Ring-Opening Metathesis of a Cyclic Imine

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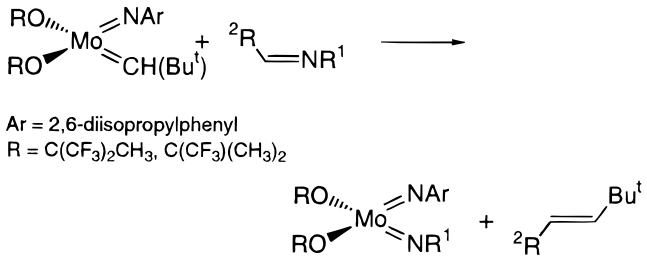
Pyrroline, a five-membered cyclic imine, undergoes ring-opening metathesis with alkylidene complexes of the class Mo(=CHR′)(=NAr)(OR)$_2$ (Ar = 2,6 diisopropylphenyl; R = CMe_3, $CMe_2(CF_3)$, $CMe(CF_3)_2$; R′ = CMe_3, $CPhMe_2$). An intermediate pyrroline-bound complex was isolated and characterized crystallographically for the R = $CMe_2(CF_3)$ derivative. This adduct, Mo(=CHBu^t)(=NAr)[$OCMe_2(CF_3)$]$_2$[pyrroline], transforms to the mixed bis(imide) product, Mo(=$NCH_2CH_2CH_2CH$=CHBu^t)(=NAr)[$OMe_2(CF_3)$]$_2$, with a first-order rate constant of 1.4 × 10^{-2} min^{-1} at 55 °C. The reaction of the R = CMe_3 derivative produces not only the ring-opened product but also a byproduct, Mo[$CH(CMe_2Ph)(C_4H_8N)$](=O)(=NAr)(OBu^t).

Introduction

The ring-opening metathesis of pyrroline presented herein represents an important milestone in our effort to generalize ring-opening metathesis polymerization (ROMP) to heteroolefinic substrates. Previously, we[1−3] and others[4] have studied metathesis activity of acyclic imine substrates with metal alkylidene and metal imide functional groups, but only recently did we observe the first ring-opening of a cyclic heteroolefin substrate.[5] In this paper we describe in detail the ring-opening of pyrroline by olefin metathesis complexes of the general formula Mo(=CHR′)(=NAr)(OR)$_2$.[6] We also discuss the mechanistic implications arising from the isolation of an intermediate and a byproduct of the metathesis reaction.

Our previous studies on the reactions of Mo(=CHR′)(=NAr)(OR)$_2$ with acyclic imine substrates had established that the fluorinated alkoxide derivatives reacted with a wide variety of imines to give mixed bis(imide) and olefin products (Scheme 1).[3] We had also reported that the metathesis rate decreased as the alkoxide groups became more electron donating and that precoordination was observed for sterically unhindered imines. That investigation as well as studies of imine/alkylidene metathesis by Rocklage and Schrock[4a,b] that preceded ours involved only acyclic imines. Herein, we describe the extension of this reactivity to a new class of substrates, cyclic imines.

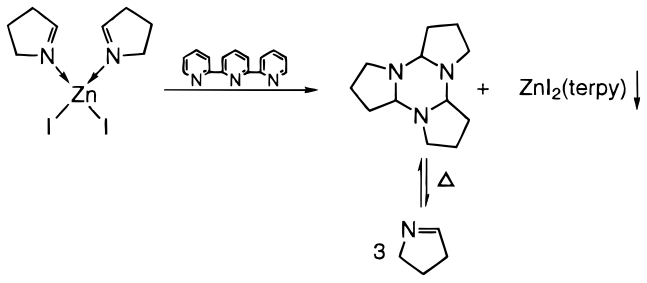
Scheme 1



Results

The cyclic imine 1-pyrroline (3,4-dihydro-2*H*-pyrrole) is a difficult reagent to use due to its volatility and tendency to trimerize in either neutral or basic solutions. Therefore, the procedure developed by Baxter et al. was used to prepare and trap monomeric pyrroline as $ZnI_2(pyrroline)_2$.[7] Free pyrroline was recovered by treating a suspension of $ZnI_2(pyrroline)_2$ in benzene (or benzene-d_6) with a coordinating base. The pyrroline was collected, along with the solvent, by trap-to-trap distillation. The best base for this procedure was terpyridine (Scheme 2); triethylenetetraamine and 1,10-phenanthroline both gave impure product. Although the pyrroline solutions thus generated comprised monomeric

Scheme 2



(1) Cantrell, G. K.; Meyer, T. Y. *J. Chem. Soc., Chem. Commun.* **1997**, 1551−1552.
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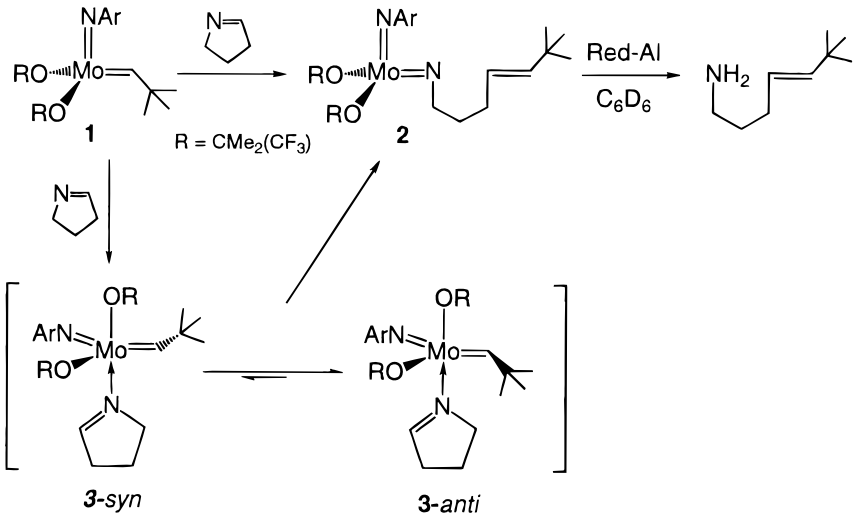
Scheme 3



and trimeric pyrroline, conversion to pure monomer could be achieved by thermolysis at 70−85 °C for 1−5 days, depending on solution concentration.

Stoichiometric Ring-Opening of Pyrroline. The molybdenum alkylidene complex Mo(=CHBu^t)(=NAr)-[(OCMe$_2$(CF$_3$)]$_2$ (**1**) reacts with a stoichiometric amount of pyrroline in C_6D_6 at 55 °C to yield the ring-opening metathesis product Mo(=NCH$_2$CH$_2$CH$_2$CH=CHBu^t)-(=NAr)[(OCMe$_2$(CF$_3$)]$_2$ (**2**), as observed by ^{1}H NMR spectroscopy (Scheme 3). The characteristic olefinic resonances of **2**, a doublet and a doublet of triplets, at δ 5.33 and 5.10, respectively, exhibit a trans coupling to each other of 15.2 Hz. The ^{13}C NMR spectrum is also consistent with this formulation. Although we were not able to isolate complex **2** from the reaction mixture, the identity of ring-opened species **2** was further confirmed by reductive cleavage of the unsaturated organic amine using sodium bis(methoxyethoxy)aluminum hydride (Red-Al).[5] The resultant organic amine fragment was isolated and its structure was confirmed by mass spectrometry and NMR spectroscopy.

NMR studies of the reaction in progress indicated the presence of pyrroline-coordinated intermediates. When complex **1** was treated with excess pyrroline (5 equiv) at room temperature, a ^{1}H NMR spectrum acquired within 10 min showed that **1** had been completely consumed, as indicated by the disappearance of the original δ 11.61 alkylidene resonance. Two new alkylidene resonances were observed at δ 12.23 and 13.18. New downfield-shifted resonances for the proton on the pyrroline sp^2-carbon at δ 7.68 and 8.30, respectively, were also located and found to correspond stoichiometrically with the new alkylidene complexes. As the reaction proceeded, the complex represented by the δ 12.23 and 7.68 pair was converted completely to that represented by the δ 13.18 and 8.30 pair. ^{13}C NMR spectroscopy of the thermodynamic isomer showed an alkylidene CH coupling constant of 139 Hz. By analogy with previous reports by Schrock and co-workers on the coordination behavior of **1** with PMe_3,[8] we have assigned the kinetic intermediate as the syn-isomer (**3-*syn***, *tert*-butyl points toward the imido ligand) and the thermodynamic species as the anti-isomer (**3-*anti***, *tert*-butyl points way from the imido ligand). It is also interesting to note that only the thermodynamic isomer was observed when the pyrroline was not used in excess.

The identity of the isolated pyrroline adduct, **3**, was confirmed by X-ray crystallography and is shown in Figure 1. The structure, which was described in detail in a preliminary communication of this work,[5] can be viewed as a distorted trigonal-bipyramid in which the alkylidene, one alkoxide, and the imido ligand occupy equatorial positions within the coordination sphere. Pyrroline and the second alkoxide occupy axial positions. The pyrroline is η^1-N-bound rather than η^2-CN-bound, and the alkylidene *tert*-butyl substituent lies in the equatorial plane and has adopted the anti-conformation. The isolated adduct is, therefore, the thermodynamic **3-*anti*** isomer.

Conversion of pyrroline adduct **3** to the ring-opened product, **2**, was quantitative and followed simple first-order kinetics. The reaction was monitored over 5 half-lives and a logarithmic fit (R = 0.994) of the concentration of pyrroline adduct **3** vs time gave a first-order rate constant of (1.4 ± 0.2) × 10^{-2} min^{-1} at 55 °C.[5]

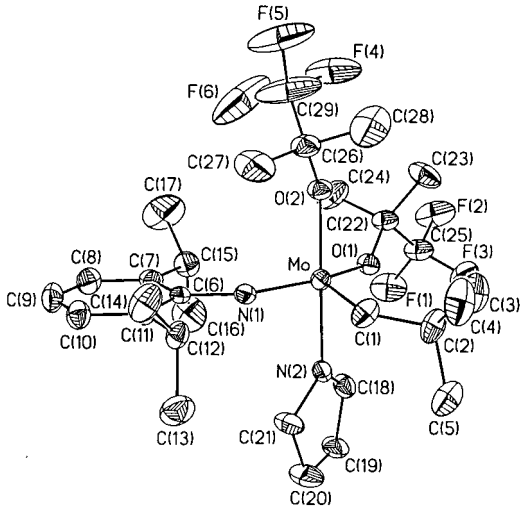


Figure 1. Molecular structure of *anti*-Mo(=CHBu^t)(=NAr)-[OCMe$_2$(CF$_3$)]$_2$(pyrroline), **3-*anti*** (one of two identical independent molecules). Hydrogen atoms have been omitted for clarity, 30% probability ellipsoids.

(8) Schrock, R. R.; Crowe, W. E.; Bazan, G., C.; DiMare, M.; O'Regan, M. B.; Schofield, M. H. *Organometallics* **1991**, *10*, 1832−1843.

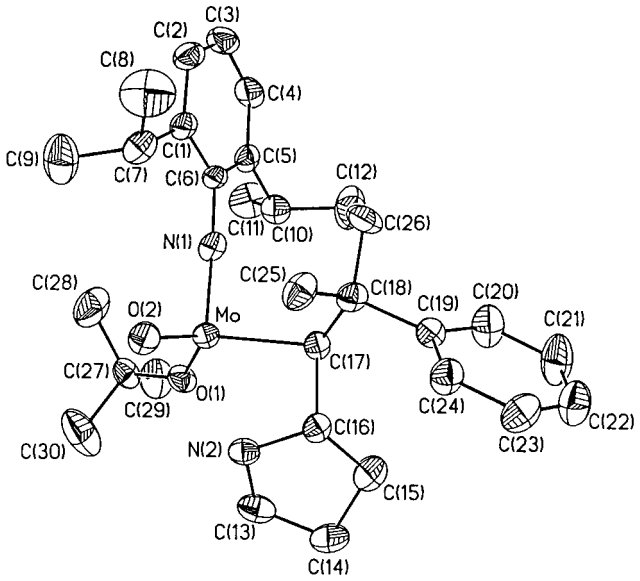


Figure 2. Molecular structure of Mo[CH(CMe$_2$Ph)(C$_4$H$_8$N)](=O)(=NAr)(OBu^t). Hydrogen atoms have been omitted for clarity, 30% probability ellipsoids.

To investigate the electronic effects of the ancillary alkoxide ligands on the ring-opening metathesis reaction, pyrroline was treated with alkylidene complexes Mo(=CHBu^t)(=NAr)[OCMe(CF$_3$)$_2$]$_2$ (**4**) and Mo[=CH-(CMe$_2$Ph)](=NAr)(OBu^t)$_2$ (**5**). The hexafluoro-*tert*-butoxide-ligated alkylidene complex, **4**, gave the expected ring-opened product, but at a significantly slower rate than that observed with **1**. When complex **4** was treated with a stoichiometric amount of pyrroline in C$_6$D$_6$, two new alkylidene resonances were observed in the ^{1}H NMR spectrum, at δ 12.41 and 13.45, indicating that two isomeric forms of the pyrroline adduct were present. After 1 day at room temperature, the compound with the δ 12.41 alkylidene resonance was quantitatively converted to the one with a δ 13.45 resonance. When heated at 65 °C for 1 day, new olefinic resonances consistent with the ring-opened product Mo[=NCH$_2$-CH$_2$CH$_2$CH=CHBu^t)(=NAr)[OCMe(CF$_3$)$_2$]$_2$ (**6**) were observed in the ^{1}H NMR spectrum. If the reaction was allowed to proceed for long periods, the spectrum became more complex; decomposition processes became dominant.

The *tert*-butoxide-ligated alkylidene complex, **5**, also reacted with pyrroline to give the ring-opened product as observed by ^{1}H NMR spectroscopy. Complex **5** was treated with 1−1.5 equiv of pyrroline in C$_6$D$_6$ at room temperature. Within 24 h, new olefinic resonances for the ring-opened product, Mo[=NCH$_2$CH$_2$CH$_2$CH=CH-(CMe$_2$Ph)](=NAr)(OBu^t)$_2$ (**7**), were observed in the ^{1}H NMR spectrum at δ 5.51 (d) and 5.22 (dt, $^1J_{HH}$ = 15.5 Hz). This reaction proceeded more slowly than those with **1** and **4**, and no precoordination was observed.

An intriguing byproduct was isolated from a preparative scale reaction of pyrroline with *tert*-butoxide-ligated **5**. Low-temperature crystallization yielded a total of three crops of solid. The first two crops were a mixture of several species, including (1) ring-opened product **7**; (2) homo bis(imide) Mo(=NAr)$_2$(OBu^t)$_2$ (**8**), which would be produced in the well-precedented comproportionation of **7**;[9] (3) residual starting material **5**; and (4) one or two minor species that could not be assigned. The byproduct was found in the third crop of crystalline solid (<10% yield), which proved to be a single species by ^{1}H NMR spectroscopy, oxo-imido complex Mo[CH(CMe$_2$Ph)-(C$_4$H$_8$N)](=O)(=NAr)(OBu^t) (**9**). Crystals suitable for single-crystal X-ray diffraction study were recovered and analyzed.

As illustrated in Figure 2, the core geometry of complex **9** can be viewed as a distorted trigonal-bipyramid in which the oxo, alkoxide, and alkylidene ligands occupy equatorial positions within the coordination sphere. The imido ligand and a dative interaction with the pyrrolidine lone pair fill axial positions. The crystal data and refinement parameters are listed in Table 1. Important bond distances and angles are listed in Table 2. All bond lengths fall within expected ranges.[10] The Mo−N(1) bond length of 1.748(5) Å is typical for an imido ligand. The compressed Mo−O(2) bond, 1.688(5) Å, is characteristic of a Mo=O multiple bond. The longer Mo−O(1) bond, 1.892(5) Å, is typical of strongly π-donating alkoxide ligands. The relatively

Table 1. Crystal Data and Data Collection and Refinement Parameters for Mo[CH(CMe$_2$Ph)(C$_4$H$_8$N)](=O)(=NAr)(OBu^t)

molecular formula	$C_{30}H_{46}MoN_2O_2$
fw	562.67
cryst syst	triclinic
space group	$P\bar{1}$
temperature	200(1) K
wavelength	0.71073 Å
unit cell dimens	a = 11.500(9) Å α = 79.44(5)°
	b = 11.604(7) Å β = 68.11(6)°
	c = 13.356(10) Å γ = 62.93(5)°
volume, Z	1472.4(18) Å^3, 2
density (calcd)	1.269 Mg/m^3
abs coeff	0.472 mm^{-1}
F(000)	596
cryst size	0.35 × 0.25 × 0.25 mm
θ range for data collection	1.97−24.00°
limiting indices	$0 \le h \le 13$, $-13 \le k \le 13$, $-15 \le l \le 15$
reflns collected	4624
unique reflns	4622 (R_{int} = 0.0775)
completeness to θ = 24.00	99.9%
max. and min. transmission	0.8910 and 0.8521
refinement method	full-matrix least-squares on F^2
no. of data/restraints/params	4622/0/352
goodness-of-fit on F^2	0.999
final R indices [$I > 2\sigma(I)$]	R1 = 0.0664, wR2 = 0.1661
R indices (all data)	R1 = 0.0858, wR2 = 0.1818
largest diff peak and hole	1.240 and −1.050 e Å^{-3}

Table 2. Selected Bond Lengths (Å) and Angles (deg) for Mo[CH(CMe$_2$Ph)(C$_4$H$_8$N)](=O)(=NAr)(OBu^t)

Bond Lengths (Å)			
Mo−O(1)	1.892 (5)	Mo−N(2)	2.297 (6)
Mo−O(2)	1.688 (5)	Mo−C(17)	2.170 (6)
Mo−N(1)	1.748 (5)	N(2)−C(16)	1.482 (9)
C(17)−C(16)	1.519 (9)	C(17)−C(18)	1.518 (9)
C(16)−C(15)	1.498 (12)		

Bond Angles (deg)			
Mo−N(1)−C(6)	175.3 (5)	O(2)−Mo−C(17)	108.5 (2)
Mo−C(17)−C(18)	124.2 (5)	O(2)−Mo−O(1)	118.7 (2)
Mo−C(17)−C(16)	97.5 (4)	O(1)−Mo−C(17)	120.5 (2)
C(17)−C(16)−N(2)	104.6 (5)	N(1)−Mo−N(2)	159.4 (2)
C(17)−C(16)−C(15)	118.7 (7)	C(16)−C(17)−C(18)	115.7 (5)

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(10) Nugent, W. A.; Mayer, J. M. *Metal−Ligand Multiple Bonds*; John Wiley & Sons: New York, 1988.

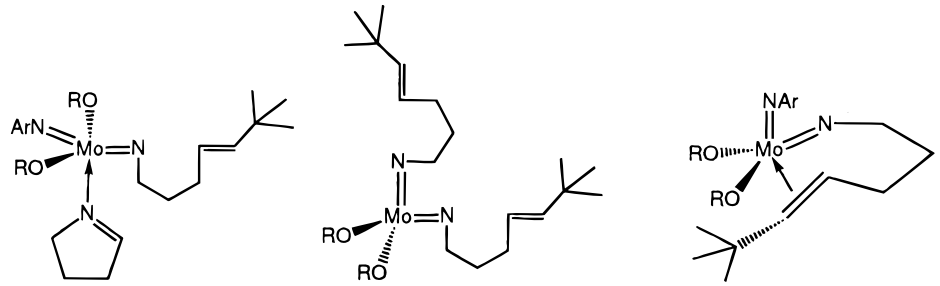

Figure 3. Possible reaction products of ring-opened species **2** that do not involve multiple ring-openings.

long Mo−N(2) bond, 2.297(6) Å, is consistent with a dative interaction between the pyrrolidine nitrogen lone pair and the molybdenum core.[11] The long Mo−C(17) bond, 2.170(6) Å, is typical for a Mo−C single bond.[12] The imido ligand is nearly linear (Mo−N(1)−C(6) = 175.3(5)°), indicating that the nitrogen is essentially sp hybridized and that there could be significant π interaction between its nitrogen lone pair and molybdenum. The angles between the atoms occupying the equatorial plane are not significantly distorted. Finally, the neophyl moiety is directed away from the axial imido ligand. This trans-orientation appears to minimize steric interaction between these two ligands.

Our investigation provides no evidence to support multiple ring-openings, even for the most effective complex, the trifluoro-*tert*-butoxide-ligated **1**. Although resonances for new species were observed in the ^{1}H NMR spectrum of reactions with excess pyrroline, integrations were not consistent with multiple pyrroline ring-openings.

Discussion

Pyrroline Adducts. The behavior of pyrroline clearly parallels that previously reported for five-coordinate base adducts of group VI alkylidene complexes.[8,13,14] Schrock et al. reported that molybdenum alkylidene complexes of the general formula M(=CHBu^t)(=NAr)-(OR)$_2$ (M = W or Mo; Ar = 2,6-diisopropylphenyl; R = Bu^t or CMe(CF$_3$)$_2$) react quantitatively with PMe$_3$ to give five-coordinate base adducts of the type M(=CH-Bu^t)(=NAr)(OR)$_2$(PMe$_3$).[8] In all cases, two isomeric forms (syn and anti), related by rotation about the Mo= C bond, were observed. Syn-rotomers are characterized by downfield shifts of the alkylidene H$_\alpha$ resonance (with respect to the four-coordinate precursor) and alkylidene J_{CH} values on the order of ~110 Hz. Anti-rotomers are characterized by even larger downfield H$_\alpha$ shifts and comparatively large J_{CH} values of 136−138 Hz. As in our case, the kinetic intermediates were found to be syn-rotomers, and the thermodynamic products were found to be trans-rotomers.[8]

Presumably, the mechanism for interconversion between alkylidene rotomers in our pyrroline-coordinated complexes involves a dissociative process since the rate

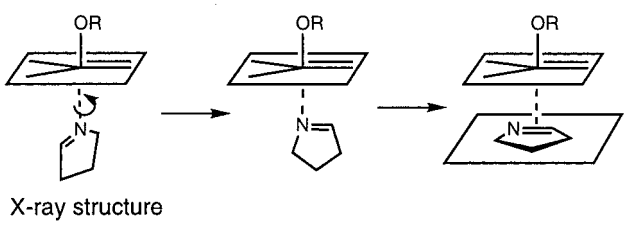

Figure 4. Orientational changes required for pyrroline adduct to undergo a [2+2] addition.

of conversion to the final isomer was retarded by excess pyrroline. The fact that alkylidene rotation is known to be relatively facile for four-coordinate alkylidene imido complexes of this type is consistent with this proposal. Finally, the observation that electrophilic complex **4** undergoes the slowest syn−anti conversion further supports a dissociative process.

Catalytic Potential. The reaction of pyrroline with these alkylidene complexes was not expected to yield polymer. We know from previous work that the alkoxide-derivatized bis(imides), analogous to ring-opened bis(imide) **2**, do not react with imines.[3] The propagation step of the catalysis should therefore be frustrated. Moreover, the pyrroline ring-strain is sufficiently small that only a low-temperature reaction could possibly yield polymer. The increased complexity of the spectrum observed when an excess of pyrroline was reacted with **1** could be explained by several possible side reactions, including coordination of the ring-opened product by pyrroline, comproportionation of the mixed bis(imides) to give Mo(=NCH$_2$CH$_2$CH$_2$CH=CHBu^t)$_2$[OCMe$_2$(CF$_3$)]$_2$ and Mo(=NAr)$_2$[OCMe$_2$(CF$_3$)]$_2$, and chelation of the olefinic chain end (Figure 3).

Mechanism of Ring-Opening. In our system, the first step in the reaction is the coordination of pyrroline. Although precoordination has been postulated as the first step for olefin metathesis, we are aware of only two isolated examples of alkylidene−olefin adducts in the literature.[15,16] Clear evidence for precoordination was observed when complexes **1** and **4** were treated with pyrroline. Since the crystal structure of complex **3** reveals that the imine is coordinated by the N-lone pair however, it is clear that some sort of isomerization or dissociation/reassociation will be required for the alkylidene carbon to access the π face of the pyrroline (Figure 4). Such a reorientation would be required for either a concerted [2+2] reaction or a less concerted nucleophilic attack/ring-closure pathway.

(11) Schrock, R. R.; S., L.; Lee, J. C., Jr.; Zanetti, N. C.; Davis, W. M. *J. Am. Chem. Soc.* **1996**, *118*, 3883−3895.
(12) McCullogh, L. G.; Schrock, R. R.; C., D. J.; Murdzek, J. S. *J. Am. Chem. Soc.* **1985**, *107*, 5987−88.
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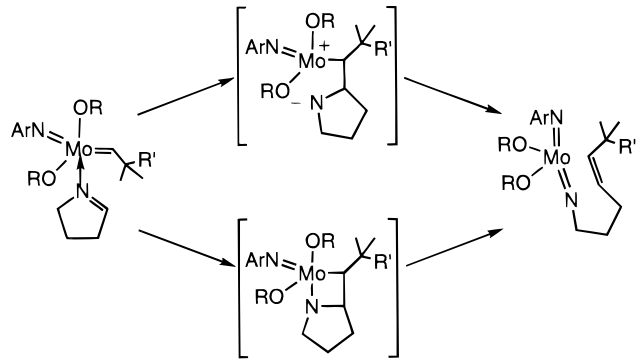
Scheme 4

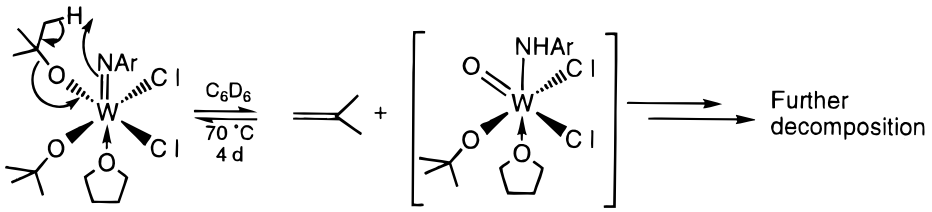


The need to access a more reactive isomer prior to ring-opening could explain both the overall slowness of the reaction of alkylidenes with imines and the lower reactivity of the hexafluoro *tert*-butoxide complex **4** compared with the trifluoro-*tert*-butoxide complex **5**. The barrier for rearrangement of precoordinated intermediates, possibly requiring dissociation, could well be rate-determining. If this is the case, then the strong binding of the electron-poor hexafluoro derivative may inhibit the necessary rearrangement relative to the weaker binding trifluoro derivative. Assuming that the pyrroline can access the correct geometry, the most likely subsequent transition state (or short-lived intermediate) involves either a traditional metallacycle or, in the case of a less concerted attack, a zwitterionic betaine-type structure (Scheme 4). Of course, these species are not observed so their nature cannot be firmly established.

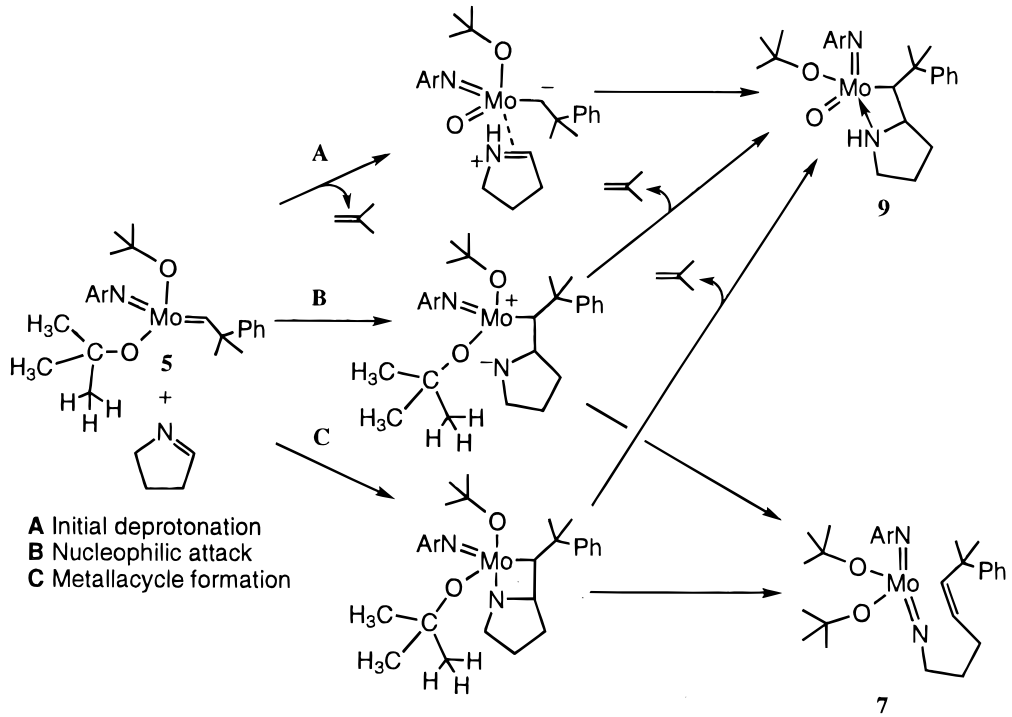
More insight into the mechanism may be gained by considering the possible origins of oxo compound **9**. This compound is particularly intriguing because it has a single bond between the alkylidene and pyrroline-derived carbon atoms. Previous investigations in our laboratory of a related tungsten imide, $W(=NAr)(OBu^t)_2Cl_2$, provide precedent for the origin of **9**. This tungsten compound was found to be thermally unstable, and the spectroscopic data were consistent with an initiation event involving deprotonation of a *tert*-butoxide by the imide ligand (Scheme 5).[17] By analogy, the pyrroline nitrogen could be expected to act as a base and deprotonate the *tert*-butoxide of **5**.

Scheme 6 summarizes three possible pathways for the formation of **9**. In pathway A, the pyrroline deprotonates the *tert*-butoxide first. Elimination of isobutylene is then followed by nucleophilic attack on the activated carbon of the pyrroline moiety. In pathway B, the reaction is initiated by nucleophilic attack of the alkylidene carbon. The resultant zwitterionic intermediate is analogous to a Wittig betaine. The negatively charged nitrogen atom then acts as a base, inducing loss of isobutylene. In pathway C, a metastable metallacyclic intermediate decomposes by deprotonation of the *tert*-butoxide. Although competing pathways involving free radical or

Scheme 5



Scheme 6



cationic butyl intermediates could be postulated, we have not observed byproducts consistent with these mechanisms. Moreover, given the presence of the readily available nitrogen base, a simple deprotonation seems most likely.

Of the three pathways, we currently favor C. Pathway A seems least likely since pyrroline is not a strong base. Of the remaining pathways, C is slightly favored over B since it involves a six-membered transition state for the 1,5-proton transfer. The 1,7-proton transfer required for B must proceed through a presumably less stable eight-membered transition state. The fact that byproducts analogous to **9** were not observed for the fluorine-containing complexes **1** and **4** can be explained if we assume that the intimate mechanism for the elimination has some E_1 character in the transition state or if the reaction is an E_1 elimination with tight ion pairing.[18] This explanation is appealing since the electron-poor molybdenum oxide anion can certainly delocalize the negative charge and the non-fluorinated *tert*-butyl group can support positive charge. Moreover, the lack of reactivity of the fluorinated alkoxide derivatives **1** and **4** can then be explained by the destabilizing effect of the electron-withdrawing groups on the positively charged *tert*-butyl transition state or intermediate.[19]

Two other possible explanations for the observed selectivity should be considered. A simple statistical argument would predict the highest reactivity toward deprotonation for the *tert*-butyl group that had the most hydrogens—the nonfluorinated one. This effect may be a contributing factor, but given the large differences in electronics, seems unlikely to be dominant. A second possible explanation for the unique reactivity of **5** relies on the differences in precoordination of pyrroline (**1** and **4** exhibit precoordination; **5** does not). This explanation is not compelling, however, since it necessitates that the reaction proceed by pathway A, which appears less likely.

The discussion of the possible mechanism of formation of oxo-complex **9** is relevant to the mechanism of the ring-opening metathesis reaction in that the intermediate of either pathway B or C could also lead to the ring-opened product. From this perspective, the deprotonation of the neighboring *tert*-butyl group could be considered a trapping reaction for the common intermediate.

Conclusion

We have reported the first example of the ring-opening metathesis of a cyclic imine, a key step in our effort to extend ROMP to heteroolefinic substrates. The fact that the N-coordinated pyrroline adduct is quite stable may partially explain the slow rates of reactions of imines relative to olefins. After reorientation of the pyrroline, the mechanism of reaction likely involves either a metallacyclic or zwitterionic intermediate that can, in the case of the *tert*-butyl derivatives, be trapped by deprotonation.

Experimental Section

Unless otherwise noted, the following methods were employed for all experiments described. Manipulations were carried out under an inert nitrogen atmosphere in a Vacuum Atmospheres drybox or with standard Schlenk or vacuum line techniques. Reagent grade ether and toluene were distilled from sodium benzophenone ketyl under nitrogen. Reagent grade hexanes was washed with concentrated sulfuric acid, passed through a column of activated alumina, and distilled from sodium benzophenone ketyl under nitrogen. Benzene-d_6 was distilled from sodium benzylphenone ketyl and stored in a glass vessel, equipped with a Teflon stopcock. Pyrroline was prepared and stored as $ZnI_2(pyrroline)_2$, as described in the literature.[7] Alkylidene complexes Mo(=CHBu^t)(=NAr)[OCMe$_2$(CF$_3$)]$_2$ and Mo(=CHBu^t)(=NAr)[OCMe(CF$_3$)$_2$]$_2$ (Ar = 2, 6-diisopropylphenyl) were prepared as described in the literature.[6] Mo[=CH(CMe$_2$Ph)](=NAr)(OBu^t)$_2$ was purchased from Strem Chemicals and used without further purification. 2,2′:6′,2″-Terpyridine was purchased from Aldrich and used without further purification. Sodium bis(methoxyethoxy)aluminum hydride (Red-Al), 70% weight solution in toluene, was purchased from Fisher Scientific and used without further purification. All synthetic reagents were purified by standard methods.

^{1}H NMR and ^{13}C spectra were obtained on a Bruker DRX 500 or a Bruker AF 300 spectrometer. NMR spectra were obtained at 25 °C unless noted otherwise. Mass spectra were acquired with a Hewlet Packard Series 5890 GC/5971A MS.

Pyrroline. $ZnI_2(pyrroline)_2$ (400 mg, 0.875 mmol) and 2, 2′:6′,2"-terpyridine (210 mg, 0.900 mmol, 1.0 equiv) were suspended in ca. 6 mL of C_6D_6. The mixture was frozen in a liquid nitrogen bath, degassed, and then warmed to room temperature. After stirring for 20 min at room temperature, pyrroline and the deuterated solvent were collected under reduced pressure. A ^{1}H NMR spectrum of the pyrroline solution revealed a mixture of pyrroline monomer and trimer. The trimer was dissociated thermally at 85 °C (7 days). ^{1}H NMR (C_6D_6) of pyrroline trimer: δ 3.03 (m, 6), 2.22 (m, 3), 1.76 (m, 9), 1.53 (m, 3). ^{1}H NMR (C_6D_6) of pyrroline monomer: δ 7.26 (s, 1, −N=C*H*CH$_2$CH$_2$CH$_2$−), 3.70 (m, 2, −N=CHC*H*$_2$-CH$_2$CH$_2$−), 1.86 (t, 2, −N=CHCH$_2$CH$_2$C*H*$_2$−, J_{HH} = 7.9 Hz), 1.26 (m, 2, −N=CHCH$_2$C*H*$_2$CH$_2$−).

Mo(=CHBu^t)(=NAr)[OCMe$_2$(CF$_3$)]$_2$[pyrroline] (3). Mo(=CHBu^t)(=NAr)[OMe$_2$(CF$_3$)]$_2$, **1** (102 mg, 0.171 mmol), was dissolved in ca. 0.5 mL of C_6D_6 and then treated with 1 equiv of pyrroline (dissolved in C_6D_6). A ^{1}H NMR spectrum was acquired to confirm that 1 equiv of pyrroline had been added. The solvent was removed in vacuo to give a brown residue. Low-temperature crystallization (−30 °C) from toluene afforded yellow crystals that were suitable for X-ray diffraction (∼25 mg, ∼20% isolated yield). ^{1}H NMR of **3-*anti*** (500 MHz, C_6D_6): δ 13.18 (s, 1, =C*H*), 8.30 (s, 1, N=CH), 7.0−6.94 (m, 3, Aryl), 4.53 (sept, 1, C*H*Me$_2$, J_{HH} = 6.9 Hz), 3.72 (sept, 1, C*H*Me$_2$, J_{HH} = 6.8 Hz), 3.50 (m, 1, CH$_2$), 3.41 (m, 1, CH$_2$), 1.98 (s, 3, OC*Me*$_2$(CF$_3$)), 1.88 (s, 3, OC*Me*$_2$(CF$_3$)), 1.56 (m, 2, CH$_2$), 1.46 (s, 3, OC*Me*$_2$(CF$_3$)), 1.39 (d, 6, CH*Me*$_2$, J_{HH} = 6.9 Hz), 1.28 (d, 3, CH*Me*$_2$, J_{HH} = 6.5 Hz), 1.22 (s, 3, OC*Me*$_2$(CF$_3$)), 1.20 (s, 9, =CH*Bu^t*), 1.0 (d, 3, CH*Me*$_2$, J_{HH} = 6.8 Hz), 0.75 (m, 1, CH$_2$), 0.65 (m, 1, CH$_2$). ^{13}C NMR (125 MHz, C_6D_6): δ 301.66 (M*o*=C*H*, $^1J_{CH}$ = 139 Hz), 174.02, 152.29, 147.99, 143.67, 127.46, 127.16(q), 124.86(q), 80.32(q), 77.45(q), 65.33, 43.97, 35.41, 31.64, 29.99, 29.50, 25.35, 24.71, 24.25, 24.50, 23.92, 23.30, 22.95, 21.27. Anal. Found: C 51.69, H 4.23, N 6.98. Calcd for $C_{29}H_{46}N_2O_2F_6Mo$: C 52.40, H 4.21, N 6.97. Note: when excess pyrroline was used, a kinetic isomer was observed. Complete conversion to the thermodynamic isomer occurred in <2 h under the reaction conditions. Partial ^{1}H NMR of **3-*syn*** (300 MHz): δ 12.23 (s, 1, =C*H*), 7.68 (s, 1, N=CH).

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(19) It should be noted that **5** also is also unique in that it has a neophylidene rather than neopentylidene group. In experiments that are not specifically discussed in this paper, however, no significant differences in reactivity were noted between neophylidenes and neopentylidenes.

3-*anti* to 2, Kinetic Study: NMR Study. Mo(=CHBu^t)(=NAr)[OMe$_2$(CF$_3$)]$_2$(pyrroline) (**3**) was dissolved in ca. 0.4 mL of C_6D_6 to give an approximately 4.5 ± 0.2 M solution in a NMR tube equipped with a Teflon stopcock. Toluene was added as an internal standard. The sample was placed into a preheated NMR probe (55 °C) and the progress of the reaction monitored by ^{1}H NMR spectroscopy. ^{1}H NMR of **2** (C_6D_6 at 55 °C) (unisolated): δ 7.10−6.94 (m, 3, Aryl), 5.33 (d, 1, CH=C*H*Bu^t, J_{HH} = 15.2 Hz), 5.10 (m, 1, C*H*=CHBu^t), 4.08 (t, 2, NC*H*$_2$CH$_2$CH$_2$, J_{HH} = 7.3 Hz), 3.65 (sept, 2, C*H*Me$_2$, J_{HH} = 7.1 Hz), 1.85 and 1.59 (m, 4, NCH$_2$*CH$_2$CH$_2$*), 1.42 (s, 12, OC*Me$_2$*-CF$_3$), 1.26 (d, 12, CH*Me$_2$*, J_{HH} = 7.3 Hz), 0.94 (s, 9, CH=CH*Bu^t*). ^{13}C NMR (75 MHz) (C_6D_6 at 25 °C): δ 154.17, 143.05, 127.40(q), 126.54, 123.86, 123.42, 123.22, 80.27(q), 67.87, 33.26, 32.98, 30.40, 30.17, 29.0, 25.30, 24.99, 24.00. Rate: (1.4 ± 0.2) × 10^{-2} min^{-1}.

Reductive Cleavage of 2. A sample of Mo(=CHBu^t)(=NAr)[OCMe$_2$(CF$_3$)]$_2$ (50 mg, 0.083 mmol) was treated with excess pyrroline in C_6D_6. After heating at 60 °C for 8 h, conversion to the ring-opened species, **2**, was complete. Solvent and excess pyrroline were removed in vacuo. The solid was treated with 4.1 equiv of Red-Al (70% by wt in toluene). After 2 h at room temperature, the reaction was quenched with H_2O. Extraction with Et_2O, drying with $MgSO_4$, and concentration yielded ~25 mg of a yellowish oil. Column chromatography on silica produced a fraction that contained a mixture of 2,6-diisopropylaniline and the reduced ligand H$_2$NCH$_2$CH$_2$CH$_2$-CH=CH(Bu^t). No further purification was attempted. Yield: ~40%. ^{1}H NMR of H$_2$NCH$_2$CH$_2$CH$_2$CH=CH(Bu^t) (C_6D_6) (unisolated): 5.42 (d, 1, CH=C*H*Bu^t, J_{HH} = 15 Hz), 5.3 (dt, 1, C*H*=CHBu^t), 2.8 (t, 2, NC*H*$_2$CH$_2$CH$_2$, J_{HH} = 7.0 Hz), 1.70 and 1.42 (m, 4, NCH$_2$*CH$_2$CH$_2$*), 1.52 (br s, 2, NH$_2$), 0.92 (s, 9, CH=CH*Bu^t*). ^{13}C NMR (75 MHz): δ 135.7, 123.1, 43.3, 33.8, 31.5, 30.40, 30.17. GC/MS (EI): 141 (M^+), 124 ($M^+ - NH_3$).

Reaction of Mo(=CHBu^t)(=NAr)[OCMe(CF$_3$)$_2$]$_2$ (4) with Pyrroline: NMR Study. Complex **4** was dissolved in a stoichiometric amount of pyrroline in C_6D_6 in an NMR tube equipped with a Teflon stopcock. A ^{1}H NMR spectrum of the mixture acquired within minutes of mixing revealed two new alkylidene species, syn- and anti-isomers of pyrroline adduct. After 1 day at room temperature only one isomer was observed in the spectrum. The sample was monitored for 1 day at room temperature and then heated to 65 °C. ^{1}H NMR (unisolated) in C_6D_6 (kinetic isomer): δ 12.41(s, 1 =C*H*Bu^t), 7.63 (s, 1, N=C*H*), 3.88 (br sept, 1, C*H*Me$_2$), 3.30 (br sept, 1, C*H*Me$_2$). Full assignment for this isomer was not possible due to overlap with resonances of the second isomer; (thermodynamic isomer) δ 13.45 (s, 1 =C*H*Bu^t), 8.26 (s, 1, N=C*H*), 7.06−6.90 (m, 3, Aryl), 4.53 (sept, 1, C*H*Me$_2$, J_{HH} = 6.9 Hz), 3.52 (sept, 1, C*H*Me$_2$, J_{HH} = 6.6 Hz), 3.43 (br t, pyrroline CH$_2$, J_{HH} = 7.5 Hz), 2.22 (s, 3, OC*Me*(CF$_3$)$_2$), 1.58 (s, 3,OC*Me*(CF$_3$)$_2$), 1.37 (d, 3, CH*Me$_2$*, J_{HH} = 6.9 Hz), 1.24 (s, 9, =CH*Bu^t*), 1.39 (m, pyrroline CH$_2$), 1.20 (d, 3, CH*Me$_2$*, J_{HH} = 7.0 Hz), 1.03 (d, 3, CH*Me$_2$*, J_{HH} = 6.6 Hz). One set of isopropyl methyl (3H) and remaining pyrroline methylenes could not be definitively assigned due to overlap with other resonances in the alkyl region of the spectrum. After heating, resonances consistent with the ring-opened species, Mo[=NCH$_2$CH$_2$CH$_2$CH=CH(CMe$_2$Ph)](=NAr)(OCMe-(CF$_3$)$_2$)$_2$, **6**, were observed at 5.46 (d, 1, CH=C*H*Bu^t, J_{HH} = 15.1 Hz) and 5.31 (dt, 1, C*H*=CHBu^t), but the reaction was slow and decomposition was competitive.

Reaction of Mo[=CH(CMe$_2$Ph)](=NAr)(OBu^t)$_2$ (5) with Pyrroline: NMR Study. Complex **5** (11 mg, 0.020 mmol) was dissolved in ca. 0.5 mL of C_6D_6 and then treated with 1.5 equiv of pyrroline (dissolved in C_6D_6) in an NMR tube equipped with a Teflon stopcock. The sample was maintained at room temperature for 2 days and then heated at 45 °C intermittently over a 4 day period (total time at 45 °C was 45 h). The progress of the reaction was monitored by ^{1}H NMR spectroscopy. Pyrroline precoordination was not observed. ^{1}H NMR of Mo[=NCH$_2$CH$_2$CH$_2$CH=CH(CMe$_2$Ph)](=NAr)(OBu^t)$_2$ (**7**) (C_6D_6) (unisolated): δ 7.45 and 7.34−6.98 (m, 3, aryl), 5.51 (d, 1, CH=C*H*(CMe$_2$Ph) J_{HH} = 15.9 Hz), 5.26 (m, 1, C*H*=CH(CMe$_2$Ph)), 4.19 (t, 2, NC*H*$_2$CH$_2$CH$_2$, J_{HH} = 7.3 Hz), 3.76 (sept, 2, C*H*Me$_2$, J_{HH} = 6.8 Hz), 2.22 and 2.04 (m, 4, NCH$_2$*CH$_2$CH$_2$*), 1.74 (s, 3, C*Me$_2$*Ph), 1.45 (s, 18, OBu^t), 1.40 (s, 3, C*Me$_2$*Ph). Isopropyl methyl resonances (6H) could not be definitively assigned due to overlap with other alkyl resonances in the spectrum. The ring-opening was still incomplete, and the reaction mixture contained other, unidentified species.

Mo[CH(CMe$_2$Ph)(C$_4$H$_8$N)](=O)(=NAr)(OBu^t) (9). Complex **5** (152 mg, 0.276 mmol) was dissolved in a solution of pyrroline (1−2 equiv) in benzene (15 mL). The reaction mixture was stirred for 19 h at room temperature and then for 21 h at 45 °C. The solvent was removed in vacuo. Low-temperature crystallization at −35 °C from a mixture of benzene/hexane yielded two crops of tan powder (~40 mg total). An ^{1}H NMR spectrum of the isolated solid revealed a complex mixture of products, which included Mo[=NCH$_2$CH$_2$CH$_2$CH=CH(CMe$_2$-Ph)](=NAr)(OBu^t)$_2$, **7**, Mo(=NAr)$_2$(OBu^t)$_2$, **8**, Mo[C(CMe$_2$Ph)-(C$_4$H$_8$N)](=O)(=NAr)(OBu^t), **9**, and residual starting material. A third crop of solid (~10 mg, <10% yield) was recovered from ether at −35 °C. Amber crystals suitable for X-ray diffraction were obtained. Partial ^{1}H NMR (C_6D_6): for **7** (unisolated) δ 5.46 (d, 1, CH=C*H*(CMe$_2$Ph), J_{HH} = 16.5 Hz), 5.20 (m, 1, C*H*=CH(CMe$_2$Ph)), 1.39 (s, 18, OBu^t). Complete assignment of this product could not be made due to the presence of multiple species in the sample; **8** (unisolated but identical to authentic sample) δ 3.84 (sept, 4, C*H*Me$_2$, J_{HH} = 6.6 Hz), 1.43 (s, 18, OBu^t), 1.18 (d, 24, CH*Me$_2$*, J_{HH} = 7.4 Hz). Aryl resonances for **7** and **8** could not be distinguished from other species due to complexity of the spectrum in that region. ^{1}H NMR (C_6D_6) for **9**: δ 7.35 (d, aromatic, J_{HH} = 7.6 Hz), 7.18−6.99 (m, aromatic), 4.59 (sept, 2, C*H*Me$_2$, J_{HH} = 6.7 Hz), 4.40 (s, 1, NH), 2.17 (d, 1, MoC*H*(CMe$_2$Ph), J_{HH} = 7.3 Hz), 1.70 (s, 3, C*Me$_2$*Ph), 1.50 (d, 6, CH*Me$_2$*, J_{HH} = 6.8 Hz), 1.46 (d, 6, CH*Me$_2$*, J_{HH} = 6.8 Hz), 1.43 (s, 3, C*Me$_2$*Ph), 1.37 (s, 9, OBu^t), 3.42, 2.98, 2.23, 2.07, 0.99, and 0.81 (m, 6, pyrrolidine CH$_2$'s). Samples of sufficient purity for analysis could not be isolated.

X-ray Structure Determination of 9. Data were collected on a Siemens P3 diffractometer with graphite-monochromated Mo Kα (λ = 0.710873 Å) radiation at −78 °C. All data were corrected for Lorentz and polarization effects. Heavy atoms were located using direct methods; remaining atoms were located from subsequent difference Fourier syntheses and refined anisotropically using the Siemens SHELXTL PLUS software package (version 5.02). Hydrogen atom positions were computed by fixing the C−H distance to 0.96 Å.

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Supporting Information Available: Tables of atom coordinates, bond distances and angles, anisotropic thermal parameters, and hydrogen coordinates for **9**. This material is available free of charge via the Internet at http://pubs.acs.org.

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