Ring-Opening of a Cyclic Imine: The First Step of Imine ROMP

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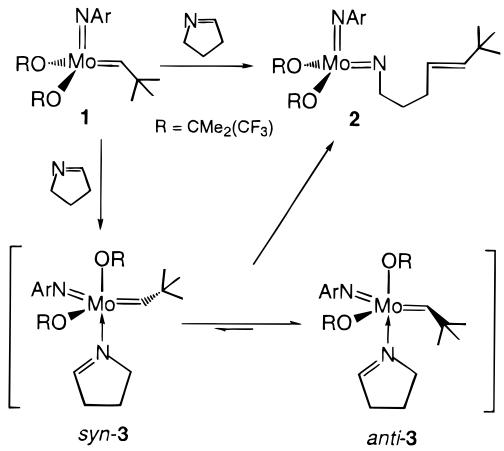
Summary: *Mo(=CH-t-Bu)(=NAr)[OCMe$_2$(CF$_3$)]$_2$ (**1**, Ar = 2,6 diisopropylphenyl) undergoes ring-opening metathesis with pyrroline (C$_4$H$_7$N) to give the mixed bis(imide) product Mo(=NCH$_2$CH$_2$CH$_2$CH=CH-t-Bu)(=NAr)[OMe$_2$(CF$_3$)]$_2$ (**2**). An intermediate N-bound pyrroline adduct Mo(=CH-t-Bu)(=NAr)[OCMe$_2$(CF$_3$)]$_2$[pyrroline], **3**, was isolated and characterized spectroscopically and by X-ray diffraction.*

We report herein the first ring-opening metathesis of a cyclic imine by a transition metal complex. Our interest in this reaction arises from our desire to understand and develop the new C=N bond-forming reaction, catalytic imine metathesis, so that it can be exploited for both small molecule synthesis and polymerization. Our group[1−3] and others[4] have observed metathetic exchange of imines with metal imide or metal alkylidene complexes, but none has yet reported the metathesis of cyclic imine substrates, the key step in a potential heteroolefin ring-opening metathesis polymerization (ROMP). Our previous studies on the reactions of acyclic imines with the Schrock-type olefin catalysts of the general formula Mo(=CHR)(NAr)(OR′)$_2$[3] suggested that these compounds would be ideal candidates for the characterization of a single ring-opening event. Ease of preparation and a minimum amount of strain determined our choice of imine, pyrroline.

Mo(=CH-*t*-Bu)(=NAr)[OCMe$_2$(CF$_3$)]$_2$ (**1**, Ar = 2,6 diisopropylphenyl) undergoes ring-opening metathesis with pyrroline (C$_4$H$_7$N) to give the mixed bis(imide) product Mo(=NCH$_2$CH$_2$CH$_2$CH=CH-*t*-Bu)(=NAr)[OCMe$_2$(CF$_3$)]$_2$ (**2**) (Scheme 1). Complex **1** was treated with a stoichiometric amount of pyrroline in C$_6$D$_6$ at room temperature. A ^{1}H NMR spectrum acquired within minutes of mixing revealed that the original alkylidene resonance at δ 11.61 had been replaced by a new resonance at δ 13.18. Downfield shifts of this magnitude are characteristic for coordination of ligands to molybdenum alkylidene complexes of this type.[5] An accompanying shift of the sp^2 C−H pyrroline resonance, from δ 7.26 to 8.30, was also observed. A spectrum acquired after 3 h in a 70 °C bath exhibited new *trans*-olefinic resonances at δ 5.33 and 5.10 (J_{HH} = 15.2 Hz for sp^2 hydrogens), which were consistent with the formation of metathesis product **2**.

Scheme 1



A shorter-lived intermediate species was observed in early spectra of reaction mixtures that contained an excess of pyrroline. The alkylidene resonance at δ 12.23 (broad), paired with a corresponding shift for a pyrroline sp^2 C−H of δ 7.68, established that this species is also a pyrroline adduct. Schrock and co-workers observed similar coordination behavior when PMe$_3$ reacted with **1**, and they identified the observed isomers as alkylidene rotomers: *syn* (*tert*-butyl points toward the imido ligand) and *anti* (*tert*-butyl points away from the imido ligand).[5] By analogy, we have assigned the kinetic δ 12.23 intermediate as the *syn*-isomer (***syn*-3**) and the thermodynamic δ 13.18 as the *anti*-isomer (***anti*-3**). The relatively large alkylidene J_{CH} of 139 Hz for the thermodynamic isomer is also consistent with the *anti*-assignment.[5] The pyrroline itself is apparently freely rotating at experimental temperatures.

Pyrroline adduct ***anti*-3** was isolated and characterized by X-ray diffraction.[6] A preparative scale reaction of **1** with pyrroline that was not allowed to proceed to the ring-opening stage yielded X-ray quality, amber-colored crystals. Although the overall quality of the structure is not exceptional, primarily due to disorder about the trifluoromethyl *tert*-butoxide ligands, it is sufficient to verify the core geometry and to identify broad structural features of the complex (Figure 1).[7] The geometry about the molybdenum core can be viewed as a distorted trigonal-bipyramid in which the alkylidene, one alkoxide, and the imido ligand occupy equatorial

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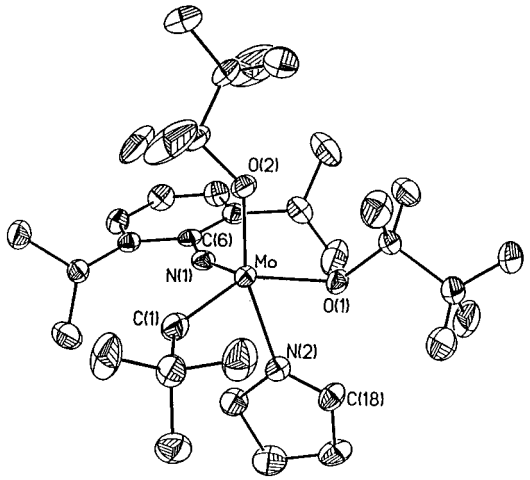


Figure 1. Molecular structure of ***anti*-3** (one of two independent molecules). Hydrogen atoms omitted for clarity, 30% probability ellipsoids. Selected interatomic distances [Å] and angles [deg]: Mo−N(1) 1.735(5), Mo−N(2) 2.237(5), Mo−C(1) 1.948(7), Mo−O(1) 1.966(4), Mo−O(2) 1.988(4), N(2)−C(18) 1.261(8), C(1)−Mo−O(2) 105.7(3), C(1)−Mo−O(1) 117.4(3), N(1)−Mo−C(1) 98.0(3), N(1)−Mo−O(1) 142.4(2), N(1)−Mo−O(2) 97.4(2), O(2)−Mo−N(2) 162.0-(2), O(1)−Mo−O(2) 85.39(18), C(6)−N(1)−Mo 160.3(5).

positions within the coordination sphere. Pyrroline and the second alkoxide occupy axial positions, and the pyrroline is rotated such that the N=C bond aligns with the equatorial alkoxide. Bond lengths are not unusual.[5,8,9]

There are two features of the crystal structure that deserve specific mention: (1) The orientation of the pyrroline ligand indicates that the dative interaction with the molybdenum core is through the nitrogen lone pair rather than the C=N π-system; (2) the imido ligand is not linear (C(6)−N(1)−Mo = 160.3(5)°). In general, diisopropylphenylimido ligands of high oxidation state complexes are nearly linear.[8] Similar trigonal-bipyramidal base adducts of this class of complexes were also found to have nonlinear imido ligands, possibly due to competing π-donation.[5,9]

A significant advantage of pyrroline complex **3** relative to the two olefin adducts that have been observed

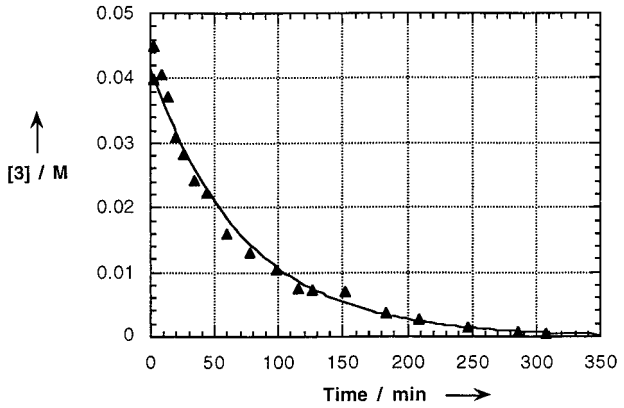
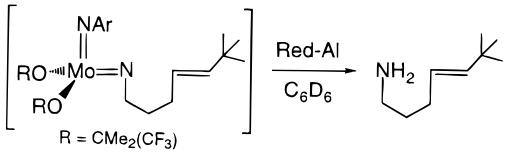


Figure 2. First-order conversion of pyrroline adduct **3** to the ring-opened product **2**: $k_1(\mathbf{3}) = 1.4 \times 10^{-2}$ min^{-1}.

Scheme 2



and shown to be active ROMP/RCM agents[10] is that the conversion to metathesized product can be monitored spectroscopically. We found that **3** reacts to form the ring-opened product, **2**, via simple first-order kinetics.[11] The reaction was monitored over >5 half-lives and a logarithmic fit ($R = 0.994$) of the concentration of the pyrroline adduct **3** vs time gave a rate constant of 1.4 $\pm$ 0.2 $\times 10^{-2}$ min^{-1} at 55 °C (Figure 2).

Although the product, **2**, could not be isolated from the reaction mixture, the olefinic NMR resonances observed for this complex correspond exactly to those for well-characterized olefins produced from the reaction of acyclic imine substrates with **1**.[3] Further confirmation that pyrroline did in fact undergo ring-opening metathesis was obtained by cleaving the product chain from the metal via reduction with sodium bis(methoxyethoxy)aluminum hydride (Red-Al) (Scheme 2). ^{1}H and ^{13}C NMR spectroscopy combined with GC/MS analysis confirmed the presence of the reductively cleaved ligand, $H_2NCH_2CH_2CH_2CH{=}CH(t\text{-Bu})$.[12] Our inability to isolate **2** may be related to either facile imide/imide exchange[3,13] or some inherent instability of the straight-chain alkyl imide. As we had expected, **2** did not react with a second equivalent of pyrroline. The lack of further reactivity can be attributed to the low ring strain of pyrroline and the inertness of fluoralkoxy-ligated bis-(imide) complexes to reaction with imines.[3]

The N-binding mode of the pyrroline adduct **3** has important implications for heteroolefin metathesis. If

(6) ***anti*-3.** Mo(=CH-*t*-Bu)(=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** (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-*t-Bu*), 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 (Mo=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.

(7) Crystal data for ***anti*-3** ($C_{29}H_{46}MoN_2O_2$): 0.41 × 0.38 × 0.38 mm, monoclinic, $P2_1/n$, a = 19.532(4) Å, b = 19.209(4) Å, c = 20.156(4) Å, β = 118.53(3)°, V = 6643(2) Å^3, Z = 8 (4 × 2 independent molecules), T = 200(2) K, ρ_{calc} = 1.329 mg/m^3; Z = 8; $R(F)$ = 0.1237, $R(wF)$ = 0.2090 (all data); GOF = 1.195.

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(11) **(*anti*-3) to (2):** Mo(=CH-*t*-Bu)(=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 $\pm$ 0.5) × 10^{-2} M solution in an 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*-*t*-Bu, J_{HH} = 15.2 Hz), 5.10 (m, 1, C*H*=CH-*t*-Bu), 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-*t-Bu*). ^{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.

the reaction proceeds through a concerted [2+2] mechanism, the pyrroline would need to reorient such that it lay parallel with the C/N/O face, double bond aligned beneath the alkylidene. Moreover, the N-bound orientation does not appear suitable for even a less concerted mechanism involving an initial nucleophilic attack by the imide on the imine. The relatively slow reactions of the pyrroline with alkylidenes, compared with those of olefins,[14] may be due to this rearrangement barrier.[15]

In summary, we have shown that the cyclic imine, pyrroline, will ring open metathetically. Moreover, we have observed and characterized an intermediate pyrroline complex and spectroscopically observed the conversion from adduct to metathesized product.

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

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(12) **Reduction of 2**: A sample of Mo(=CH-*t*-Bu)(=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, **3**, 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 RT, 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. No further purification was attempted. ^{1}H NMR of $H_2NCH_2CH_2CH_2CH$=CH(*t*-Bu) (C_6D_6) (unisolated): 5.42 (d, 1, CH=C*H*-*t*-Bu, J_{HH} = 15 Hz), 5.3 (dt, 1, C*H*=CH-*t*-Bu), 2.8 (t, 2, $NCH_2CH_2CH_2$, J_{HH} = 7.0 Hz), 1.70 and 1.42 (m, 4, $NCH_2CH_2CH_2$), 1.52 (br s, 2, NH_2), 0.92 (s, 9, CH=CH-*t-Bu*). ^{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 ($M^+ - NH_3$).

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(15) The "rearrangement" may involve dissociation and recoordination.