dewar, M. J. S.; Nahlovsky, B. D. *J. Am. Chem. Soc.* **1974**, *96*, 460. **7** and **8:** Reference 5f. **12**: (c) Bunina-Krivorukova, L. I.; Feoktistov, V. M.; Aleksandrova, E. K.; Bal'yan, Kh. V. *Zh. Org. Khim.* **1982**, *18*, 859. (d) Julia, M.; Nel, M.; Uguen, D. *Bull. Soc. Chim. Fr.* **1987**, 487. (e) De Renzi, A.; Panunzi, A.; Saporito, A.; Vitagliano, A. *J. Chem. Soc., Perkin Trans. 2* **1983**, 993. **13**: Reference 18c,d. (h) Baird, K. J.; Grundon, M. F. *J. Chem. Soc., Perkin Trans. 1* **1980**, 1820. **15**: (f) Ballester, P.; Capo, M.; Saa, J. M. *Tetrahedron Lett.* **1990**, *31*, 1339. (g) Araki, S.; Manabe, S.; Butsugan, Y. *Chem. Lett.* **1982**, 797.

(19) **16** (*E*): (a) Manhart, E.; von Werner, K. *Synthesis* **1978**, 705. (b) Hassner, A.; Fibiger, R.; Andisik, D. *J. Org. Chem.* **1984**, *49*, 4237. (c) Murahashi, S.; Taniguchi, Y.; Imada, Y.; Tanigawa, Y. *J. Org. Chem.* **1989**, *54*, 3292. (d) Viaud, M. C.; Rollin, P. *Synthesis* **1990**, 130. (e) Kanai, T.; Kanagawa, Y.; Ishii, Y. *J. Org. Chem.* **1990**, *55*, 3274. (f) Hung, R. R.; Straub, J. A.; Whitesides, G. M. *J. Org. Chem.* **1991**, *56*, 3849. (g) Blart, E.; Genet, J.-P.; Safi, M.; Savignac, M.; Sinou, D. *Tetrahedron* **1994**, *50*, 505. (h) Alvarez, S. G.; Alvarez, M. T. *Synthesis* **1997**, 413. (i) Rosen, T.; Lico, I. M.; Chu, D. T. W. *J. Org. Chem.* **1988**, *53*, 1580. **16** (*E*/*Z*): (j) Balderman, D.; Kalir, A. *Synthesis* **1978**, 24. (k) Yang, C.-H.; Shen, H.-J. *Tetrahedron Lett.* **1993**, *34*, 4051. (l) Koziara, A.; Zwierzak, A. *Synthesis* **1992**, 1063. **17** (*E*): (m) Murahashi, S.; Taniguchi, Y.; Imada, Y.; Tanigawa, Y. *J. Org. Chem.* **1989**, *54*, 3292. **19**: (n) Kanai, T.; Kanagawa, Y.; Ishii, Y. *J. Org. Chem.* **1990**, *55*, 3274. (o) Banert, K.; Groth, S. *Angew. Chem.* **1992**, *104*, 865. **22**: (p) Mizuno, M.; Shioiri, T. *Chem. Commun.* **1997**, 2165. (q) Breton, G. W.; Daus, K. A.; Kropp, P. J. *J. Org. Chem.* **1992**, *57*, 6646. **23**: (r) Grieco, P. A.; DuBay, W. J.; Todd, L. J. *Tetrahedron Lett.* **1996**, *37*, 8707. (s) Grieco, P. A.; Handy, S. T. *Tetrahedron Lett.* **1997**, *38*, 2645. **25**: (t) Hassner, A.; Fowler, F. W. *J. Org. Chem.* **1968**, *33*, 2684. (u) Blond, A.; Platzer, N.; Guy, A.; Dhotel, H.; Serva, L. *Bull. Soc. Chim. Fr.* **1996**, *133*, 283. (v) Chmielowiec, U.; Uzarewicz, I.; Uzarewicz, A. *Pol. J. Chem.* **1990**, *64*, 613. (x) Hassner; Fowler, F. *J. Org. Chem.* **1968**, *33*, 2684, 2686. **28**: Reference 17. **29**: Reference 17. (y) Loibner, H.; Zbiral, E. *Helv. Chim. Acta* **1976**, *59*, 2100.

Aromatics as Nucleophiles. $(acac)_2MoCl_2$ complex[6b] (10 mg, 0.027 mmol, 2.7 mol %) was added to a stirred solution of the allylic substrate (1 mmol) and an electron-rich aromatic nucleophile (1.3 mmol) in CH_2Cl_2 (5 mL) at room temperature, followed by addition of solid silver hexafluoroantimonate (10 mg, 0.029 mmol). The mixture was stirred under nitrogen at room temperature for 10−30 min 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 the text.

1-Phenyl-3-(4″-hydroxyphenyl)-1-propene (6).[18a,b] Obtained from **4** and PhOH as a colorless oil (58%). **6**: ^{1}H NMR δ 3.46 (d, J = 6.0 Hz, 2 H, 3-H), 5.01 (s, 1 H, OH), 6.31 (dt, J = 15.9, 6.0 Hz, 1 H, 2-H), 6.42 (d, J = 16.0 Hz, 1 H, 1-H), 6.84 (d, J = 8.5 Hz, 2 H, 3″-H, 5″-H), 7.13 (d, J = 8.5 Hz, 2 H, 2″-H, 6″-H), 7.17−7.35 (m, 5 H, arom); ^{13}C NMR δ 38.9 (3-CH_2), 115.8 (3″,5″-CH), 126.6 (CH), 127.5 (CH), 129.0 (CH), 130.1 (CH), 130.3 (CH), 131.2 (1-CH), 132.8 and 138.0 (1′-C and 1″-C), 154.3 (4″−C); MS (EI) m/z 210 (100, $M^{\bullet+}$).

1-Phenyl-3-(4″-hydroxyphenyl)-1-butene (7).[5f] Obtained from **4** and PhOMe as a colorless oil (79%). **7**: ^{1}H NMR δ 1.41 (d, J = 6.9 Hz, 3 H, Me), 3.56 (m, 1 H, 3-H), 5.08 (brs, 1 H, OH), 6.36 (m, 2 H, 1-H, 2-H), 6.75 (d, J = 8.5 Hz, 2 H, 3″-H, 5″-H), 7.11 (d, J = 8.5 Hz, 2 H, 2″-H, 6″-H), 7.17−7.36 (m, 5 H, arom); ^{13}C NMR δ 21.8 (Me), 42.1 (3-CH), 115.8 (3″,5″-CH), 126.6 (CH), 127.5 CH), 128.8 (CH), 129.0 (CH), 130.2 (CH), 136.1 (1-CH), 138.1 and 138.3 (1′, 1″-C), 154.3 (4″-C); MS (EI) m/z 224 (73, $M^{\bullet+}$), 209 (100).

1-Phenyl-3-(4″-methoxyphenyl)-1-butene (8).[5f] Obtained from **5** and PhOMe as a colorless oil (90%). **8**: ^{1}H NMR δ 1.43 (d, J = 6.9 Hz, 3 H, Me), 3.58 (m, 1 H, 3-H), 3.76 (s, 3 H, OMe), 6.37 (m, 2 H, 1-H, 2-H), 6.85 (d, J = 8.8 Hz, 2 H, 3″-H, 5″-H), 7.17 (d, J = 8.8 Hz, 2 H, 2″-H, 6″-H), 7.20−7.36 (m, 5 H, arom); ^{13}C NMR δ 21.3 (Me), 41.7 (3-CH), 55.2 (OMe), 113.8 (3″,5″-CH), 126.1 (CH), 127.0 (CH), 128.2 (CH), 128.3 (CH), 128.5 (CH), 135.6 (1-CH), 137.6 and 137.7 (1′-C and 1″-C), 158.0 (4″-C); MS (EI) m/z 238 (71, $M^{\bullet+}$), 223 (100).

3,4-Dihydro-2,2-dimethyl-2*H*-benzopyran (13).[18c−e] Obtained as a colorless oil (28% from **9** + **11**; 46% from **10** + **11**). **13**: ^{1}H NMR δ 1.33 (s, 6 H, 2 × 2-CH_3), 1.80 (m, 2 H, 3-H), 2.77 (t, J = 6.9 Hz, 2 H, 4-H), 6.71−7.11 (m, 4 H, arom); ^{13}C NMR δ 22.9 (3-CH_2), 27.3 (2 × 2-Me), 33.2 (4-CH_2), 74.5 (2-C), 117.7 and 120.0 (6- and 8-CH), 121.3 (4a-C), 127.7 and 129.8 (5- and 7-CH), 154.4 (8a-C).

1-(4′-Methoxyphenyl)-3,7-dimethyl-2,6-octadiene (15).[18f,g] Obtained from **14** and PhOMe as a colorless oil (30%). **15**: ^{1}H NMR δ 1.61 (s, 3 H, 3-Me), 1.71 (s, 6 H, 7,8-Me), 1.90−2.21 (m, 4 H, 4,5-H), 3.29 (m, 2 H, 1-H), 3.79 (s, 3 H, OMe), 5.11 (m, 1 H, 6-H), 5.33 (m, 1 H, 2-H), 6.83 (d, J = 8.8 Hz, 2 H, 3′-H, 5′-H), 7.09 (d, J = 8.8 Hz, 2 H, 2′-H, 6′-H).

General Procedure for the Allylic Substitution Reactions Catalyzed by Complex B and with Trimethylsilyl Azide as Nucleophile. $(acac)_2MoCl_2$ complex[6b] (5 mg, 0.014 mmol, 1.9 mol %) was added to a stirred solution of allylic alcohol (0.75 mmol) and trimethylsilyl azide (103 mg, 0.90 mmol, 1.2 equiv) in dry CH_2Cl_2 (10 mL), followed by addition of solid silver triflate (10 mg, 0.039 mmol, 5.2 mol %), and the mixture was stirred at room temperature for 10 min. The volume of the solvent was then reduced to ∼1/5 by evaporation in vacuo at 20 °C, and the residue was chromatographed on a column of silica gel (90 g) with an 80:20 petroleum ether−ether mixture or a 90:10 hexanes−ethyl acetate mixture. For details and the yields see the text.

***(E)*-3-Azido-1-phenyl-1-propene 16.**[19a−i] Obtained as a pale yellow oil (65% from **5**; 57% from **18**). **16**: ^{1}H NMR δ 3.92 (2 H, d, J = 6.6 Hz, CH_2N_3), 6.22 (dt, J = 15.7, 6.6 Hz, 1 H, CH=C*H*CH_2), 6.63 (d, J = 15.7 Hz, 1 H, PhC*H*=H), 7.22−7.43 (m, 5 H, arom); ^{13}C NMR δ 53.1 (t), 122.4 (d), 126.7 (d), 128.2 (d), 128.7 (d), 134.6 (s); IR ν(N_3) 2094 cm^{-1}; MS (EI) m/z 159 ($M^{+\bullet}$, 19), 117 ($M^+ - N_3$, 100).

***(E)*-3-Azido-1-phenyl-1-butene 17.**[19c,m] Obtained from **5** as a pale yellow oil (30%). **17**: ^{1}H NMR δ 1.35 (3 H, d, J = 7.0 Hz, CH_3), 4.10 (1 H, m), 6.09 (dd, J = 6.6 and 16.1 Hz, 1 H, PhCH=C*H*), 6.60 (d, J = 16.1 Hz, 1 H, PhC*H*=H), 7.05−7.55 (m, 5 H, arom); ^{13}C NMR δ 20.6 (q), 60.1 (d), 127.1 (d), 128.5 (d), 128.8 (d), 129.1 (d), 132.6 (d), 136.5 (s); IR ν(N_3) 2094 cm^{-1}.

1-Azido-3-methylbut-2-ene 19.[19e,n,o] Obtained as from **10** a pale yellow oil (20%): ^{1}H NMR δ 1.72 (s, 3 H). 1.81 (s, 3 H), 3.75 (d, J = 7.5 Hz, 2 H) 5.34 (t, J = 7.0 Hz, 1 H); IR ν(N_3) 2100 cm^{-1}.

1-Azidocyclohex-2-ene 22.[19p,q] Obtained from **20** as a pale yellow oil (61%). **22**: ^{1}H NMR δ 1.74 (m, 4 H), 2.11 (m, 2 H), 3.85 (br m, 1 H, C*H*N_3), 5.69 (ddt, J = 2.2, 3.9 and 10 Hz, 1 H, N_3CHC*H*=CH), 6.01 (ddt, J = 1.5, 3.9, 10 Hz, 1 H, N_3CHCH=C*H*); IR ν(N_3) 2100 cm^{-1}.

1-Azido-3,5,5-trimethylcyclohex-2-ene 23.[19r,s] Obtained from **21** as a pale yellow oil (89%). **23**: ^{1}H NMR δ 0.89 (s, 3 H), 1.01 (s, 2 H), 1.26−1.38 (m, 1 H), 1.60−1.92 (m, 1 H), 1.70 (s, 6 H), 3.90 (br m, 1 H), 5.38 (d, J = 0.93 Hz, 1 H); ^{13}C NMR δ 24.0 (q), 26.2 (q), 31.0 (s), 31.3 (q), 41.1 (t), 44.2 (t), 57.6 (d), 118.9 (d), 138.8 (s); IR ν(N_3) 2100 cm^{-1}; MS (CI) m/z 166 ($M^{+\bullet}$, 6), 138 ($M^{\bullet+}$ + H − N_2, 14), 123 ($M^+ - N_3$, 100).

1-Azidocyclopent-2-ene 25.[19t−x] Obtained from **24** as a pale yellow oil (54%). **25**: ^{1}H NMR δ 1.40−2.62 (m, 4 H), 3.91−4.53 (m, 1 H, C*H*N_3), 5.63−6.18 (m, 2 H); IR ν(N_3) 2100 cm^{-1}.

***3β*-Azido-cholest-4-ene (28) and 3α-Azido-cholest-4-ene (29).** $(acac)_2MoCl_2$ complex[6b] (5 mg, 0.014 mmol, 3.6 mol %) was added to a solution of cholest-4-en-3*β*-ol (**26**) (150 mg, 0.39 mmol) and trimethylsilyl azide (54 mg, 0.47 mmol, 1.2 equiv) in dry CH_2Cl_2 (10 mL), followed by addition of silver triflate (10 mg, 0.039 mmol, 10 mol %), and the mixture was stirred at room temperature for 10 min. The volume of the solvent was then reduced to ∼1/5 by evaporation in vacuo at 20 °C, and the residue was chromatographed on a column of silica gel (90 g) with an 80:20 petroleum ether−ether mixture to afford a 15:85 mixture of **28**[17] and **29**[17] (128 mg, 80%) as a colorless oil. **28:** ^{1}H NMR (measured in a mixture with the 3α-isomer) δ 0.68 (s, 3 H, 18-H), 1.05 (s, 3 H, 19-H), 3.80 (m, W = 19.5 Hz, 1 H, 3α-H), 5.24 (br s, 1 H, 4-H), in accordance with the literature.[17] **29**: ^{1}H NMR (measured in a mixture with the 3*β* isomer) δ 0.70 (s, 3 H, 18-H), 0.95 (s, 3 H, 19-H), 3.84 (m, $W \cong$ 28 Hz, 1 H, 3*β*-H), 5.38 (br d, J = 3.5 Hz, 1 H, 4-H), in accordance with the literature.[17,19y]

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Supporting Information Available: MS and HRMS data for the compounds described. This material is available free of charge via the Internet at http://pubs.acs.org.

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