^{1}H NMR Binding Studies. In a typical experiment, a 4 mM solution of host **4** (2.5 mg in 500 μL of $CDCl_3$) was prepared, and the solution ^{1}H NMR spectrum was recorded. A small aliquot of potential guest in $CDCl_3$ was added via syringe to the host solution (overall guest concentration ranging from 40–400 mM), and the ^{1}H NMR spectrum was recorded. The process was repeated at least ten times in each case to generate enough points for a binding constant calculation. The spectra were taken at 200 MHz at 298 K and were referenced to the residual proton peak of 99.99% $CDCl_3$.

Crystal Structure Determination. Compound **4**·$2C_6H_6$ crystallizes from C_6H_6 as colorless plates in the tetragonal system $I4_1/a$. Unit cell dimensions are as follows: a = 25.147 (2), c = 14.972 (1) Å, v = 9468 Å^3, Z = 4 (each molecule has $\bar{4}$ (S_4) symmetry). This host has two clefts and each cleft contains a (disordered) benzene molecule. This benzene molecule has four C···C distances of 3.6 Å to one of the dibenzofuran fragments of the macrocycle and the plane of the benzene ring is nearly parallel to the plane of that dibenzofuran (within 8°). The crystal was examined on a modified Syntex $P\bar{1}$ diffractometer, Cu Kα radiation, at 298 K. The structure was determined by direct methods. Refinement of 167 parameters (1679 reflections with $I > 3\sigma(I)$) has an agreement value, R, currently at 0.103. Details will be published elsewhere.

Compound **8** crystallizes from CH_2Cl_2/MeOH as colorless parallelepipeds in the triclinic system $P\bar{1}$. Unit cell dimensions are as follows: a = 11.1041 (9) Å, b = 13.083 (1) Å, c = 16.973 (2) Å, α = 78.047 (5)°, β = 85.090 (5)°, γ = 65.753 (5)°, v = 2180 Å^3, Z = 2. The crystal was examined on a modified Syntex $P\bar{1}$ diffractometer, Cu Kα radiation, at 298 K. The structure was determined by direct methods. Refinement of 259 parameters (3100 reflections with $I > 3\sigma(I)$) has an agreement value, R, currently at 0.118. Details will be published elsewhere.

This molecule forms centrosymmetric dimers with the following short intermolecular contacts: H···H < 2.7 Å 6, C···H < 3.2 Å 24, C···C < 3.7 Å 24, and O···H < 3.0 Å 2.

Compound **6** crystallizes from CH_2Cl_2/$(C_2H_5)_2O$ as colorless parallelepipeds in the monoclinic system $P2_1/n$. Unit cell dimensions are as follows: a = 16.280 (2) Å, b = 23.417 (4) Å, c = 16.735 (2) Å, β = 102.715 (4)°, v = 6224 Å^3, Z = 8. The crystal was examined on a modified Picker FACS-1 diffractometer, Mo Kα radiation, at 298 K. The structure was determined by direct methods. Refinement of 377 parameters (2869 reflections with $I > 2\sigma(I)$) has an agreement value, R, currently at 0.15.

The crystal contains two independent macrocycles. These form dimers by close contacts between dibenzofuran units from each of the two cycles. There are nine C···C contacts between 3.4 and 3.6 Å and the two dibenzofurans are nearly parallel (within 14°) although only one benzene ring from each dibenzofuran nearly overlaps one from the other dibenzofuran. The crystal contains both solvents used in the crystallization. Details will be published elsewhere.

Supplementary Material Available: Experimental details of the crystal structure determination, atom positions and thermal parameters, and bond lengths and angles (26 pages). Ordering information is given on any current masthead page.

Exo-Selective Diels–Alder Reactions of Aminocarbene Complexes

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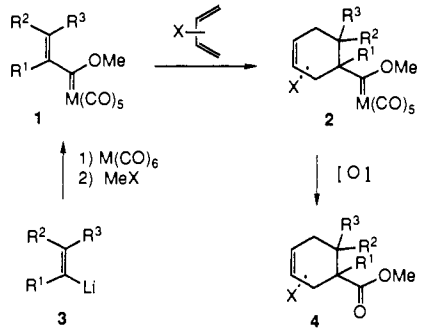
Abstract: The first examples of intermolecular Diels–Alder reactions of aminocarbene complexes are described. Various members of both the alkylamino and acylamino families of complexes are investigated. The E-isomer of [*trans*-propenyl(methylamino)methylene]pentacarbonyltungsten (**22**) will react with Danishefsky's diene and 1-methoxy-1,3-butadiene, but the *Z*-isomer will not. The yields are good only for the more reactive Danishefsky's diene, but all reactions with acyclic dienes are completely selective for the exo cycloadduct (≥96:4). The [*trans*-propenyl(*N*-methyl-*N*-benzoylamino)methylene]pentacarbonyltungsten(0) (**35**) is more reactive than **22**, and if it is converted into the chelated complex **42**, where the oxygen of the benzoyl group replaces a carbon monoxide ligand on the metal, a highly reactive dienophile is obtained. Complex **42** will react with Danishefsky's diene within minutes at room temperature, and although the yields are low (~30%) due to competing dinuclear carbene complex formation, the cycloaddition again occurs with complete exo selectivity (≥97:3). The cycloaddition of **42** with cyclopentadiene is not stereoselective and gives approximately a 1:1 mixture of endo and exo isomers. Possible sources of the unique reactivity and high exo selectivity of these complexes with acyclic dienes are discussed in terms of their solution spectra and the solid-state structures of complexes **22-E**, **22-Z**, and **34**.

Alkenyl alkoxycarbene Fischer carbene complexes of the type **1** were first identified as reactive Diels–Alder dienophiles in 1983.[2] The reaction rates, the endo/exo selectivities, and the regioselectivies were found to be comparable to Lewis acid catalyzed reactions of their corresponding esters.[2,3] Since the metal can be oxidatively removed from the product to give esters, these alkoxy carbene complexes can serve as synthons for esters in the Diels–Alder reaction (Scheme I). Furthermore, Fischer carbene complexes are compatible with sensitive diene functionalities that are not tolerated by the Lewis acidic conditions typically required for Diels–Alder reactions. Alkoxy-substituted Fischer carbene complexes, therefore, have real advantages to offer as synthons for the Diels–Alder reactions.

Scheme I



Although the preparation of alkenylaminocarbene complexes of the type **5** should be trivial (Scheme II), there are no reports

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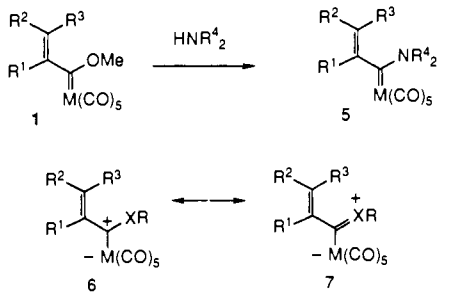
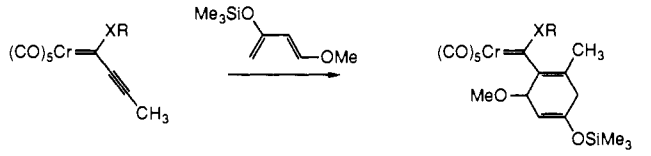
Scheme II



Scheme III

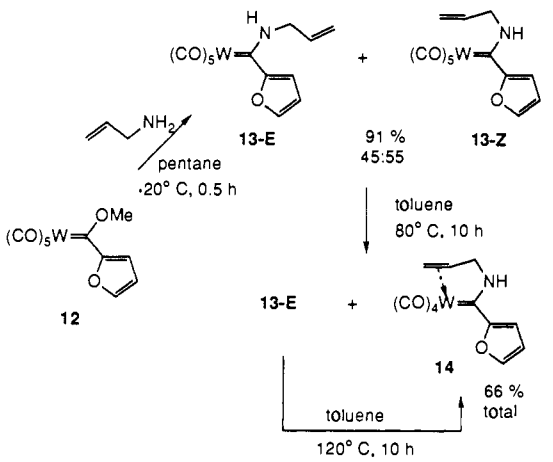


Complex	XR	solvent	conditions	Yield
8a	OMe	benzene (2 M)	25° C, 10 min	**9a** 100 %
8b	NMe_2	neat	25° C, 5 days	**9b** not observed

Complex	XR	solvent	conditions	Yield
10a	OMe	neat	25° C, 2 hours	**11a** 57 %
10b	NMe_2	neat	130° C, hours	**11b** not observed

of intermolecular Diels–Alder reactions of alkenylaminoacarbene complexes in the literature.[4] One of our interests in amino complexes lies with their potential for asymmetric Diels–Alder reactions employing complexes derived from readily available chiral amines. However, it was quickly anticipated that alkenyl amino complexes of the type **5** would be significantly less reactive than alkoxy complexes in [4 + 2] cycloadditions with 1,3-dienes. The high reactivity of alkenylalkoxycarbene complexes as dienophiles correlates with the electrophilicity of the carbene carbon, which dominates most of the reaction patterns of these complexes.

Scheme IV



In addition to structure **1**, the resonance forms **6** and **7** are thought to be important in determining the electronic structure of Fischer carbene complexes.[5] If resonance structures of the type **6** are important in imparting high dienophilicity to these complexes, then it would be anticipated that replacing the alkoxy group in **1** with an amino group would lead to a decrease in reactivity toward 1,3-dienes as a consequence of the greater contribution of resonance structure **7** due to the better π-backbonding ability of nitrogen versus oxygen. In this report, we describe the first examples of intermolecular Diels–Alder reactions of alkenylaminocarbene complexes and find that they are much less reactive than their corresponding alkoxy complexes. We describe a solution to the relative low reactivity and also report the unexpected finding that the Diels–Alder reactions of alkenylamino complexes are highly exo selective with acyclic dienes.[6]

Background

In an attempt to directly compare the influence of amino and alkoxy ancillaries of Fischer carbene complexes on the Diels–Alder reaction, the complexes **8a** and **8b** were reacted with Danishefsky's diene. A 2 M solution of the methoxy complex **8a** in benzene reacts at room temperature in 10 min to give a quantitative yield of the adduct **9a** (Scheme III).[3a] In contrast, the dimethylamino complex **8b** was exposed to neat Danishefsky's diene at room temperature for 5 days, but no detectable amount of the cycloadduct was formed and the reaction mixture consisted largely of unreacted **8b**.[7] The reaction of the alkoxy complex **8a** with Danishefsky's diene cannot be run under neat conditions, since an attempt to do so led to a reaction exothermic enough to cause significant decomposition of the carbene complex and a large drop in yield. It has also been reported that, whereas the tungsten alkoxy complex **10a** will undergo [4 + 2] cycloaddition with cyclopentadiene rapidly at room temperature, the reaction of the corresponding amino complex did not produce the cycloadduct **11b** in an autoclave after several hours at 130 °C.[3b] These two examples clearly illustrate that, as expected, the substitution of an amino group for an alkoxy group in an α,β-unsaturated Fischer carbene complex greatly decreases the rates of Diels–Alder reactions of these complexes and makes it understandable why there are no reports of intermolecular Diels–Alder reactions of aminocarbene complexes in the literature.

Despite the dramatically reduced dienophilicity of aminocarbene complexes, three successful examples of intramolecular Diels Alder reactions of aminocarbene complexes have been described.[3f,l] One of these examples is particularly intriguing and involves the intramolecular [4 + 2] cycloaddition of an alkylamine function and a furan.[3l] The monoallylamine complex **13** was prepared in high

(1) (a) American Chemical Society Organic Division Rohm and Haas Fellow 1989–90. William Rainey Harper Fellow 1990–91. (b) Department of Education GAANN fellow 1991–92.

(2) (a) Wulff, W. D.; Yang, D. C. *J. Am. Chem. Soc.* **1983**, *105*, 6726. A full account of this work has appeared: (b) Wulff, W. D.; Bauta, W. E.; Kaesler, R. W.; Lankford, P. J.; Miller, R. A.; Murray, C. K.; Yang, D. C. *J. Am. Chem. Soc.* **1990**, *112*, 3642.

(3) For other Diels–Alder reactions of carbene complexes, see: (a) Wulff, W. D.; Yang, D. C. *J. Am. Chem. Soc.* **1984**, *106*, 7656. (b) Dötz, K. H.; Kuhn, W. *J. Organomet. Chem.* **1985**, *286*, C23. (c) Wulff, W. D.; Tang, P. C.; Chan, K. S.; McCallum, J. S.; Yang, D. C.; Gilbertson, S. R. *Tetrahedron* **1985**, *41*, 5813. (d) Dötz, K. H.; Werner, K.; Mueller, G.; Huber, B.; Ali, H. G., *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 812. (e) Paquette, L. A.; Gugelchuk, Y. L.; Hsu, Y. L., *J. Org. Chem.* **1986**, *51*, 3864. (f) Dötz, K. H.; Noack, R.; Müller, G. *J. Chem Soc., Chem. Commun.* **1988**, 302. (g) Wulff, W. D.; Yang, D. C.; Murray, C. K. *Pure Appl. Chem.* **1988**, *110*, 2653. (h) Faron, K. L.; Wulff, W. D. *J. Am. Chem. Soc.* **1988**, *110*, 8727. (i) Huy, N. H. T.; Maihey, F. *Organometallics*, **1988**, *7*, 2233. (j) De Meijere, A.; Kaufmann, A.; Lackman, R.; Militzer, H. A.; Reiser, O.; Schömenauer, S.; Weier, A. In *Organometallics in Organic Synthesis*; Erker, G., Werner, H., Eds.; Springer: Heidelberg, 1989; Vol. II, p 255. (k) Wulff, W. D. In *Advances in Metal-Organic Chemistry*; Liebeskind, L. S., Ed.; JAI Press Inc.: Greenwich, CT, 1989; Vol 1, pp 209–393. (l) Dötz, K. H.; Noack, R.; Harms, K.; Mueller, G. *Tetrahedron* **1990**, *46*, 1235. (m) Wang, S. L. B.; Wulff, W. D. *J. Am. Chem. Soc.* **1990**, *112*, 4550. (n) Park, J.; Kang, S.; Whang, D.; Kim, K. *Organometallics* **1991**, *10*, 3413. (o) Merlic, C. A.; Xu, D. *J. Am. Chem. Soc.* **1991**, *113*, 7418. (p) Wulff, W. D. In *Comprehensive Organic Synthesis*; Trost, B. M.; Fleming, I., Eds.; Pergamon Press: New York, 1991; Vol 5, pp 1065–1113. (q) Bao, J.; Dragisich, V.; Wenglowsky, S.; Wulff, W. D. *J. Am. Chem. Soc.* **1991**, *113*, 9873.

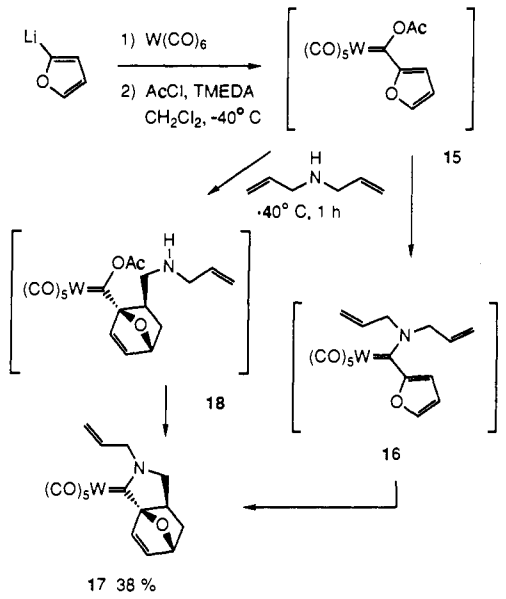
(4) For reviews on the synthesis and utility of amino complexes, see: (a) Dötz, K. H.; Fischer, H.; Hofmann, P.; Kreissel, F. R.; Schubert, U.; Weiss, K. *Transition Metal Carbene Complexes*; Verlag Chemie; Deerfield Beach, FL, 1984. (b) Schwindt, M. A.; Miller, J. R.; Hegedus, L. S. *J. Organomet. Chem.* **1991**, *413*, 143. (c) Grotjahn, D. G.; Dötz, K. H. *Synlett* **1991**, 381.

(5) For a discussion see Hoffman in ref 4a.

(6) Anderson, B. A.; Wulff, W. D.; Powers, T. S.; Tribbitt, S.; Rheingold, A. L. *Abstracts of Papers*, 200th National Meeting of the American Chemical Society, Washington, DC, August 26–31, 1990; American Chemical Society: Washington, DC, 1990; ORG 107.

(7) Wulff, W. D.; Bos, M. E., unpublished results.

Scheme V

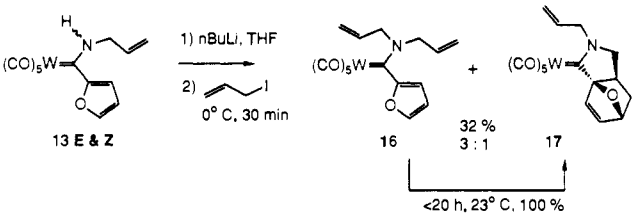


yield as indicated in Scheme IV and obtained as a 45:55 mixture of *E*- and *Z*-isomers. This particular set of isomeric amino complexes could not be separated, but like most isomers of aminocarbene complexes, they do not interconvert. The barrier to rotation about the C_{carb}–N bond in a typical aminocarbene complex is ≥25 kcal/mol, and this can be attributed to the high degree of delocalization from nitrogen to carbon. The thermolysis of a mixture of **13-E** and **13-Z** at 80 °C did not produce any cycloadducts but instead resulted in the formation of the alkene-chelated complex **14** and the recovery of the *E*-isomer in pure form. Thermolysis of pure **13-E** at 120 °C likewise did not produce a cycloadduct but rather the alkene chelate **14**, presumably via an isomerization of **13-E** to **13-Z**. Although this reaction did not produce Diels–Alder products, it is of interest since it is one of the rare examples in which the rotamers of aminocarbene complexes have been thermally interconverted.

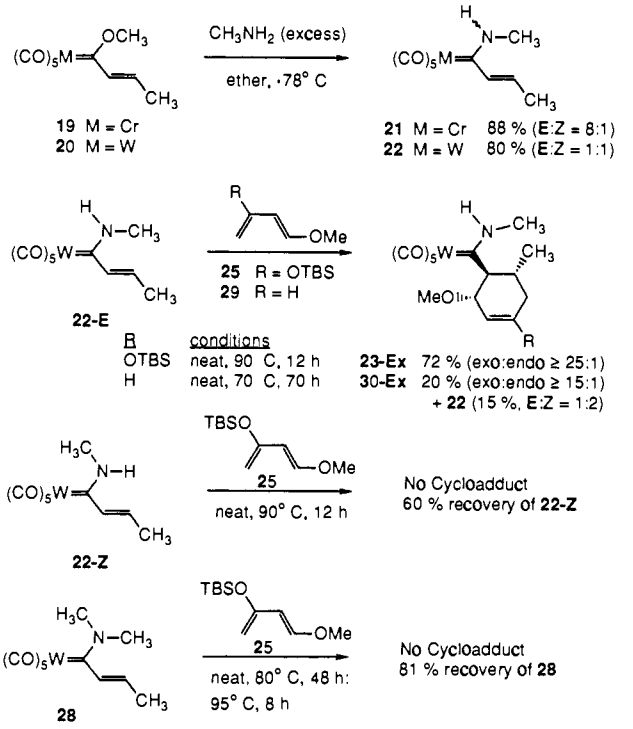
While neither the *E*- nor the *Z*-isomer of complex **13** would undergo an intramolecular Diels–Alder reaction at 80 °C, it was reported that the diallyl analog **16** underwent such a facile intramolecular Diels–Alder reaction at −40 °C that it could not be isolated.[3] This is a fascinating result, considering that the *E*-isomer of **13** has the allyl and furan substituents syn and yet no cycloaddition occurred. Complex **16** is constrained to have one of the allyl groups syn to the furan unit, but it is certainly not obvious why the presence of the second allyl group on nitrogen would so greatly enhance the intramolecular Diels–Alder reaction of the syn allyl group. Each of the ally groups in **16** has 2 degrees of freedom that permit the access of reactive (?) conformations resulting from rotation about a carbon–carbon and a carbon–nitrogen single bond. If this is the source of the difference in the reactivities of complexes **13-E** and **16**, then it is surprising that the preferred conformations of the anti allyl group could so strongly affect the populations of conformers of the syn allyl group that the thermal requirements for these Diels–Alder reactions could be affected by more than 100 °C.

An alternate explanation for the discrepancy between the rates of the intramolecular Diels–Alder reactions of **13-E** and **16** is the fact that **17** is not formed from the intramolecular cyclization of **16** but rather from an intermolecular Diels–Alder reaction of the acetoxy complex **15** with diallylamine to give the adduct **18**, which then produces **17** by an intramolecular aminolysis (Scheme V). This possibility could not be ruled out on the basis of the reported data, since complex **16** was not isolable. The formation of **18** by an intermolecular Diels–Alder reaction of the acetoxy complex **15** is not unreasonable, since the acetoxy complex would be expected to be a highly reactive dienophile on the basis of the arguments presented above, which correctly anticipated the decreased reactivity of amino complexes relative to alkoxy complexes.

Scheme VI



Scheme VII



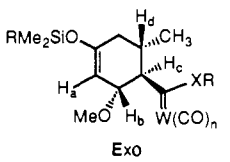
It has been reported that acetoxy complexes are much more reactive than alkoxy complexes in [2 + 1] cycloadditions leading to cyclopropane products.[8] In order to address the issue of how complex **17** is formed, we sought to prepare the allyl complex **16** by an independent method. Alkylation of a mixture of *E*- and *Z*-isomers of the (monoallylamino)carbene complex **13** led to the isolation of the diallylamino complex **16** (Scheme VI). When complex **16** was purified from the crude reaction mixture by chromatography on silica gel at room temperature, complex **16** was obtained as an inseparable mixture with the Diels–Alder adduct **17** in a 3:1 ratio. The diallylamino complex **16** is not very stable at room temperature. Upon standing at ambient temperature, the 3:1 mixture of **16** and **17** had completely converted to **17** within 20 h. While our results prove that the **18** need not be an intermediate in the formation of **17**, still unexplained is why the intramolecular Diels–Alder reaction of **16** is possible and the same reaction for the monoallylamino complex **13-E** is not.

Intermolecular Diels–Alder Reactions of Methyl Amino Complexes. Attempted intermolecular Diels–Alder reactions of α,β-unsaturated aminocarbene complexes have been described in the literature (Scheme III), but none were successful. It was clear from what was known at the time this work was started that more forcing conditions would be necessary to effect the cycloaddition reactions of amino complexes as compared to alkoxy complexes, but this constraint was not considered severe enough to preclude the possibility of finding such a reaction, given the greater thermal stability of aminocarbene complexes.

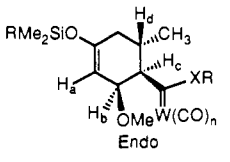
The complexes examined in this work were limited to *trans*-propenylaminocarbene complexes. The monomethyl complexes

(8) Murray, C. K.; Yang, D. C.; Wulff, W. D. *J. Am. Chem. Soc.* **1990**, *112*, 5660.

Table I. Selected Coupling Constants for 3-Cyclohexenyl Carbene Complexes



Exo



Endo

carbene complex[a]	stereochemistry	R	XR	J_{ab} (Hz)	J_{bc} (Hz)	J_{cd} (Hz)
26-Ex	exo	Me	OMe	1.7	8.3	8.3[b]
27-Ex	exo	*t*-Bu	OMe	<1.5	8.7	8.1
23-Ex	exo	*t*-Bu	*E*-NHMe	<1.5	8.4	11.0
37-Ex	exo	*t*-Bu	NMeCOPh	<1.5	8.4	11.0
26-En	endo	Me	OMe	5.4	3.6	11.4[b]
27-En	endo	*t*-Bu	OMe	4.0	3.5	11.4
23-En	endo	*t*-Bu	*E*-NHMe	4.3	2.5	12.2
37-En	endo	*t*-Bu	NMeCOPh	5.0	3.9	12.3

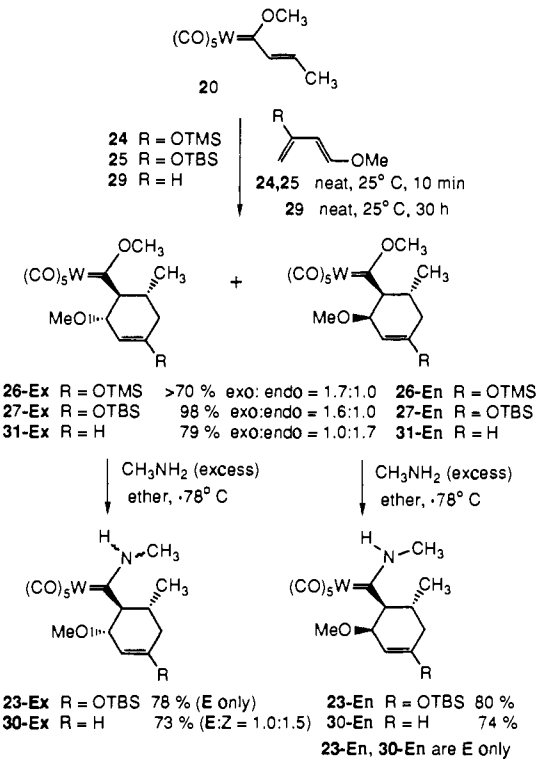
[a] Pentacarbonyl complexes (n = 5) in all cases except **37-Ex** and **37-En**, which are tetracarbonyl chelates (n = 4). [b] Reference 2b.

21 and **22** were prepared by the standard aminolysis method from the corresponding *trans*-propenylmethoxy complexes (Scheme VII).[2b] Low-temperature treatment with the amine prevented competing **1,4** addition,[9] and the extremely stable aminocarbene complexes **21** and **22** could be isolated in high yields for both chromium and tungsten. It is somewhat surprising that of the several alkenylaminocarbene complexes that have been prepared, only one previous synthesis has been reported by the aminolysis route.[31] Specialized methods have accounted for the remaining preparations of alkenylaminocarbene complexes which by and large are useful for the preparation of only specially substituted alkenyl complexes.[10]

Both the chromium and tungsten complexes **21** and **22** were formed as mixtures of *E*- and *Z*-isomers which could easily be separated by silica gel chromatography. The assignments of the stereochemistry about the carbene carbon–nitrogen bond were made on the basis of the observation by Fischer that the ^{1}H NMR shifts of the α-hydrogens of an alkyl group on the nitrogen atom are downfield for the *Z*-isomers relative to those for the *E*-isomers.[11,12] In this case, for example, the *N*-methyl group in **22-E** is at δ = 3.15 and that for **22-Z** is δ = 3.54. These stereochemical assignment for **22-E** and **22-Z** were also confirmed by X-ray spectroscopy (vide infra).

The first reactions of the alkenylaminocarbene complexes were surveyed using 1-methoxy-3-(*tert*-butyldimethylsiloxy)-1,3-butadiene (**25**) not only because of the importance of this diene in organic synthesis[13] but also to take advantage of the high reactivity of this electron-rich diene. The reaction of complex **22-E** with diene **25** proceeded at 90 °C in 12 h to give a 72% yield of the cycloadduct **23-Ex**. In light of the success of this reaction, it was quite surprising to find that under the same conditions the *Z*-isomer of **22** failed to produce any cycloadducts and led only to a 60% recovery of **22-Z**. An additional surprise was that the reaction of **22-E** with Danishefsky's diene gives exclusively the

Scheme VIII



exo cycloadduct **23-Ex**, whose stereochemistry was determined by spectroscopic analysis and independent synthesis as shown in Scheme VIII. It was surprising that this reaction was highly exo selective, because neither the methoxy complex **20** nor *trans*-methyl crotonate display this high degree of exo selectivity with Danishefsky's diene: both the complex **20**[2b] and *trans*-methyl crotonate[14] give ~2:1 mixture of isomers in favor of the exo cycloadduct. The Diels–Alder reaction is generally endo selective, and there are no known general methods for obtaining high selectivities for exo products. The observation that the reaction of **22-E** with **25** gives only the exo product **23-Ex** is quite significant and will be discussed in further detail in the Results and Discussion section.

Authentic samples of both the exo and endo isomers of the cycloadduct **23** were prepared by aminolysis of the corresponding methoxy complexes **27** as indicated in Scheme VIII. The

(9) Fischer, E. O.; Kalbfus, H. J. *J. Organomet. Chem.* **1977**, *131*, 57.
(10) (a) Aumann, R. Heinrich, H.; Dartmann, M.; Krebs, B. *Chem. Ber.* **1991**, *124*, 2343. (b) Macomber, D. W.; Hung, M. H.; Madhuker, P.; Liang, M. *Organometallics*, **1991**, *10*, 737. (c) Schwindı, M. A.; Lejon, T.; Hegedus, L. S. *Organometallics*, **1990**, *9*, 2814. (d) Imwinkelreid, R.; Hegedus, L. S. *Organometallics*, **1988**, *7*, 702. (e) Dötz, K. H.; Pruskil, I. *Chem. Ber.*, **1978**, *111*, 2059. (f) Dötz, K. H., *Chem. Ber.*, **1977**, *110*, 78. (g) Dötz, K. H.; Pruskil, I. *J. Organomet. Chem.*, **1977**, *132*, 115. (h) Dötz, K. H.; Krieter, C. G. *J. Organomet. Chem.* **1975**, *99*, 309. (i) Huttner, G.; Lang, S. *Chem. Ber.* **1970**, *103*, 3149. (j) Fischer, E. O.; Aumann, R. *Chem. Ber.* **1968**, *101*, 954.
(11) It should be noted that terms *Z* and *E* used here to describe the stereochemistry of the two rotamers about the carbene carbon–nitrogen bond are reversed from the usage employed by Fischer for this same purpose.[12]
(12) (a) Moser, E.; Fischer, E. O. *J. Organomet. Chem.* **1969**, *16*, 275. (b) Fischer, E. O.; Leupold, M. *Chem. Ber.* **1972**, *105*, 599.
(13) (a) Danishefsky, S. *Chemtracts. Org. Chem.* **1989**, *2*, 273–297. (b) Danishefsky, S. *Acc. Chem. Res.* **1981**, *14*, 400. (c) Fringuelli, F.; Taticchi, A. *Dienes in the Diels–Alder Reaction*; John Wiley & Sons, Inc.: New York, 1990.
(14) (a) Danishefsky, S.; Kitahara, T.; Yan, C. F.; Morris, J. *J. Am. Chem. Soc.* **1979**, *101*, 6996. (b) Vorndam, P. E. *J. Org. Chem.* **1990**, *55*, 3693. (c) Ibuka, T.; Mori, Y.; Inubushi, Y. *Chem. Pharm. Bull.* **1978**, *26*, 2442. (d) Rosen, T.; Taschner, M. J.; Thomas, J. A.; Heathcock, C. H. *J. Org. Chem.* **1985**, *50*, 1190.

Diels–Alder reaction of the *trans*-propenyl methoxy tungsten complex **20** with Danishefsky's diene has been previously reported to give a 1.7:1.0 mixture of the exo and endo cycloadducts **26**.[2b] The *tert*-butyldimethylsilyl analog of Danishefsky's diene **25** was employed here so that the products **27-Ex** and **27-En** would be stable to silica gel. The reaction of **20** with **25** gives **27** in a total yield of 98% as a 1.6:1.0 mixture of the exo and endo isomers **27-Ex** and **27-En**, which were easily separated by silica gel chromatography. The treatment of each isomer of **27** with methylamine at low temperature independently gave pure samples of the exo isomer of **23** and the endo isomer of **23**. These reactions produced **23-Ex** and **23-En** in each case as a single rotamer about the carbene carbon–nitrogen bond. The stereochemistry was assigned as that of the *E*-rotamer, since the product **23-Ex** from this reaction was spectroscopically identical to the product obtained from the reaction of **22-E** with diene **25**. On this basis, the rotamer of **23-En** produced from the reaction of **27-En** with methylamine was assumed to be the *E*-isomer. The exo and endo cycloadducts are normally readily identifiable by proton–proton coupling constants between the ring protons. This has been reported for the trimethylsiloxy derivatives **26-Ex** and **26-En** and has also been found to be the case here for the compounds **27-Ex** and **27-En**, as well as for the amino-substituted cycloadducts **23-Ex** and **23-En** (Table I). Particularly diagnostic are the coupling constants J_{ab} and J_{bc}, where it was found that J_{ab} is significantly larger for the endo adducts and J_{bc} is significantly larger for the exo adducts. With authentic samples of **23-Ex** and **23-En** in hand, the exo:endo selectivity for the reaction of **22-E** with diene **25** could be established as ≥25:1 by analysis of the crude reaction mixture by ^{1}H NMR.

Given the drastic difference in the reactivity of the *E*-isomer of the complex **22**, with the *N*-methyl syn to the propenyl ligand, and the *Z*-isomer of **22**, with the *N*-methyl group anti to the propenyl ligand, the reaction of the (dimethylamino)carbene complex **28** with diene **25** was investigated (Scheme VII). This complex would not react to give any detectable amount of cycloadduct under conditions for which **22-E** readily reacted. After the neat mixture of **28** and diene **25** was heated at 80 °C for 48 h and then at 95 °C for 8 h, the complex **28** could be recovered from the reaction mixture in pure form in 81% yield. Therefore, steric interactions between the *N*-methyl and propenyl groups do not explain why **22-E** is more reactive than **22-Z** (Scheme VII).

The scope of the reactivity of **22-E** appears to be limited to highly activated dioxygenated dienes. The reaction of **22-E** with 1-methoxy-1,3-butadiene at 70 °C for 70 h gave the Diels–Alder product in only 20% yield along with 15% recovery of the starting carbene complex, which was obtained as a 1:2 mixture of *E*- and *Z*-isomers (Scheme VII). It is not clear how the *Z*-rotamer of **22** was formed. Thermal isomerization is a possibility, but is unlikely given the relatively low reaction temperature. Base-catalyzed isomerization, either by deprotonation or by reversible 1,4 addition, is more reasonable. The two most likely sources of base could be either the amine liberated by decomposed starting carbene complex or the 1-methoxybutadiene.[15] Although the efficiency of the cycloaddition is severely limited, the selectivity of the reaction remained exceptionally high, giving only the exo isomer of the cycloadduct **30**. The level of the stereoselectivity can be set at ≥15:1 in favor of the exo isomer on the basis of analysis of the crude reaction mixture by ^{1}H NMR and comparison with the spectral data for authentic samples of the exo and endo isomers of **30**, which were prepared by the procedure outlined in Scheme VIII.

The Diels–Alder reaction of the *trans*-propenyl methoxy tungsten complex **20** with 1-methoxybutadiene is known to give a 1.0:1.7 mixture of exo:endo isomers in a total 79% yield.[2b] These two complexes are chromatographically separable and were used to prepare authentic samples of the exo and endo isomers of **30** by treatment with methylamine. As indicated in Scheme VIII, these two reactions proceeded smoothly to give the exo adduct **30-Ex** in 73% yield and the endo adduct **30-En** in 74% yield. The exo adduct **30-Ex** was obtained as a 1.0:1.5 mixture of *E*- and *Z*-isomers about the carbene carbon–nitrogen bond, whereas, the endo isomer **30-En** was obtained as a single rotamer. Since the spectral data for both rotamers of **30-Ex** were available, the *E*-isomer could be assigned as the one with the *N*-methyl group furthermost upfield.[11,12] The stereochemistry about the carbon–nitrogen bond in **30-Ex** obtained from the Diels–Alder reaction of **22-E** with diene **29** was thereby established as that of the *E*-isomer, the same as the starting dienophile **22-E**. The stereochemistry of the exo and endo adducts of **30** were also confirmed by proton–proton couplings constants, as detailed in the Experimental Section.

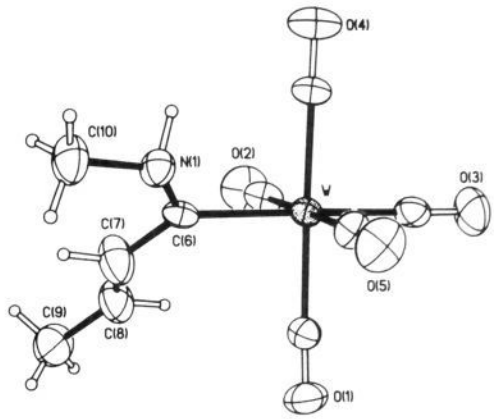


Figure 1. ORTEP diagram of **22-E**.

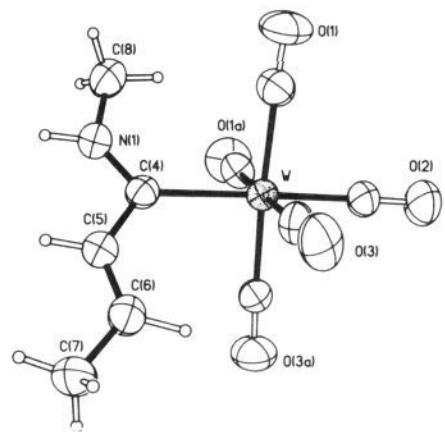


Figure 2. ORTEP diagram of **22-Z**.

Solid-State Structures of the *E*- and *Z*-Isomers of the Monomethyl Complexes 22. The solid-state structures of **22-E** and **22-Z** were determined to confirm the stereochemistry about the carbene carbon–nitrogen bond and to reveal obvious structural differences between the two that might explain their greatly dissimilar reactivities with Danishefsky's diene. As indicated by the ORTEP drawings in Figures 1 and 2, the determination of stereochemistry made on the basis of the chemical shifts of the *N*-methyl did lead to the correct structural assignment.[11,12] Unfortunately, no conclusions concerning the enhanced reactivity of the *E*-isomer could be drawn from the structural data. The crystal structures of the two compounds are very similar, and aside from the different relative geometries of the methyl group about the nitrogen, no other significantly distinguishing characteristics are evident (Table II) which could explain the differences in the reactivities of **22-E** and **22-Z**.

The double bonds of both **22-E** and **22-Z** are in s-cis conformations with respect to the metal pentacarbonyl. The *Z*-isomer has a mirror plane, and therefore, the dihedral angle containing tungsten, the carbene carbon, and the double bond carbons,

(15) It has been shown that a *cis*-propenylcarbene complex can be epimerized in the presence of a trioxygenated diene, presumably via reversible 1,4-addition;[2b] however, it also possible that isomerization could be caused by a reversible 1,2-addition: Wulff, W. D.; Yang, D. C.; Murray, C. K. *J. Am. Chem. Soc.* **1988**, *110*, 2653.

Table II. Selected Bond Lengths and Bond Angles for **22-E** and **22-Z**

22-E		22-Z	
	Bond Length (Å)		
W-C(6)	2.243 (10)	W-C(4)	2.258 (9)
C(6)-N(1)	1.309 (10)	C(4)-N(1)	1.314 (15)
N(1)-C(10)	1.468 (2)	N(1)-C(8)	1.450 (16)
C(6)-C(7)	1.460 (14)	C(4)-C(5)	1.473 (14)
C(7)-C(8)	1.214 (14)	C(5)-C(6)	1.325 (18)
C(8)-C(9)	1.508 (20)	C(6)-C(7)	1.501 (16)
W-C(1)	2.061 (9)	W-C(2)	1.983 (10)
W-C(3)	2.004 (11)	W-C(3)	2.040 (9)
O(1)-C(1)	1.112 (12)	O(2)-C(2)	1.195 (14)
O(3)-C(3)	1.160 (14)	O(3)-C(3)	1.188 (18)
	Bond Angle (deg)		
W-C(6)-N(1)	119.6 (7)	W-C(4)-N(1)	125.7 (7)
W-C(6)-C(7)	125.3 (6)	W-C(4)-C(5)	126.2 (8)
C(6)-N(1)-C(10)	128.7 (9)	C(4)-N(1)-C(8)	129.5 (9)
N(1)-C(6)-C(7)	115.0 (9)	N(1)-C(4)-C(5)	108.2 (9)
C(6)-C(7)-C(8)	133.1 (12)	C(4)-C(5)-C(6)	128.6 (10)
C(7)-C(8)-C(9)	130.8 (12)	C(5)-C(6)-C(7)	123.2 (11)
	Dihedral Angle (deg)		
W-C(6)-C(7)-C(8)	0.15	W-C(4)-C(5)-C(6)	0.0
C(5)-W-C(6)-N(1)	48.2	C(1)-W-C(4)-N(1)	46.5

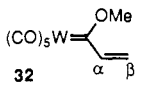
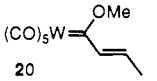
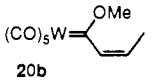
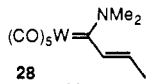
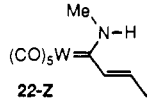
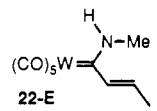
W-C(4)-C(5)-C(6), is 0°.[16] The corresponding angle for the *E*-isomer, W-C(6)-C(7)-C(8), is 0.15°. The double bonds for both complexes are in appropriate conformations which would allow conjugation with the metal pentacarbonyl. The *Z*-isomer double bond C(5)-C(6) distance is 1.325 (18) Å, whereas the corresponding double bond C(7)-C(8) of the *E*-isomer is 1.214(14) Å. The latter bond distance is inexplicably short by any chemical rationale but may be an artifact of unresolved structural disorder. That is, the location of one or both atoms is the average of two (or more) disordered positions and does not represent a physically real atomic position. In neither case, however, is the β-carbon of the propenyl group within bonding distance to the metal center. The W-C(6) distance is 3.72 (1) Å for **22-Z**, and the distance W-C(8) in **22-E** is 3.71 (1) Å.

In summary, no significant solid-state structural evidence was found that would indicate why one isomer is more reactive toward cycloaddition. Because notable differences in the solution-phase spectral properties were observed for **22-E** and **22-Z** (vide infra), it is not unreasonable to suspect that the solid-phase conformations might not necessarily reflect the reactive conformations of the two isomers in solution.

Solution Spectra of 22-E and 22-Z. Alkene IR C–C bond stretches for the *E*- and *Z*-isomers of **22** might provide evidence concerning the relative extent of conjugation for the two isomers. The appropriate bands cannot, however, be unequivocally assigned, since they are relatively weak compared to metal carbonyl absorptions and characteristic aminocarbene complex absorptions are expected in the 1500–1600 cm^{-1} region of the IR.[17] The solution-phase IR spectra of the two isomers do differ to some extent. The CO bands for the *Z*-isomer are shifted to slightly higher energies (2062, 1971, and 1929 cm^{-1}) compared to those of the reactive *E*-isomer (2050, 1963, 1910, and 1903 cm^{-1}). This shift indicates that more electron density is centered on the metal in the *E*-isomer, since distribution of the electron density into the anti-bonding orbitals of the carbon monoxides would be expected to decrease the energy of the CO stretches.

The most notable differences between the spectral features of the *E*- and *Z*-isomers of **22** are the relative ^1H and ^{13}C shifts of the alkenyl constituents (Table III). In the unreactive *Z*-isomer,

Table III. Selected Chemical Shifts of Alkenylcarbene Complexes[a]

carbene complex	δ (ppm) H_α	H_β	C_α	C_β	C_{carb}
 **32**	7.38[b]	5.28 5.72	152.6	119.4	313.0
 **20**	7.22[b]	6.55	149.3[c]	137.2[c]	309.7
 **20b**	7.19[b]	5.54	147.6[c]	130.5[c]	316.9
 **28**	6.38[d]	5.23	142.3	122.7	252.0
 **22-Z**	6.75	5.90	146.8	130.8	247.0
 **22-E**	6.48	6.67	136.5	149.1	249.3

[a] All chemical shifts in $CDCl_3$. H_α and H_β were assigned by proton–proton coupling, and C_α and C_β were assigned by HETCOR from the proton assignments. [b] Reference 2b. [c] The vinyl carbons were not assigned in the original report and were determined in the present work by HETCOR experiments. [d] From the HETCOR experiments the *Z*-methyl carbon can be assigned as δ = 53.70 and the *E*-methyl carbon as δ = 43.64.

the ^1H and ^{13}C shift of the β-proton and β-carbon appear upfield from the shifts of the α-proton and α-carbon. This trend was previously observed for the analogous alkoxycarbene complex **20**, as well as for the parent vinyl(methoxy)carbene tungsten complex **32**.[2b] The vinyl carbon assignments for **28**, **22-Z**, and **22-E**, as well as for the previously unassigned **20** and **20b**, were determined by HETCOR experiments. In contrast to all of the other examples in Table III, the reactive *E*-rotamer of the aminocarbene complex **22** demonstrates an opposite trend. The α-proton and α-carbon are shifted upfield relative to the β-constituents.

The chromium analog of unsubstituted vinyl tungsten complex **32** has very similar shifts in the ^1H and ^{13}C NMR. For the chromium analog of **32**, it has been suggested that these NMR shifts can be accounted for by a preference for a conformation about the carbene carbon–vinyl carbon bond, in which the vinyl group and the carbene ligand are perpendicular. The deshielding of the α-vinyl carbon was attributed to an inductive electron-withdrawing effect of the carbene carbon. If this is true, then it can be concluded that for all of the complexes in Table III (except, perhaps, for **22-E**) there is a preference for conformations about the carbene carbon–vinyl bond that are nonplanar. The solution spectra suggest that the structure of complexes **22-E** and **22-Z** are different in solution than they are in the solid state where both complexes have planar vinyl groups (Figures 1 and 2). From the information we have at this time, however, it is not clear why in solution a planar conformation of the propenyl group in **22-E** would be preferred to a greater extent than it is in **22-Z**.

Intermolecular Diels–Alder Reactions of *N*-Benzoylamino Complexes. Given that the ultimate goal of this work was to develop asymmetric Diels–Alder reactions with chiral aminocarbene complexes, the not unexpected finding that the reaction of **22-E** with 1-methoxy-1,3-butadiene was quite sluggish (as compared to **20**) indicated that designs for increasing the reactivity of the aminocarbene complex had to be considered. Because the low reactivity was probably due to lone pair donation from the nitrogen into the carbene carbon (in the planar conformation), a straightforward solution called for the preparation of derivatives with electron-withdrawing substituents on nitrogen. The appropriate class of derivatives was suggested by reports that unsaturated imides were considerably more reactive dieneophiles than related

(16) For another example of a solid-state structure of an alkenylaminocarbene complex with a mirror plane, see: Hutlner, G.; Lange, S. *Chem. Ber.* **1970**, *103*, 3149.
(17) Moser, E.; Fischer, E. O. *J. Organomet. Chem.* **1969**, *16*, 275.
(18) Wilson, J. W.; Fischer, E. O. *J. Organomet. Chem.* **1973**, *57*, C63.
(19) Chan, K. S.; Wulff, W. D. *J. Am. Chem. Soc.* **1986**, *108*, 5229.
(20) (a) Strobel, M. P.; Andrieu, C. G.; Paquer, D.; Vazeux, M.; Pham, C. C. *Nouv. J. Chim.* **1980**, *4*, 101. (b) Taskinen, E. *Tetrahedron* **1978**, *34*, 425.

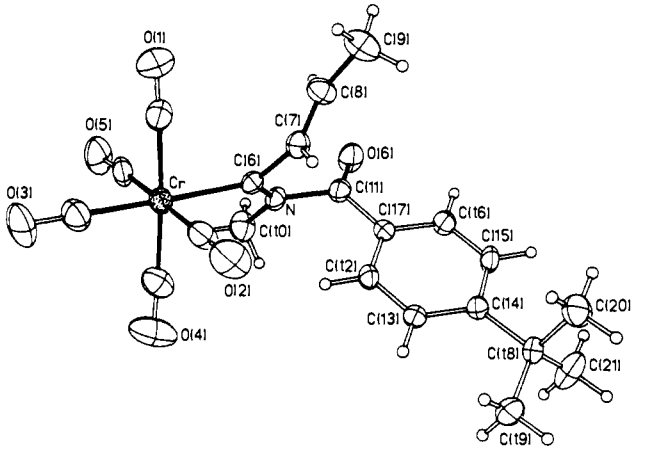
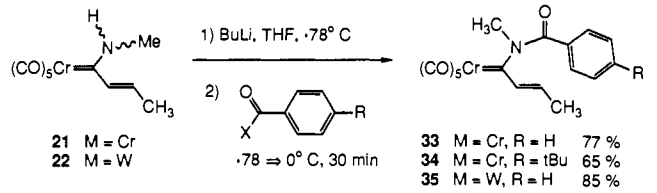


Figure 3. ORTEP diagram of **34**.

Scheme IX



esters and much more reactive dieneophiles than the parent amides.[21] Deprotonation of the **22** with butyllithium followed by addition of a benzoyl halide led to the isolation of a single isomer of the relatively stable *trans*-propenyl(*N*-methyl-*N*-benzoylamino)carbene complex **35** (Scheme IX). An identical product was isolated regardless of which isomer of the (methylamino)carbene complex was used, but higher yields of **35** were obtained starting from the *Z*-rotamer. The complex was most conveniently prepared from a 1:1 mixture of *E*- and *Z*-isomers of **22** (85% yield). The analogous chromium complexes **33** and **34** were prepared in a similar fashion and also were each obtained as a single isomer.

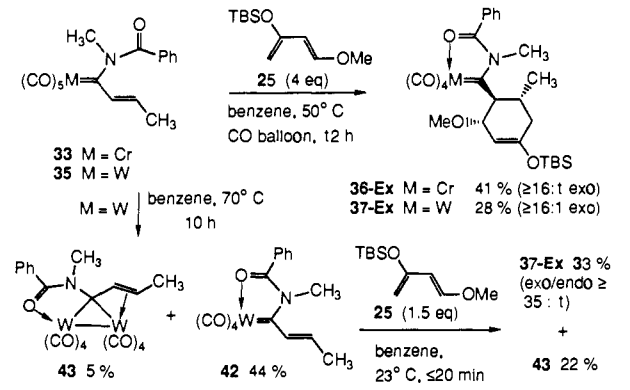
The chromium and tungsten complexes **33** and **35** were both oils and thus could not be characterized in the solid state. However, the *p-tert*-butylbenzoyl derivative **34** was crystalline, and several interesting structural features were revealed in the solid state by X-ray analysis (Table IV). The first is the finding that the stereochemistry about the carbene carbon–nitrogen bond has the benzoyl group oriented away from the metal (Figure 3). The C–C double bond of the propenyl group is out of the metal–carbene carbon–nitrogen plane, which is indicated by the dihedral angle Cr–C(6)–C(7)–C(8) of −188.7°. The appended *N*-benzoyl unit has essentially no influence on the $N–C_{carb}$ (1.320 Å) and $Cr–C_{carb}$ (2.092 Å) bond lengths when compared to typical aminocarbene complexes. The *N*-benzoyl moiety is severely distorted out of an orientation that would allow for nitrogen lone pair conjugation into the carbonyl (the dihedral angle C(6)–N–C(11)–O(6) is −114.4°). The N–CO bond length (1.487 Å) is extremely long, even when compared with that of orthogonal amides.[22] The solid-state structure of **34** suggests that the *N*-benzoyl group does not compete favorably with the carbene carbon for the nitrogen lone pair. The spectra of **34** in solution also suggest that the carbon–oxygen bond of the carbonyl group is not in conjugation with the nitrogen and aminocarbene ligand. A distorted orientation of the N–CO bond is most consistent with the relatively high-energy carbonyl IR stretch (1725 cm^{-1}) compared to that of typical amides (~1630–1680 cm^{-1}) or even imides (~1710 cm^{-1}).[22] The shift of the vinyl hydrogens in the ^1H NMR spectrum of **34** more closely resembles the unreactive *Z*-isomer of **22** than the reactive *E*-isomer (δ = 6.60 (vinyl CH_α), δ = 5.10 (vinyl CH_β)). Regardless of the structural features indicated by the spectral data, the *N*-benzoyl moiety did have an influence on the cycloaddition reactivity of the carbene complex.

(21) Vedejs, E.; Gadwood, R. C. *J. Org. Chem.* **1978**, *43*, 376.
(22) Bennet, A. J.; Wang, O.-P.; Slebocka-Tilk, H.; Somayaji, V.; Brown, R. S.; Santarsiero, B. D. *J. Am. Chem. Soc.* **1990**, *112*, 6383.

Table IV. Selected Bond Lengths and Bond Angles for **34**

Bond Length (Å)	
Cr–C(1)	1.908 (6)
Cr–C(3)	1.872 (5)
Cr–C(6)	2.092 (4)
N–C(6)	1.320 (5)
N–C(10)	1.469 (7)
N–C(11)	1.487 (5)
O(6)–C(11)	1.193 (5)
C(6)–C(7)	1.487 (7)
C(7)–C(8)	1.305 (6)
C(8)–C(9)	1.489 (8)
C(11)–C(17)	1.473 (6)
O(1)–C(1)	1.136 (7)
O(3)–C(3)	1.148 (6)
Bond Angle (deg)	
C(6)–N–C(10)	124.8 (3)
C(6)–N–C(11)	124.0 (4)
C(10)–N–C(11)	111.2 (3)
Cr–C(6)–N	130.7 (3)
Cr–C(6)–C(7)	116.9 (3)
N–C(6)–C(7)	112.3 (3)
C(6)–C(7)–C(8)	126.1 (4)
C(7)–C(8)–C(9)	126.4 (5)
N–C(11)–O(6)	119.1 (4)
N–C(11)–C(17)	114.9 (3)
O(6)–C(11)–C(17)	125.8 (4)
Dihedral Angle (deg)	
Cr–C(6)–C(7)–C(8)	−188.7
C(6)–N–C(11)–O(6)	−114.4

Scheme X



The red-to-orange *N*-benzoyl complexes **33–35** could be handled in air, were stable to water, and could be purified on silica gel. However, they do slowly decompose to give highly-colored organometallic compounds. Initially, these compounds were not identified, but it was found that the decomposition could be slowed in the presence of CO. The Diels–Alder reaction of **35** with **25** was therefore carried out under CO atmosphere for 12 h at 50 °C (Scheme X). When compared to the conditions necessary to give a Diels–Alder product from **22-E**, the pendent benzoyl group had an obvious effect. In the former cases, the reactions were carried out in neat diene at 90 °C, whereas the reaction of 35 was run in benzene solution with only 4 equiv of **25** at a much lower temperature. The ^1H NMR of the crude reaction mixture indicated the presence of a single Diels–Alder adduct (28%, 35% based on unrecovered **35**) as well as some residual starting carbene complex **35** (20% recovery). By comparison of the diagnostic chemical shifts and coupling constants (Table I), the product was assigned as the exo stereoisomer **37-Ex**. The chromium *N*-benzoyl complex **33** was completely consumed under similar conditions and, likewise, led to a single Diels–Alder product which was

Table V. Selected Spectral Data for Carbene Complexes **35** and **42**[a]

	carbene complex	
	35	**42**
IR CO_{metal}	2063 m cm^{-1}	2011 m cm^{-1}
	1974 (sh)	1902 vs
	1910 vs	1839 s
IR CO_{amide}	1725 m	nd[b]
$C_{benzoyl}$	175.9 ppm	183.1 ppm
C_{carb}	258.3	282.3
H_α	6.48 ppm	6.65 ppm
H_β	5.29	7.85
C_α	145.7 ppm	139.9 ppm
C_β	126.4	151.2

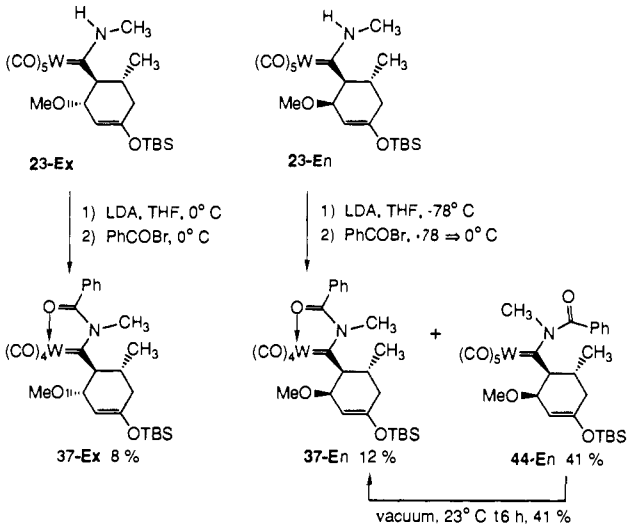
[a] All NMR spectra in $CDCl_3$. IR spectra as thin film. H_α and H_β were assigned by proton–proton coupling, and C_α and C_β were assigned by HETCOR from the proton assignments. [b] Not detected.

assigned as the exo cycloadduct **36-Ex**. Additionally, as described below, authentic samples of both the endo and exo adducts of **37** were prepared, and thereby, from a ^1H NMR analysis of the crude mixture from the reaction of **35** with **25**, a threshold on the exo:endo selectivity could be set at ≥16:1.

It was clear from the IR, ^{13}C NMR, and elemental analyses that the Diels–Alder adducts **36-Ex** and **37-Ex** were not pentacarbonyl complexes. Potentially, either the carbonyl oxygen of the benzoyl group or the oxygen of the methoxy group could chelate to the metal and occupy the sixth coordination site. Chelation of a methoxy group to the chromium center has been observed in related Diels–Alder adducts but only for the endo isomers and not the exo isomers.[2b] Similar methoxy chelates have also been observed for endo cycloadducts of tungsten carbene complexes.[2b] Examples of chelated carbonyl oxygens of *N*-acyl complexes have been recently reported by Dötz, Grotjahn, and Harms.[23] In the present case, the benzoyl-chelated structure **37-Ex** would be most consistent with the fact that the *N*-benzoyl carbonyl absorbance was no longer observed at 1725 cm^{-1} and could not be unambiguously located. The assignment of the *O*-benzoyl chelate **37-Ex** was also confirmed by the reactions shown in the bottom of Scheme X.

The reactions shown in the bottom of Scheme X were carried out to address the issue of which happened first in the reaction of **35** with **25**, chelation of the benzoyl group or the Diels–Alder reaction. This point was addressed by beginning with a careful analysis of the previously observed purple and greenish-brown decomposition products of **35**. As noted, decomposition of **35** had been slowed by stirring the carbene complex **35** under a CO atmosphere. Thermolysis of **35** in the absence of CO or application of dynamic vacuum to a concentrated sample of **35** provided the decomposition products in quantities sufficient for characterization. The moderately stable, deep purple organometallic product proved to be a tetracarbonyl carbene complex that had spectral characteristics consistent with the chelated carbene complex **42**. The carbene carbon and benzoyl carbon resonances of **42** are shifted downfield with respect to the starting pentacarbonyl carbene complex **35** (Table V). The relative α- and β-vinyl proton shifts follow the same general trend that had been found for the reactive *E*-isomer of **22** (Table III), but an even more dramatic downfield shift of H_β is observed for **42** (δ = 7.85, H_β). The stereochemistry about the carbene carbon–nitrogen bond in **35** is assumed to have the benzoyl group anti to the metal, on the basis of the solid-state structure of **34**, and therefore the barrier to rotation about this bond is greatly reduced with respect to normal amino complexes, given that the chelate **42** can be generated from **35** under conditions at which rotamers of amino complexes cannot be interconverted. The greenish-brown organometallic product from the thermolysis of **35** has been assigned as the binuclear μ-carbene complex **43**, which has a coordinated propenyl group and benzoyl oxygen to either tungsten.[24,25]

Scheme XI



The chelated propenylcarbene complex **42** is remarkably reactive in Diels–Alder reactions. It is more reactive than any other aminocarbene complex that has been examined and is equal in reactivity with the methoxypropenyl carbene complex **20**. The reaction of the chelated carbene complex **42** with **25** was carried out under the same dilution as the reaction with the pentacarbonyl complex **35** and was complete in less than 20 min at room temperature to give the spectroscopically identical exo product **37-Ex** along with a 22% yield (based on W) of the dinuclear decomposition product **43**. Notice that this is the same order of reactivity that was observed for the methoxy complex **20**, which proceeded at room temperature under neat conditions in 10 min. The rate at which the complex **35** decomposes to **42** is on the order of the rate at which **35** undergoes Diels–Alder reaction with **25**, and thus it is suspected that chelation precedes cycloaddition. What is clear, however, is that the chelated complex **42** is much more reactive than the nonchelated complex **35**.

The stereochemical assignment of the cycloadduct **37-Ex** was confirmed by its spectral data and by an independent synthesis of both the endo and exo isomers of **37**. Independent conversion of the exo and endo cycloadducts of **23** to the chelated complexes by N-deprotonation with LDA, followed by treatment with benzoyl bromide, was carried out as indicated in Scheme XI. These reactions were not optimized, but it was found that higher yields could be obtained by deprotonating and initiating the acylation at lower temperatures. The acylation of **23-En** gave both chelated and nonchelated complexes, and the latter could be converted to the former under vacuum. Purified samples of both **37-Ex** and **37-En** could thus be obtained. The coupling constants observed for key proton–proton coupling of ring protons also confirm the exo and endo assignments (Table I). Armed with the spectra data of both the endo and exo cycloadducts of **37**, the level of the selectivity of the Diels–Alder reaction **42** with **25** could be set at exo:endo ≥ 35:1 from the ^1H NMR spectrum of the crude reaction mixture.

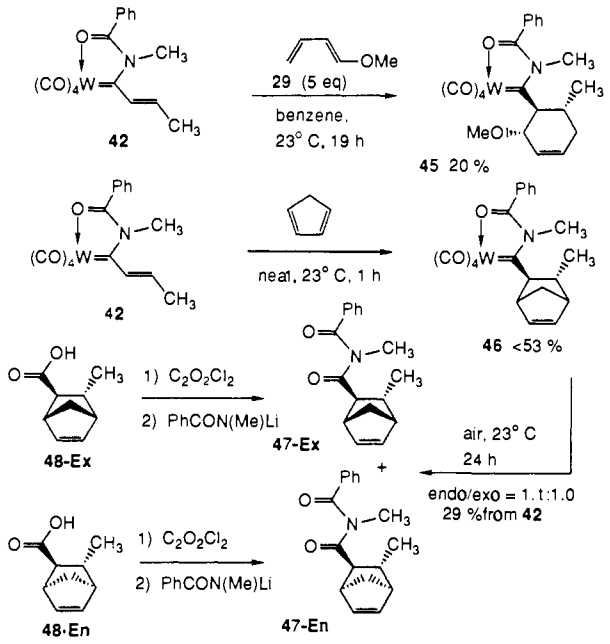
With a sample of the endo Diels–Alder adduct **37-En** in hand, it was possible to determine whether thermodynamic equilibration to the exo adduct **37-Ex** under the reaction conditions was responsible for the observed exo selectivity. Stirring **37-En** at room temperature in the presence of excess diene **25** did not lead to detectable quantities of **37-Ex**. Considerable decomposition of **37-En** was noted, and, while a 53% recovery of **37-En** was observed after 20 min at room temperature, complete loss of **37-En** was observed at higher temperatures. The instability of these com-

(23) (a) Dötz, K. H.; Grotjahn, D.; Harms, K. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 1384. (b) Dötz, K. H.; Grotjahn, D.; Harms, K. *J. Organomet. Chem.* **1989**, *375*, C47.

(24) A complex related to 43 has been characterized by X-ray diffraction: Wulff, W. D.; Powers, T. A.; Rheingold, A. L., unpublished results.

(25) For characterization of other types of μ-binuclear tungsten carbene complexes, see: Macomber, D. W.; Hung, M. H.; Madhukar, P.; Liang, M.; Rogers, R. D. *Organometallics* **1991**, *10*, 737 and references therein.

Scheme XII



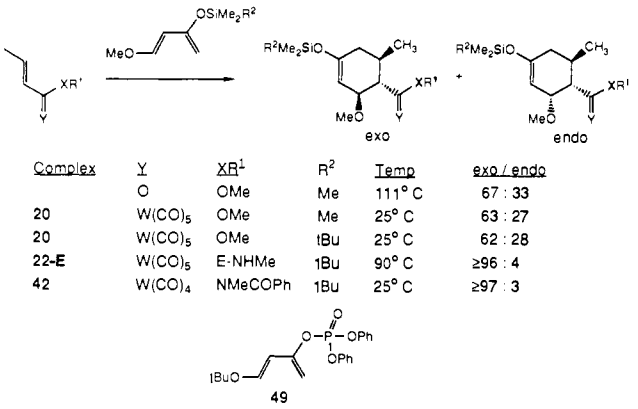
plexes may be in part responsible for the low yields in these reactions. It can be concluded that the exo selectivity of this Diels–Alder reaction is not due to thermodynamic equilibration of initially formed **37-En**. Also, since **37-En** can be isolated and is reasonably stable, it can also be concluded that if it were formed it would probably be detectable.

High exo selectivity and large rate enhancements were also found for the reaction of **42** with **1**-methoxy-1,3-butadiene. The reaction was carried out with 5 equiv of diene in benzene for 19 h at room temperature to give the exo complex **45** as the exclusive Diels–Alder product (Scheme XII). The yield of the reaction, as was the case with **22-E**, was low. The reaction of **42** with cyclopentadiene was the only unselective reaction encountered. Cycloaddition in neat diene was complete within 1 h at room temperature. The diastereomeric products could not be isolated with sufficient purity, so the carbene complexes were directly air-oxidized and the organic imides were characterized. The oxidation product was a 1.1:1 (endo:exo) mixture of stereoisomers. The structural assignments of the imides **47** were made by an independent synthesis from the corresponding endo and exo carboxylic acids **48**.[26] It was not determined whether the dinuclear product **43**, the decomposition product of the chelated carbene complex **42**, was formed in the reactions shown in Scheme XII.

Results and Discussion

Synthetic Potential and Exo Selectivity of the Reactions of 22-E and 42. There are two aspects of the Diels–Alder reactions of complexes **22-E** and **42** that give promise for potential applications in synthetic organic chemistry: (1) their very high exo selectivity with acyclic dienes and (2) their high reactivity with, and at the same time their tolerance of, the sensitive functionality in the highly electron-rich dienes **25** and **29**. Both of these facets of the Diels–Alder reactions of carbene complexes should be useful in countering shortcomings of conventional Diels–Alder reactions. Diels–Alder reactions in principle can give eight possible products composed of different regioisomers, diastereomers, and enantiomers. In general, the utilization of the Diels–Alder reaction has been limited to those four products from the endo domain. There is no general method by which exo products can be obtained from the Diels–Alder reaction.[28] There are a few Diels–Alder

Scheme XIII



Complex	Y	XR^1	R^2	Temp	exo / endo
	O	OMe	Me	111° C	67 : 33
20	$W(CO)_5$	OMe	Me	25° C	63 : 27
20	$W(CO)_5$	OMe	tBu	25° C	62 : 28
22-E	$W(CO)_5$	E-NHMe	tBu	90° C	≥96 : 4
42	$W(CO)_4$	NMeCOPh	tBu	25° C	≥97 : 3

reactions that are exo selective, but these are restricted to limited cases which, by and large, are composed of those with furans as dienes,[29] with α-substituted dienophiles,[30] or with those dienophiles that are locked into s-cis conformations.[31,32] However, to our knowledge there are no Diels–Alder reactions of crotonate dienophiles that are highly exo selective, and thus the reactions of **22-E** and **42** with dienes **25** and **29** represent the first selective entry to exo cycloadducts with a crotonate dienophile (Scheme XIII).[33,34,35] The implications for the expanded scope of these reactions are clear when it is considered that exo-selective reactions with monosubstituted dienophiles are exceptionally rare.[36]

The tolerance of these carbene complexes for sensitive dienes such as **25** also overcomes a current limitation of the application of the Diels–Alder reactions of these dienes. More often than not, thermal Diels–Alder reactions are only marginally endo selective; however, in most cases the endo selectivity can be significantly enhanced by the use of Lewis acids. This, however, has not been possible in the case of 1,3-dioxygenated dienes due to the sensitivity of these dienes to the Lewis acids that are typically employed.[37] There is only a single report of a Diels–Alder reaction of an acyclic 1,3-diene in this class that has been accelerated with a Lewis acid.[38,39] This involved the reaction of the deactivated diene **49** with a phosphate ester substituent with a chiral dienophile, which was reported to be accelerated by trifluoroacetic anhydride and to give a 99:1 selectivity for the endo adduct.[38] The rather special diene **49** was designed for its ability to tolerate Lewis acids, and it was reported that 3-[(trimethylsilyl)oxy]-1-*tert*-butoxy-1,3-

(26) Poos, G. I.; Lehman, M. M. *J. Org. Chem.* **1961**, *26*, 2576.
(27) (a) O'Connor, J. M.; Uhrhammer, R.; Rheingold, A. L.; Staley, D. L.; Chandha, R. K. *J. Am. Chem. Soc.* **1990**, *112*, 7585. (b) DeShong, P.; Slough, G. A. Sidler, D. R.; Rybczynski, P. J.; Von Philipsborn, W.; Kunz, R. W.; Bursten, B. E.; Clayton, T. W. *Organometallics* **1989**, *8*, 1381.
(28) For recent citations to the literature, see: Oppolzer, W. In *Comprehensive Organic Synthesis*; Trost, B. M.; Fleming, I., Eds.; Pergamon Press: New York, 1991; Vol 5, pp 315–399.
(29) Lee, M. W.; Herndon, W. C. *J. Org. Chem.* **1978**, *43*, 518.
(30) (a) Creary, X.; Inocencio, P. A.; Underiner, T. L.; Kosiromin, R. *J. Org. Chem.* **1985**, *50*, 1932. (b) Seguchi, K.; Sera, A.; Otsuki, Y.; Maruyama, K. *Bull. Chem. Soc. Jpn.* **1975**, *48*, 3641. (c) Kobuke, Y.; Fueno, T.; Furukawa, J. *J. Am. Chem. Soc.* **1970**, *92*, 6548. (d) Martin, J. G.; Hill, R. K. *Chem. Rev.* **1961**, *61*, 537.
(31) (a) Roush, W. R.; Essenfeld, A. P.; Warmus, J. S.; Brown, B. B. *Tetrahedron Lett.* **1989**, *30*, 7305. (b) Adam, W.; Alberi, R.; Hasemann, L.; Nava Salgado, V. O.; Nesiler, B.; Peters, E. M.; Peters, K.; Prechtl, F.; von Schnering, H. G. *J. Org. Chem.* **1991**, *56*, 5782. (c) Fotiadu, F.; Michel, F.; Buono, G. *Tetrahedron Lett.* **1990**, *31*, 4863. (d) Maitay, J.; Mertes, J.; Maas, G. *Chem. Ber.* **1989**, *122*, 327.
(32) Roush, W. R.; Brown, B. B. *J. Org. Chem.* **1992**, *57*, 3380 and references therein.
(33) Exo-selective reactions have been observed for acrylate and methacrylate derivatives of bimetallic carbene complexes: Finn, M. G. 43rd Southeast Regional Meeting of the American Chemical Society, Richmond, VA, November 12–15, 1991; ORG 229.
(34) Exo selective reactions have been observed for crotonate derivatives of binuclear iron acyl complexes with Danishefsky's diene: Gilbertson, S. R., personnal communication.
(35) Furan gives a 1:1 mixture of isomers with methylcrotonate: Dauben, W. C.; Krabbenhoft, H. O. *J. Am. Chem. Soc.* **1976**, *98*, 1992.
(36) (a) Lamy-Schelken, H.; Ghosez, L. *Tetrahedron Lett.* **1989**, *30*, 5891. (b) Lamy-Schelkens, H.; Giomi, D.; Ghosez, L. *Tetrahedron Lett.* **1989**, *30*, 5887.
(37) See ref 13a, 280.
(38) Kouklovsky, C.; Pouilhes, A.; Langlois, Y. *J. Am. Chem. Soc.* **1990**, *112*, 6672.
(39) For an example with a cyclic diene, see ref 36.

butadiene was not stable in the presence of trifluoroacetic anhydride.

Factors Affecting Reactivity and Selectivity. One of the interesting observations made in the above work is that of the source of the difference in the reactivity of the complexes **22-E**, **22-Z**, and **28**; however, at this time sufficient data is not available to identify the source of these differences. There is also the issue of the decreased reactivity of the amino complexes relative to the methoxy complexes. This would not be predicted from the chemical shifts of the vinyl protons and the vinyl carbons that are indicated in Table III. With the reasonable assumption that the transition state of the Diels–Alder reaction of these complexes requires a planar conformation of the vinyl group, it would be expected, for example, that the methoxy complex **20** would react more slowly than the amino complex **22-E**, since the vinyl proton and carbon shifts indicate that there is a greater preference for nonplanar conformations for **20** than for **22-E** for the reasons discussed above (Table III). This can be explained by a situation in which the planar conformations in the alkoxy complexes are so much more reactive than the planar conformations of **22-E** that the change of conformational preferences can be offset. As indicated by the data in Table III, the greater reactivity of alkoxy complexes over amino complexes in the Diels–Alder reaction correlates with the chemical shift of the carbene carbon. Therefore, it would be expected that the planar conformation for complexes **20** and **32** would be more reactive dienophiles than the planar conformations of **22** or **28** if it is true, as suggested, that the carbon shifts of carbene complexes are at least an indicator of electron deficiency at the carbene carbon.[40] Furthermore, it is not unreasonable to evoke an activation of the vinyl group of the dienophile by delocalization of electron density into the carbene carbon, since for alkynylcarbene complexes (of the type **8** and **10**, Scheme III), where the carbene substituent is configurationally restricted in an orientation that allows conjugation, it has in fact been shown that the β-carbon is shifted downfield relative to the α-carbon.[19] Thus, the overall observed reactivities of the complexes in Table III could correlate with the combined effects of the nature of the heteroatom stabilizing group and the preferred conformation of the alkenyl substituent of the carbene carbon.

Another key issue raised in this work is the increased reactivity of the chelated complex **42** relative to its pentacarbonyl analog **35**. It seems counterintuitive that the loss of a CO ligand from the metal pentacarbonyl unit should lead to a more reactive dienophile. This phenomenon can be better understood if the crystal structure of the *N*-benzoyl pentacarbonyl complex **34** is reconsidered. It is evident from the data previously discussed that in solution for the complex **34**, the distorted *N*-benzoyl carbonyl experiences little electronic interaction with the lone pair from the basic nitrogen. By chelating to the metal, the carbonyl is now fixed into a conformation that allows delocalization of the nitrogen lone pair into the *N*-benzoyl carbonyl. Apparently, in terms of their ability to remove electron density from the metal, the loss of a carbon monoxide ligand during chelation is more than offset by the gain in withdrawal of electron density from the metal via the *N*-benzoyl group. Whether there is any special stabilization in the chelated complex **42** that is related to aromaticity cannot be determined with the data that we have at this time.[27] That the chelated complex **42** is approximately as reactive as the methoxy complex **20** in reactions with diene **25** is probably partly due to a decrease of electron density at the carbene carbon in **42**, as indicated by the shift of the carbene carbon from complex **35** to **42**, and partly due to the fact that, as indicated by the NMR data, there is a much larger preference for conformations that have the alkenyl group in conjugation with the carbene complex for **42** (Table V) than there is for **20** (Table III).

Finally, perhaps the most important observation to be made from this work is that of the exo-selective nature of the Diels–Alder reactions of complexes **22-E** and **42**. An s-cis conformation of the propenyl group was assumed for the reactive configuration of complex **22** in the preceding discussion. This assumption also leads to a reasonable explanation of the stereoselectivity of these reactions. The unique exo selectivity that distinguishes these reactions is most likely a consequence of the metal pentacarbonyl fragment sterically preventing the more typical endo configuration of the diene and forcing the approach away from the metal, thereby giving the observed exo product (Figure 4). This model also accounts for the lack of selectivity observed in the reaction with cyclopentadiene where there would be expected to be significant steric interactions with the metal pentacarbonyl group in either the exo or endo transition states.

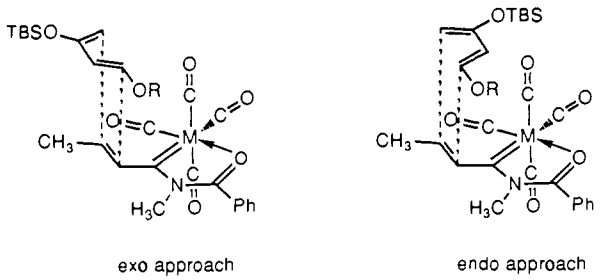


Figure 4.

Summary

The long-range goal that prompted the present study is the development of asymmetric Diels–Alder reactions of aminocarbene complexes having a chiral amine as an auxiliary. As a prelude, the present work has resulted in the development of the first intermolecular Diels–Alder reactions of aminocarbene complexes and has established the necessary design features for a chiral system. At the same time, it was discovered that the intermolecular Diels–Alder reactions of these complexes are highly exo selective with acyclic dienes. The low reactivity of the alkylamino complexes can be overcome by derivatization of the nitrogen with an electron-withdrawing *N*-benzoyl group. The greatest reactivity was for the tetracarbonyl complexes in which the benzoyl carbonyl oxygen is chelated to the metal.

The methoxycarbene complexes had previously been demonstrated to be synthons for α,β-unsaturated carbonyl dienophiles, and it had been specifically pointed out that the methoxy complexes had specific advantages as synthons relating to rate and increased regio- and stereoselectivity and increased tolerance of sensitive dienes.[2b] Whereas the methoxy complexes offer advantages, the amino complexes offer options: the opportunity to selectively obtain exo adducts from the Diels–Alder reaction. The main drawback of the activated complex **42** developed in this work is its relative instability, which is most likely the source of the low yields in its Diels–Alder reactions. The mild reaction conditions necessary for the cycloaddition reaction and the unique exo selectivity that is observed, nonetheless, makes continued development of this methodology appealing.

Experimental Section

All reagents were obtained from commercial suppliers and used without further purification unless otherwise indicated. Tetrahydrofuran (THF), ether, and benzene were distilled from benzophenone ketyl under nitrogen. Chromatographic purifications were performed on silica gel (230–400 mesh) under gravity or by flash technique. Unless otherwise specified, the solvent mixture employed is a mixture of ether, methylene chloride, and hexanes in a ratio that is indicated in each section in parentheses. Proton NMR data were obtained either on a University of Chicago-built DS-1000 500-MHz instrument or a General Electric QE-300-MHz instrument. Carbon-13 spectra were obtained on the QE-300 instrument at 75 MHz or on a Varian XL-400 instrument at 100 MHz. HETCOR experiments were obtained either on a General Electric Ω-300- or Ω-500-MHz instrument. Infrared spectra were taken on a Nicolet 20SX FTIR. Low-resolution mass spectra were recorded on a Finnigan 1015 mass spectrometer. High-resolution mass spectra were recorded on a VG 70-250 instrument or obtained from the Midwest Center for Mass Spectrometry in Lincoln, NE. Elemental analyses were done by Galbraith Laboratories in Knoxville, TN.

Preparation of [2-Furyl(diallylamino)methylene]pentacarbonyltungsten(0) (16). To a solution of **13**[31] (mixture of *E*- and *Z*-isomers)

(40) For leading references, see: Casey, C. P.; Albin, L. D.; Saeman, M. C.; Evans, D. H. *J. Organomet. Chem.* **1978**, *155*, C37.

Table VI. Crystallographic Data for **22-E**, **22-Z**, and **34**

	22-E	22-Z	34
	(a) Crystal Parameters		
formula	$W(CO)_5(C_5H_9N)$	$W(CO)_5(C_5H_9N)$	$Cr(CO)_5(C_{12}H_{13}ON)$
crystal system	monoclinic	monoclinic	monoclinic
space group	$P2_1/c$ (No. 14)	$A2/m$ (No. 12)	$P2_1/n$ (No. 14)
a, Å	13.970 (4)	12.372 (3)	11.219 (2)
b, Å	6.539 (2)	7.782 (2)	10.870 (2)
c, Å	15.176 (5)	13.475 (3)	18.990 (8)
β, deg	111.34 (2)	99.87 (2)	107.22 (3)
V, Å^3	1291.3 (7)	1278.2 (5)	2212.0 (14)
Z	4	4	4
cryst dimens, nm	0.26 × 0.32 × 0.40	0.30 × 0.40 × 0.28	0.38 × 0.38 × 0.38
cryst color	yellow	yellow	orange
d(calc), g cm^{-3}	2.093	2.115	1.307
μ(Mo Kα), cm^{-1}	94.70	95.45	5.36
T, K	297	297	297
T(max)/T(min)	2.360	2.400	1.109
	(b) Data Collection		
diffractometer	Nicolet R3m		
monochromator	graphite		
radiation	Mo Kα (λ = 0.71073 Å)		
2θ scan range, deg	4–50	4–50	4–46.5
data collected (h,k,l)	±17,+8,+19	±15,+10,+16	±13,+13,+22
rflns, collected	2592	2835	3485
indpt rflns	2274	1365	3174
indpt obsvd rflns $F_o > n\sigma(F_o)$ (n = 5)	1773	1181	2082
std rflns	3 std/197 rflns	3 std/197 rflns	3 std/197 rflns
	(c) Refinement		
$R(F)$, %	3.61	3.07	4.93
R(wF), %	3.70	3.46	5.31
Δ/σ (max)	0.003	0.020	0.011
Δ (ρ), eÅ$^-$	1.347	1.313	0.305
N_o/N_v	11.4	11.8	8.0
GOF	1.068	0.849	1.304

(0.285 g, 0.620 mmol) in 5 mL of THF was added a solution of *n*-butyllithium (0.40 mL, 1.55 M, 0.62 mmol) in hexane at −78 °C under an argon atmosphere. After 15 min, allyl iodide (0.22 g, 1.31 mmol) was injected, and the solution was warmed to 0 °C for 30 min. The reaction was quenched by the rapid addition of a saturated NH_4Cl solution. The mixture was diluted with ether and washed with water and brine, and the organics were dried over $MgSO_4$. The solution was filtered and concentrated by rotary evaporation in a slightly warm water bath. The product was purified by silica gel chromatography (1:1:4) to give **16** (0.158 g, 0.317 mmol) as a 4:1 mixture with the Diels–Alder adduct **17** (R_f = 0.32).[31] The following spectral data for **16** were taken from the spectrum of the 4:1 mixture: R_f = 0.74; ^{1}H NMR ($CDCl_3$) δ 4.14 (d, 2 H, J = 4.9 Hz), 4.84 (d, 2 H, J = 5.5 Hz), 5.18 (m, obscured, 1 H), 5.33 (m, obscured, 2 H), 5.44 (d, 1 H, J = 10.2 Hz), 5.75 (m, 1 H), 5.95 (m, 1 H), 6.40 (m, 2 H), 7.47 (s, 1 H). The alkylation product **16** was completely converted to the Diels–Alder adduct **17** within 20 h at room temperature.

Preparation of [*trans*-Propenyl(methylamino)methylene]pentacarbonylchromium(0) (21). Carbene complex **19**[2b] (0.4211 g, 1.53 mmol) was dissolved in 3 mL of ether and cooled to the freezing point (−110 °C, ethanol, liquid N_2). A solution of methylamine (0.90 mL, 0.63 g, 20.3 mmol) in 3 mL of ether was transferred into the carbene complex solution via cannula, and the mixture was allowed to thaw and warm to room temperature. The mixture was concentrated by rotary evaporation. Silica gel chromatography (1:1:4) led to the isolation of two yellow organometallic compounds which were identified as the **21-E** rotomer (0.331 g, 1.203 mmol) in 79% and the **21-Z** rotomer (0.0382 g, 0.139 mmol) in 9% yield. The following spectral data were collected for **21**: ^{1}H NMR ($CDCl_3$) (*E*-isomer) δ 1.98 (dd, 3 H, J = 1.0, 6.7 Hz), 3.16 (d, 3 H, J = 5 Hz), 6.29 (m, 1 H), 6.87 (br d, 1 H, J = 17 Hz), 8.53 (br s, 1 H, NH); (*Z*-isomer) δ 1.82 (d, 3 H, J = 7 Hz), 3.61 (d, 3 H, J = 5 Hz), 5.57 (dq, 1 H, J = 17, 7 Hz), 6.86 (d, 1 H, J = 17 Hz), 8.67 (br s, 1 H, NH); ^{13}C NMR ($CDCl_3$) (*Z*-isomer) δ 19.30, 36.35, 136.13, 141.00, 218.00, 222.98, 272.21; IR (thin film) ν 2051 m, 1920 sh, 1898 vs, 1886 vs, 1547 w, 1513 w; MS, m/z (relative intensity) 276 (4) M^+ + 1, 275 (11) M^+, 247 (12), 219 (6), 191 (9), 163 (19), 136 (18), 135 (100), 120 (7). Anal. Calcd for $C_{10}H_9O_5CrN$: C, 43.64; H, 3.27; N, 5.09. Found (from mixture): C, 44.17; H, 3.51; N, 5.10.

Preparation of [*trans*-Propenyl(methylamino)methylene]pentacarbonyltungsten(0) (22). A solution of carbene complex **20**[2b] (1.07 g, 2.61 mmol) in 20 mL of ether was cooled to −78 °C under an argon atmosphere. Methylamine was bubbled through the solution in brief intervals until a yellow solution persisted and TLC indicated that all of the starting material had been consumed. The solution was diluted with ether and washed with dilute HCl (0.1 N), water, $NaHCO_3$ (saturated, aqueous), and brine. The ethereal extract was dried over anhydrous magnesium sulfate, filtered through Celite, and concentrated. The ^{1}H NMR of this crude mixture indicated complete conversion to the desired product **22** as a 1:1.2 (*E*:*Z*) mixture of rotamers. Silica gel chromatography (1:1, hexanes:ethyl acetate) of the mixture led to the isolation of pure *E*-rotamer (0.316 g, 0.78 mmol) in 30% yield as a yellow solid; a 1:4.5 (*E*:*Z*) mixture of rotamers (0.387 g, 0.95 mmol); and pure *Z*-rotamer (0.0724 g, 0.18 mmol) in 7% yield as a yellow solid. The combined yield of the reaction (0.776 g, 1.907 mmol) was 73%. Spectral data for **22-E**: R_f = 0.77; mp 107–108 °C; ^{1}H NMR ($CDCl_3$) δ 2.03 (dd, 3 H, J = 10, 6.6 Hz, CH_3), 3.15 (d, 3 H, J = 5.23 Hz, NCH_3), 6.48 (dd, 1 H, J = 1, 15 Hz, CH_α), 6.67 (dq, 1 H, J = 15, 6.7 Hz, CH_β), 8.36 (br s, 1 H, NH); ^{13}C NMR ($CDCl_3$) δ 19.53, 35.93, 136.50, 149.12, 199.00 (J_{cw} = 126 Hz), 202.94, 250.05; (C_6D_6) δ 19.02, 34.68, 136.73 (C_α), 147.92 (C_β), 199.71, 202.89, 249.28. The carbon resonances were assigned by a HETCOR experiment, correlating the proton doublet and doublet of quartets with the corresponding carbons: IR (thin film) ν 2058 w, 1965 sh, 1899 s, 1879 s, 1532 w; (chloroform) 2050 m, 1963 sh, 1910 s, 1903 s; MS m/z (relative intensity) 207 (20) M^+, 379 (18), 351 (10), 321 (27), 295 (76), 265 (100), 237 (53), 222 (42), 209 (29), 197 (12), 132 (18). Anal. Calcd for $C_{10}H_9O_5WN$: C, 29.52; H, 2.23; N, 3.44. Found: C, 29.58; H, 2.28; N, 3.54. This product was further characterized by X-ray crystallography (vide infra). Spectral data for **22-Z**: R_f = 0.70; mp 91–92 °C; ^{1}H NMR ($CDCl_3$) δ 1.91 (d, 3 H, J = 6.22 Hz, CH_3), 3.54 (d, 3 H, J = 5.1 Hz, NCH_3), 5.90 (dq, 1 H, J = 15, 6.6 Hz, CH_β), 6.75 (d, 1 H, J = 15 Hz, CH_α), 8.5 (br s, 1 H, NH); ^{13}C NMR ($CDCl_3$) δ 17.97, 41.58, 130.08, 146.81, 198.28, 203.37, 249.32; (C_6D_6) δ 17.67, 41.07, 131.22 (C_β), 146.46 (C_α), 198.88 (J_{cw} = 126 Hz), 203.73, 246.99. The carbon resonances were assigned from a HETCOR experiment, correlating the proton doublet and doublet of quartets with the corresponding carbons: IR (thin film) ν 2063 m, 1969 sh, 1910 vs, 1554 m; (chloroform) 2062 m, 1970 sh, 1929 s; MS m/z (relative intensity) 407 (24) M^+, 379 (17), 351 (13), 321 (32), 295 (88), 265 (100), 237 (42), 222 (26), 209 (10), 133 (31). Anal. Calcd for $C_{10}H_9O_5WN$: C, 29.51; H, 2.23; N, 3.44. Found: C, 29.58; H, 2.28; N, 3.54. This

product was further characterized by X-ray crystallography (vide infra).

Crystal Structure Determination for the Monomethylamino Complexes 22-E and 22-Z and for the *p*-*tert*-Butylbenzoylamino Complex 34. Crystal, data collection, and refinement parameters are collected in Table VI. A well-formed crystal each of **22-E** grown from petroleum ether/diethyl ether, of **22-Z** grown from ether/pentane, and of **34** grown from pentane was mounted on a fine glass fiber with epoxy cement. The unit cell parameters of **22-E**, **22-Z**, and **34** were each obtained from the least-squares fit of 25 reflections ($20° \leq \theta \leq 25°$). Preliminary photographic characterizations showed $2/m$ Laue symmetry for **22-E**, **22-Z** and **34**. The systematic absences in the diffraction data of **34** established the space group as $P2_1/n$ (No. 14). The systematic absences in the diffraction data of **22-E** uniquely established the space group as $P2_1/c$ (No. 14). The systematic absences in the diffraction data established that the space group of **22-Z** was either $A2$ (No. 5), Am (No. 8), or $A2/m$ (No. 12) (nonstandard $C2$, Cm, and $C2/m$, respectively). The E-statistics suggested the centrosymmetric alternative and the chemically sensible results of refinement indicated that $A2/m$ is the correct space group for **22-Z**. An empirical absorption correction was applied to the data sets of **22-E** and **22-Z** (216 ψ-scan reflections, pseudoellipsoid model). An absorption correction was not applied to the data set for **34** (low μ, well-shaped crystal, $T_{max}/T_{min} = 1.109$).

Structure Solution and Refinement. The structure of **22-E** was solved by heavy-atom methods, and **22-Z** was solved by direct methods, each of which located the W atom in **22-E** and **22-Z**, respectively. The structure of **34** was solved by a Patterson solution, which located the Cr atom. In **22-E**, **22-Z**, and **34**, the remaining nonhydrogen atoms were located through subsequent difference Fourier and least-squares syntheses. All hydrogens were included as idealized isotropic contributions ($d_{CH} = 0.960$ Å, $U = 1.2\ U$ for attached C) except for hydrogens on carbons C(5) and C(6) and on N(1) of **22-Z**, which were located and refined isotropically. In complex **22-Z**, all non-hydrogen atoms with the exception of C(1), O(1), C(3), and O(3) lie on a mirror plane. Tables of complete positional parameters and bond distances and bond angles for all complexes can be found in the supplementary material. Selected bond lengths and angles can be found in Table II for **22-E** and **22-Z** and in Table IV for complex **34**. All computer programs and the sources of the scattering angles are contained in the SHELXTL program library (5.1) (G. Sheldrick; Nicolet(Siemens), Madison, WI).

Diels–Alder Reaction of the Methoxy Complex 20 with Diene 25. Carbene complex **20**[1b] (0.241 g, 0.589 mmol) was dissolved in 1-methoxy-3-(*tert*-butyldimethylsiloxy)-1,3-butadiene (**25**)[41] (0.455 g, 2.13 mmol). A slightly exothermic reaction ensued, and after 10 min the volatiles were removed by high vacuum. The residue was purified by silica gel chromatography (1:1:10) to give the exo product **27-Ex** (0.228 g, 0.367 mmol) in 62% yield and the endo product **27-En** (0.1312 g, 0.211 mmol) in 36% yield. Spectral data for **27-Ex**: $R_f = 0.77$ (1:1:10); ^{1}H NMR ($CDCl_3$) δ 0.17 (s, 3 H, SiCH), 0.18 (s, 3 H, SiCH), 0.93 (s, 9 H, $C(CH)_3$), 0.98 (d, 3 H, $J = 6.31$ Hz), 1.93–2.04 (m, 3 H), 3.21 (s, 3 H), 4.01–4.10 (m, 2 H), 4.68 (s, 3 H), 4.90 (br s, 1 H); ^{13}C NMR ($CDCl_3$) δ −4.53 (q, $J = 119$ Hz), −4.50 (q, $J = 119$), 17.89 (s), 18.91 (q, $J = 125$ Hz), 25.50 (q, $J = 125$ Hz), 32.87 (d, $J = 132$ Hz), 38.89 (t, $J = 128$ Hz), 55.95 (q, $J = 140$ Hz), 70.23 (q, $J = 148$ Hz), 78.25 (d, $J = 130$ Hz), 81.31 (d, $J = 146$ Hz), 103.83 (d, $J = 156$ Hz), 151.63 (s), 197.34 ($J_{cw} = 126$ Hz), 204.07 (s), 348.21 (s); IR (thin film) ν 2955 w, 2922 w, 2848 w, 2070 s, 1986 sh, 1917 vs, 1657 m, 1451 m, 1218 m, 832 m. Spectral data for **27-En**: $R_f = 0.47$ (1:1:10), 0.71 (1:1:4); ^{1}H NMR ($CDCl_3$) δ 0.177 (s, 3 H, SiMe), 0.183 (s, 3 H, SiMe), 0.91 (d, 3 H, $J = 6.5$ Hz, CH_3), 0.94 (s, 9 H, CMe_3), 1.79 (dd, 1 H, $J = 11.2$, 17.5 Hz), 2.08 (dd, 1 H, $J = 5.5$, 17.6 Hz), 2.37 (m, 1 H), 3.19 (s, 3 H, OCH_3), 3.97 (dd, 1 H, $J = 3.5$, 11.4 Hz), 4.24 (br t, 1 H, $J = 4$ Hz), 4.68 (s, 3 H, OCH_3), 5.13 (br d, 1 H, $J \sim 3.5$ Hz); ^{13}C NMR ($CDCl_3$) δ −4.53 (q, $J = 119$ Hz), 17.95 (s), 19.45 (q, $J = 125$ Hz), 25.51 (q, $J = 125$ Hz), 27.48 (q, $J = 133$ Hz), 38.59 (t, $J = 129$ Hz), 56.53 (q, $J = 136$ Hz), 70.85 (q, $J = 148$), 74.64 (d, $J = 137$ Hz), 78.84 (d, $J = 135$ Hz), 101.89 (d, $J = 158$ Hz), 154.76 (s), 197.48 ($J_{cw} = 126$ Hz), 202.94 (s), 340.53 (s); IR (thin film) ν 2946 w, 2927 w, 2847 w, 2071 s, 1971 sh, 1919 vs, 1660 w, 1448 m, 1236 m, 831 m. Anal. Calcd for $C_{21}H_{30}O_8WSiN$: C, 40.52; H, 4.86. Found: C, 40.45; H, 5.07. The stereochemistry of **27-Ex** and **27-En** was confirmed by an analysis of coupling constants (Table I).

Diels–Alder Reaction of the Monomethylamino Complex 22-E with Diene 25 and an Independent Synthesis of the Cycloadduct 27-Ex. A round-bottom flask with a high-vacuum screw cap[42] was charged with carbene complex **22-E** (0.116 g, 0.287 mmol), which ws dissolved in 1-methoxy-3-(*tert*-butyldimethylsiloxy)-1,3-butadiene (**25**)[41] (0.850 g, 3.97 mmol). The solution was deoxygenated by the freeze–thaw method (−196 to 0 °C, 3 cycles), backfilled with argon, and stirred at 90 °C for 12 h. The volatiles were removed under high vacuum, and the residual oil was purified by silica gel chromatography (1:1:4) to give the exo Diels-Alder adduct **23-Ex** (0.128 g, 0.206 mmol) in 72% yield as a yellow solid. Spectral data for **23-Ex**: mp 119–123 °C; ^{1}H NMR ($CDCl_3$) δ 0.20 (s, 3 H, 6 H, $Si(CH)_2$), 0.87 (d, 3 H, $J = 6.31$ Hz), 0.95 (s, 9 H, $C(CH)_3$), 1.93 (dd, 1 H, $J = 10.6$, 17.2 Hz), 2.18 (dd, 1 H, $J = 5.3$, 17.2 Hz), 2.35–2.41 (m, 1 H), 2.48 (dd, 1 H, $J = 11$, 8.4 Hz), 3.24 (d, 3 H, $J = 5.0$ Hz), 3.28 (s, 3 H), 4.53 (br d, 1 H, $J = 8$ Hz), 5.12 (br s, 1 H), 9.03 (br s, 1 H, NH); ^{13}C NMR ($CDCl_3$) δ −4.44, 17.98, 20.01, 25.57, 33.54, 36.86, 37.84, 55.24, 58.84, 78.65, 80.90, 100.93, 152.63, 198.66, 200.83, 269.43; IR (thin film) ν 3375 br w, 2948 m, 2922 m, 2855 w, 2061 s, 1966 sh, 1904 vs, 1664 m, 1524 m, 1205 m, 839 m, 605 m; MS m/z (relative intensity) 621 (1) M^+, 593, 563 (3), 535 (9), 505 (12), 479 (24), 447 (18), 432 (9), 273 (22), 250 (25), 209 (33), 165 (100), 89 (95). Anal. Calcd for $C_{21}H_{31}O_7WNSi$: C, 40.58; H, 5.03; N, 2.25. Found: C, 41.01; H, 4.96; N, 2.29. The exo stereochemistry of **23-Ex** was confirmed by an independent synthesis and by an analysis of coupling constants (Table I). Analysis of the crude mixture from the reaction of **22-E** and **25** by ^{1}H NMR revealed that the stereoselectivity was greater than 25:1 in favor of exo.

An authentic sample of **23-Ex** was prepared by the aminolysis of **27-Ex**. A solution of **27-Ex** (0.481 g, 0.773 mmol) in 15 mL of ether was treated with portions of methylamine at −78 °C until a yellow color persisted and TLC indicated that the starting material had been consumed. The solution was diluted with ether, washed with water, dried over $MgSO_4$, filtered through a plug of Celite, and concentrated. Silica gel chromatography (1:3, ethyl acetate:hexane), led to the isolation of **23-Ex** (0.373 g, 0.601 mmol) in 78% yield. The product from this reaction had a ^{1}H NMR spectrum identical with that obtained from the reaction of **22-E** and **25**.

Attempted Diels–Alder Reaction of the Monomethylamino Complex 22-Z with Diene 25. A round-bottom flask with a high-vacuum screw cap[42] was charged with carbene complex **22-Z** (0.0482 g, 0.118 mmol), which was dissolved in 1-methoxy-3-(*tert*-butyldimethylsiloxy)-1,3-butadiene (**25**)[41] (0.376 g, 1.757 mmol). The solution was deoxygenated by the freeze–thaw method (−196 °C to 0 °C, 3 cycles), backfilled with argon, and stirred at 90 °C for 12 h. The volatiles were removed under high vacuum, and the residual oil was purified by silica gel chromatography (1:1:4) to give the starting carbene complex **22-Z** (0.0287 g, 0.071 mmol) in 60% recovery.

Preparation of 23-En by Aminolysis of 27-En. Carbene complex **27-En** (0.338 g, 0.544 mmol) was dissolved in 15 mL of ether. The solution was cooled to −78 °C under an argon atmosphere, and methylamine was bubbled through the solution in brief intervals until a yellow solution persisted and TLC indicated all of the starting material had been consumed. The solution was diluted with ether and washed with water (3×). The ethereal extract was dried over anhydrous magnesium sulfate, filtered through Celite, and concentrated. Silica gel chromatography led to the isolation of the desired product **23-En** (0.272 g, 0.44 mmol) as a single rotamer in 80% yield. Spectral data for **23-En**: ^{1}H NMR ($CDCl_3$) δ 0.17 (s, 3 H, SiCH), 0.18 (s, 3 H, Si CH), 0.92 (s, 9 H, $C(CH)_3$), 1.05 (d, 3 H, $J = 6.6$ Hz, CH_3), 1.78 (dd, 1 H, $J = 10.8$, 17.5 Hz), 2.12 (dd, 1 H, $J = 5.1$, 17.3 Hz), 2.46 (m, 1 H), 3.29 (s, 3 H, OCH_3), 3.38 (d, 3 H, $J = 5.6$ Hz, NCH_3), 3.88 (dd, 1 H, $J = 2.5$, 12.2 Hz), 4.25 (br t, 1 H, $J = 4.4$ Hz), 5.2 (br d, 1 H, $J \sim 4.3$ Hz); ^{13}C NMR ($CDCl_3$) δ −4.68, −4.39, 17.99, 19.18, 25.54, 28.65, 29.67, 39.91, 41.24, 56.30, 70.40, 74.73, 101.97, 154.48, 199.35 ($J_{cw} = 128$ Hz), 202.70, 266.90; IR (thin film) ν 3365 w, 2958 m, 2930 m, 2853 m, 2060 s, 1965 sh, 1908 vs, 1656 m, 1533 m, 1455 m, 840 m. Anal. Calcd for $C_{21}H_{31}O_7WNSi$: C, 40.58; H, 5.03; N, 2.25. Found: C, 40.75; H, 5.28; N, 2.19. The endo stereochemistry of **23-En** was confirmed by an analysis of coupling constants (Table I).

Preparation of [*trans*-Propenyl(dimethylamino)methylene]pentacarbonyltungsten(0) (28). To a solution of carbene complex **22** (0.2697 g, 0.663 mmol) in 10 mL of THF was added a solution of *n*-butyllithium (0.27 mL, 2.5 M, 0.66 mmol) in hexanes at −78 °C under an argon atmosphere. After 15 min, methyl fluorosulfonate (0.060 mL, 0.085 g, 0.75 mmol) was injected, and the solution was stirred for 30 min. The reaction was quenched by the addition of a saturated aqueous solution of $NaHCO_3$. The mixture was diluted with ether and washed with water and brine. The ethereal extract was dried over anhydrous magnesium sulfate, filtered through Celite, and concentrated. The product was purified by silica gel chromatography (1:1:4) to give **28** (0.136 g, 0.322 mmol) as a yellow solid in 48% yield. Spectral data for **28**: $R_f = 0.5$; mp 53–55 °C, ^{1}H NMR ($CDCl_3$) δ 1.91 (d, 3 H, $J = 6.6$ Hz, CH_3), 3.35 (s, 3 H, NCH_3), 3.77 (s, 3 H, NCH_3), 5.23 (dq, 1 H, $J = 16$, 6.6 Hz,

(41) Danishefsky, S.; Bednarsky, M.; Izawa, T.; Maring, C. *J. Org. Chem.* **1984**, *49*, 2290.

(42) Chan, K. S.; Peterson, G. A.; Brandvold, T. A.; Faron, K. L.; Challener, C. A.; Hyldahl, C.; Wulff, W. D. *J. Organomet. Chem.* **1987**, *334*. 9.

CH_β), 6.38 (d, 1 H, J = 16 Hz, CH_α); ^{13}C NMR ($CDCl_3$) δ 17.86, 43.64 (E-NCH_3), 53.70 (Z-NCH_3), 122.70 (=$CHCH_3$), 142.29 (=CHC_{carb}), 198.70 (J_{cw} = 128 Hz), 203.88, 252.01; IR (thin film) ν 2059 m, 1962 sh, 1895 s, 1879 s, 1536 m, 1405 w; MS m/z (relative intensity) 421 (2) M^+, 393 (21), 365 (6), 337 (21), 323 (1), 307 (48), 279 (85), 251 (26), 235 (31), 222 (31), 209 (20), 138 (19), 97 (67). Anal. Calcd for $C_{11}H_{11}O_5WN$: C, 31.38; H, 2.63; N, 3.33 Found: C, 31.40; H, 2.65; N, 3.31. The vinyl carbons and the N-methyl carbons were assigned by proton–carbon HETCOR experiments.

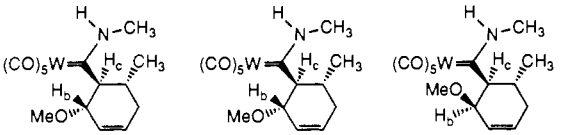
An alternate preparation of this compound by the addition of excess anhydrous dimethylamine to the methoxy complex **20** at −90 °C in THF led to only a 27% yield of **28**, and the other products from this reaction were not characterized. An improvement to this procedure was attempted according to the recent report by Merlic.[43] The addition of 3.0 equiv of anhydrous dimethylamine to THF solution of **20** at −78 °C was directly followed by the addition of 1.5 equiv of sodium methoxide (as a 25% by wt solution in methanol) and led to a 43% yield of **28** after silica gel chromatography. It should be pointed out that none of the above procedures for the preparation of **28** have been optimized, and each has been carried out only once.

Attempted Diels–Alder Reaction of the Dimethylamino Complex 28 with Diene 25. A round-bottom flask with a high-vacuum screw cap[42] was charged with carbene complex **28** (0.0887 g, 0.210 mmol) dissolved in 1-methoxy-3-(*tert*-butyldimethylsiloxy)-1,3-butadiene (**25**)[41] (0.420 g, 1.96 mmol). The solution was degassed by the freeze–thaw method (−196 to 0 °C, 3 cycles), backfilled with argon, and stirred at 80 °C for 48 h. No reaction was observed by TLC, so the mixture was warmed to 95 °C for 8 h. The volatiles were removed under high vacuum, and the residual oil was purified by silica gel chromatography (1:1:4) to give the starting carbene complex **28** (0.0716 g, 0.170 mmol) in 81% recovery.

Diels–Alder Reaction of the Monomethylamino Complex 22-E with 1-Methoxy-1,3-butadiene (29) and an Independent Synthesis of the Cycloadduct 30-Ex. A round-bottom flask with a high-vacuum screw cap[42] was charged with carbene complex **22-E** (0.1123 g, 0.275 mmol) dissolved in 1-methoxy-1,3-butadiene (0.47 g, 5.6 mmol). The solution was deoxygenated by the freeze–thaw method (−196 to 0 °C, 3 cycles), backfilled with argon, and stirred at 70 °C for 70 h. The volatiles were removed under high vacuum, and the ^1H NMR spectrum of the crude reaction mixture was recorded, which indicated that the E-rotamer of exo product **30-Ex** was the only Diels–Alder adduct present (**30-Ex**:**30-En** ≥ 15:1). The residual oil was purified by silica gel chromatography (1:1:4) to give the starting E-rotamer of carbene complex **22** (6 mg, 0.015 mmol, 5%) and a fraction (35.8 mg) containing a 1.8:1 mixture of **30-Ex** (20%) and the Z-rotamer of **22** (10%). Adduct **30-Ex** was obtained only as the E-rotamer and was identical to the E-rotamer of **30-Ex** prepared by the independent synthesis described below.

An authentic sample of the exo Diels–Alder adduct **30-Ex** was prepared by the aminolysis of the alkoxycarbene complex **31-Ex**. A solution of carbene complex **31-Ex**[2b] (0.0579 g, 0.118 mmol) in 10 mL of ether was stirred at −78 °C under an argon atmosphere. Methylamine was bubbled through the solution in brief intervals until a yellow solution persisted and TLC indicated all of the starting material had been consumed. The solution was diluted with ether and washed with water. The ethereal extract was dried over anhydrous magnesium sulfate, filtered through Celite, and concentrated. Silica gel chromatography (1:1:3) led to the isolation of the E-rotomer of **30-Ex** (0.0161 g, 0.034 mmol) in 29% yield and the Z-rotamer of **30-Ex** (0.0252 g, 0.051 mmol) in 44% yield. Spectral data for **30-Ex** (E-rotamer): R_f = 0.63 (1:1:3); mp 110–120 °C dec; ^1H NMR ($CDCl_3$) δ 0.87 (d, 3 H, J = 6.1 Hz, CH_3), 1.77–1.83 (m, 1 H), 2.27–2.35 (m, 2 H), 2.56 (m, 1 H), 3.24 (d, 3 H, J = 5.1 Hz, NCH_3), 3.35 (s, 3 H, OCH_3), 4.42 (dd, 1 H, J = 1.7, 8.8 Hz), 5.84–5.96 (m, 2 H), 9.05 (br s, 1 H, NH); ^{13}C NMR ($CDCl_3$) δ 20.39, 33.30, 33.51, 36.99, 55.86, 59.04, 80.37, 124.11, 128.84, 198.91, 200.84, 269.72; IR (thin film) ν 3385 w, 2058 m, 1957 sh, 1953 s, 1897 vs, 1542 m; MS m/z (relative intensity), 489 (12) M^+, 461 (18), 377 (12), 349 (71), 321 (25), 136 (100), 79 (31); calcd for $C_{15}H_{17}O_6W^{182}N$ m/z 489.0538; measd m/z 489.0539. Anal. Calcd for $C_{15}H_{17}O_6WN$: C, 36.68; H, 3.49; N, 2.85. Found: C, 36.98; H, 3.71; N, 2.89. Spectral data for **30-Ex** (Z-rotamer): R_f = 0.44 (1:1:3); mp 135–137 °C dec; ^1H NMR ($CDCl_3$) δ 0.89 (d, 3 H, J = 6.4 Hz), 1.76–1.82 (m, 1 H), 2.17–2.33 (m, 3 H), 3.35 (s, 3 H), 3.58 (d, 3 H, J = 4.9 Hz), 4.30 (br d, 1 H, J = 9 Hz), 5.82–5.91 (m, 2 H), 8.85 (br s, 1 H, NH); ^{13}C NMR ($CDCl_3$) δ 20.54, 32.14, 33.65, 42.48, 56.03, 74.08, 78.65, 124.60, 128.99, 198.53 (J_{cw} = 126 Hz), 201.48, 267.36; IR (thin film) ν 3217 m, 2059 m, 1960 sh, 1900 s, 1569 w, 1076 m; MS m/z (relative intensity), 461 (50) M^+ − (CO), 252 (70), 235 (38), 140 (100), 123 (90); calcd for $C_{14}H_{17}O_5W^{182}N$ m/z 461.0590; measd m/z 461.0599. Anal. Calcd for $C_{15}H_{17}O_6WN$: C, 36.68; H, 3.49; N, 2.85. Found: C, 36.98; H, 3.71; N, 2.89.

The minor isomer was assigned as the E-isomer on the basis that the N-methyl group (δ = 3.24) was further upfield than the N-methyl group of the Z-isomer (δ = 3.58).[11,12] The exo stereochemistry of both rotamers of the cycloadduct **30-Ex** was confirmed by a comparison of the coupling constant J_{bc} with that for the known methoxy complex **31-Ex**.[37] The coupling constant J_{bc} for each of the rotamers of **30-Ex** was found to be 9 Hz (also 9 Hz for **31-Ex**).



30-Ex (E·rotamer) **30-Ex** (Z·rotamer) **30-En** (E·rotamer)

Independent Synthesis of the 1-Methoxy-1,3-butadiene Cycloadduct 30-En by Aminolysis of 31-En. Carbene complex **31-En**[2b] (0.0882 g, 0.179 mmol) was dissolved in 10 mL of ether and cooled to −78 °C under an argon atmosphere. Methylamine was bubbled through the solution in brief intervals until a yellow solution persisted and TLC indicated all of the starting material had been consumed. The solution was diluted with ether and washed with water. The ethereal extract was dried over anhydrous magnesium sulfate, filtered through Celite, and concentrated. Silica gel chromatography (1:1, hexane:ethyl acetate) led to the isolation of a single rotamer (assumed to be E) of the product **30-En** (0.0650 g, 0.132 mmol) in 74% yield. Spectral data for **30-En**: R_f = 0.78; mp 137–139 °C dec; ^1H NMR ($CDCl_3$) δ 1.07 (d, 3 H, J = 6.5 Hz), 1.69–1.75 (m, 1 H), 2.19–2.34 (m, 3 H), 3.38 (s, 3 H), 3.42 (d, 3 H, J = 5.6 Hz), 3.96 (dd, 1 H, J = 3.5, 12.3 Hz), 4.15 (m, 1 H), 5.90–5.93 (m, 1 H), 6.02–6.04 (m, 1 H), 9.0 (br s, 1 H); ^{13}C NMR ($CDCl_3$) δ 19.32, 28.17, 35.32, 41.24, 57.32, 70.79, 73.85, 124.76, 130.65, 199.36, 202.57, 266.97; IR (thin film) ν 3371 m, 2058 m, 1964 sh, 1930 s, 1910 s, 1885 s, 1551 m, 1459 m; MS m/z (relative intensity), 463 (87) M^+ − (CO), 435 (18), 351 (10), 252 (65), 235 (32), 140 (100), 123 (90); calcd for $C_{14}H_{17}O_5W^{182}N$ m/z 461.0588; measd m/z 461.0582. Anal. Calcd for $C_{15}H_{17}O_6WN$: C, 36.68; H, 3.49; N, 2.85. Found: C, 36.92; H, 3.59; N, 3.10. The exo stereochemistry of the cycloadduct **30-En** was confirmed by a comparison of the coupling constant J_{bc} with that for the known methoxy complex **31-En**.[44] The coupling constant J_{bc} for **30-En** was found to be 3.5 Hz (3.8 Hz reported for **31-En**).

Preparation of [*trans*-Propenyl(*N*-methyl-*N*-benzoylamino)methylene]pentacarbonylchromium(0) (33). To a solution of **21** (0.1004 g, 0.365 mmol) in 3 mL of THF was added a solution of n-butyllithium (0.23 mL, 1.6 M, 0.36 mmol) in hexanes at −78 °C under an argon atmosphere. After 10 min, benzoyl bromide (0.070 g, 0.38 mmol) was injected, and the solution was warmed to 0 °C for 20 min. The reaction was quenched by the addition of a saturated (aqueous) solution of $NaHCO_3$. The solution was diluted with ether and washed with water and brine. The ethereal extract was dried over anhydrous magnesium sulfate, filtered through Celite, and concentrated. The product was isolated by silica gel chromatography (1:1:10) to give **33** (0.1068 g, 0.283 mmol) as a red oil in 77% yield. Spectral data for **33**: R_f = 0.60 (1:1:10); ^1H NMR ($CDCl_3$) δ 1.54 (d, 3 H, J = 6.6 Hz, CH_3), 4.04 (s, 3 H, NCH_3), 5.06 (dq, 1 H, J = 15.7, 6.7 Hz, CH_β), 6.62 (d, 1 H, J = 15.7 Hz, CH_α), 7.48–7.66 (m, 5 H, ArH); ^{13}C NMR ($CDCl_3$) δ 17.74, 45.56, 121.76, 129.42, 129.55, 131.86, 134.56, 175.86, 217.13, 223.68, 281.46; IR (thin film) ν 2352 w, 2331 w, 2049 m, 1971 sh; 1900 vs, 1718 m, 1591 w. Anal. Calcd for $C_{17}H_{13}O_6CrN$: C, 53.83; H, 3.45; N, 3.69. Found: C, 53.28; H, 4.14; N, 3.59.

From *Z*-rotamer. The identical procedure given above was carried out using the purified E-rotamer of the carbene complex **21** (0.0330 g, 0.120 mmol) in ether. After deprotonation with a solution of n-butyllithium (0.075 mL, 1.6 M, 0.120 mmol) and reaction with benzoyl chloride (0.020 g, 0.14 mmol), the desired product was isolated after silica gel chromatography (1:1:4) to give **33** (0.039 g, 0.103 mmol) in 86% yield.

From *E*-rotamer. The identical procedure given above was carried out using the purified Z-rotamer of the carbene complex **21** (0.331 g, 1.20 mmol). After deprotonation with a solution of n-butyllithium (0.75 mL, 1.6 M, 1.20 mmol) and reaction with benzoyl chloride (0.17 g, 1.2 mmol), the desired product was isolated after silica gel chromatography (1:1:4) to give **33** (0.176 g, 0.460 mmol) in 39% yield.

Preparation of [*trans*-Propenyl(*N*-methyl-*N*-benzoylamino)methylene]pentacarbonyltungsten(0) (35). To a solution of carbene complex **22** (1:1.1, E:Z; 0.7498 g, 1.84 mmol) in 10 mL of THF was added a solution of fresh n-butyllithium (1.15 mL, 1.6 M, 1.84 mmol) in hexanes at −78 °C under an argon atmosphere. After 15 min, benzoyl bromide (0.38 g, 2.05 mmol) was injected. The solution was warmed to 25 °C for 30 min, and the reaction was quenched by the addition of a saturated (aqueous) solution of $NaHCO_3$. The solution was diluted with

(43) Merlic, C. A.; Xu, D.; Khan, S. I. *Organometallics* **1992**, *11*, 412.
(44) Reference 2b, 3649.

ether and then washed with water and brine. The ethereal extract was dried over anhydrous magnesium sulfate, filtered through Celite, and concentrated by rotary evaporation. The residual was purified by silica gel chromatography (1:1:4) to give **35** (0.570 g, 0.112 mmol) as a red oil in 61% yield.

The yield of **35** can be improved if the aqueous workup is omitted. After being warmed to room temperature for 30 min, the dark red solution was concentrated on a rotary evaporator, and the reddish-brown residue was directly transferred to a silica gel column. Elution (1:1:4) gave pure **35** in 85% yield. Spectral data for **35**: R_f = 0.65; ^{1}H NMR ($CDCl_3$, 23 °C) δ 1.61 (d, 3 H, J = 6.5 Hz, CH_3), 3.88 (s, 3 H, NCH_3), 5.29 (dq, 1 H, J = 15.3, 6.5 Hz, CH_β), 6.48 (d, 1 H, J = 15.5 Hz, CH_α), 7.47–7.63 (m, 5 H, ArH); (−70 °C) 3.99 (NCH_3), 2.25 (1 H, CH_β), other resonances not recorded at −70 °C; ^{13}C NMR ($CDCl_3$) δ 17.81 (CH_3), 47.29 (NCH_3), 126.36 (=$CHCH_3$), 129.56, 129.65, 131.22, 134.81, 145.73 (=CHC_{carb}), 175.91, 197.94 (J_{cw} = 128 Hz), 203.60, 258.35; IR (thin film) ν 2063 s, 1975 sh, 1910 vs, 1725 m, 1445 m, 1227 m, 1021 m; MS m/z (relative intensity) 511 (1) M^+, 483 (2), 427 (4), 399 (4), 371 (10), 187 (10), 135 (15), 134 (19), 118 (88), 105 (100), 77 (86); calcd for $C_{17}H_{13}O_6W^{182}N$ m/z 511.0252; measd m/z 511.0280. Anal. Calcd for $C_{17}H_{13}O_6WN$: C, 39.94; H, 2.56; N, 2.74. Found: C, 40.11; H, 2.77; N, 2.78. The vinyl and methyl carbons were assigned by proton–carbon HETCOR experiments.

From *Z*-rotamer. The procedure given above (aqueous workup) was carried out using the enriched *Z*-rotamer (4:1) of the carbene complex **22** (0.0326 g, 0.080 mmol). After deprotonation with a solution of *n*-butyllithium (0.050 mL, 1.6 M, 0.080 mmol) and reaction with benzoyl bromide (0.0240 g, 0.13 mmol), the desired product was isolated by silica gel chromatography (1:1:4) to give **35** (0.030 g, 0.059 mmol) in 73% yield.

From *E*-rotamer. The procedure given above (aqueous workup) was carried out using the enriched *E*-rotamer (16:1) of the carbene complex **22** (0.0490 g, 0.120 mmol). After deprotonation with a solution of *n*-butyllithium (0.080 mL, 1.6 M, 0.120 mmol) and reaction with benzoyl bromide (0.0270 g, 0.14 mmol), the desired product was isolated by silica gel chromatography (1:1:4) to give **35** (0.03116 g, 0.062 mmol) in 52% yield.

Preparation of [*trans*-Propenyl(*N*-methyl-*N*-(*p*-*tert*-butylbenzoyl)-amino)methylene]pentacarbonylchromium(0) (34). Carbene complex **21** (0.3295 g, 1.198 mmol) in 6 mL of THF was treated with a solution of *n*-butyllithium (0.75 mL, 1.6 M, 1.20 mmol) in hexanes at −78 °C under an argon atmosphere. After 10 min, 4-*tert*-butylbenzoyl chloride (0.250 g, 1.25 mmol) was added, and the solution was warmed to 0 °C. The reaction was quenched after 30 min by the addition of a saturated (aqueous) solution of $NaHCO_3$. The solution was diluted with ether and washed with water and brine. The ethereal extract was dried over anhydrous magnesium sulfate, filtered through Celite, and concentrated. The product was isolated by silica gel chromatography (1:1:5) to give **34** (0.337 g, 0.775 mmol) in 65% yield as an orange solid (mp 73–75 °C dec). Spectral data for **34**: ^{1}H NMR ($CDCl_3$) δ 1.36 (s, 9 H, CMe_3), 1.58 (dd, 3 H, J = 0.9, 6.6 Hz, CH_3), 3.98 (s, 3 H, NCH_3), 5.10 (dq, 1 H, J = 15.8, 6.6 Hz, CH_β), 6.60 (d, 1 H, J = 15.8 Hz, CH_α), 7.43–7.54 (m, 4 H, ArH); ^{13}C NMR ($CDCl_3$) δ 17.80, 30.92, 35.41, 45.47, 122.08 (=$CHCH_3$), 126.62, 128.19, 129.71, 144.60 (=CHC_{carb}), 159.10, 175.58, 217.21, 223.63, 278.72; IR (thin film) ν 2967 m, 2055 s, 1976 sh, 1925 vs, 1725 m, 1604, m, 1475 m, 1384 m, 1251 m; MS m/z (relative intensity), 407 (55) M^+ − (CO), 391 (25), 364 (30), 252 (70), 235 (40), 140 (100), 123 (90); calcd for $C_{20}H_{21}O_5Cr^{52}N$ m/z 407.0824; measd m/z 407.0820. The vinyl carbons were assigned by proton–carbon HETCOR experiments. The product was structurally characterized by X-ray crystallography (vide supra).

Diels–Alder Reaction of *N*-Benzoylamino Pentacarbonyltungsten Complex 35 with Diene 25. A 25-mL round-bottom flask fit with a 3-way stopcock was charged with carbene complex **35** (0.0685 g, 0.130 mmol) and 1-methoxy-3-(*tert*-butyldimethylsiloxy)-1,3-butadiene (**25**)[41] (0.110 g, 0.50 mmol) dissolved in 1 mL of benzene. The solution was deoxygenated by the freeze–thaw method (−196 to 0 °C, 3 cycles), backfilled with a carbon monoxide atmosphere which was maintained by an attached balloon. The contents were warmed to 47 °C for 12 h. The solution was diluted with pentane, filtered through Celite, and concentrated by rotary evaporation. The ^{1}H NMR spectrum of the crude reaction mixture was recorded which indicated the presence of only starting material **35** and the single Diels–Alder product **37-Ex** (exo:endo ≥ 17:1). The mixture was purified by silica gel chromatography (1:1:4) to give the starting carbene complex **35** (0.0140 g, 0.026 mmol) in 20% recovery and the chelated, tetracarbonyl Diels–Alder adduct **37-Ex** (0.0265 g, 0.0357 mmol) as a green oil in 28% yield. Spectral data for **37-Ex**: ^{1}H NMR ($CDCl_3$) δ 0.24 (s, 3 H, SiCH), 0.25 (s, 3 H, SiCH), 0.86 (d, 3 H, J = 6.4 Hz), 2.01–2.05 (m, 1 H), 2.24 (dd, 1 H, J = 5.4, 17 Hz), 2.76 (m, 1 H), 2.95 (dd, 1 H, J = 8.4, 11 Hz), 3.28 (s, 3 H, NCH_3), 3.76 (s, 3 H, OCH_3), 4.98 (br d, 1 H, J = 8.4 Hz), 5.21 (m, 1 H), 7.45–7.63 (m, 5 H, ArH); ^{13}C NMR (C_6D_6) δ −4.24, 18.29, 20.07, 25.86, 36.26, 39.23, 55.22, 63.54, 85.38, 102.50, 130 (obs), 131.73, 131.93, 132.03, 152.25, 183.44, 190.99, 191.31, 191.64, 309.16; IR (thin film) ν 2956 w, 2930 w, 2018 s, 1912 vs, 1853 s, 1671 m, 1211 m, 839 m. Anal. Calcd for $C_{27}H_{35}O_7WN$: C, 46.49; H, 5.06; N, 2.01; found: C, 46.87; H, 5.49; N, 2.05. The exo stereochemistry of **37-Ex** was confirmed by the independent synthesis described below and by an analysis of coupling constants (Table I).

Preparation of the Chelated Exo Cycloadduct 37-Ex by Acylation of 23-Ex. To a solution of diisopropylamine (0.020 g, 0.20 mmol) in 3 mL of THF was added a solution of methyllithium (0.11 mL, 1.7 M, 1.9 mmol) in pentane at 0 °C under an argon atmosphere. This solution was transferred via cannula to a solution of **23-Ex** (0.117 g, 0.189 mmol) in 5 mL of THF at 0 °C. After 15 min, benzoylbromide (0.040 g, 0.22 mmol) was added, and the resulting mixture was stirred for 30 min before the reaction was quenched by the addition of a saturated solution (aqueous) of $NaHCO_3$. The solution was diluted with ether and then washed with water and brine. The ethereal extract was dried over magnesium sulfate, filtered, and concentrated. The residual oil was maintained under high vacuum for 24 h. The mixture was purified by silica gel chromatography to give the desired product **37-Ex** (0.010 g, 0.014 mmol) in 8% yield. This compound was found to have a ^{1}H NMR spectrum identical with that obtained from the cycloadducts from the reaction of **35** and **42** with diene **25**.

Independent Synthesis of the Chelated Endo Cycloadduct 37-En by the Acylation of 23-En. To a solution of diisopropylamine (0.116 g, 1.15 mmol) in 3 mL of THF was injected a solution of *n*-butyllithium (0.35 mL, 2.5 M, 0.87 mmol) in hexanes at −78 °C under an argon atmosphere. After 10 min, the solution was transferred via cannula to a solution of the carbene complex **23-En** (0.359 g, 0.58 mmol) in 5 mL of THF at −78 °C. The solution was stirred 15 min, warmed to 0 °C for 10 min, and then recooled to −78 °C. Benzoyl bromide (0.19 g, 1.02 mmol) was injected, and after 15 min the mixture was warmed to 0 °C for 15 min before the reaction was quenched by the addition of a saturated (aqueous) NH_4Cl solution. The mixture was diluted with ether and then washed with water and brine. The ethereal extract was dried over magnesium sulfate, filtered through silica gel, and concentrated. Silica gel chromatography (1:1:10) led to the isolation of the yellow pentacarbonyl complex **44-En** (0.172 g, 0.237 mmol) in 41% and the green chelated tetracarbonyl complex **37-En** (49.3 mg, 0.071 mmol) in 12% yield. The pentacarbonyl complex **44-En** (0.172 g, 0.237 mmol) was converted to the chelated complex **37-En** (66.9 mg, 0.096 mmol) in 41% by exposure to vacuum for 16 h. Spectral data for **44-En**: ^{1}H NMR ($CDCl_3$) δ 0.19 (s, 3 H, $SiCH_3$), 0.21 (s, 3 H, $SiCH_3$), 0.95 (s, 9 H, $C(CH_3)_3$), 1.22 (d, 3 H, J = 6.5 Hz), 1.89 (dd, 1 H, J = 10.8, 17.2 Hz), 2.21 (dd, 1 H, J = 4.9, 17.3 Hz), 2.60–2.7 (m, 1 H), 3.46 (s, 3 H, NCH_3), 3.80 (s, 3 H, OCH_3), 4.37 (dd, 1 H, J = 3.3, 12.2 Hz), 4.49 (br t, 1 H, $J \approx 4$ Hz), 5.31 (br d, 1 H, J = 4.4 Hz), 7.5–7.7 (m, 5 H, ArH). Spectral data for **37-En**: R_f = 0.29 (1:1:10); ^{1}H NMR ($CDCl_3$) δ 0.24 (s, 6 H, $Si(CH_3)_2$), 0.97 (s, 9 H, $C(CH_3)_3$), 1.06 (d, 3 H, J = 6.4 Hz), 1.95 (dd, 1 H, J = 10.7, 17.2 Hz), 2.20 (dd, 1 H, J = 5.2, 17.4 Hz), 2.64 (m, 1 H), 3.24 (s, 3 H, NCH_3), 3.98 (s, 3 H, OCH_3), 4.54 (dd, 1 H, J = 3.9, 12.3 Hz), 4.64 (br t, 1 H, J = 4.4 Hz), 5.27 (dd, 1 H, J = 5.0, 1 Hz), 7.50–7.68 (m, 5 H, ArH); ^{13}C NMR (C_6D_6) δ −4.64, −4.26, 18.25, 19.94, 28.31, 40.25, 42.66, 55.67, 69.70, 78.76, 102.74, 128.47, 128.53, 128.60, 131.68, 132.34, 154.51, 184.31, 214.09, 309.63; IR (thin film) ν 2948 w, 2922 w, 2848 w, 2017 s, 1911 vs, 1853 s, 1657 w, 1464 w, 1205 m, 832 m. The endo stereochemistry of the adduct **37-En** was confirmed by an analysis of coupling constants (Table I).

Diels–Alder Reaction of the *N*-Benzoylamino Pentacarbonylchromium Complex 33 with Diene 25. A 25-mL round-bottom flask fit with a 3-way stopcock was charged with carbene complex **33** (0.0523 g, 0.132 mmol) and 1-methoxy-3-(*tert*-butyldimethylsiloxy)-1,3-butadiene (**25**)[41] (0.080 g, 0.37 mmol) dissolved in 1 mL of benzene. The solution was deoxygenated by the freeze–thaw method (−196 to 0 °C, 3 cycles) and backfilled with a carbon monoxide atmosphere maintained by an attached balloon. The contents were warmed at 50 °C for 12 h. The solution was diluted with pentane, filtered through Celite, and concentrated by rotary evaporation. A ^{1}H NMR spectrum of the crude reaction mixture was recorded which indicated the presence of a single Diels–Alder product. The mixture was purified by silica gel chromatography (1:1:4) to give the chelated tetracarbonyl Diels–Alder adduct **36-Ex** (0.031 g, 0.0533 mmol) as a green oil in 40% yield. Spectral data for **36-En**: ^{1}H NMR ($CDCl_3$) δ 0.22 (s, 3 H, SiMe), 0.23 (s, 3 H, SiMe), 0.86 (d, 3 H), 0.96 (s, 9 H, $Si(CH_3)_3$), 1.95–2.05 (m, 1 H), 2.30 (dd, 1 H, J = 5.4, 17.1 Hz), 2.90–2.98 (m, 1 H), 3.06 (dd, 1 H, J = 8.1, 11.2 Hz), 3.29 (s, 3 H), 3.70 (s, 3 H), 5.17 (br d, 1 H, J = 8.1 Hz), 5.28 (br t, 1 H, J = 2.1 Hz), 7.47–7.58 (m, 5 H, ArH); ^{13}C NMR ($CDCl_3$) δ −4.36, 20.33, 25.62, 30.02, 35.65, 38.71, 39.19, 55.05, 62.91, 83.67, 101.45, 128.75, 128.45,

131.99, 132.11, 152.29, 182.02, 340.63; IR (thin film) ν 2959 w, 2927 w, 2013 s, 1919 vs, 1853 m, 1672 w.

Isolation of [*trans*-Propenyl(*N*-methyl-*N*-benzoylamino)methylene]-tetracarbonyltungsten(0) 42 and the Dinuclear μ-Carbene Complex 43. Thermolysis of 35. A solution of carbene complex **35** (1.00 g, 1.95 mmol) in 100 mL of THF was placed in a flask with a high-vacuum screw cap. The contents were deoxygenated by the freeze-thaw method (−196 to 0 °C, 3 cycles), and the solution was heated to 70 °C for 1 h. The solution was concentrated, and the residue was loaded onto a silica gel column and eluted with a 1:1:4 mixture of ether, methylene chloride, and hexanes. Three colored bands separated on the column, which, in order of elution, were red (R_f = 0.65), greenish-brown (R_f = 0.40), and purple (R_f = 0.35). The red band was identified as the starting carbene complex **35** (0.105 g, 0.206 mmol, 11% recovery), the greenish-brown band as the dinuclear complex **43** (0.075 g, 0.10 mmol, 5% yield), and the purple band as the chelated complex **42** (0.417 g, 0.86 mmol, 44% yield). Spectral data for **42**: R_f = 0.35 (1:1:4), mp = 73–75 °C dec; ^{1}H NMR ($CDCl_3$) δ 1.91 (dd, 3 H, J = 0.9, 7.1 Hz, CH_3), 3.67 (s, 3 H, NCH_3), 6.65 (dd, 1 H, $J \approx$ 1 Hz, J = 14.6 Hz, CH_α), 7.40–7.62 (m, 5 H, ArH), 7.85 (dq, 1 H, J = 14.1, 7.0 Hz, CH_β); ^{13}C NMR ($CDCl_3$) (+23 °C) δ 21.22, 38.78, 128.03, 128.50, 128.85, 128.85, 132.26, 139.91 (=CHC_{carb}), 151.22 (=$CHCH_3$), 183.06, 213.29 (J_{cw} = 126 Hz), 282.26; (−50 °C) δ 21.77, 39.21, 128.67, 128.79, 131.06, 132.47, 139.66, 153.38, 183.35, 283.37; IR (thin film) ν 2011 m, 1902 vs, 1839 s. The compound was insufficiently stable to obtain an acceptable elemental analysis. Anal. Calcd for $C_{16}H_{13}O_5WN$: C, 39.77; H, 2.71; N, 2.89. Found: C, 40.86; H, 3.27; N, 2.74. The vinyl carbons were assigned by proton–carbon HETCOR experiments. Spectral data for **43**: R_f = 0.40 (1:1:4), mp = 153–155 °C dec; ^{1}H NMR ($CDCl_3$) δ 2.28 (d, 3 H, J = 6.1 Hz, CH_3), 3.42 (dq, 1 H, J = 6.0, 3.7 Hz, =$CHCH_3$), 3.75 (s, 3 H, NCH_3), 6.17 (dd, 1 H, J = 9.8, 1 Hz, =CHC_{carb}), 7.43–7.57 (m, 5 H, ArH); ^{13}C NMR ($CDCl_3$) δ 19.92, 39.43, 83.36, 90.61, 130.01, 130.50, 131.29, 134.11, 181.03, 210 (broad hump), 217.69, 292.44; IR (thin film) ν 2057 vs, 2008 vs, 1958 vs, 1919 vs, 1475 w, 1442 w, 1400 m, 1064 m, 1026 m. Anal. Calcd for $C_{20}H_{13}O_9W_2N$: C, 30.82; H, 1.68; N, 1.79. Found: C, 30.19; H, 1.67; N, 1.58.

Diels–Alder Reaction of the Chelated *trans*-Propenyl Tungsten Complex 42 with Diene 25. Carbene complex **42** (0.0671 g, 0.139 mmol) and 1-methoxy-3-(*tert*-butyldimethylsiloxy)-1,3-butadiene (**25**)[41] (51 mg, 0.238 mmol) were dissolved in 1.6 mL of benzene. An effort was made to degas the solution, but a reaction was immediately apparent. TLC indicated that the starting material had been consumed within 10 min. The solution was concentrated and the mixture was purified by preparatory thin layer chromatography (2:1, hexane:ethyl acetate) and then column chromatography (1:1:10) to give the Diels–Alder adduct **37-Ex** (0.032 g, 0.046 mmol) in 33% yield. Only the exo adduct was observed in the ^{1}H NMR spectrum of the crude reaction mixture (exo:endo ≥ 35:1). Also isolated from this reaction mixture was a 22% yield (based on tungsten) of the dinuclear complex **43**.

Attempted Thermodynamic Equilibration of the Chelated Endo Cycloadduct 37-En. A solution of carbene complex **37-En** (0.051 g, 0.106 mmol) and 1-methoxy-3-(*tert*-butyldimethylsiloxy)-1,3-butadiene (**25**)[41] (0.048 g, 0.22 mmol) in 1 mL of benzene was stirred at 23 °C for 25 min. A portion (one-half) of the mixture was removed and concentrated. The crude ^{1}H NMR spectrum of the aliquot indicated that no exo product was present. After silica gel chromatography, the starting carbene complex **37-En** (14 mg) was isolated in 53% recovery. An attempt to bring about equilibration at higher temperatures (45 °C) resulted in complete decomposition of the carbene complex.

Diels–Alder Reaction of the Chelated Tungsten Complex 42 with 1-Methoxy-1,3-butadiene (29). A round-bottom flask fit with a 3-way stopcock was charged with a solution of carbene complex **42** (0.0841 g, 0.174 mmol) and 1-methoxy-1,3-butadiene dissolved in 1.7 mL of benzene. The contents were deoxygenated by the freeze–thaw method (−196 to 0 °C) and backfilled with a carbon monoxide atmosphere maintained by a balloon. The solution was stirred at 23 °C for 19 h, and the mixture was concentrated under reduced pressure. Only one Diels–Alder adduct was observed in the ^{1}H NMR spectrum of the crude reaction mixture. Silica gel chromatography (1:1:4) gave a product that was slightly contaminated with diene polymer. The product **45** (20 mg, 0.035 mmol) was isolated in pure form from a second column (1:1, hexane:ethyl acetate) as a green oil in 20% yield. Spectral data for **45**: R_f = 0.30 (1:1:4), then R_f = 0.60 (1:1); ^{1}H NMR ($CDCl_3$) δ 0.87 (d, 3 H, J = 6.5 Hz), 1.89–1.94 (m, 1 H), 2.33–2.39 (m, 1 H), 2.70–2.73 (m, 1 H), 3.04 (br t, 1 H, $J \approx$ 10 Hz), 3.35 (s, 3 H), 3.76 (s, 3 H), 4.88 (br d, 1 H, $J \approx$ 8.4 Hz), 5.92–5.95 (m, 1 H), 6.05–6.03 (m, 1 H), 7.52–7.68 (m, 5 H, ArH); ^{13}C NMR (C_6D_6) δ 20.28, 34.49, 36.31, 39.19, 55.45, 63.34, 84.60, 125.47, 128.49, 128.55, 131.74, 183.47, 214.2 (br), 309.71; IR (thin film) ν 2016 s, 1905 vs, 1844 s, 1088 w, 1049 w, 1020 w. Anal. Calcd for $C_{21}H_{21}O_6WN$: C, 44.46; H, 3.73; N, 2.47. Found: C, 44.43; H, 3.64; N, 2.48.

Diels–Alder Reaction of the Chelated Tungsten Complex 42 with Cyclopentadiene. Carbene complex **42** (0.0709 g, 0.147 mmol) was dissolved in 1 mL of freshly distilled cyclopentadiene. After 1 h, the volatiles were removed under reduced pressure. The reaction mixture was passed through a short silica gel column (3:1, hexane:ethyl acetate) to give the green organometallic product **46** (0.0431 g). The product **46** could not be isolated in a pure form, so the mixture was oxidized by dissolution in 10 mL of a (1:1) hexane:ethyl acetate mixture and stirring in air for 24 h. The solution was filtered through Celite and concentrated. The ^{1}H NMR spectrum of the crude mixture indicated the presence of the endo and exo Diels–Alder adducts **47** in a 1.1:1.0 ratio. Silica gel chromatography (1:1:4) led to the isolation of **47** (11.5 mg, 0.043 mmol) as a 1.1:1 (endo:exo) mixture in a combined yield of **29%** based on **42**.

Independent Synthesis of the Endo Cycloadduct 47-En. The endo carboxylic acid **48-En**[26] (0.354 g, 2.33 mmol) was dissolved in 5 mL of dichloromethane and stirred at 0 °C under argon while oxalyl chloride (0.86 mL) was added. After 30 min, the mixture was warmed to 23 °C, and stirring was continued for 2 h. The volatiles were removed by reduced pressure, and the residue was dissolved in 1 mL of dichloromethane. The dichloromethane solution was added to a solution of the amide (0.318 g, 2.36 mmol) in THF which had been treated with a solution of *n*-butyllithium (1.5 mL, 1.6 M, 2.4 mmol) at 0 °C 10 min prior. The resulting solution was stirred at 23 °C for 45 min before the reaction was quenched by the addition of a saturated (aqueous) solution of $NaHCO_3$. The mixture was diluted with ether and then washed with water and brine. Silica gel chromatography (1:1, hexane:ethyl acetate) led to the isolation of the product **47-En** (0.508 g, 1.9 mmol) as a clear colorless oil in 81% yield. Spectral data for **47-En**: ^{1}H NMR ($CDCl_3$) δ 1.06 (d, 3 H, J = 7.1 Hz), 1.26 (t, 1 H, J = 7.1 Hz), 1.36–1.39 (m, 1 H), 1.51 (m, 1 H), 2.05–2.15 (m, 1 H), 2.47 (br s, 1 H), 3.04–3.07 (m, 2 H), 3.17 (s, 3 H, NCH_3), 5.88–5.19 (m, 1 H, CH), 6.33–6.36 (m, 1 H), 7.46–7.66 (m, 5 H, ArH); ^{13}C NMR ($CDCl_3$) δ 20.46, 34.68, 37.37, 46.60, 47.35, 49.32, 53.79, 128.40, 128.73, 131.44, 132.29, 135.36, 139.05, 174.42, 178.07; IR (thin film) ν 3052 w, 2962 m, 2919 w, 2862 w, 1660 sh, 1440 m, 1320 s, 1200 m, 1062 s, 1012 m; MS m/z (relative intensity) 270 (4) M^+ + 1, 269 (8) M^+, 204 (26), 203 (56), 136 (63), 134 (22), 105 (100), 77 (44), 69 (67); calcd for $C_{17}H_{19}O_2N$ m/z 269.1415, measd m/z 269.1393.

Independent Synthesis of the Exo Cycloadduct 47-Ex. A procedure identical with that described above led to the conversion of the exo carboxylic acid **48-Ex**[26] (0.125 g, 0.82 mmol) and the *N*-methylbenzamide (0.115 g, 0.85 mmol) to the desired compound **47-Ex** (0.144 g, 0.54 mmol) in 65% yield. Spectral data for **47-Ex**: ^{1}H NMR ($CDCl_3$) δ 0.76 (d, 3 H, J = 6.9 Hz), 1.38 (dd, 1 H, J = 1, 8.4 Hz), 1.86 (br d, 1 H, J = 8.4 Hz), 2.13 (dd, 1 H, J = 1, 4.9 Hz), 2.5–2.59 (m, 1 H), 2.70 (br s, 1 H), 2.89 (br s, 1 H), 3.25 (s, 3 H, NCH_3), 6.08 (br, s, 2 H), 7.44–7.64 (m, 5 H); ^{13}C NMR ($CDCl_3$) δ 19.60, 35.36, 39.87, 47.71, 48.20, 49.97, 53.99, 129.13, 129.49, 132.98, 136.43, 137.42, 175.12, 180.43; MS m/z (relative intensity) 270 (1) M^+ + 1, 269 (4) M^+, 204 (44), 136 (56), 105 (100), 77 (70), 69 (67), 66 (62); calcd for $C_{17}H_{19}O_2N$ m/z 269.1415; measd m/z 269.1393.

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Supplementary Material Available: X-ray crystallographic data for compounds **22-E**, **22-Z**, and **34**, including tables of fractional coordinates, isotropic and anisotropic thermal parameters, bond distances, and bond angles (13 pages); tables of observed and calculated structure factor amplitudes for **22-E**, **22-Z**, and **34** (16 pages). Ordering information is given on any current masthead page.