Registry No. 3, 129648-64-2; **4**, 129648-66-4; **7**, 129648-69-7; **8**, 129678-22-4; $POCl_3$, 10025-87-3; 1,3-diaminopropane, 109-76-2; 5-(*n*-heptyloxy)isophthalic acid, 129648-65-3; oxalyl chloride, 79-37-8; 2,6-diaminopyridine, 141-86-6; 1,3-bis[[(6-aminopyrid-2-yl)amino]-carbonyl]-5-(heptyloxy)benzene, 129648-67-5; propionyl chloride, 79-03-8; 5-nitroisophthalic acid, 618-88-2; 1,3-bis[[(6-aminopyrid-2-yl)-amino]carbonyl]-5-nitrobenzene, 129648-68-6; butyryl chloride, 141-75-3; diglycolic acid, 110-99-6; bis[[[(6-aminopyrid-2-yl)amino]-carbonyl]methyl] ether, 129648-70-0; hexanoyl chloride, 142-61-0; *N*-butylamine, 109-73-9.

Ligand Dependence of Molybdenum-Catalyzed Alkylations. Molybdenum–Isonitrile Complexes as a New Class of Highly Reactive Alkylation Catalysts

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Abstract: A series of molybdenum complexes bearing α-diimine, *N,N'*-diarylideneethylenediamine, and isonitrile ligands have been prepared and evaluated for their ability to catalyze alkylations by using allyl acetates and especially allyl sulfones. $(bpy)Mo(CH_3CN)(CO)_3$ proved to be a very effective catalyst in contrast to $bpyMo(CO)_4$. The addition of isonitrile ligands to molybdenum hexacarbonyl generates the most effective molybdenum catalysts known to date. The reactive catalyst proved to be $Mo(RNC)_4(CO)_2$. With this new catalyst, a much broader range of substrates can be employed including many that failed or reacted very poorly by using molybdenum hexacarbonyl. The regioselectivity also differs from that obtained with molybdenum hexacarbonyl. The stereochemistry of the reaction proceeds with very clean net retention of configuration even under conditions that produced diastereomeric mixtures with molybdenum hexacarbonyl. A mechanistic rationale that accounts for the seemingly disparate complexes that are catalysts is presented.

Metal-catalyzed allylic alkylations for building molecular frameworks and for protecting group chemistry continues to enjoy explosive growth. Their attractiveness derives from their attributes of chemo-, regio-, and diastereoselectivity. Nevertheless, numerous opportunities exist to expand the scope of such processes. Many questions can be posed. What types of leaving groups at the allylic position suffice? Of special significance are those groups which normally do not participate in substitution reactions. Can regioselectivity of reactions with unsymmetrical allyl substrates be altered at will? While low valent palladium complexes have proven to be the most general and versatile catalysts,[1] will other less expensive low valent metal complexes[2,3] prove effective? To what extent can chiral metal complexes control absolute stereochemistry?[4] The beauty of metal-catalyzed reactions, in part, lies in the ability to broach these and other questions by "tuning" the catalyst via metal and ligand variation.

We have begun to seek solutions to a number of the questions posed above. While these questions can be approached individually, at times they overlap. For example, we sought to control regioselectivity by altering the low valent metal complex, especially by focusing on those derived from less expensive metals. Of these molybdenum catalysts, notably molybdenum hexacarbonyl, has proven especially interesting since it strongly promoted regioselective attack of malonate anion at the more substituted terminus of an unsymmetrical allyl system.[3] Our attempts to utilize this catalyst system to control regioselectivity of alkylation of allyl sulfones demonstrated a limitation since the reactions became almost stoichiometric in the molybdenum catalyst. We attributed a partial source of the problem to the facile disengagement of carbon monoxide which led to new molybdenum complexes that no longer functioned as catalysts. Earlier work noted that clearly ligand substitution was occurring under our alkylation conditions although we do not know the exact nature of the substitution. Therefore, we turned to the question of ligand choice.

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Part I. The Catalysts

Imine Ligands. Our early work demonstrated the feasibility of replacing several CO ligands of molybdenum hexacarbonyl with 2,2'-bipyridyl (bpy) and 1,2-bis(diphenylphosphino)ethane (dppe), but both complexes were significantly less reactive catalysts.[3a] The

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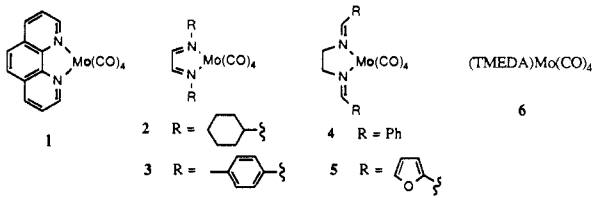
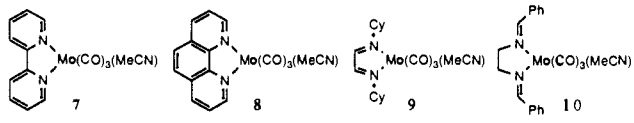
higher reactivity of the bipyridyl-ligated molybdenum complex led us to synthesize a family of imine complexes **1–5** which were prepared by the simple ligand exchange with molybdenum hexacarbonyl in refluxing toluene.[5,6] In addition, the saturated amine complex **6** was prepared for comparison.[5f] All complexes were air stable crystalline solids varying in color to dark red to deep purple for **1–3** indicative of a strong metal-to-ligand charge-transfer transition[5] to yellow to light orange for **4–6** as expected for weak π-acceptor ligands.



NMR spectroscopy reveals complexes **4** and **5** to be isomeric mixtures. For example, the spectrum of complex **5** shows the signals for the bridging methylene protons at δ 3.98 (1.5 H, m), 4.12 (1.5 H, m), and 4.20 (1 H, s) and that for the imine protons at δ 8.40 (0.75 H, s), 8.55 (0.5 H, s), and 8.67 (0.75 H, s). Furthermore, the ^{95}Mo spectrum showed two signals at −1170 and −1165 ppm in a 3:1 ratio. Combining the above data with the fact that the combustion analysis indicates the mixture must be that of isomers, we assign the singlets to the symmetrical trans, trans complex and the multiplets to the unsymmetrical cis, trans complex in a 3:1 ratio. Since the starting ligand was geometrically pure, isomerization must have been promoted by complexation as a result of unfavorable steric interactions between the aryl groups of the ligand and the metal fragment.

Envisioning the need for facile ligand dissociation to achieve catalytic activity, we also prepared a parallel set of complexes **7–10**



in which one carbonyl group was replaced by acetonitrile. In situ preparation of tris(acetonitrile)molybdenum tricarbonyl[7] followed by addition of the imine ligand provided the complexes.[8] Complexes **7–9** were dark blue to purple crystalline solids and complex **10** was isolated as red crystals. Unlike the tetracarbonyl complexes, the tricarbonyl complexes were air sensitive, especially in solution. Unlike complex **4**, the tricarbonyl complex **10** shows a single symmetrical pattern for the imine ligand consistent with either a cis, cis, or trans, trans geometry. Since the starting ligand was pure anti, we favor the latter geometry for the complex. The CO stretching region of the infrared spectra of all the complexes are similar. The absorptions at 1915 and 1800 cm^{-1} for **9** are consistent with a *fac*-$Mo(CO)_3L_2L'$ complex with weak to moderate π-acceptor ligands.[9,10] This geometry appears to be the same for all.

Table I. Isonitrile Complexes

entry	isonitrile	isolated yields: *cis*-$Mo(CO)_4(CNR)_2$	*fac*-$Me(CO)_3(CNR)_3$	*cis*-$Mo(CO)_2(CNR)_4$
1	t-C_4H_9NC			**15**, 66%
2	n-C_4H_9NC		**16**, 10%	**14**, 38%
3	PhNC			**18**, 55%
4	2,6-$(CH_3)_2$-C_6H_3NC		**19**, 62%	**20**, 22%
5	$PhCH_2NC$		**21**, 63%	
6	CH_3NC	**22**, 39%	**23**, 43%	

Isonitrile Ligands. Isonitriles, which are isoelectronic with carbon monoxide but are retained in solution if dissociated from the metal, appeared to be promising ligand candidates. Though well studied by organometallic chemists, isonitriles are seldom used as ancillary ligands in homogeneous catalysts, perhaps because of their proclivity to undergo insertion reactions.[11] However, molybdenum π-allyl complexes do not appear to insert isonitriles.[12]

A series of isonitrile compelxes beginning with those derived from *tert*-butylisonitrile [$Mo(CO)_n(CNC_4H_9$-$t)_{6-n}$, n = 5 (**11**), n = 4 (**12**), n = 3 (**13**), and n = 2 (**14**)] were prepared by the procedure of Coville and Albers in which carbonyl substitution was promoted by cobalt chloride[13,14] (see eq 1 and Table I). The

$$Mo(CO)_6 + RNC \xrightarrow[\text{PhMe } 111^\circ C]{0.1 \text{ eq } CoCl_2\,2H_2O} Mo(CO)_n(CNR)_{6-n} \quad (1)$$

complexes were purified by flash chromatography with hexane–methylene chloride mixtures, the polarity increasing with increasing isonitrile substitution. All of the complexes were white to yellow crystalline solids except for the n-butyl complexes which were yellow oils.

Infrared spectroscopy proved most helpful in characterizing the complexes. For example, *cis*-$Mo(CO)_2(CNC_4H_9$-$n)_4$ exhibits carbonyl absorptions at 1885 and 1825 cm^{-1}, *fac*-$Mo(CO)_3(CNC_4H_9$-$n)_3$ at 1945 and 1870 cm^{-1}, and *cis*-$Mo(CO)_4(CNCH_3)_2$ at 2020 and 1920 cm^{-1}, all analogous to similar reported complexes.[13]

The failure to obtain the tetrasubstituted complex with benzylisonitrile is surprising, and no rationale is evident. The low boiling point of methylisonitrile necessitated a lower temperature to avoid excessive loss; thus, benzene was substituted for toluene. The lower reaction temperature may account for the fact that only trisubstitution could be achieved.

^{95} NMR Spectra. ^{95}Mo NMR shifts provide insight into the electronic characteristics of the complexes in which the molbydenum signal moves downfield with decreasing π-acceptor ability.[15,16] It should be recalled that molybdenum shifts occur in the shielded range upfield from disodium molybdate in deu-

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Table II. ^{95}Mo NMR Shifts[a]

entry	complex	compd no.	compd shift	entry	complex	compd no.	compd shift
1	$Mo(CO)_6$ [Mo–C]		−1858	11[b]	*fac*-$Mo(CO)_3(CNPh)_3$		−1772
2	$Mo(CO)_5(CNCH_3)$		−1850	12	*cis*-$Mo(CO)_2(CNC_4H_9$-*n*$)_4$	**17**	−1731
3	$Mo(CO)_5(CNC_4H_9$-*t*$)$	**11**	−1849	13	*cis*-$Mo(CO)_2(CNC_4H_9$-*t*$)_4$	**14**	−1714
4	*cis*-$Mo(CO)_4(CNCH_3)_2$	**22**	−1829	14	*cis*-$Mo(CO)_2[2,6(CH_3)_3C_6H_3NC]$	**20**	−1711
5	*cis*-$Mo(CO)_4(CNC_4H_9$-*t*$)_2$	**12**	−1825	15	*cis*-$Mo(CO)_2(CNPh)_4$	**18**	−1699
6	*fac*-$Mo(CO)_3(CNCH_2Ph)_3$	**21**	−1792	16	$(CyNCH)_2Mo(CO)_4$	**2**	−7209
7	*fac*-$Mo(CO)_3(CNC_4H_9$-*n*$)$	**16**	−1791	17	$(PhCHNCH_2)_2Mo(CO)_4$	**5**	−1170
8	*fac*-$Mo(CO)_3(CNCH_3)$	**23**	−1786				−1165
9	*fac*-$Mo(CO)_3[2,6(CH_3)_2C_6H_3NC]$	**19**	−1783	18	$[(2\text{-furyl})CHNCH_2]_2Mo(CO)_4$	**4**	−1153
10	*fac*-$Mo(CO)_3(CNC_4H_9$-*t*$)_3$	**13**	−1782	19[c]	$Mo(CO)_4$bpy		−1150
				20	$Mo(CO)_4$TMEDA	**6**	−1010

[a] All shifts are recorded in methylene containing 10% benzene-d_6 (for locking) unless otherwise noted and are reported in ppm upfield from the reference disodium molybdate in D_2O at pH 11. [b] This complex was detected as an impurity in **18**. [c] DMF was employed as solvent.

Table III. Ligand Properties

entry	ligand (L_2)	pK_a for conjugate acid	qualitative π-acceptor ability	ν(CO) cm^{-1} for $L_2Mo(CO)_4$	av ν(CO)
1	TMEDA	9.0	none	2010, 1890, 1870, 1830	1900
2	bpy	4.5	weak	2017, 1909, 1878, 1829	1908
3	$(PhCH{=}NCH_2)_2$		weak	2010, 1910, 1880, 1835	1909
4	$(C_6H_{11}N{=}CH)_2$		weak	2010, 1920, 1895, 1845	1918
5	dppe	>2.7	good	2020, 1919, 1907, 1881	1932
6	$(t\text{-}C_4H_9NC)_2$		strong	2015, 1942, 1932, 1923	1953
7	$(CO)_2$	≪−10	very strong	2004	2004

terium oxide at pH 11. The series of complexes listed in Table II follows the previously reported trend of a downfield shift with more σ donation and less π acceptance. The relatively small shifts observed by replacing CO with isonitriles supports our assumption that isonitrile complexes should be good substitutes for molybdenum hexacarbonyl. The relatively narrow line widths (<10 Hz) presumably reflect the good π acceptor ability and high symmetry of the isonitrile ligands.

Discussion

Tuning reactivity and selectivity of transition-metal-catalyzed reactions requires a detailed study of the effects of ligands. In allylic alkylations, the steric and electronic properties of the ligands can influence each of the four stages—(1) initial olefin coordination of the substrate, (2) ionization of the allylic substituent, (3) nucleophilic attack on the π-allyl complex, and (4) decomplexation of the product—in different and sometimes contradictory fashion. While minimizing nonbonded interactions should be beneficial for all stages, electronic effects can be quite variable. Enhancing the electrophilic properties of the metal should facilitate stages 1, 3, and 4, whereas increasing electron density of the metal should facilitate the ionization step 2.

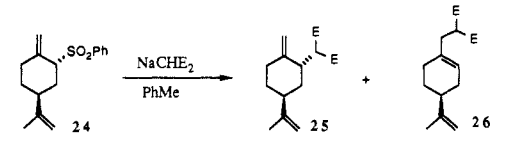
The effect of a ligand on the electronic properties of molybdenum consists of both σ- and π-bonding components. The net effect is reflected in the stretching frequencies of coordinated carbonyl groups in the infrared spectra which are listed in Table III.[10,17] The pk_a of the conjugate acid is a measure of the σ-component (the weaker the acid the better the σ-donation). An evaluation of the π-component derives from a qualitative evaluation of the difference in energy between the HOMO of molybdenum and the LUMO of the ligand. The π-acceptor properties of nitrogen ligands derives from spectroscopic studies (IR, UV, and ^{1}H, ^{13}C, and ^{31}P NMR)[5] and calculations.[19] By using the average carbonyl frequency as a measure of the net effect, the ligands are listed in decreasing order of σ-donation and increasing order of π-acceptance. A comparison of Tables III and II reveals the ^{95}Mo chemical shifts also follow the same order with TMEDA causing greatest shielding and CO greatest deshielding. The much broader range of NMR chemical shifts makes this technique a more sensitive one for evaluating ligand effects.

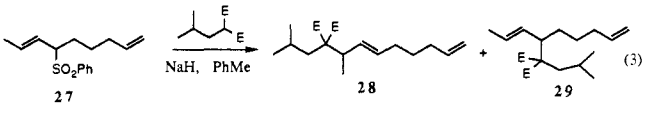
Table IV. Catalytic Activity of Isonitrile Complexes with Allyl Sulfones

catalyst	at 6 h (%)	at 12 h (%)
$Mo(CO)_6$	6	28
$Mo(CO)_5(CNC_4H_9$-*t*$)$	11	17
$Mo(CO)_4(CNC_4H_9$-*t*$)_2$	0	5
$Mo(CO)_3(CNC_4H_9$-*t*$)_3$	8	24
$Mo(CO)_2(CNC_4H_9$-*t*$)_4$[MoBl4]	92	97

Part II. The Catalytic Reaction

Alkylations with Allyl Sulfones. Our interest in employment of organosulfones as chemical chameleons[20] led us to examine allyl sulfones[21,22] as initial test substrates (eqs 2 and 3). For comparison, each reaction was performed with 10 mol % molybdenum hexacarbonyl (Mo–C) as catalyst in refluxing toluene. Alkylation of malonate anion with sulfone **24** produces exclusively the more substituted product **25** in 45% yield—a regioselectivity consistent with that observed for allyl acetates (vide infra).[3] The substituted malonate reacts with allyl sulfone **27** to give a 59% yield of a 4:1





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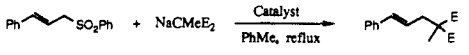
(22) For Lewis acid catalyzed reactions of allyl sulfones, see: Trost, B. M.; Ghadiri, M. R. *J. Am. Chem. Soc.* **1984**, *106*, 7260; **1986**, *108*, 1098.

Table V. Effect of Isonitrile Ligand with Allyl Sulfones

entry	catalyst	time (h)	ratio 25	ratio 26	yield (%)
1	$Mo(CO)_6$	24	100	0	45
2	$Mo(CO)_6$ + t-C_4H_9NC	24	79	21	80
3	$Mo(CO)_2(CNC_4H_9$-$t)_4$ (**14**)	10	69	31	89
4	$Mo(CO)_2(CNC_4H_9$-$n)_4$ (**17**)	8	83	17	86
5	$Mo(CO)_2(CNPh)_4$ (**18**)	24	86	14	37
6	$Mo(CO)_2[2,6$-$(CH_3)_2C_6H_3NC]_4$ (**20**)	24	79	21	26
7	$Mo(CO)_3[2,6$-$(CH_3)_2C_6H_3NC]_3$ (**19**)	24			0
8	$Mo(CO)_3(CNCH_2Ph)_3$ (**21**)	24	86	14	31
9	$Mo(CO)_3(CNCH_3)_3$ (**23**)	24	89	11	26

mixture of **28** and **29**. Addition of 4 equiv of *tert*-butylisonitrile to each of these reactions led to dramatic improvements in yields to 80% and 72%, respectively. While in eq 2 some deterioration in regioselectivity occurred (**25**:**26**, 79:21), enhanced regioselectivity was observed in eq 3 (**28**:**29**, >95:<5).

In order to establish which of the possible in situ formed isonitrile complexes might be the active catalyst, the alkylation of eq 4 was performed with each of the *tert*-butylisonitrile complexes.

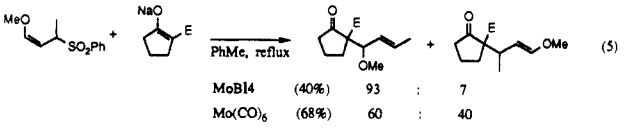


(4)

The results, summarized in Table IV, are dramatic; a quantum difference in reactivity occurs upon going to the MoBI4 catalyst.[23]

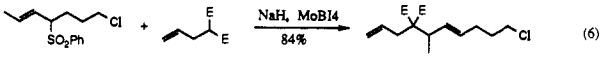
The effect of the isonitrile structure was explored in the context of the reaction of eq 2. The results summarized in Table V indicate the butylisonitrile catalysts are superior with the *n*-butylisonitrile complex **17** providing somewhat better regioselectivity than the *tert*-butylisonitrile complex **14**. Because the former complex is an oil which made it somewhat more difficult to handle and sensitive to air, we preferred the crystalline *tert*-butylisonitrile complex for further exploratory chemistry.

Questions of chemo- and regioselectivity with allyl sulfones were further explored. Equation 5 reveals the compatibility of an enol ether and the enhanced regioselectivity for attack α to oxygen with



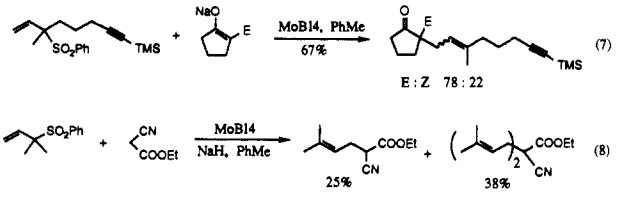
(5)

MoBI4. Equation 6 reveals the dramatic effect of metal catalysts on the relative leaving group abilities of allylic substituents. Thus, a sulfone, which is a nonleaving group in the absence of a catalyst, wins over a more conventional chloride leaving group in the



(6)

presence of MoBI4. The excellent regioselectivity in this case (>95:<5) is enhanced over that obtained with molybdenum hexacarbonyl (85:15). Acetylenes have proven to be incompatible with molybdenum hexacarbonyl. On the other hand, such groups appear to cause no difficulties using MoBI4 (eq 7). MoBI4 also overcomes the low yields of alkylation with ethyl cyanoacetate although polyalkylation, a common problem with cyano stabilized anions, becomes an issue (see eq 8).



(7)
(8)

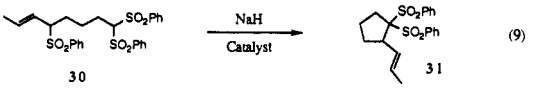
(23) Abbreviations of the form MoAln were chosen as a shorthand representation for molybdenum isonitrile complexes which have rather long IUPAC names. Mo stands for molybdenum, A is the first letter in the name of the alkyl or aryl residue in the isonitrile ligand, l stands for isonitrile, and *n* is the number of isonitrile ligands. Thus, $Mo(CO)(CNPh)_5$ is designated MoP15.

Table VI. Effect of Imine Ligands with Allyl Acetates

entry	catalyst	time (h)	ratio 35	ratio 36[a]	yield (%)
1	$Mo(CO)_6$	8	100	0	73
2	$Mo(CO)_4$bpy	36	40	60 (1.3:1)	70
3	$Mo(CO)_3(CH_3CN)$bpy (**7**)	9	30	70 (1.5:1)	70
4	$Mo(CO)_3(CH_3CN)$phen (**8**)	24	40	60 (2.3:1)	55
5	$Mo(CO)_4(CH_2N{=}CHC_4H_3O$-$2)_2$ (**5**)	24	90	10	70
6	$Mo(CO)_4(CH_2N{=}CHPh)_2$ (**4**)	24	100	0	32
7	$Mo(CO)_4$TMEDA (**6**)	24	100	0	21
8	$Mo(CO)_4(CH{=}NC_6H_4CH_3$-$4)_2$ (**3**)	24	nr[b]	nr[b]	
9	$Mo(CO)_4(CH{=}NC_6H_{12})_2$ (**2**)	24	nr[b]	nr[b]	
10	$Mo(CO)_3(CH_3NC)(CH{=}NC_6H_{11})_2$ (**9**)	24	nr[b]	nr[b]	

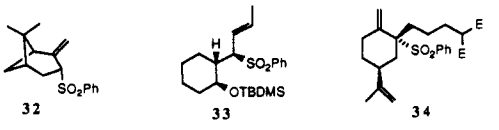
[a] Numbers in parentheses are diastereomeric ratios. [b] No reaction.

Cyclizations are another reaction type in which molybdenum hexacarbonyl had only limited success. Tris-sulfone **30** cyclized to cyclopentane **31** in only 15% yield with MoC, but switching to MoBI4 almost tripled the yield to 44% with an 82% yield based on recovered starting material (eq 9).

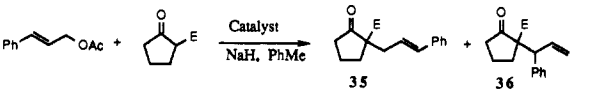


(9)

While the MoBI4 catalyst appears to be generally useful for activating allyl sulfones, we have had some failures. Thus, neither **32** and **33** serves as substrates for any of our molybdenum catalysts nor does **34** cyclize. Steric hindrance to approach of the molybdenum templates to the face of the olefin distal to the sulfone may account for these failures. None of the imine-ligated catalysts effect reaction of allyl sulfones.

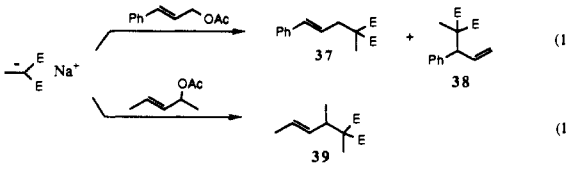


Alkylations with Allyl Carboxylates. To examine the effect of a leaving group on ligand choice, we examined the more common allyl acetate substrates. The alkylation of 2-(methoxycarbonyl)cyclopentanone with (*E*)-cinnamyl acetate[3] was used as a test reaction for the effect of imine ligands (eq 10, Table VI).



(10)

The data of Table V reveal two important features. First, the incorporation of an easily dissociable ligand like acetonitrile in the catalyst bearing a bpy ligand tremendously increases the reactivity such that **7** rivals molybdenum hexacarbonyl in its rate but provides complementary regioselectivity. Second, the α-diimine ligands create inactive catalysts, which is quite surprising since such ligands are the best π-acceptors of those tested and the resultant complexes might have been thought to be most similar to molybdenum hexacarbonyl. To determine whether the nucleophile inhibited catalytic activity of these complexes, we employed dimethyl sodiomethylmalonate as a nucleophile (eqs 11 and 12). In contrast to the earlier reaction, catalysts **2** and

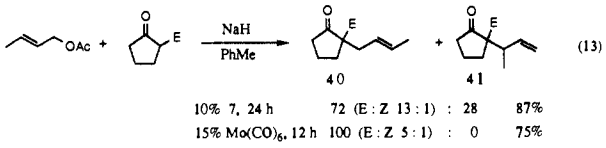


(11)
(12)

9 do lead to the alkylation products (**37**:**38** is 72:28 in 40% with **2** and 75:25 in 20% with **9**; **39** in 56% with **2** and 55% with **9**) but in diminished yields compared to molybdenum hexacarbonyl (**37**:**38** 100:0 in 90%; **39**, 75%).

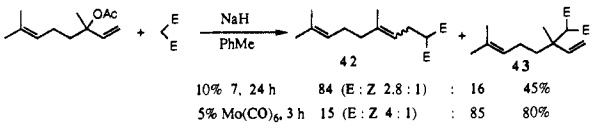
The excellent reactivity of the monoacetonitrile complexes **7** and **8** led us to focus on the general properties of the former, especially as it contrasts with molybdenum hexacarbonyl. BSA proved superior as a base in molybdenum hexacarbonyl reactions; however, it kills catalytic activity of **7**, strongly implicating its role as a ligand to molybdenum. Thus, sodium hydride was employed in all cases.

Equations 13–17 contrasts the two new catalysts with molybdenum hexacarbonyl. Catalyst **7** appears comparable in reactivity to molybdenum hexacarbonyl but can give complementary (eq 14) or enhanced (eqs 15 and 16) regioselectivity depending upon the degree of substitution of the π-allyl intermediate.



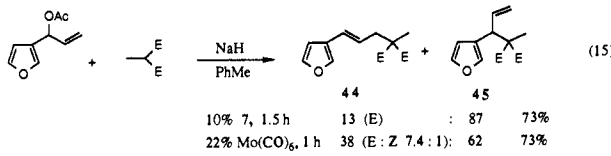
(13)

10% 7, 24 h 72 (E:Z 13:1) : 28 87%
15% $Mo(CO)_6$, 12 h 100 (E:Z 5:1) : 0 75%



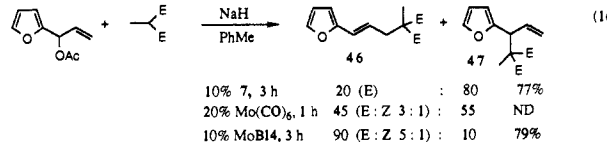
(14)

10% 7, 24 h 84 (E:Z 2.8:1) : 16 45%
5% $Mo(CO)_6$, 3 h 15 (E:Z 4:1) : 85 80%



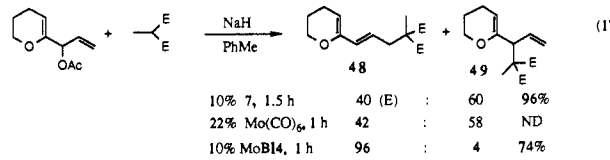
(15)

10% 7, 1.5 h 13 (E) : 87 73%
22% $Mo(CO)_6$, 1 h 38 (E:Z 7.4:1): 62 73%
10% MoBI4, 1 h 78 (E:Z 9:1) : 22 90%



(16)

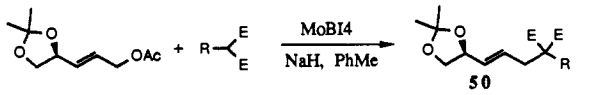
10% 7, 3 h 20 (E) : 80 77%
20% $Mo(CO)_6$, 1 h 45 (E:Z 3:1) : 55 ND
10% MoBI4, 3 h 90 (E:Z 5:1) : 10 79%



(17)

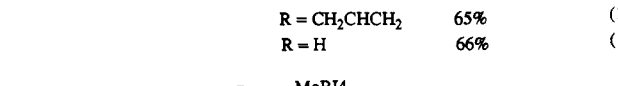
10% 7, 1.5 h 40 (E) : 60 96%
22% $Mo(CO)_6$, 1 h 42 : 58 ND
10% MoBI4, 1 h 96 : 4 74%

The isonitrile complexes, however, appear to be superior to molybdenum hexacarbonyl with allyl acetate substrates (cf. eqs 15–17). The yields are as good or higher; the regioselectivity is good to excellent and is complementary, i.e., the major product with MoBI4 is the minor product with molybdenum hexacarbonyl. Most importantly, alkylations that proceed only poorly (eq 18a) or not at all (eqs 18b–21) with molybdenum hexacarbonyl now proceed smoothly.



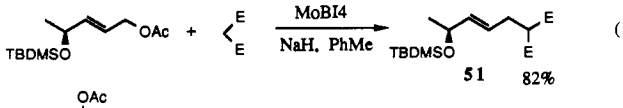
(18a)

$R = CH_2CHCH_2$ 65%



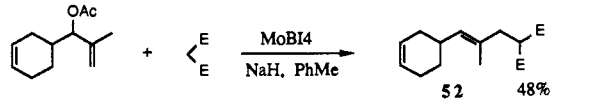
(18b)

$R = H$ 66%



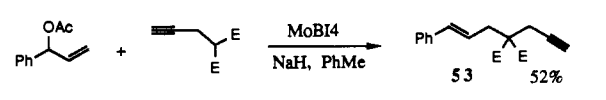
(19)

51 82%



(20)

52 48%



(21)

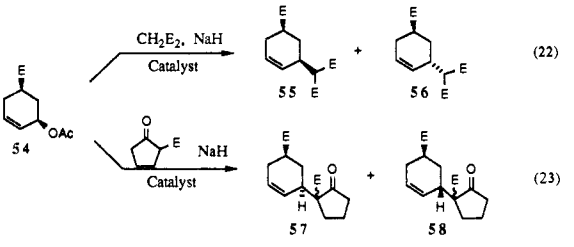
53 52%

The stereochemistry of the MoBI4-catalyzed reactions was briefly examined with our standard test substrate **54**. Again, a striking contrast exists between molybdenum hexacarbonyl and MoBI4 (eqs 22 and 23, Table VII). Thus, under otherwise identical conditions, a reaction which was stereorandom with molybdenum hexacarbonyl (entries 1 and 5) becomes highly selective for the product of net retention of configuration (entries 3 and 7).

Table VII. Stereochemistry of Alkylation of *cis*-3-Acetoxy-5-(methoxycarbonyl)cyclohexane[a]

entry	eq	catalyst	base	time (h)	ratio 55 or 57	ratio 56 or 58	yield (%)
1[b]	22	$Mo(CO)_6$	NaH	48	1	1	50
2[b]	22	$Mo(CO)_6$	BSA	48	>10	<1	75
3	22	MoBI4	NaH	24	99	1	70
4	22	MoBI4	BSA	24			nr[c]
5[b]	23	$Mo(CO)_6$	NaH	48	1 (1:1)	1 (1:1)	57
6[b]	23	$Mo(CO)_6$	BSA	48	>99 (6:1)	<1	50
7	23	MoBI4	NaH	24	>99 (1:2)	<1	41

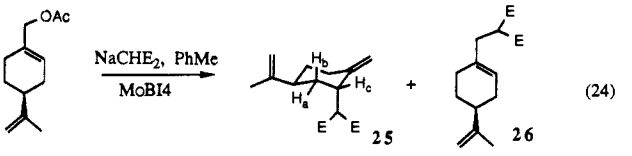
[a] All reactions employed 20 mol % catalyst except entry 1 wherein 40 mol % was employed. [b] Reference 3. [c] No reaction.



(22)

(23)

The diastereoselectivity was also examined in an example where the stereochemistry of the intermediate π-allylmolybdenum complex is not determined by the leaving group. Alkylation of (*S*)-perillyl acetate produced a 36:64 mixture of regioisomers **25** and **26** in 77% based upon recovered starting material (eq 24).



(24)

The product of alkylation at the ring carbon **25** is a single diastereomer, the same as that derived from alkylation of the sulfone **24** (eq 2). Upon the basis of the observation of only small couplings between H_c (δ 3.22) and H_a (δ 1.30) and H_b (δ 1.57) and of only one axial–axial coupling (J = 12.8 Hz) to H_b, the stereochemistry depicted in **25** is assigned.

Discussion

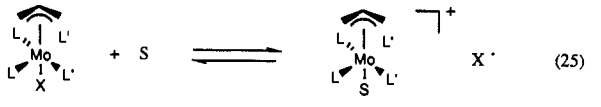
Comparison of Tables III and VI indicates the relationship between such electronic properties and catalytic activity is not simple. Catalysts bearing stronger σ-donating ligands (as in Table III, entries 1–3) or stronger π-accepting ligands (as in Table III, entries 6 and 7) are better catalysts than those that have ligands where such properties are more balanced (as in Table III, entries 4 and 5). This effect does not arise from a differing ability of the various complexes to open a coordination site. While ligand expulsion to create an open coordination site for the allylic substrate does influence the reaction (see Table VI, entries 2 and 3), the inactive catalysts bearing an α-diimine ligand remain inactive after introducing a more dissociable ligand (see Table VI, entries 9 and 10).

The dramatic effect of the isonitrile ligands may be attributed to the claim that they are both good σ-donors as well as π-acceptors in contrast to carbon monoxide.[24] Thus, the ambident properties would allow them to stabilize both low and higher oxidation states of metals, both of which are involved in the

(24) Singleton, E.; Dosthuizen, H. E. *Adv. Organomet. Chem.* **1983**, *22*, 209. Yamamoto, Y. *Coord. Chem. Rev.* **1980**, *32*, 193. Treichel, P. M. *Adv. Organomet. Chem.* **1983**, *11*, 21. Malatesta, L.; Bonati, F. *Isonitrile Complexes of Metals*; Wiley: New York, 1969.

catalytic cycle. Nevertheless, the data of Tables II and III do not suggest that they are particularly good σ-donors. While such characteristics of the isonitrile ligand may contribute somewhat to their beneficial effect, such an explanation appears unlikely to be of major importance.

The seemingly contradictory relationship between electronic properties of the ligand and the reactivity of the corresponding complexes appear to correlate best with the ability of the intermediate π-allylmolybdenum complex to suffer nucleophilic attack. We have established the importance of ionization in the reactions of π-allylpalladium complexes with nucleophiles.[25] With the stronger donor ligands, the equilibrium shown in eq 25 may occur.



(25)

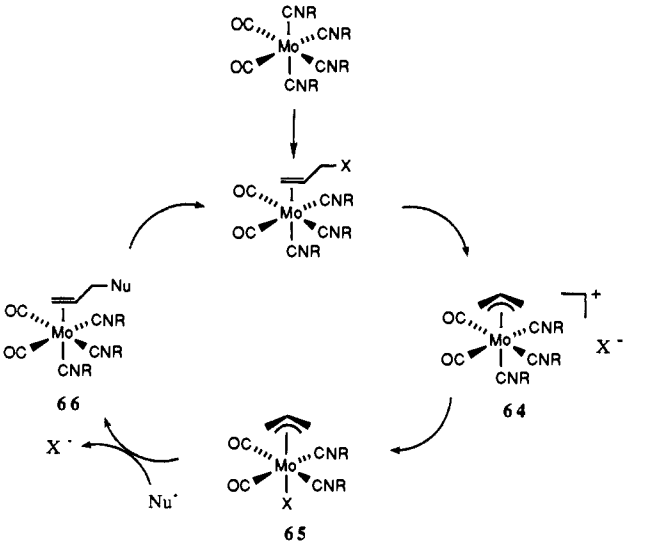
59 **60**

The resultant cationic complex **60** should be sufficiently electrophilic to be reactive toward the stabilized nucleophiles explored herein. However, with the poorer σ-donating ligands of Table III, entries 4–7, such an equilibrium may not occur. The poorer electrophilic properties of **59** when L′ is either an α-diimine or a bis-phosphine prevent its reaction with nucleophiles. On the other hand, if all four neutral ligands are sufficiently electron withdrawing, as in Table III, entries 6 and 7, then the neutral complex **59** is sufficiently electrophilic to participate in alkylation reactions. This explanation also encompasses our earlier observations regarding the effect of BSA and dimethyl sodiomalonate on the reactivity of the molybdenum hexacarbonyl catalyzed reactions. The earlier suggestions[3] that such molecules enter the coordination sphere of molybdenum and thereby alter its catalytic reactivity appear substantiated by the current results. Reactivity and diastereoselectivity comparisons support this thesis. The stronger ligating properties and poorer volatility of the isonitrile ligands compared to CO prevent replacement of a neutral ligand by malonate anion. Thus, substrates that failed to react with molybdenum hexacarbonyl as catalysts now participate in alkylations (eqs 18–20). Substrates bearing an acetylenic group that also previously failed to react, presumably because of coordination of the acetylene with molybdenum, participate in alkylations with catalysts bearing the isonitrile ligands (eq 21).

The stereochemical results of Table VII also support these conclusions. The dichotomy between sodium hydride and BSA as base in providing products of net retention of configuration in molybdenum hexacarbonyl catalyzed reactions was attributed to preferential coordination of BSA over the stabilized anion in the product-determining step. This difference disappears with MoBI4.

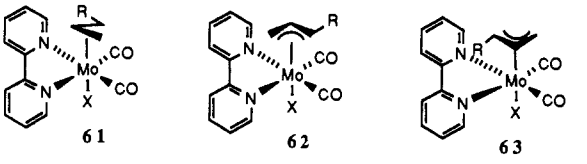
Complex **7** rivals molybdenum hexacarbonyl in its reactivity but has the interesting property of promoting alkylation at the more substituted allyl terminus to a greater extent than molybdenum hexacarbonyl (eqs 10, 13, 15–17) except for dimethyl malonate (eq 14). We have previously delineated a number of factors that affect regioselectivity in palladium-catalyzed allylic alkylations including (1) steric hindrance of the regioisomeric alkylation sites, (2) steric hindrance of the attacking nucleophile, (3) charge distribution and orbital coefficients in the intermediate π-allyl complex, (4) relative stability of the two possible product olefin–metal complexes, (5) asymmetric coordination of the π-allyl moiety to the metal, and (6) reactivity of the nucleophiles. While these factors undoubtedly also play a role in molybdenum-catalyzed reactions, the use of molybdenum complexes bearing more than one type of ligand raises the question of proximal ligand effects on regioselectivity as probed by the experimental studies of Faller[26] and the theoretical studies of Curtis and Eisenstein.[27]

Scheme I. A MoBI4 Catalytic Cycle



66 **64** **65**

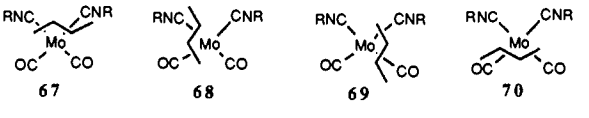
Alkylation should occur at the allyl terminus syn to the more electronegative ligand. Regioselectivity then depends upon rotamer populations and/or kinetics. Of the three rotamers **61–63** for the bpy catalysts, rotamer **61** would have no proximal ligand effect but sterically should be the most disfavored. Of the remaining two, rotamer **62** should favor attack at the more substituted



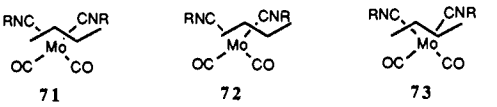
61 **62** **63**

position, but the reverse should be true for rotamer **63**. Since steric factors should favor **62**, the increased bias of these complexes to favor attack at the more substituted position compared to molybdenum hexacarbonyl may derive from this proximal ligand effect. It also should be noted that the bpy complex **7** enhances geometric purity of the olefins to 13:1 to >99:1 from 3:1 to 7:1 which has been typical for many molybdenum hexacarbonyl catalyzed reactions.

Extrapolating this argument to the isonitrile complexes becomes clouded by the conjecture as to the structure of the catalytic intermediate. The sequential substitution of isonitrile for CO starting from molybdenum hexacarbonyl suggests that the poor catalytic activity of complexes **11–13** stem, in part, from poor ligand dissociation of either CO or isonitrile. For MoBI4, dissociation of CO under the catalytic conditions appears highly unlikely.[13,14,24] The tightness of coordination of the CO groups is clearly revealed by the rather low carbonyl stretching frequencies of 1864 and 1818 cm^{-1} (cf. 1946 and 1860 for MoBI3). Thus, the catalytic cycle likely begins by dissociation of an isonitrile. Such a dissociation should be easier for MoBI4 since the isonitrile that departs can be trans to another isonitrile whose stronger donor properties should facilitate that dissociation compared to CO (see Scheme I). The better σ-donor properties of isonitrile ligands should also facilitate the ionization step leading to the electrophilic complex **67** that suffers nucleophilic attack to produce the product



67 **68** **69** **70**



71 **72** **73**

olefin complex **66** which simply exchanges olefin ligands to initiate another cycle. The discussion of the nature of the ionization step

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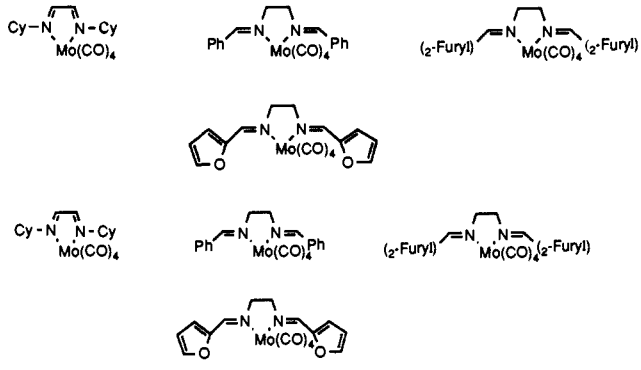
and the possible intervention of an ion pair **64** is deferred. The fact that isonitrile ligands can dissociate and associate as required combined with the better ionization properties of isonitrile complexes account for the greater superiority of MoBI4. The above suggests that the homoleptic complex hexakis(*tert*-butylisonitrile)molybdenum[28] should be as good if not better as a catalyst. A preliminary examination using an impure sample of this uneasily obtained complex confirmed this prediction.

This picture, which invokes the intermediacy of **65**, permits an understanding of the regioselectivity of alkylation with such catalysts. In all the results presented, MoBI4 is consistently more regioselective for alkylation at the less hindered carbon than molybdenum hexacarbonyl. Of several contributing effects, the predominant factor is probably steric hindrance of nucleophilic attack at the regioisomeric alkylation sites. The charge distribution in the intermediate π-allyl complex, which favors alkylation at the more substituted site, is not important. MoBI4 is less electronegative than molybdenum hexacarbonyl so there should be less charge on the allyl fragment. Equations 16–18 best illustrate this effect since the electronic properties of the substrate had less effect on the MoBI4-catalyzed reaction than on the molybdenum hexacarbonyl catalyzed one. Even the bias for internal attack by the small malonate nucleophile can be overcome. Combination of catalyst and substrate steric effects in eq 20 lead to formation of only the primary alkylation product **52**. The stability of the two possible metal–olefin (product) complexes should play a minor role. Alkylation at the more hindered site is favored because the less substituted olefin–metal complex is preferred on steric and electronic (better π-backbonding) grounds. The result in eq 6 could not be explained by this effect.



Returning to the differences among the various isonitrile complexes in Table V, it is interesting to speculate on the mechanistic cause of varying regiochemistry with changing ligand size. Ligand steric bulk may affect approach of the nucleophile (but only if the approach trajectory is proximal to a ligand) or it may affect coordination of the π-allyl. Coordination effects include rotation, cant, and asymmetry.[24,27,29] While effects due to rotation and cant appear to be so small to be inconsequential, asymmetric coordination may augment the basic steric preference for attack at the less substituted carbon to account for the differences between MoBI4 and molybdenum hexacarbonyl catalyzed reactions.

The most significant chemoselectivity result with the MoBI4 catalyst is the absence of isonitrile insertion products. Only alkylated products were isolated and in high yield. Thus MoBI4 joins a select group of zerovalent transition-metal isonitrile catalysts. For example, MoBI6 initiates the polymerization of methyl methacrylate in the presence of alkyl halides such as CCl_4.[30] Homoleptic chromium isonitrile complexes have been used for butadiene polymerization.[31] Copper(0) isonitrile complexes promote alkylations and cyclizations of alkyl halides.[32] Gold isonitrile complexes catalyze the aldol and related reactions.[33]

Chemoselectivity is exhibited in the presence of alkyl halides, allyl ethers, silyl ethers, and enol ethers. Enhanced chemoselectivity over molybdenum hexacarbonyl is seen in reactions involving acetonides and nitriles. The Lewis acidity of molybdenum hexacarbonyl[19,34] should be greatly attenuated in MoBI4 due to the better σ-donor isonitrile ligands. The tolerance of acetylenes is a particular advantage of MoBI4 catalysis. Molybdenum hexacarbonyl has been reported to effect acetylene trimerizations,[35] and molybdenum acetylene complexes are known.[36] It should also be noted that nucleophiles can add to isonitriles,[37] and condensation of dimethyl malonate with isonitriles is catalyzed by cobalt isonitrile complexes.[38] Such competing reactions were not observed here.

MoBI4-catalyzed allylic alkylations, like those catalyzed by molybdenum hexacarbonyl, are stereoselective for trans olefins. The MoBI4 reactions are modestly more selective (eqs 15 and 16). For disubstituted olefins the geometric selectivity ranges from 5:1 to 100:1. As in the case with many olefination reactions, conjugation to a phenyl group (eqs 4 and 21) or the presence of α-branching (eqs 18–20) greatly enhances selectivity for the trans olefin. Formation of trisubstituted olefins has shown varying selectivity depending upon substitution (cf. eq 20 vs 7).

As in other transition-metal-catalyzed allylic alkylations, formation of trans olefinic products reflects the thermodynamic preference for formation of syn-π-allylmolybdenum complexes over anti complexes. Interconversion between the two occurs via single bond rotation in a σ-allyl complex. Because this occurs via a 16-electron intermediate, it should be facilitated in the more electron rich isonitrile complex.

With regard to reactivity, MoBI4 is sensitive to the same substrate structural features as molybdenum hexacarbonyl and palladium catalysts. That is, substrates with monosubstituted olefins and tertiary leaving groups react much faster than substrates with trisubstituted olefins and primary leaving groups. The less substituted olefin facilitates coordination of the metal, while the tertiary leaving group facilitates oxidative addition, which has more S_N1 than S_N2 character. Sterically encumbered allylic compounds are poor substrates with MoBI4 as they are with other catalysts.

The stereochemistry proceeds with clean net retention of configuration. Two steps are involved in determining the overall stereochemistry—the oxidative addition and the reductive elimination or substitution. The net retention demands that both involve either retention or inversion processes. Analogy to the palladium-catalyzed reactions suggests the double inversion sequence.[1] Many of the ligand effects seen here and in our earlier studies are also best in accord with such an interpretation. Nevertheless, this question must now be considered open in light of the studies of Faller and Linebarrier[39] wherein they observed oxidative addition proceeded with retention suggesting a double retention mechanism. Since ligand environment has such a major effect on these molybdenum-catalyzed reactions, the quite different reaction conditions of Faller preclude any firm conclusions at this time.

Conclusions. Tetrakis(*tert*-butylisonitrile)dicarbonylmolybdenum(0) has been shown to be a superior catalyst compared to molybdenum hexacarbonyl. It has enhanced reactivity as well as chemo-, regio-, and stereoselectivity in allylic alkylation reactions. The catalyst is regioselective for alkylation at the less

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substituted allylic carbon due primarily to steric control. The product stereochemistry is that of net retention. The (bpy)Mo(CO)$_3$(CH$_3$CN) complex also proves to be an effective catalyst that provides complementary regioselectivity to that of MoBI4. The availability of these two new catalysts greatly enhances the utility of molybdenum-catalyzed allylic alkylations and allows their extension to new types of substrates.

Experimental Section

General Techniques. Reactions were generally run under a positive pressure of dry nitrogen in glassware which was flame dried under a stream of dry nitrogen. Anhydrous solvents or reaction mixtures were transferred by oven dried syringe or cannula. Solvents and reagents were generally distilled before use: acetonitrile, dichloromethane, dichloroethane, diisopropylamine, and dimethylformamide from calcium hydride; benzene, dioxane, ether, tetrahydrofuran (THF), and toluene from sodium benzophenone ketyl; pyridine and triethylamine from potassium hydroxide. Molybdenum hexacarbonyl was used as received as a gift from the Pressure Chemical Company. Sodium hydride was employed as a 50 wt % dispersion in mineral oil, and weights are recorded for the dispersion. Flash chromatography following the method of Still employed E. Merck silica gel Kieselgel 60, 200–400 mesh. Analytical thin-layer chromatograhy was performed with 0.2 mm coated commercial silica gel plates (E. Merck, DC-Plastikfolien, Kieselgel 60 F_{254}). Melting points were obtained on a Thomas-Hoover apparatus in open capillary tubes and are uncorrected. Boiling points are also uncorrected.

Proton nuclear magnetic resonance (^{1}H-NMR) spectra were recorded on a Bruker WP-200 (200 MH), Bruker WP-270 (270 MHz), or Bruker AM-500 (500 MHz) instrument. Chemical shifts are reported in delta (δ) units, parts per million (ppm) downfield from tetramethylsilane. Splitting patterns are designated as s, singlet; d, doublet; t, triplet; q, quartet; quin, quintet; m, multiplet; br, broad. Coupling constants are reported in hertz (Hz). Carbon-13 nuclear magnetic resonance (^{13}C-NMR) spectra were recorded on a Joel FX-60 (15 MHz), Joel FX-200 (50.1 MHz), or Bruker AM-500 (125 MHz) instrument and are reported in ppm relative to the center line of a triplet at 77.00 ppm for deuterochloroform. Molybdenum-95 nuclear magnetic resonance (^{95}Mo-NMR) spectra were recorded on a Bruker AM-360 instrument at 23.45 MHz. The spectra were taken at 300 K, with active temperature control and with broadband proton decoupling (WALTZ-16, using 1 W). Methylene chloride with 10% benzene-d_6 added for locking purposes and acetonitrile-d_3 were used as solvents. Acquisition times were typically twice the inverse of the expected line width, with a pulse angle of approximately 30° and no delay between scans. Chemical shifts are reported with respect to an external standard of Na_2MoO_4 in D_2O, pH 11, and are corrected for the difference in chemical shift between D_2O and the lock solvent used for each complex.

Infrared (IR) spectra were recorded in 0.1 mm path length sodium chloride cavity cells on a Beckman acculab 7, Perkin-Elmer 1420, or Mattson Polaris. Mass spectra (MS) were recorded on an AE1-MS902, Kratos MS25, or Kratos MS80 spectrometer at an ionizing current of 98 mA and an ionizing voltage of 70 eV, unless otherwise noted, and are reported as *m/e* (relative intensity). Microanalyses were performed by Spang Microanalytical Laboratories, Eagle Harbor, MI.

Preparation of Ligands. The ligands were prepared according to well-established literature procedures: *N,N'*-bis(cyclohexyl)ethylenediimine, mp 146–8 °C (lit.[40] mp 145–7 °C); *N,N'*-bis(*p*-tolyl)ethylenediimine, mp 162–5 °C (lit.[40] mp 164–5 °C); *N,N'*-bis(benzylidene)-ethylenediamine, mp 51–3 °C (lit.[41] mp 53–4 °C); *N,N'*-bis(furfurylidene)ethylenediamine, mp 53–54.5 °C (lit.[42] mp 53–4 °C).

Preparation of [*N,N'*-Bis(cyclohexyl)ethylenediimine]tetracarbonylmolybdenum(0) (2).[22] A solution of hexacarbonylmolybdenum (0.72 g, 2.73 mmol) and *N,N'*-bis(cyclohexyl)ethylenediimine (0.60 g, 2.72 mmol) in toluene (15 mL) was refluxed for 1.5 h. After cooling, the toluene was removed in vacuo. The solid was recrystallized from chloroform and hexane yielding 0.95 g (82%) of **2** as deep purple crystals: IR (CHCl$_3$) 2010, 1920, 1895, 1845, 1500 cm^{-1}; ^{1}H NMR (200 MHz, CDCl$_3$) δ 1.20–2.10 (20 H, m), 3.65–3.85 (2 H, m), 8.25 (2 H, s); ^{95}Mo NMR (23.45 MHz, CH$_2$Cl$_2$) δ −1209 (1/2 = 57 Hz); ^{95}Mo NMR (23.45 MHz, CH$_3$CN) δ −1240 (1/2 = 37 Hz). Anal. Calcd for $C_{18}H_{24}MoN_2O_4$: C, 50.48; H, 5.65; N, 6.54; MW, 428.0776. Found: C, 50.18; H, 5.43; N, 6.66; MW, 428.0790.

Preparation of [*N,N'*-Bis(*p*-tolyl)ethylenediimine]tetracarbonylmolybdenum(0) (3).[22] A solution of hexacarbonylmolybdenum (0.335 g, 1.27 mmol) and *N,N'*-bis(*p*-tolyl)ethylenediimine (0.300 g, 1.27 mmol) in toluene (10 mL) was refluxed for 1.5 h. The deep purple solution was cooled and concentrated to 5 mL. Hexane (5 mL) was added, and the resultant crystals were filtered and washed with hexane (10 mL) to yield 0.302 g (54%) of the product as deep purple crystals: IR (CHCl$_3$) 2010, 1930, 1865, 1500, 1455 cm^{-1}; ^{1}H NMR (200 MHz, CDCl$_3$) δ 2.35 (6 H, s), 6.66 (4 H, d, *J* = 8.5 Hz), 7.02 (4 H, d, *J* = 8.5 Hz), 7.58 (2 H, s); mass calcd for $C_{20}H_{16}{}^{100}MoN_2O_4$ 448.0182, found 448.0189.

Preparation of [*N,N'*-Bis(benzylidene)-1,2-ethylenediamine]tetracarbonylmolybdenum(0) (4). A solution of hexacarbonylmolybdenum (0.4073 g, 1.543 mmol) and *N,N'*-bis(benzylidene)-1,2-ethylenediamine (0.3646 g, 1.543 mmol) in toluene (10 mL) was refluxed for 1.5 h. After cooling, hexane (20 mL) was slowly added. The precipitated material was filtered, washed with hexane (10 mL), and dried in vacuo to yield 0.384 g (56%) of the product (1:4 mixture of trans–trans and cis–trans ligand isomers) as a yellow powder: IR (CHCl$_3$) 2010, 1910, 1880, 1835 cm^{-1}; ^{1}H NMR (200 MHz, CDCl$_3$) δ 4.00 (4 H, m), 7.46–7.60 (8 H, m), 7.90 and 8.05 (2 H, m), 8.73 and 8.79 and 9.05 (2 H, s, 2:1:2); ^{95}Mo NMR (23.45 MHz, CH$_2$Cl$_2$) δ −1153 ($\Delta\nu_{1/2}$ = 61 Hz). Anal. Calcd for $C_{20}H_{16}MoN_2O_4$: C, 54.07; H, 3.63; N, 6.31. Found: C, 52.91; H, 3.68; N, 6.42.

Preparation of [*N,N'*-Bis(furfurylidene)-1,2-ethylenediamine]tetracarbonylmolybenum(0) (5). Following the procedure for **3**, hexacarbonylmolybdenum (0.610 g, 2.31 mmol) and *N,N'*-bis(furfurylidene)ethylenediamine (0.500 g, 2.31 mmol) in toluene (7 mL) gave 0.913 g (93%) of the product (1:1 mixture of trans–trans and cis–trans ligand isomers) as an orange powder: IR (CHCl$_3$) 3020, 2010, 1900, 1875, 1825, 1625, 1470, 1395, 1150, 1020, 925, 885, cm^{-1}; ^{1}H NMR (200 MHz, CDCl$_3$) δ 3.98 (1.5 H, m), 4.12 (1.5 H, m) 4.2 (1 H, s), 6.63 (2 H, m), 6.95 (1.5 H, m), 7.60 and 7.65 and 7.75 (2.5 H, m), 8.40 (0.75 H, s), 8.55 (0.5 H, s), 8.67 (0.75 H, s); ^{95}Mo NMR (23.45 MHz, CH$_2$Cl$_2$) δ −1170 ($\Delta\nu_{1/2}$ = 150 Hz), −1165 ($\Delta\nu_{1/2}$ = 60 Hz), (3:1). Anal. Calcd for $C_{16}H_{12}MoN_2O_6$: C, 45.30; H, 2.85; N, 6.60.. Found: C, 45.27; H, 2.84; N, 6.74.

Preparation of (Acetonitrile)[*N,N'*-bis(cyclohexyl)ethylenediimine]-tricarbonylmolybdenum(0) (9). Hexacarbonylmolybdenum (0.538 g, 2.04 mmol) was refluxed in acetonitrile (5 mL) for 5 h. The yellow solution was cooled to room temperature, and *N,N'*-bis(cyclohexyl)ethylenediimine (0.449 g, 2.04 mmol) in acetonitrile (4 mL) was added. The resulting dark blue solution was concentrated to 2 mL. The precipitated product was filtered, washed with hexane (2 × 2 mL), and dried in vacuo to yield 0.511 g (57%) of the product as dark blue crystals: IR (CH$_3$CN) 1915, 1800 cm^{-1}; ^{1}H NMR (200 MHz, CD$_3$CN) δ 1.15–1.55 (8 H, m), 1.58–2.10 (12 H, m), 2.18 (3 H, s), 3.55–3.80 (2 H, m), 8.30 (2 H, s). Anal. Calcd for $C_{19}H_{27}MoN_3O_3$: C, 51.71; H, 6.17; N, 9.52. Found: C, 51.38; H, 6.15; N, 9.05.

Preparation of (Acetonitrile)[*N,N'*-bis(benzylidene)ethylenediamine]-tricarbonylmolybdenum(0) (10). Hexacarbonylmolybdenum (0.600 g, 2.27 mmol) was refluxed in acetonitrile (4 mL) for 5 h. The yellow solution was cooled to room temperature, and *N,N'*-bis(benzylidene)-ethylenediamine (0.537 g, 2.27 mmol) in acetonitrile (2 mL) was added. The resulting red solution was stirred for 10 min, stood for 45 min, and chilled at −20 °C overnight. The cold solvent was removed from the precipitated product, hexane (5 mL) was added, and the mixture was warmed to room temperature. The product was filtered, washed with hexane (2 × 2 mL), and dried in vacuo to yield 0.672 g (65%) of the product as red crystals: IR (CH$_3$CN) 1925, 1800 cm^{-1}; ^{1}H NMR (200 MHz, CD$_3$CN) δ 2.18 (3 H, s), 3.90 (4 H, s), 7.35–7.46 (6 H, m), 7.64–7.74 (4 H, m), 8.30 (2 H, s). Anal. Calcd for $C_{21}H_{14}MoN_3O_3$: C, 55.16; H, 4.19; N, 9.19. Found: C, 55.06; H, 4.08; N, 9.33.

Preparation of *cis*-Tetrakis(*tert*-butylisonitrile)dicarbonylmolybdenum (MoBI4) (15). In a modification of Albers and Coville's procedure,[13] a solution of hexacarbonylmolybdenum (0.792 g, 3.0 mmol) and cobalt dichloride dihydrate (0.050 g, 0.3 mmol) in toluene (10 mL) was refluxed for 5 min in an oil bath preheated to 120 °C. The purplish slurry was cooled to ca. 80 °C, and *tert*-butylisonitrile (1.50 g, 18.0 mmol) was added. After the vigorous evolution of gas subsided, the green solution was refluxed for 6 h. The solvent was removed in vacuo, and the green mixture was purified by flash chromatography (methylene chloride) collecting the second yellow band to elute. After concentration, the product was filtered through a plug of silic gel with methylene chloride, and the solvent was removed in vacuo yielding 0.952 g (66%) of MoBI4 as a yellow solid: IR (CHCl$_3$) 2980, 2130, 2090, 2030, 1870, 1820, 1370, 1210 cm^{-1}; lit.[9] ν(CN), 2140, 2092, 2055, 2025; ν(CO), 1864, 1818 cm^{-1}; ^{1}H NMR (270 MHz, CDCl$_3$) δ 1.42 (18 H, s), 1.45 (18 H, s); ^{95}Mo NMR (23.45 MHz, CH$_2$Cl$_2$) δ −1714 ($\Delta\nu_{1/2}$ = 6.2 Hz); MS mass calcd for $C_{22}H_{36}{}^{98}MoN_4O_2$ 486.1894, found 486.1886.

Preparation of *fac*-Tris(*n*-butylisonitrile)tricarbonylmolybdenum (16) and *cis*-Tetrakis(*n*-butylisonitrile)dicarbonylmolybdenum (17). Following the above procedure, hexacarbonylmolybdenum (0.528 g, 2.0 mmol), anhydrous cobalt dichloride (0.026 g, 0.2 mmol), and *n*-butylisonitrile

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(1.25 mL, 12 mmol) in toluene (8 mL) gave after purification by flash chromatography (75:25 methylene chloride–hexane) 0.089 g (10%) of the tris complex **16** as a colorless oil (R_f = 0.60) and 0.368 g (38%) of **17** as a yellow oil (R_f = 0.30). **16**: IR ($CHCl_3$) 2960, 2880, 2165, 2130, 1940, 1870 (br), 1440, 1360 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) δ 0.98 (9 H, t, J = 7.1 Hz), 1.43–1.59 (6 H, m), 1.69 (6 H, quin, J = 6.5 Hz), 3.54 (6 H, t, J = 6.5 Hz); ^{95}Mo NMR (23.45 MHz, CH_2Cl_2) δ −1791 ($\Delta\nu_{1/2}$ = 4.1 Hz); MS, mass calcd for $C_{18}H_{27}{}^{98}MoN_3O_3$ 431.1108, found 431.1099. **17**: IR ($CHCl_3$) 2960, 2880, 2150, 2090, 2060, 1875, 1830, 1450, 1350 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) δ 0.95 (6 H, t, J = 7.1 Hz), 0.96 (6 H, t, J = 7.1 Hz), 1.43–1.60 (4 H, m), 1.61–1.75 (4 H, m), 3.53 (8 H, t, J = 6.5 Hz); ^{95}Mo NMR (23.45 MHz, CH_2Cl_2) δ −1731 ($\Delta\nu_{1/2}$ = 4.3 Hz).

Preparation of *cis*-Tetrakis(phenylisonitrile)dicarbonylmolybdenum (18). By using the above procedure, hexacarbonylmolybdenum (0.792 g, 3.0 mmol) cobalt dichloride dihydrate (0.050 g, 0.3 mmol) and phenylisonitrile (2.00 g, 19 mmol) in toluene (10 mL) gave after 2 h reaction time, purification by flash chromatography (60:40 hexane–methylene chloride) and recrystallization (2:1 hexane–chloroform) of 0.934 g (55%) of **18** as a yellow powder: IR ($CHCl_3$) 2120, 2020, 1990, 1900 (br), 1590, 1485 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) δ 7.17–7.40 (20 H, m); ^{95}Mo NMR (23.45 MHz, CH_2Cl_2) δ −1699 ($\Delta\nu_{1/2}$ = 4.5 Hz); $Mo(CO)_3(CNPh)_3$ impurity observed at −1772 ppm.

Preparation of *fac*-Tris(2,6-dimethylphenylisonitrile)tricarbonylmolybdenum (19). Following the above procedure, hexacarbonylmolybdenum (0.528, 2.0 mmol), cobalt dichloride dihydrate (0.033 g, 0.2 mmol), and 2,6-dimethylphenylisonitrile (0.918 g, 7.0 mmol) in toluene (10 mL) gave after 15 min reaction time and after purification by flash chromatography (75:25 hexane–methylene chloride) (R_f = 0.25) 0.706 g (62%) of **19** as a bright yellow solid, mp 130 °C dec: IR ($CHCl_3$) 2130, 2065, 1950, 1900 (br) 1470 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) δ 2.43 (18 H, s), 7.02–7.12 (9 H, m); ^{95}Mo NMR (23.45 MHz, CH_2Cl_2) δ −1783 ($\Delta\nu_{1/2}$ = 1.6 Hz). Anal. Calcd for $C_{30}H_{27}MoN_3O_3$: C, 62.83; H, 4.74. Found: C, 63.07; H, 4.87.

Preparation of *cis*-Tetrakis(2,6-dimethylphenylisonitrile)dicarbonylmolybdenum (20). Following the above procedure, hexacarbonylmolybdenum (0.528 g, 2.0 mmol), cobalt dichloride dihydrate (0.033 g, 0.2 mmol), and 2,6-dimethylphenylisonitrile[43] (1.574 g, 12.0 mmol) in toluene (10 mL) gave, after purification by flash chromatography (75:25 hexane–methylene chloride) (R_f = 0.15) 0.296 g (22%) of **20** as a dark yellow solid: IR ($CHCl_3$) 3020, 2120, 2030, 2000, 1900, 1880, 1050, 930 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) δ 2.43 (12 H, s), 2.44 (12 H, s), 7.00–7.05 (12 H, m); ^{95}Mo NMR (23.45 MHz, CH_2Cl_2) δ −1711 ($\Delta\nu_{1/2}$ = 5.2 Hz). Anal. Calcd for $C_{38}H_{36}MoN_4O_2$: C, 67.45; H, 5.36. Found: C, 67.83; H, 5.43.

Preparation of *fac*-Tris(benzylisonitrile)tricarbonylmolybdenum (21). Following the above procedure, hexacarbonylmolybdenum (0.264 g, 1.0 mmol) and cobalt dichloride dihydrate (0.0166 g, 0.1 mmol) in toluene (5 mL) gave, after purification by flash chromatography (55:45 hexane–methylene chloride) (R_f = 0.18), 0.334 g (63%) of **21** as a light yellow solid: IR ($CHCl_3$) 2160, 2120, 1950, 1880, 1495, 1450, 1440, 1350 cm^{-1}; lit.[11] ν(CN), 2165, 2120; ν(CO), 1947, 1883 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) δ 4.78 (6 H, s), 7.32 (15 H, s); ^{95}Mo NMR (23.45 MHz, CH_2Cl_2) δ −1792 ($\Delta\nu_{1/2}$ = 3.8 Hz). Anal. Calcd for $C_{27}H_{21}MoN_3O_3$: C, 61.02; H, 3.98. Found: C, 60.83; H, 3.88.

Preparation of *cis*-Bis(methylisonitrile)tetracarbonylmolybdenum (22) and *fac*-Tris(methylisonitrile)tricarbonylmolybdenum (23). A solution of hexacarbonylmolybdenum (1.056 g, 4.0 mmol) and cobalt dichloride dihydrate (0.066 g, 0.4 mmol) in benzene (20 mL) was refluxed for 5 min in an oil bath preheated to 90 °C. The purplish slurry was cooled to ca. 70 °C, methylisonitrile[44] (1.4 mL, 27 mmol) (caution: extreme strench) was added, and the green solution was refluxed 8 h. The benzene was distilled, and the green mixture was purified by flash chromatography (70:30 gradient to 40:60 hexane–methylene chloride) to provide 0.448 g (39%) of the bis(methylisonitrile) complex **22** as white needles (150 °C dec, R_f 0.50) and 0.523 g (43%) of the tris(methylisonitrile) complex **23** as fine white needles (mp 177 °C dec, lit.[45] mp 177 °C, R_f 0.15). **22**: IR ($CHCl_3$) 2180, 2150, 2020, 1920 (br), 1415 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) δ 3.36 ($\Delta\nu_{1/2}$ = 1.6 Hz); ^{95}Mo NMR (23.45 MHz, CH_2Cl_2) δ −1829 ($\Delta\nu_{1/2}$ = 4.2 Hz). Anal. Calcd for $C_8H_6MoN_2O_4$: C, 33.13; H, 2.08; MW, 291.9388. Found: C, 33.33; H, 2.04; MW, 291.9396.

Molybdenum-Catalyzed Alkylation. General Procedure. Toluene was added to a flask containing sodium hydride (washed two times with hexane) followed by dropwise addition of the nucleophile to the stirred suspension. The mixture was heated at 100 °C for 15 min, and then the allylic substrate followed by the catalyst (10 to 20 mol %) were added. The reaction was heated at reflux until TLC indicated disappearance of starting material or no further progress of reaction after 24 h. The reaction was worked up by diluting the mixture with ether and washing the organic solution twice with 10% aqueous potassium hydroxide solution and once with saturated aqueous sodium chloride solution. The ether layer was dried over magnesium sulfate, and then the solvent was removed in vacuo. The crude product was purified by flash chromatography.

Alkylation of (2*R*,4*S*)-4-Isopropenyl-1-methylene-2-(phenylsulfonyl)-cyclohexane (24). Procedure 1. Following the general procedure, dimethyl malonate (0.132 g, 1.0 mmol), sodium hydride (0.0432 g, 0.9 mmol), allyl sulfone **24** (0.138 g, 0.5 mmol), and hexacarbonylmolybdenum (0.0264 g, 0.1 mmol) in toluene (4 mL) were combined, *tert*-butylisonitrile (46 μL, 0.4 mmol) was added, and the reaction was heated at reflux for 24 h. Standard workup and flash chromatography (92:8 hexane–ethyl acetate) yielded 0.107 g (80%) as a colorless oil identified by GC (180 °C, 25 m × 0.25 mm, SE-30) as a 79:21 mixture of **25** (2.52 min) and **26** (3.38 min). **25**: IR ($CDCl_3$) 1750, 1725, 1640, 1430 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) δ 1.18–1.40 (1 H, m), 1.57 (1 H, td, J = 12.8, 4.8 Hz), 1.69 (3 H, s), 1.65–1.80 (1 H, m), 1.80–1.95 (1 H, m), 2.15–2.30 (3 H, m), 3.22 (1 H, dm, J = 11.6 Hz), 3.66 (3 H, s), 3.75 (3 H, s) 3.82 (1 H, d, J = 11.9 Hz), 4.68 (1 H, s), 4.70 (1 H, s), 4.70 (1 H, s), 4.76 (1 H, s); ^{13}C NMR (125 MHz, $CDCl_3$) δ 168.6, 168.4, 148.9, 146.9, 111.3, 109.1, 53.8, 52.4, 52.2, 43.3, 39.2, 34.9, 32.8, 31.1, 20.8; calcd for $C_{15}H_{22}O_4$ 266.1518, found 266.1524.

Procedure 2. Following the general procedure, dimethyl malonate (0.132 g, 1.0 mmol), sodium hydride (0.0432 g, 0.9 mmol), allyl sulfone **24** (0.138 g, 0.5 mmol), and MoBl4 (0.0484 g, 0.1 mmol) in toluene (5 mL) were combined and heated at reflux for 10 h. Standard workup and flash chromatography (92:8 hexane–ethyl acetate) yielded 0.118 g (89%) of alkylated products (2*R*,4*S*)-2-[bis(methoxycarbonyl)methyl]-4-isopropenyl-1-methylenecyclohexane (**25**) and (4*S*)-4-isopropenyl-1-[2′,2-bis(methoxycarbonyl)ethyl]cyclohexene (**26**) as a colorless oil in a 69:31 ratio as determined by GC (180 °C, 25 m × 0.25 mm, SE-30).

Alkylation of 6-(Phenylsulfonyl)-1,7-(*E*)-nonadiene (27). Following the general procedure, dimethyl isobutylmalonate (0.188 g, 1.0 mmol), sodium hydride (0.0432 g, 0.9 mmol), allyl sulfone **27** (0.132 g, 0.5 mmol), and hexacarbonylmolybdenum (0.0264 g, 0.1 mmol) in toluene (3 mL) were combined, *tert*-butylisonitrile (46 μL, 0.4 mmol) was added, and the reaction was heated at reflux for 24 h. Standard workup and flash chromatography (93:7 hexane–ethyl acetate) yielded 0.111 g (72%) of **28** as the only detectable product by ^1H NMR: IR ($CDCl_3$) 1720, 1640, 1450, 1430, 1380 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) δ 0.80–0.93 (6 H, m), 1.05 (3 H, d, J = 6.8 Hz), 1.35–1.50 (2 H, m), 1.52–1.90 (3, H, m), 1.92–2.12 (4 H, m), 2.82 (1 H, quin, J = 6.8 Hz), 3.71 (6 H, s), 4.90–5.05 (2 H, m), 5.30 (1 H, dd, J = 15.5, 9.0 Hz), 5.37–5.50 (1 H, m), 5.70–5.84 (1 H, m); ^{13}C NMR (50.1 MHz, $CDCl_3$) δ 171.8, 171.3, 138.7, 131.8, 131.1, 114.4, 61.0, 51.5, 51.4, 43.2, 42.3, 33.1, 31.9, 28.7, 24.6, 24.1, 23.4, 17.5; mass calcd for $C_{18}H_{30}O_4$ 310.2144, found 310.2134.

Alkylation of 1-Methoxy-3-(phenylsulfonyl)-1-(*Z*)-butene with 2-(Methoxycarbonyl)cyclopentanone. Procedure 1. 2-(Methoxycarbonyl)cyclopentanone (0.142 g, 1.0 mmol) was added to a suspension of sodium hydride (0.0432 g, 0.9 mmol) (washed with 1 mL of hexane) in toluene (4 mL). The solution was warmed to 100 °C and stirred 15 min. Then 1-methoxy-3-(phenylsulfonyl)-1-(*Z*)-butene (0.113 g, 0.5 mmol) and hexacarbonylmolybdenum (0.0264 g, 0.1 mmol) were added, and the solution was refluxed 24 h. The mixture was added to ether (30 mL) and washed with 10% aqueous potassium hydroxide solution (2 × 30 mL) and saturated aqueous sodium chloride solution (30 mL). The ether solution was dried ($MgSO_4$), and the solvent was removed in vacuo. The crude material was purified by flash chromatography (90:10 hexane–ethyl acetate) to yield 0.046 g (41%) of 2-(methoxycarbonyl)-2-(1′-methoxy-2′-(*E*)-buten-1′-yl)cyclopentanone (**I**) (1:1 diasteromeric mixture by ^1H NMR) and 0.031 g (27%) of 2-(methoxycarbonyl)-2-(1′-methoxy-1′-buten-3′-yl)cyclopentanone (**II**) (ca. 1:1:1:1 isomeric mixture of *E* and *Z* olefins and diastereomers of each by ^1H NMR) as colorless oils.

Procedure 2. Following the general procedure, 2-carbomethoxycyclopentanone (0.142 g, 1.0 mmol), sodium hydride (0.0432 g, 0.9 mmol), 1-methoxy-3-(phenylsulfonyl)-1-(*Z*)-butene (0.113 g, 0.5 mmol), and MoBl4 (0.0484 g, 0.1 mmol) in toluene (4 mL) were combined and heated at reflux for 24 h. As TLC indicated remaining starting material, another portion of MoBl4 (0.0484 g, 0.1 mmol) was added, and the reaction was refluxed an additional 12 h. Standard workup and flash

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chromatography (90:10 hexane–ethyl acetate) yielded 0.026 g (23%) of one diastereomer of **1** and 0.019 g (17%) of the other diastereomer of **1** and 5% of the regioisomer **11** as colorless oils for an overall 93(1.6:1):7 ratio of **1** and **11**. **1**: IR ($CHCl_3$) 1750, 1715, 1450, 1435 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) major diastereomer δ 1.72 (3 H, dd, J = 6.5, 1.5 Hz), 1.84–2.08 (2 H, m), 2.15–2.51 (4 H, m), 3.17 (3 H, s), 3.67 (3 H, s), 4.28 (1 H, d, J = 8.0 Hz), 5.23 (1 H, ddq, J = 15.4, 8.0, 1.5 Hz), 5.77 (1 H, dq, (1 H, dq, J = 15.4, 6.5 Hz); ^1H NMR (270 MHz, $CDCl_3$) minor diastereomer δ 1.71 (3 H, dd, J = 6.5, 1.5 Hz), 1.88–2.00 (2 H, m), 2.05–2.65 (4 H, m), 3.23 (3 H, s), 3.73 (3 H, s), 4.25 (1 H, d, J = 8.0 Hz), 5.33 (1 H, ddq, J = 15.4, 8.0, 1.5 Hz), 5.73 (1 H, dq, J = 15.4, 6.5 Hz); ^{13}C NMR (50.1 MHz, $CDCl_3$) δ 212.7, 212.3, 169.5, 168.7, 132.1, 130.9, 126.3, 126.1, 83.7, 83.1, 65.7, 65.3, 56.6, 56.5, 52.5, 52.4, 39.0, 38.8, 33.2, 28.2, 26.9, 19.9, 17.7, 17.2; mass calcd for $C_{12}H_{18}O_4$ 226.1205, found 226.1210. **11**: IR ($CHCl_3$) 1720 (br), 1435, 1150 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) 1:1:1:1 mixture of E and Z olefins and diastereomers of each, δ 0.95–1.0 (3 H, m), 1.65–2.55 (6 H, m), 3.47 (1.5 H, s), 3.55 (0.75 H, s), 3.57 (0.75 H, s), 3.65–3.73 (3 H, m), 4.15 (0.25 H, dd, 10.2, 6.3 Hz), 4.28 (0.25 H, dd, 10.2, 6.3 Hz), 4.48 (0.25 H, dd, 12.6, 9.6 Hz), 4.53 (0.25 H, dd, 12.6, 9.0 Hz), 5.86 (0.25 H, d, 6.3 Hz), 5.88 (0.25 H, d, 6.3 Hz), 6.28 (0.25 H, d, 12.6 Hz), 6.35 (0.25 H, d, 12.6 Hz); mass calcd for $C_{12}H_{18}O_4$ 226.1205, found 226.1207.

Alkylation of 1-Chloro-4-(phenylsulfonyl)-(*E*)-5-heptene. Following the general procedure, dimethyl allylmalonate (0.172 g, 1.0 mmol), sodium hydride (0.0432 g, 0.9 mmol), 1-chloro-4-(phenylsulfonyl)-5-(*E*)-heptene (0.136 g, 0.5 mmol), and MoBl4 (0.0484 g, 0.1 mmol) in toluene (4 mL) were combined and heated at reflux for 8 h. Standard workup and flash chromatography (95:5 hexane–ethyl acetate) yielded 0.127 g (84%) of 4,4-bis(methoxycarbonyl)-10-chloro-5-methyl-(*E*)-1,6-decadiene and a trace of the regioisomeric product as a colorless oil: IR ($CHCl_3$) 3030, 2950, 1730, 1640, 1440 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) δ 1.08 (3 H, d, J = 7.1 Hz), 1.82 (2 H, quin, J = 6.5 Hz), 2.11–2.21 (2 H, m), 2.55–2.70 (2 H, m), 2.83 (2 H, quin, J = 7.1 Hz), 3.52 (2 H, t, J = 6.5 Hz), 3.71 (3 H, s), 3.72 (3 H, s), 5.00–5.15 (2 H, m), 5.33–5.53 (2 H, m), 5.65–5.85 (1 H, m); ^{13}C NMR (50.1 MHz, $CDCl_3$) **142** δ 170.7, 170.6, 133.3, 132.1, 130.2, 118.1, 61.8, 51.7, 44.0, 41.1, 38.6, 32.1, 29.5, 17.0. Anal. Calcd for $C_{15}H_{23}ClO_4$: C, 59.50; H, 7.66; MW, 303.1363. Found: C, 59.85; H, 8.01; MW, 303.1369.

Alkylation of 3-Methyl-3-(phenylsulfonyl)-8-(trimethylsilyl)oct-1-en-7-yne with 2-(Methoxycarbonyl)cyclopentanone. Following the general procedure, 2-(methoxycarbonyl)cyclopentanone (0.142 g, 1.0 mmol), sodium hydride (0.0432 g, 0.9 mmol), 3-methyl-3-(phenylsulfonyl)-8-(trimethylsilyl)oct-1-en-7-yne (0.167 g, 0.5 mmol), and MoBl4 (0.0484 g, 0.1 mmol) in toluene (4 mL) were combined and heated at reflux for 24 h. Standard workup and flash chromatography (95:5 hexane–ethyl acetate) yielded 0.112 g (67%) of alkylated product as a colorless oil which GC indicated was a 78:22 E:Z ratio (220 °C, 25 m × 0.25 mm SE-30): IR ($CHCl_3$) 2950, 2170, 1750, 1720, 1435 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) δ 0.15 (9 H, s), 1.53–1.68 (2 H, m), 1.61 (2.3 H, s), 1.69 (0.7 H, s), 1.85–2.52 (11 H, m), 2.63 (0.8 H, dd, J = 14.2, 7.7 Hz), 3.70 (3 H, s), 4.98–5.09 (1 H, m); ^{13}C NMR (50.1 MHz, $CDCl_3$) E, δ 214.4, 171.4, 138.2, 119.2, 107.1, 84.6, 60.3, 52.3, 38.6, 38.1, 32.1, 32.0, 26.7, 19.6, 19.1, 16.0, 0.1; ^{13}C NMR (50.1 MHz, $CDCl_3$) Z, partial, δ 214.2, 171.4, 138.4, 119.7, 31.7, 30.8, 23.4; vinyl methyl ^{13}C resonance from INEPT experiment E, 15.9; Z, 23.4. Anal. Calcd for $C_{19}H_{30}O_3Si$: C, 68.22; H, 9.04; MW, 319.1729. Found: C, 68.54; H, 9.26; MW, 319.1734.

Alkylation of Ethyl Cyanoacetate with 1,1-Dimethylallyl Phenyl Sulfone. Following the general procedure, ethyl cyanoacetate (0.226 g, 2.0 mmol), sodium hydride (0.0864 g, 1.8 mmol), 3-methyl-3-(phenylsulfonyl)-1-butene (0.210 g, 1.0 mmol), and MoBl4 (0.0484 g, 0.1 mmol) in toluene (6 mL) were combined and heated at reflux for 10 h. Standard workup and flash chromatography (93:7 hexane–ethyl acetate) yielded 0.045 g (25%) of the monoalkylated product (**1**) and 0.048 g (38%) of the dialkylated product (**11**) as colorless oils. **1**: IR ($CHCl_3$) mixture 2240, 1740 (br), 1440, 1365 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) δ 1.32 (3 H, t, J = 7.1 Hz), 1.67 (3 H, s), 1.78 (3 H, s), 2.65 (2 H, t, J = 7.1 Hz), 3.49 (1 H, t, J = 7.1 Hz), 4.26 (2 H, q, J = 7.1 Hz), 5.17 (1 H, t, J = 7.1 Hz); mass calcd for $C_{10}H_{15}NO_2$ 181.1099, found 181.1102. **11**: IR ($CHCl_3$) 2240, 1740, 1620, 1450, 1380 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) δ 1.29 (3 H, t, J = 7.1 Hz), 1.65 (6 H, s), 1.74 (6 H, s), 2.51 (2 H, dd, J = 14.2, 7.1 Hz), 2.62 (2 H, dd, J = 14.2, 7.1 Hz), 4.22 (2 H, q, J = 7.1 Hz), 5.18 (2 H, t, J = 7.1 Hz). Anal. Calcd for $C_{15}H_{23}NO_2$: C, 72.25; H, 9.30; MW, 249.1729. Found: C, 72.55; H, 9.04; MW, 249.1730.

Cyclization of 1,1,5-Tris(phenylsulfonyl)-(*E*)-6-octene (30). 1,1,5-Tris(phenylsulfonyl)-6-(*E*)-octene (0.213 g, 0.4 mmol) was added to a suspension of sodium hydride (0.0192 g, 0.4 mmol) (washed with 0.5 mL hexane) in toluene (4 mL). The solution was warmed to 100 °C and stirred for 15 min. Then MoBl4 (0.0388 g, 0.08 mmol) was added, and the solution was refluxed for 24 h. Standard workup, purification by flash chromatography (80:20 hexane–ethyl acetate), and recrystallization (80:20 hexane–chloroform) yielded 0.069 g (44%, 82% based on recovered starting material) of cyclopentane **30** as white crystals, mp 176–178 °C, and 0.099 g (45%) of starting material: IR ($CHCl_3$) 3010, 2960, 1515, 1440, 1325, 1305, 1135, 1070, 1040, 925 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) δ 1.45 (3 H, d, J = 6.6 Hz), 1.50–1.75 (1 H, m), 1.85–2.10 (3 H, m), 2.48–2.75 (2 H, m), 3.20–3.34 (1 H, m), 4.99 (1 H, dqd, J = 15.2, 6.6, 0.9 Hz), 5.65 (1 H, ddq, J = 15.2, 7.6, 1.5 Hz), 7.45–7.78 (6 H, m), 8.04–8.21 (4 H, m). Anal. Calcd for $C_{20}H_{22}O_4S_2$: C, 61.51; H, 5.68; MW (M + 1), 391.1038. Found: C, 61.39; H, 5.90; MW (M + 1), 391.1034.

Alkylation of 2-(Methoxycarbonyl)cyclopentanone with Crotyl Acetate. Following the general procedure, 2-(methoxycarbonyl)cyclopentanone (0.284 g, 2.0 mmol), sodium hydride (0.0864 g, 1.8 mmol), crotyl acetate (0.114 g, 1.0 mmol), and $Mo(CO)_3(CH_3CN)$bipy (**7**) (0.0377 g, 0.1 mmol) in toluene (6 mL) were combined and heated at reflux for 24 h. Standard workup and flash chromatography (9:1 hexane–ethyl acetate) yielded 0.171 g (87%) of a 67:5:28 mixture of (*E*)-**40**:(*Z*)-**40**:**41** as determined by GC (120 °C, 25 m × 0.25 mm SE-30): IR ($CHCl_3$) mixture 2950, 1750, 1720, 1435, 1150, 970 cm^{-1}; spectral data for (*E*)-**40** ^1H NMR (270 MHz, $CDCl_3$) δ 1.65 (3 H, dd, J = 6.5, 1.5 Hz), 1.80–2.55 (7 H, m), 2.60 (1 H, dd, J = 13.9, 7.1 Hz), 3.71 (3 H, s), 5.21–5.35 (1 H, m), 5.52 (1 H, dq, J = 15.1, 6.5 Hz); ^{13}C NMR (50.1 MHz, $CDCl_3$) δ 214.0, 171.2, 129.4, 125.1, 60.0, 52.1, 37.8, 36.4, 31.8, 19.2, 17.6; partial spectral data for (*Z*)-**40** ^{13}C NMR (50.1 MHz, $CDCl_3$) δ 127.5, 124.2, 31.9, 30.6, 12.6; mass calcd for $C_{11}H_{16}O_3$ 196.1100, found 196.1099; partial spectral data for **41** (1:1 diastereomeric mixture) ^1H NMR (270 MHz, $CDCl_3$) δ 0.97 (1.5 H, d, J = 7.1 Hz), 1.00 (1.5 H, d, J = 6.8 Hz), 1.80–2.55 (16 H, m), 3.08–3.18 (1 H, m), 3.71 (3 H, s), 5.00–5.12 (1 H, m), 5.55–5.73 (1 H, m); ^{13}C NMR (50.1 MHz, $CDCl_3$) δ 213.4, 213.3, 170.2, 170.1, 138.9, 138.2, 116.6, 115.6, 64.7, 64.3, 52.2, 41.3, 38.7, 38.5, 28.3, 28.0, 19.5, 19.3, 14.96, 14.8.

Alkylation of Dimethyl Malonate with Linalyl Acetate. Following the general procedure, dimethyl malonate (0.264 g, 2.0 mmol), sodium hydride (0.0864 g, 1.8 mmol), linalyl acetate (0.196 g, 1.0 mmol), and $Mo(CO)_3(CH_3CN)$bipy (**14**) (0.377 g, 0.1 mmol) in toluene (10 mL) were combined and heated at reflux for 24 h. Standard workup and flash chromatography (95:5 hexane–ethyl acetate) yielded 0.121 g (45%) of a 62:22:16 mixture of (*E*)-**42**:(*Z*)-**42**:**43**[45] as determined by GC (180 °C, 25 m × 0.25 mm, (SE-30)).

Alkylation of Dimethyl Methylmalonate with 1-(3′-Furyl)allyl Acetate. Procedure 1. Following the general procedure, dimethyl methylmalonate (0.234 g, 1.6 mmol), sodium hydride (0.0691 g, 1.4 mmol), the (3′-furyl)allyl acetate (0.133 g, 0.8 mmol), and $Mo(CO)_3(CH_3CN)$bipy (**7**) (0.0302 g, 0.08 mmol) in toluene (4 mL) were combined and heated at reflux for 1.5 h. Standard workup and flash chromatography (90:10 hexane–ethyl acetate) yielded 0.148 g (73%) of a 87:13 (by ^1H NMR) mixture of **45** and (*E*)-**44**.

Procedure 2. Following the general procedure, dimethyl methylmalonate (0.234 g, 1.6 mmol), sodium hydride (0.0691 g, 1.4 mmol), (3′-furyl)allyl acetate (0.133 g, 0.8 mmol), and MoBl4 (0.388 g, 0.08 mmol) in toluene (4 mL) were combined and heated at reflux for 1.5 h. Standard workup and flash chromatography (90:10 hexane–ethyl acetate) yielded 0.183 g (90%) of a 78(9:1 *E*:*Z*):22 (by ^1H NMR) mixture of **44** and **45**: IR ($CHCl_3$) mixture 1735, 1440 cm^{-1}; (*E*)-**44**, ^1H NMR (270 MHz, $CDCl_3$) δ 1.43 (3 H, s), 2.72 (2 H, dd, J = 7.4, 1.2 Hz), 3.73 (6 H, s), 5.79 (1 H, dt, J = 15.4, 7.4 Hz), 6.30 (1 H, dt, J = 15.4, 1.2 Hz), 6.49 (1 H, s), 7.27–7.37 (2 H, m); ^{13}C NMR (50.1 MHz, $CDCl_3$) δ 172.0, 143.2, 139.8, 123.8, 123.6, 123.4, 107.4, 53.8, 52.2, 39.2, 19.7; (*Z*)-**44**, ^1H NMR (270 MHz, $CDCl_3$) δ 1.42 (3 H, s), 2.88 (2 H, dd, J = 7.1, 1.8 Hz), 3.74 (6 H, s), 5.42 (1 H, dt, J = 11.6, 7.1 Hz); ^{13}C NMR (50.1 MHz, $CDCl_3$) δ 170.2, 142.7, 140.8, 124.6, 121.8, 110.6, 45.6, 34.8, 13.4; mass calcd for $C_{13}H_{16}O_5$ 252.0998, found 252.0995; **45**, ^1H NMR (270 MHz, $CDCl_3$) δ 1.41 (3 H, s), 3.67 (3 H, s), 3.70 (3 H, s), 4.12 (1 H, d, J = 8.6 Hz), 5.09–5.18 (2 H, m), 6.09 (1 H, ddd, J = 17.5, 9.8, 8.6 Hz), 6.30 (1 H, s), 7.26–7.29 (1 H, m), 7.33–7.35 (1 H, m); ^{13}C NMR (50.1 MHz, $CDCl_3$) δ 171.2, 171.0, 142.3, 140.6, 136.0, 122.6, 117.5, 110.8, 58.3, 52.2, 45.4, 17.6; mass calcd for $C_{13}H_{16}O_5$ 252.0998, found 252.0998.

Alkylation of Dimethyl Methylmalonate with 1-(2′-Furyl)allyl Acetate. Procedure 1. With catalyst **7**: Following the general procedure, dimethyl methylmalonate (0.234 g, 1.6 mmol), sodium hydride (0.0691 g, 1.4 mmol), 1-(2′-furanyl)-prop-2-en-1-yl acetate[47] (**32**) (0.133 g, 0.8 mmol), and $Mo(CO)_3(CH_3CN)$bipy (**14**) (0.0302 g, 0.08 mmol) in toluene (4 mL) were combined and heated at reflux for 3 h. Standard workup provided red crystals in an oil. The red crystals were separated by filtration and washing with ether to provide 8.3 mg (28%) of $Mo(CO)_4$bipy as identified by IR spectroscopy.[5a] The oil was purified by flash chromatography (90:10 hexane–ethyl acetate) to yield 0.156 g

(77%) of a 80:20 mixture (by ^{1}H NMR) of **47** and (*E*)-**46**.

Procedure 2. With MoBl4: Following the general procedure, dimethyl methylmalonate (0.234 g, 1.6 mmol), sodium hydride (0.0691 g, 1.4 mmol), and 2'-furylallyl acetate (0.133 g, 0.8 mmol), and MoBl4 (0.0388 g, 0.08 mmol) in toluene (4 mL) were combined and heated at reflux for 3 h. Standard workup and flash chromatography (90:10 hexane–ethyl acetate) yielded 0.160 g (79%) of a 90(5:1 *E*:*Z*):10 mixture (by ^{1}H NMR) of **46**:**47**: IR ($CHCl_3$) mixture 1740, 1440 cm^{-1}; (*E*)-**46**, ^{1}H NMR (270 MHz, $CDCl_3$) δ 1.44 (3 H, s), 2.74 (2 H, dd, J = 7.7, 1.2 Hz), 3.73 (6 H, s), 6.0 (1 H, dt, J = 15.5, 7.7 Hz), 6.15–6.19 (1 H, m), 6.28 (1 H, dt, J = 15.5, 1.2 Hz), 6.32–6.36 (1 H, m), 7.29–7.33 (1 H, m); ^{13}C NMR (50.1 MHz, $CDCl_3$) δ 172.0, 152.3, 141.6, 122.6, 122.3, 111.0, 107.1, 53.7, 52.4, 39.1, 19.8; (*Z*)-**46**, ^{1}H NMR (270 MHz, $CDCl_3$) δ 1.45 (3 H, s), 3.11 (2 H, dd, J = 7.7, 1.6 Hz), 3.71 (6 H, s), 5.40 (1 H, dt, J = 11.9, 7.4 Hz); ^{13}C NMR (50.1 MHz, $CDCl_3$) δ 172.2, 152.5, 123.3, 120.0, 109.9, 53.4, 34.9; mass calcd for $C_{13}H_{16}O_5$ 252.0998, found 252.0998; **47**, ^{1}H NMR (270 MHz, $CDCl_3$) δ 1.43 (3 H, s), 3.67 (3 H, s), 3.72 (3 H, s), 4.35 (1 H, d, J = 8.6 Hz), 5.17 (1 H, d, J = 18.4 Hz), 5.19 (1 H, d, J = 10.4 Hz), 6.09 (1 H, ddd, J = 18.4, 10.4, 8.6 Hz), 6.11–6.15 (1 H, m), 6.27–6.31 (1 H, m), 7.30–7.35 (1 H, m); ^{13}C NMR (50.1 MHz, $CDCl_3$) δ 170.8, 170.6, 152.6, 141.6, 133.8, 118.6, 110.0, 107.9, 58.0, 52.4, 47.9, 17.3; mass calcd for $C_{13}H_{16}O_5$: 252.0998, found 252.0997.

Alkylation of Dimethyl Methylmalonate with 1-(3,4-Dihydro-2*H*-pyran-6-yl)allyl Acetate. Procedure 1. With catalyst **7**: Following the general procedure, dimethyl methylmalonate (0.234 g, 1.6 mmol), sodium hydride (0.0691 g, 1.4 mmol), the allyl acetate[47] (0.146 g, 0.8 mmol), and $Mo(CO)_3(CH_3CN)$bipy (**7**) (0.0302 g, 0.08 mmol) in toluene (4 mL) were combined and heated at reflux for 1.5 h. Standard workup and flash chromatography (90:10 hexane–ethyl acetate) yielded 0.206 g (96%) of a 60:40 mixture (by ^{1}H NMR) of **49**:(*E*)-**48**.

Procedure 2. With MoBl4: Following the general procedure, dimethyl methylmalonate (0.234 g, 1.6 mmol), sodium hydride (0.0691 g, 1.4 mmol), 1-(3,4-dihydro-2*H*-pyran-6-yl)prop-2-en-1-yl acetate[47] (**38**) (0.146 g, 0.8 mmol), and MoBl4 (0.0388 g, 0.08 mmol) in toluene (4 mL) were combined and heated at reflux for 1 h. Standard workup and flash chromatography (90:10 hexane–ethyl acetate) yielded 0.159 g (74%) of a 96 (15:1:*E*:*Z*):4 mixture (by ^{1}H NMR) of **48** and **49**: IR ($CHCl_3$) mixture 3030, 2950, 1730, 1440 cm^{-1}; (*E*)-**48**, ^{1}H NMR (270 MHz, $CDCl_3$) δ 1.40 (3 H, s), 1.75–1.88 (2 H, m), 2.05–2.15 (2 H, m), 2.64 (2 H, d, J = 6.2 Hz), 3.72 (6 H, s), 4.02 (2 H, t, J = 5.1 Hz), 4.70 (1 H, t, J = 4.0 Hz), 5.65–5.83 (2 H, m); ^{13}C NMR (50.1 MHz, $CDCl_3$) δ 172.0, 150.5, 129.9, 121.3, 101.6, 65.7, 53.7, 52.2, 38.6, 22.2, 20.6, 19.6; (*Z*)-**48**, ^{1}H NMR (270 MHz, $CDCl_3$) δ 1.42 (3 H, s), 3.05 (2 H, d, J = 8.0 Hz), 3.74 (6 H, s), 4.75 (1 H, t, J = 4.0 Hz); mass calcd for $C_{14}H_{20}O_5$ 268.1311, found 268.1300; **49**, ^{1}H NMR (270 MHz, $CDCl_3$) δ 1.45 (3 H, s), 1.70–1.85 (2 H, m), 1.97–2.05 (2 H, m), 3.54 (1 H, d, J = 8.6 Hz), 3.69 (3 H, s), 3.72 (3 H, s), 3.85–3.93 (2 H, m), 3.63 (1 H, t, J = 3.7 Hz), 5.10–5.25 (2 H, m), 5.98 (1 H, ddd, J = 17.2, 10.4, 8.6 Hz); ^{13}C NMR (50.0 MHz, $CDCl_3$) δ 171.5, 171.1, 152.0, 134.7, 117.4, 99.3, 65.9, 56.9, 53.4, 52.0, 51.9, 21.9, 20.1, 18.2; mass calcd for $C_{14}H_{20}O_5$ 268.1311, found 268.1289.

Alkylation of (4*S*)-2,2-Dimethyl-4-(3'-acetoxyprop-(*E*)-1'-en-1'-yl)-1,3-dioxolane. Procedure 1. With dimethyl malonate: Following the general procedure, dimethyl malonate (0.132 g, 1.0 mmol), sodium hydride (0.0432 g, 0.9 mmol), the title allyl acetate (**20**) (0.100 g, 0.5 mmol), and MoBl4 (0.484 g, 0.1 mmol) in toluene (6 mL) were combined and heated at reflux for 4 h. Standard workup and flash chromatography (80:20 hexane–ethyl acetate) yielded 0.090 g (66%) of **50** (R = H) as a colorless oil: IR ($CHCl_3$) 1730, 1440, 1230, cm^{-1}; ^{1}H NMR (270 MHz, $CDCl_3$) δ 1.37 (3 H, s), 1.41 (3 H, s), 2.65 (2 H, t, J = 7.7 Hz), 3.45 (1 H, t, J = 7.7 Hz), 3.54 (1 H, t, J = 7.9 Hz), 3.73 (3 H, s), 3.74 (3 H, s), 4.06 (1 H, dd, J = 8.0, 6.2 Hz), 4.45 (1 H, q, J = 6.8 Hz), 5.56 (1 H, dd, J = 15.1, 7.1 Hz), 5.74 (1 H, dt, J = 15.1, 7.7 Hz); mass calcd for $C_{12}H_{17}O_6$ (M – CH_3) 257.1025, found 257.1016.

Procedure 2. With dimethyl allylmalonate: Following the general procedure, dimethyl allymalonate (0.172 g, 1.0 mmol), sodium hydride (0.0432 g, 0.9 mmol), the title allyl acetate (0.100 g, 0.5 mmol), and MoBl4 (0.484 g, 0.1 mmol) in toluene (4 mL) were combined and heated at reflux for 1.5 h. Standard workup and flash chromatography (85:15 hexane–ethyl acetate) yielded 0.101 g (65%) of **50** (R = CH_2=$CHCH_2$) as a colorless oil: $[\alpha]^{24}_{589}$ = 18.8° (*c* 1.17, $CHCl_3$); IR ($CHCl_3$) 1730, 1440, 1380 cm^{-1}; ^{1}H NMR (270 MHz, $CDCl_3$) δ 1.37 (3 H, s), 1.41 (3 H, s), 2.60–2.73 (4 H, m), 3.53 (1 H, t, J = 8.0 Hz), 3.71 (6 H, s), 4.06 (1 H, dd, J = 8.0, 6.2 Hz), 4.46 (1 H, q, J = 6.8 Hz), 5.10 (1 H, d, J = 15.7 Hz), 5.11 (1 H, d, J = 12.2 Hz), 5.48–5.62 (3 H, m); mass calcd for $C_{16}H_{24}O_6$ 312.1572, found 312.1573.

Alkylation of Dimethyl Malonate with 4*S*-(*tert*-Butyldimethylsiloxy)but-2(*E*)-enyl Acetate. Following the general procedure, dimethyl malonate (0.132 g, 1.0 mmol), sodium hydride (0.0432 g, 0.9 mmol), the title allyl acetate (0.129 g, 0.5 mmol), and MoBl4 (0.0484 g, 0.1 mmol) in toluene (6 mL) were combined and heated at reflux for 6 h. Standard workup and flash chromatography (93:7 hexane–ethyl acetate) yielded 0.136 g (82%) of **51** as a colorless oil: $[\alpha]^{23}_{589}$ = 1.68° (*c* 1.43, $CHCl_3$); IR ($CHCl_3$) 1735, 1450, 1260 cm^{-1}; ^{1}H NMR (270 MHz, $CDCl_3$) δ 0.03 (3 H, s), 0.04 (3 H, s), 0.88 (9 H, s), 1.16 (3 H, d, J = 6.2 Hz), 2.62 (2 H, t, J = 6.7 Hz), 3.43 (1 H, t, J = 7.5 Hz), 3.72 (3 H, s), 3.73 (3 H, s), 4.19–4.27 (1 H, m), 5.45–5.63 (2 H, m). Anal. Calcd for $C_{16}H_{30}O_5Si$: C, 58.15; H, 9.15; MW (M – 1), 329.1784. Found: C, 58.41; H, 9.36; MW (M – 1), 329.1779.

Alkylation of Dimethyl Malonate with 1-(3'-Cyclohexenyl)-2-methyl-2-propenyl Acetate. Following the general procedure, dimethyl malonate (0.066 g, 0.5 mmol), sodium hydride (0.0216 g, 0.45 mmol), 1-(cyclohex-3'-enyl)-2-methylprop-2-enyl acetate[44] (**211**) (0.0486 g, 0.25 mmol), and MoBl4 (0.0242 g, 0.05 mmol) in toluene (3 mL) were combined and heated at reflux for 24 h. As TLC indicated remaining starting material, another portion of MoBl4 (0.0242 g, 0.05 mmol) was added, and the reaction was refluxed 24 h. Standard workup and flash chromatography (95:5 hexane–ethyl acetate) yielded 0.0319 g (48%) of **52** as a colorless oil: IR ($CHCl_3$) 1740, 1440, 1230 cm^{-1}; ^{1}H NMR (270 MHz, $CDCl_3$) δ 1.23–1.43 (1 H, m), 1.55–1.80 (2 H, m), 1.65 (3 H, s), 1.95–2.13 (3 H, m), 2.35–2.51 (1 H, m), 2.58 (2 H, d, J = 8.0 Hz), 3.58 (1 H, t, J = 8.0 Hz), 3.71 (6 H, s), 5.10 (1 H, d, J = 8.9 Hz), 5.66 (2 H, s); ^{13}C NMR (50.1 MHz, $CDCl_3$) δ 169.4, 133.2, 129.7, 126.9, 126.1, 52.2, 50.8, 38.7, 32.7, 31.5, 28.7, 24.6, 15.7; mass calcd for $C_{15}H_{22}O_4$ 266.1518, found 266.1514.

Alkylation of Dimethyl Propargylmalonate with 3-Acetoxy-3-phenyl-1-propene. Following the general procedure, dimethyl propargylmalonate (0.272 g, 1.6 mmol), sodium hydride (0.0691 g, 1.4 mmol), 3-acetoxy-3-phenyl-1-propene (0.141 g, 0.8 mmol) and MoBl4 (0.0388 g, 0.08 mmol) in toluene (4 mL) were combined and heated at reflux for 2 h. Standard workup and flash chromatography (93:7 hexane–ethyl acetate) yielded 0.119 g (52%) of **53** as a colorless oil: IR ($CHCl_3$) 3310, 1735, 1600, 1430, 1300 cm^{-1}; ^{1}H NMR (270 MHz, $CDCl_3$) δ 2.07 (1 H, t, J = 2.7 Hz), 2.85 (2 H, d, J = 2.7 Hz), 2.97 (2 H, d, J = 7.7 Hz), 3.75 (6 H, s), 6.00 (1 H, dt, J = 15.7, 7.7 Hz), 6.52 (1 H, d, J = 15.7 Hz), 7.17–7.27 (5 H, m); mass calcd for $C_{17}H_{19}O_4$ (M + 1) 287.1283, found 287.1286.

Alkylation with *cis*-3-Acetoxy-5-(methoxycarbonyl)cyclohexene (54). Procedure 1. With dimethyl malonate: Following the general procedure, dimethyl malonate (0.132 g, 1.0 mmol), sodium hydride (0.0432 g, 0.9 mmol), **54** (0.100 g, 0.5 mmol), and MoBl4 (0.0484 g, 0.1 mmol) in toluene (5 mL) were combined and heated at reflux for 24 h. Standard workup and flash chromatography (80:20 hexane–ethyl acetate) yielded 0.095 g (70%) of the known **55** as a colorless oil.

Procedure 2. With 2-(methoxycarbonyl)cyclopentanone: Following the general procedure, 2-(methoxycarbonyl)cyclopentanone (0.142 g, 1.0 mmol), sodium hydride (0.0432 g, 0.9 mmol), **54** (0.100 g, 0.5 mmol), and MoBl4 (0.0484 g, 0.1 mmol) in toluene (4 mL) were combined and heated at reflux for 24 h. Standard workup and flash chromatography (80:20 hexane–ethyl acetate) yielded 0.057 g (41%, 77% based on recovered starting material) of **57** and 0.047 g (47%) of starting material **54** as colorless oils.

Alkylation of (*S*)-Perillyl Acetate. Following the general procedure, dimethyl malonate (0.132 g, 1.0 mmol), sodium hydride (0.0432 g, 0.9 mmol), (*S*)-perillyl acetate (0.097, 0.5 mmol), and MoBl4 (0.0242 g, 0.05 mmol) in toluene (5 mL) were combined and heated at reflux for 24 h. As TLC indicated remaining starting material, another portion of MoBl4 (0.0242 g, 0.05 mmol) was added, and the reaction was refluxed an additional 24 h. Standard workup and flash chromatography (92:8 hexane–ethyl acetate) yielded 0.0694 g (52%, 77% based on recovered starting material) of a 36:64 mixture of **25** and **26** as determined by GC (180 °C, 25 m × 0.25 mm, SE-30): **26**, ^{1}H NMR (270 MHz, $CDCl_3$) partial, δ 1.72 (3 H, s), 2.56 (2 H, d, J = 8.0 Hz), 3.58 (1 H, t, J = 8.0 Hz), 3.73 (6 H, s), 5.48 (1 H, br s); ^{13}C NMR (50.1 MHz, $CDCl_3$) δ 169.5, 149.5, 133.3, 123.2, 108.5, 52.3, 50.4, 40.7, 36.5, 30.6, 28.4, 27.6, 20.7; mass calcd for $C_{15}H_{224}$ 266.1518, found 266.1524.

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