Molybdenum and Tungsten Alkylidene and Metallacyclobutane Complexes that Contain a Dianionic Biphenolate Pincer Ligand

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ABSTRACT: Molybdenum imido alkylidene and tungsten oxo alkylidene complexes that contain a tridentate "pincer" [ONO] ligand have been prepared and treated with ethylene to give unsubstituted metallacyclobutane complexes that have a 16e count. Both Mo and W metallacyclobutane complexes exchange C5D5 into the metallacyclobutane ring at 22 °C at a rate that is first order in metal and zero order in C5D5. These metallacycles lose ethylene at least 104 to 105 times slower than reported 14e unsubstituted Mo and W metallacyclobutane complexes that have been explored in the literature that have a TBP geometry with the metallacyclobutane ring bound in the equatorial positions. Our studies suggest that breaking up the metallacyclobutane ring in these 16e [Mo or W complexes is slow because a 14e TBP metallacyclobutane complex cannot be accessed readily.

Alkylidene complexes of molybdenum and tungsten with the formula M(Z)(CHR)(X)(Y), where X and Y are monodentate monoanionic ligands and Z is an imido (M = Mo or W) or oxo (M = W) ligand, have been explored extensively as initiators for the controlled metathesis of olefins.1 If X and Y are not strong π bonding ligands, and Z (NR or O) is, then M(Z)(CHR)(X)(Y) complexes have a 14 electron count at the metal and 14e five-coordinate trigonal bipyrimal metallacyclobutane complexes made from them upon addition of olefin are the key intermediates in the metathesis reaction.2 In a recent investigation of W(O)(CHR)(OAr)2(L) complexes (L = a phosphine or acetonitrile) for ring-opening metathesis polymerization3 it was found that 16e W(O)(CHR)(OAr)2(L) complexes behave as initiators for ROMP to give polymers that are highly biased toward cis,isotactic structures, while 14e W(O)(CHR)(OAr)2 analogous yield polymers that are highly biased toward cis,syndiotactic structures. These results suggest that the presence of the 2e donor (L) changes the selectivity of the ROMP reaction. Fischer reported4 that Mo alkylidyne complexes that contain the [ONO]2− "pincer" ligand shown in Figure 1 are efficient catalysts for the living ring-opening polymerization of cyclooctynes at 90 °C; the initiators are essentially inactive at 22 °C. In response to the above findings we became interested in preparing and exploring 16e imido alkylidene complexes that contain the [ONO]2− ligand shown in Figure 1. Coordination of the pyridyl nitrogen should essentially guarantee that a 16e count is maintained throughout the metathesis process.

The reaction between Mo(NC5F5)2(CH2CMe2Ph) and H2[ONO] in benzene at 60 °C (12 h) led to formation of C6F5NH2, CPhMe2, and Mo(NC5F5)(CHCMe2Ph)(ONO) (1) as the only products (eq 1), according to NMR data; 1 could be isolated in only ~30% yield starting with 0.30 g of Mo(NC5F5)2(CH2CMe2Ph) as a consequence of its relatively high solubility in pentane. This is the only example of forming an imido alkylidene complex employing a (bi)phenol as an acid whose pKa is not as low as that for C6F5OH. Pentafluorophenol has been employed to protonate the t-butylimido ligand in Mo(N-t-Bu)(CH2CMe2Ph) to yield Mo(N-t-Bu)(CH-t-Bu)(OC5F5)2(NH-t-Bu) and neopentane,5,6 but protonation of a pentafluorophenylimido nitrogen in compounds of this general type also was not known.

\[
\text{C}_6\text{F}_5\text{N} + \text{H}_2\text{[ONO]} \rightarrow \text{C}_6\text{F}_5\text{NH}_2 + \text{CPhMe}_2
\]

An X-ray structure of Mo(NC5F5)(CHCMe2Ph)(ONO) shows it to be essentially a square pyramid (Figure 2) in which the neophylidene ligand is in the apical position and in a syn orientation (in which the substituent points toward the imido nitrogen atom). The N-Mo-N2 angle is 140.9(2), the O-Mo-O angle is 153.4(2)°, and the Mo=N-C angle is 159.1(6)°. The neophylidene ligand has a relatively large Mo-C1-C2 angle (150.7(6)°) and a small Mo-C1-H1 angle (96.1(5)°). The value for \( J_{\text{CH}} \) (120 Hz) is typical for a syn alkylidene isomer.6,7,8

An attempt to prepare 1 in a reaction between Li2ONO and Mo(NC5F5)(CHCMe2Ph)(1,2-dimethoxyethane)(OTf)2 led to formation of Mo(NC5F5)(CHCMe2Ph)(ONO)(OTf)(DMEO)(Li) (1LiOTf). An X-ray structural study shows 1LiOTf to be

![Figure 1. The [ONO]2− ligand.](image1.png)

Figure 1. The [ONO]2− ligand.

![Figure 2. Thermal ellipsoid drawing (50% probability) of 1.](image2.png)

Figure 2. Thermal ellipsoid drawing (50% probability) of 1. (The solvent and all hydrogens except H1 were omitted for clarity.)
essentially an octahedral complex in which triflate is bound to the metal and the lithium ion is coordinated to dimethoxyethane and the two [ONO] ligands (Figure 3). This circumstance forces the [ONO] ligand to be in an unusual fcc configuration with the O1-Mo-O2 angle being 79.6(2)°. (The [ONO]+ ligand is close to a mer geometry in all previously reported octahedral complexes.4,5) The N1-Mo-O1 and N1-Mo-O2 bond angles are 76.6(2)° and the Mo-O1 and Mo-O2 bond lengths (2.244 and 2.118 Å, respectively) are significantly longer than the Mo-O bond distances (1.988 and 2.001 Å) found in the octahedral molybdenum alkylidyne complex reported by Fischer, et al.4 Recrystallization of [LiOTf] from toluene and pentane multiple times yields 1, which confirms that LiOTf is lost readily from [LiOTf] in C6D6 at 22 °C.

Figure 3. Thermal ellipsoid drawing (50% probability) of I(LiOTf). (The solvent, several atoms, and several tert-butyl groups were omitted in order to reveal other details).

Compound 1 reacts slowly with ethylene (1 atm) over a period of 4 h at 22 °C to yield the six-coordinate unsubstituted metallacyclobutane complex, Mo(NC6F5)(CH2CH2CH3)(ONO) (2) instead of the five-coordinate methylidene complex, Mo(NC6F5)(CH3)(ONO) that we expected. An X-ray structure of 2 (Figure 4) showed that N1 and N2 are essentially trans to one another (178.4(2)°), the O1-Mo-O2 angle is 122.7(1)°, and the Mo-N2 distance is 2.377(3) Å.

Complex 2 is one of four unsubstituted molybdenocyclotubane complexes to be isolated; the other three are five-coordinate TBP complexes that contain the 2,6-disopropylphenylimido ligand (NAr), and only one of the three, Mo[NAr](C6H5)(Me2P)2(OBtBr2),6 has been characterized in an X-ray study. As far as we are aware the only six-coordinate Mo or W metallacyclobutane complex in this family is W[CH(t-Bu)CH2CH2(O2Me)]2([NAr][OCMe2(CF3)])2,10 in which the carbonyl oxygen in the carbomethoxy group is bound weakly to the metal trans to the imido nitrogen with the W-O distance being 2.376(6) Å. Other square pyramidal metallacyclobutane complexes in this class of Mo or W complexes that have been characterized structurally include five-coordinate W[NAr][CH(t-Bu)CH2][OCMe2(CF3)]2,11 W[O(C6H5)]2(OHMT)[OSi(t-Bu)3] (OHMT = O-2,6-(2,4,6-Me3C6H2)3C6H3)12 and a trisubstituted metallacycle formed through addition of 5,6-bistrifluoromethylphenoxoboradiene to W[NAr](CH-t-Bu)O(t-Bu)2,13 The metallacyclobutane ring in 2 and in SP metallacycles are all somewhat bent with M-C, distances of ~2.78 Å and other angles and bond distances are distinctly different from what they are in TBP metallacycles (Figure 5).14,15 It has been proposed that five-coordinate TBP metallacycles are the crucial intermediates in metathesis reactions; the M-C, distances are relatively short (2.3-2.4 Å; see Figure 5) and the olefin therefore able to be lost readily via what could be described as a transition state with a significant degree of olefin/alkylidyne character.14,15 One five-coordinate tungstacyclobutane complex has been observed in the solid state in which the distorted WC3 ring spans apical and basal positions and appears to be on its way to losing ethylene.16

Figure 4. Thermal ellipsoid drawing (50% probability) of 2. (The solvent and all of hydrogen atoms were omitted for clarity). Selected bond lengths (Å) and angles (deg): Mo(1)- C(1) = 2.049(4), Mo(1)-C(3) = 2.195(4), C(1)-C(2) = 1.519(6), C(2)-C(3) = 1.517(6), O(1)-Mo(1)-O(2) = 122.7(1), N(1)-Mo(1)-N(2) = 178.4(2), C(1)-Mo(1)-C(3) = 62.1(2), C(1)-C(2)-C(3) = 96.8(3).

Compound 2 decomposes slowly in C6D6 at room temperature in the absence of ethylene to yield what we propose to be the ethylene complex, Mo(NC6F5)(CH2CH3)(ONO) (3), and free ethylene; no propylene, the product that would be formed through rearrangement of the metallacycle, is observed in the proton NMR spectrum. We propose that 2 loses ethylene slowly to give Mo(NC6F5)(CH3)(ONO). Bimolecular coupling of the methylidene ligands in Mo(NC6F5)(CH3)(ONO), possibly via a bis-µ-methylidene bimetallic complex, then leads to

Figure 5. Approximate distances (Å) and angles (°) in metallacyclobutane rings in TBP versus SP or Octahedral complexes.

3 in the presence of the one equivalent of ethylene that was lost from 2. Bimolecular decomposition of d6 methylidene complexes, first observed in 18e C6Ta(CH2)Me18 is relative-
ly common, although some 14e molybdenum and tungsten imido methyldiene complexes are relatively stable and have been structurally characterized. Mo(NC₆F₃)(CH₂) is not observed under the conditions where 2 decomposes, which suggests that bimolecular coupling is fast relative to the rate of loss of ethylene from 2.

Decomposition of 2 at elevated temperatures leads to mixtures that contain decomposition products other than 3, and therefore to significantly lower yields of 3.

Exchange of C₅D₅ into 2 at 760 mm Hg partial pressure in C₅D₅ at 22 °C can be observed by following the disappearance of one of the H₃ resonances in the proton NMR spectrum of 2. The H₃ resonance in 2 in solution under 760 mm of Hg partial pressure of C₅D₅ disappears at a rate that depends to the first order on the concentration of 2 with k = 8.8 x 10⁵ s⁻¹. The result under 380 mm Hg partial pressure of C₅D₅ is 7.5 x 10⁵ s⁻¹, which suggests that the two rate constants are the same (3σ = 1.9 x 10⁵) and that the rate limiting step is loss of ethylene from 2 to give intermediate Mo(NC₆F₃)(CH₃)(ONO).

The first order decomposition of an H₃ resonance also suggests that 2-d₃(α-CH₃) does not rearrange intramolecularly to give 2-d₃(β-CH₃) before D₅=C(CH₃)₂ is lost from 2-d₃(α-CH₃) to give 2-d₃(eq) in the presence of C₅D₅. It is worth noting that the rate constant for loss of 1-butylethylene from square pyramidal W(NAr)[CH₂CH₂Bu][O Me₂(CF₃)]₂ is 23.7 °C is 7.6 x 10⁵ s⁻¹, which is an order of magnitude faster than loss of ethylene from 2.

We turned to tungsten oxo chemistry and encountered a second example of an unusually stable metallacylobutane. The reaction between Li₂[ONO] and tungsten oxo complexes of the type W(O)(CHMe₂Ph)L₂Cl₂ where L = PMe₂Ph, PMe₂Ph, or PMe₃ leads to complexes of the type W(O)(CHMe₂Ph)(ONO)(L) (4(PMe₂Ph), 4(PMe₂Ph), and 4(PMe₃), respectively). The phosphine ligand in all three complexes rapidly dissociates to a significant extent in solution and the alkylidene H₃ resonances at 22 °C consequently are relatively broad in the ¹H NMR spectrum and do not show resolved coupling to ³P. All 4 complexes also react readily with ethylene (1 atm) to give the phosphine-free metallacylobutane complex, W(O)(CH₂CH₂CH₃)(ONO) (5), which can be isolated in 55-75% yield as a consequence of its relatively low solubility in pentane. Proton and carbon NMR spectra of 5 show the metallacylobutane proton and carbon resonances in essentially the same positions as in 2, which suggest that the structure of 5 is analogous to that of 2.

The exchange of C₅D₅ into the metallacycle in 5 was also found to be first order in metal and zero order in C₅D₅ at 760 and 380 mm Hg partial pressures of C₅D₅. However, the rate constants (k = 8 x 10⁵ s⁻¹ and 10 x 10⁵ s⁻¹, respectively) are approximately an order of magnitude smaller in 5 than in 2, and the half-life approximately 21 h for exchange of C₅D₅ into 5 versus 2.4 h for exchange of C₅D₅ into 2.

Loss of ethylene from 16e 2 and 5 is dramatically slower than the rate of loss of ethylene from 14e unsubstituted TBP metallacylobutane complexes that have been explored through NMR methods. Rate constants for loss of ethylene from molybdenacylobutane complexes are >10⁷ s⁻¹. The rate of loss of ethylene from 2 is at least 10⁷ times slower and the rate of loss of ethylene from 5 is at least 10⁶ times slower than loss of ethylene from observable TBP molybdenacylobutane complexes.

There is some evidence from experimental studies, but little from theoretical studies, for an alkylidene/olefin transition state in forming a high oxidation state Mo or W metallacylobutane complex or losing an olefin from a metallacylobutane complex. The studies reported here provide convincing evidence that access to what is close to an alkylidene/olefin transition state is crucial to the olefin metathesis process and that 14e TBP intermediates are close to that transition state. An inability to access the 18e alkylidene/olefin state is a viable explanation as to why the metallacycles in 2 and 5 are not destabilized in the presence of the pyridine donor, but in fact stabilized toward loss of olefin, which is contrary to what we expected. Because there is no evidence for rearrangement of 2-d₃(α-CH₂) to 2-d₃(β-CH₂) in 2 and 5 (equation 2), ethylene must be lost faster than the metallacycle can reform from any alkylidene/olefin intermediate. This circumstance has also been observed in NMR studies of TBP metallocycles where ethylene loss is fast. Rearrangement of an SP complex to a TBP complex provides an indirect pathway for loss of olefin, but in six-coordinate 2 and 5 the metallacylobutane ring is effectively “locked” in a pseudo-octahedral form.

Preliminary experiments with 2 and 5 have shown that they are extremely slow catalysts for the metathesis of ordinary olefins, and even polymerization of norbornene, at 22 °C, as one would expect on the basis of the ethylene exchange reactions that have been observed here. The room temperature results did not eliminate the possibility that 16e complexes such as 2 and 5 could be useful for olefin metathesis at high temperatures, especially if both bimolecular decomposition and metallacylobutane rearrangement to an olefin are slower relative to the rate of olefin metathesis. However, at loadings of 5 mol % 2 homocoupling of 1-hexene progresses to only 28 % conversion to 5-decene over 4 days at room temperature and at 50 °C to 24 % conversion over 24 h. Catalyst 5 in similar experiments gives 20 % conversion to 5-decene over 4 days at room temperature, and 7 % conversion at 50 °C over 24 h. Both catalysts also decompose in the 50 °C experiments.

The results presented here suggest that a 2e donor ligand can block loss of an olefin from a metallacycle. An important remaining question then is how can a donor ligand dramatically alter the course of facile metathesis reactions? A clue may lie in the finding that donor ligands also can catalyze rearrangement of four-coordinate alkylidene complexes through formation of five-coordinate adducts, as has been observed for diastereomers of four-coordinate imido alkylidene complexes that contain a stereogenic metal center. Studies aimed toward answering questions concerning the role of donor ligands (including solvents) are being addressed.

ASSOCIATED CONTENT

Supporting Information. Experimental details for the synthesis of all compounds and a description of the x-ray structural studies. This material is available free of charge via the Internet at http://pubs.acs.org.

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Supporting Information for

Molybdenum and Tungsten Alkylidene and Metallacyclobutane Complexes that Contain a Dianionic Biphenolate Pincer Ligand

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General Experimental Procedures. All procedures and manipulations were performed under an argon or nitrogen atmosphere using standard Schlenk and glovebox techniques unless stated otherwise. All glassware was oven-dried or flame-dried prior to use unless stated otherwise. Ether, pentane, toluene, dichloromethane, toluene, and benzene were degassed with dinitrogen and passed through activated alumina columns under nitrogen unless stated otherwise. All dried and deoxygenated solvents were stored over molecular sieves in a nitrogen-filled glovebox. Deuterated solvents were purchased from Cambridge Isotope Laboratories, degassed, and dried over activated molecular sieves prior to use. Mo(NC₆F₅)₂(Ph)(OTf)(DME), H₂[ONO]⁻, W(O)(CHCMe₂Ph)(PMepPh₃)Cl₂, and W(O)(CHCMe₂Ph)(PMepPh₃)Cl₃ were synthesized according to literature procedures. NMR spectra were recorded on 600, 500 or 300 MHz spectrometers at ambient temperature. The ¹H and ¹³C NMR spectra were measured relative to partially deuterated solvent peaks, but are reported relative to tetramethylsilane. All ¹⁹F chemical shifts were measured relative to fluorobenzene (-113.15 ppm) as an external reference. All ³¹P chemical shifts were measured relative to triphenylphosphine (-6.00 ppm) as an external reference. Elemental analyses were performed at the CENTC Elemental Analysis Facility at the University of Rochester.

Modified Synthesis of Mo(NC₆F₅)₂Cl₂(DME). The following procedure was adapted from Fox, H. H. et al.⁴ A Schlenk flask was charged with 2.00 g of (NH₄₂)₃MoO₆ (1 equiv, 10.2 mmol) and a magnetic stir bar. DME (40 mL) was then added to the flask followed by 11.4 mL NEt₃ (8.00 equiv, 81.6 mmol), 22.0 mL TMSCl (17.0 equiv, 173 mmol), 7.46 g C₆F₅NH₂ (4.00 equiv, 40.7 mmol), and 60 mL of DME. The mixture was heated overnight (18 h) at 70 °C. The red reaction mixture was allowed to cool to room temperature and the mixture was filtered through a short Celite plug. The filter cake was rinsed thoroughly with DME and the volatile components were removed from the filtrate in vacuo to yield a sticky tar. The residue was extracted with 500 mL of diethyl ether and the extract was then concentrated to ~30 mL in vacuo. The resulting slurry was stirred for several hours before the solid was isolated on a glass frit and washed with small amounts of cold diethyl ether. The product was dried in vacuo to give a red powder; yield = 4.9 g (94%). All spectroscopic data match the data reported previously.

Figure S1. Labelling for the ONO ligand aromatic proton resonances, the neophylidene aromatic proton resonances, the phosphine ligand aromatic proton resonances, and the imido fluorine resonances.

Synthesis of Mo(NC₆F₅)₂(CH₂CMe₂Ph)₂. Mo(NAr³)₂(CH₂CMe₂Ph)₂ was reported previously as a dark red oil by Yuan, J. et al.¹ The procedure described here yielded a solid product. A suspension of 6.50 g Mo(NAr³)Cl₂(DME) (1 equiv, 10.5 mmol) in 100 mL of diethyl ether was chilled to -30 °C for 1 h and then 42.0 mL of chilled 0.5 M ClMgCHCMe₂Ph in Et₂O (2 equiv, 21.0 mmol) was added. The mixture was allowed to warm to room temperature and was stirred overnight before removing the solvent in vacuo. The resulting red residue was dissolved in pentane and the mixture was filtered through a plug of Celite. The solution was then concentrated and cooled to -30 °C. The mother liquor was decanted and the resulting red crystals were washed with a small amount of cold pentane before drying in vacuo; yield = 4.9 g (65%): ¹H NMR (500 MHz, C₆D₆) δ 7.22 (app d, 4H, Aromatic-CH), 7.06 (app t, 4H, Aromatic-CH), 6.90 (app t, 2H, Aromatic-CH), 1.93 (s, 4H, CH₂), and 1.36 (s, 12H, CH₃) ppm; ¹⁹F NMR (300 MHz, C₆D₆) δ -149.17 (d, 3J₉F = 21.5 Hz), -159.56 (t, 3J₉F = 21.8 Hz), and -164.09 (ap t) ppm; ¹³C
NMR (125 MHz, CDCl₃) δ 150.08 (s, Aromatic-C), 141.52 (dm, Aromatic-C), 1/2JCF = 249.2 Hz), 138.97 (dm, Aromatic-C), 1/2JCF = 252.2 Hz), 137.82 (dm, Aromatic-C), 1/2JCF = 250.0 Hz, 132.22-131.78 (m, Aromatic-C), 128.64 (s, Aromatic-CH), 126.37 (s, Aromatic-CH), 126.10 (s, Aromatic-CH), 86.60 (s, Mo-CH₃), 41.59 (s, C(CH₃)₃Ph), and 32.17 (s, CH₃) ppm. Anal. Calcd for C₃H₅F₅MoN₂O₂: C, 53.05; H, 3.62; N, 3.87. Found: C, 53.18; H, 3.76; N, 3.65.

**Mo(NcF₃)(CHCMe₂Ph)(ONO)(OTf)(DME)(Li) (1(LiOTf))**. A solution of 99 mg of Li₂ONO·(THF)₄ (1 equiv, 0.125 mmol) in 5 mL benzene was added to a solution of 0.100 g Mo(NAr₅)(CHC(CH₃)₃Ph)(OTf)₂(DME) (1 equiv, 0.125 mmol). After 2 h, the solution was filtered through Celite, the solvent was removed under reduced pressure, and the resulting dark brown residue was redissolved in 5 mL toluene. The solvent was then removed in vacuo, and the resulting residue was redissolved in ~2 mL pentane and 3-5 drops DME. The suspension was stirred for 2 h and then cooled to -30 °C overnight. The precipitate was isolated by filtration, washed with a small amount of cold pentane, and dried under high vacuum to yield an orange powder. Crystals suitable for X-ray diffraction studies were obtained from a pentane solution cooled to -30 °C; yield 0.0754 g (52.8%): 1H NMR (500 MHz, CDCl₃, δ 10.55 (s, Mo=CH), 285.13 (s, Mo=CH), 163.15 (s, Aromatic-C), 141.52 (dm, Aromatic-C), 140.78 (s, Aromatic-C), 139.26 (s, Aromatic-C), 139.04 (dm, Aromatic-C), 1/2JCF = 249.7 Hz), 138.27 (s, Aromatic-C), 137.82 (dm, Aromatic-C), 136.14 (s, Aromatic-C), 128.64 (s, Aromatic-C), 128.55 (s, Aromatic-C), 126.53 (s, Aromatic-C), 126.38 (s, Aromatic-C), 125.78 (s, Aromatic-CH), 122.96 (s, Aromatic-CH), 52.86 (s, C(CH₃)₃Ph), 35.74 (s, C(CH₃)₃), 34.57 (s, C(CH₃)₃), 31.80 (s, C(CH₃)₃), 30.60 (s, C(CH₃)₃), and 29.82 (s, CH₃) ppm. Anal. Calcd for C₃H₅F₅MoN₂O₂·C₆H₅F₅MoN₂O₂·C₆H₅F₅MoN₂O₂: C, 56.84; H, 5.74; N, 2.46. Crystals were submitted for analysis three times: C, 59.072; H, 5.754; N, 2.518: C, 58.510; H, 5.707; N, 2.469: C, 59.663; H, 6.374; N, 2.103. The high and variable analyses for carbon suggest that the samples were a mixture of 1(LiOTf) and 1.

**Mo(NcF₃)(CHCMe₂Ph)(ONO) (1)**. A solution of 0.300 g H₂ONa (1 equiv, 0.615 mmol) in 15 mL benzene was added to a solution of 0.447 g Mo(NAr₅)(CHC(CH₃)₃Ph)(OTf)₂ (1 equiv, 0.615 mmol) in 15 mL benzene. The reaction mixture was then heated in a sealed vessel at 60 °C for 12 h. The reaction was cooled to room temperature and the solvent was removed under reduced pressure. The dark residue was dissolved in ~10 mL pentane and the mixture was filtered through Celite. The solven was removed under reduced pressure and the dark residue was dried under high vacuum. The residue was redissolved in ~2 mL pentane and the mixture was stirred for 1 h. The resulting suspension was cooled to -30 °C for several hours. The product was isolated by filtration, washed with small amounts of cold pentane, and dried under high vacuum to yield a bright yellow powder; yield 0.1532 g (27.8%). Crystals suitable for X-ray diffraction studies were obtained from a pentane solution cooled to -30 °C. All NMR spectroscopic data were identical to 1(LiOTf) as a consequence of loss of LiOTf from 1(LiOTf) in solution. Anal. Calcd for C₆H₅F₅MoN₂O₂: C, 65.76; H, 6.19; N, 3.13. Found: C, 65.96; H, 6.37; N, 2.91.

**Mo(NcF₃)(CH₂CH₂CH₂)(ONO) (2)**. A solution of 0.085 g of 1 (0.095 mmol) in 10 mL pentane was placed under one atmosphere of ethylene using a freeze-pump-thaw cycle and the vessel was sealed. The reaction was stirred for 4 h, after which time the reaction volume was reduced to ~2 mL and the resulting suspension was cooled to -30 °C overnight. The product was isolated by filtration, washed with small amounts of cold pentane, and dried under high vacuum to give an orange powder; yield 0.0463 g (60.6%). Crystals suitable for X-ray diffraction studies were obtained from a pentane solution cooled to -30 °C: 1H NMR (500 MHz, CDCl₃, δ 7.73 (d, 2H, H⁺, or H⁻, 1/2JHH = 2.4 Hz), 7.47 (d, 2H, H⁺), 1/2JHH = 2.4 Hz), 7.15 (d, 2H, H⁺, 1/2JHH = 7.7 Hz), 6.98 (dd, 1H, H⁺, 1/2JHH = 8.2, 1/2JHH = 7.7 Hz),
3.83-3.72 (m, 1H, CH$_2$-CH/H-CH$_3$), 3.18-3.06 (m, 1H, CH$_2$-CHH-CH$_3$), 2.75-2.66 (m, 2H, Mo-CH$_2$-CH$_3$), 1.65 (s, 18H, CH$_3$), 1.39 (s, 18H, CH$_3$), and 1.01-0.91 (m, 2H, Mo-CH$_2$-CH$_3$) ppm; $^{19}$F NMR (300 MHz, C$_6$D$_6$) δ -146.56 (d, F$^a$, $^3$J$_{FF}$ = 18.4 Hz), -159.15 (t, F$^c$, $^3$J$_{FF}$ = 22.4 Hz), and -163.43 (td, F$^b$, $^3$J$_{FF}$ = 22.4 Hz, $^4$J$_{FF}$ = 4.6 Hz) ppm; $^{13}$C NMR (125 MHz, C$_6$D$_6$) δ 156.57 (s, Aromatic-CH), 156.39 (s, Aromatic-CH), 144.11 (s, Aromatic-CH), 143.29 (dm, Aromatic-CF, $^1$J$_{CF}$ = 247.1 Hz), 139.49 (s, Aromatic-C), 138.43 (s, Aromatic-C), 137.60 (dm, Aromatic-CF, $^1$J$_{CF}$ = 247.4 Hz), 131.00-130.59 (m, Aromatic-CF), 126.07 (s, Aromatic-CH), 125.13 (s, Ar-C), 124.41 (s, Ar-CH), 45.36 (s, Mo-CH$_2$), 35.62 (s, C(CH$_3$)$_3$), 34.71 (s, C(CH$_3$)$_3$), 34.41 (s, CH$_3$), 31.75 (s, CH$_3$), and 29.93 (s, CH$_3$) ppm. Anal. Calcd for C$_8$H$_{40}$F$_3$MoN$_2$O$_2$: C, 62.68; H, 6.14; N, 3.48. Found: C, 62.64; H, 6.06; N, 3.44.

**Alternative Synthesis of 2.** A solution of 0.300 g of H$_2$ONO (1 equiv, 0.615 mmol) in 15 mL benzene was added to a solution of 0.447 g Mo(NAr)$^3$)(CH$_2$CMe$_3$Ph)$_2$ (1 equiv, 0.615 mmol) in 15 mL benzene. The reaction mixture was then heated in a sealed vessel at 60 °C for 12 h. The reaction was cooled to room temperature and the solvent was removed under reduced pressure. The dark residue was dissolved in ~20 mL of pentane and the mixture was filtered through Celite. The pentane filtrate was then placed under an atmosphere of ethylene using one freeze-pump-thaw cycle, and the vessel was closed. The reaction was stirred for 4 h, after which time the reaction volume was reduced to ~2 mL, and the resulting suspension was cooled to -30 °C overnight. The product was isolated by filtration, washed with small amounts of cold pentane, and dried under high vacuum to give an orange powder; yield 0.191 g (38.6%).

**Mo(NC$_6$F$_3$)(CH$_2$CH$_2$)(ONO) (3).** A solution of 0.050 g of 2 (6.21 μmol) in 2 mL benzene was stirred in a closed vial for 1 week. The solvent was removed under reduced pressure, and the dark residue triturated with ~4 mL pentane overnight. The solution was filtered and the filtrate stored at -30 °C for several days. The product was isolated by filtration, washed with a small amount of cold pentane, and dried under high vacuum to yield a tan powder; yield 0.0123 g (25.0%): $^1$H NMR (500 MHz, C$_6$D$_6$) δ 7.74 (d, 2H, H$^a$ or H$^c$, $^3$J$_{HH}$ = 2.5 Hz), 7.31 (d, 2H, H$^a$ or H$^c$, $^3$J$_{HH}$ = 2.3 Hz), 7.07 (d, 2H, H$^b$, $^3$J$_{HH}$ = 7.9 Hz), 6.95 (t, 1H, H$^c$, $^3$J$_{HH}$ = 7.9 Hz), 3.04-2.99 (m, 2H, Mo-CHH), 1.68 (s, 9H, CH$_3$), 1.37 (s, 9H, CH$_3$), and 1.06-1.00 (m, 2H, Mo-CHH) ppm; $^{19}$F NMR (300 MHz, C$_6$D$_6$) δ -149.43 (d, F$^a$, $^3$J$_{FF}$ = 18.5 Hz), -159.86 (t, F$^c$, $^3$J$_{FF}$ = 22.8 Hz), and -163.31 (app t, F$^b$, $^3$J$_{FF}$ = 22.8 Hz) ppm; $^{13}$C NMR (100 MHz, C$_6$D$_6$) δ 160.53 (s, Aromatic-C), 157.37 (s, Aromatic-C), 143.03 (s, Aromatic-C), 138.78 (Aromatic-CH), 138.55 (s, Aromatic-C), 133.23-132.48 (m, Aromatic-CF), 129.29 (s, Aromatic-C), 124.98 (s, Aromatic-CH), 124.20 (s, Aromatic-CH), 123.04 (s, Aromatic-CH), 55.86 (br s, Mo-CH$_2$), 35.58 (s, C(CH$_3$)$_3$), 34.63 (s, C(CH$_3$)$_3$), 31.79 (s, CH$_3$), 29.94 (s, CH$_3$), and 23.05 (s, Mo-CH$_2$-CH$_2$) ppm. Anal. Calcd for [C$_4$H$_8$F$_3$MoN$_2$O$_2$]: C, 62.27; H, 5.99; N, 3.54. Samples were found to decompose slowly over time and did not pass elemental analyses.
**W(O)(CHCMe₂Ph)(PMe₂)₂Cl₂.** This starting material was synthesized using an adapted version of the procedure described by Peryshkov et al.³ To a suspension of 3.00 g W(O)(bipy)(CH₂CMe₂Ph)₂ (1 equiv, 4.70 mmol) and 1.10 g ZnCl₂ (dioxane) (1.05 equiv, 4.93 mmol) in 30 mL toluene was added 10 mL of 1.0 M PMe₂ (2 equiv, 9.40 mmol) in toluene. The mixture was cooled to -30 °C and 1.17 g TMSCI (2.3 equiv, 10.8 mmol) was added slowly. The mixture was stirred for 30 min and then heated to 100 °C for 4 h. The solution was cooled to 50 °C and the solvent removed under reduced pressure. The dark residue was dissolved in 40 mL benzene and the solution was filtered through Celite. The solvent was removed and filtered in vacuo and the dark residue was stirred in ~10 mL CH₂CN overnight. The resulting slurry was filtered and the yellow precipitate was washed with cold CH₂CN and dried under high vacuum. The filtrate was stored at -30 °C for several days and yellow crystals formed. The crystals were isolated by filtration, washed with cold CH₂CN, dried under high vacuum, and combined with the yellow precipitate; yield 0.881 g (33.8%): ¹H NMR (500 MHz, C₆D₆) δ 11.94 (t, 1H, W=CH, ³Jₚ₢H = 3.9 Hz), 7.32-7.28 (m, 2H, H³ or H⁴), 7.10-7.05 (m, 2H, H⁵ or H⁶), 7.00-6.96 (m, 1H, H⁷), and 1.69 (s, 6H, CH₃), and 1.27-1.23 (m, 18H, P-CH₃ ppm); ³¹P NMR (162 MHz, C₆D₆) δ -5.06 (m) ppm; ¹³C NMR (125 MHz, C₆D₆) δ 312.51 (m, W=CH), 150.44 (t, Aromatic-C, ³JₚₚC = 2.5 Hz), 128.76 (s, Aromatic-CH), 126.75 (s, Aromatic-CH), 51.45 (s, C(CH₃)₂Ph), 31.69 (s, CH₃), and 15.29 (t, P-CH₃, ¹JₚₚC = 16.2 Hz) ppm. Anal. Calc'd for C₁₅₆H₃₁₂Cl₅O₂W: C, 34.62; H, 5.45. Found: C, 34.98; H, 5.39.

**W(O)(CHCMe₂Ph)(ONO)(PPh₂Me) (4(PPh₂Me)).** A solution of 0.200 g W(O)(CHCMe₂Ph)(PPh₂Me)₂Cl₂ (1 equiv, 0.249 mmol) in 20 mL benzene was added to 0.235 g Li₂ONO·(THF)₄ (1 equiv, 0.249 mmol) and the mixture was stirred for 2 h. The orange solution was filtered through Celite and the solvent was removed in vacuo. The resulting residue was dissolved in ~10 mL DCM and the mixture was filtered through a 0.45 μm micropore frit. The solvent was removed under reduced pressure and the resulting residue stirred in ~5 mL pentane for 30 min. The product was isolated by filtration, washed with pentane, and dried under high vacuum to yield an orange powder; yield 0.198 g (78.4%): ¹H NMR (500 MHz, C₆D₆) δ 8.28 (s, 1H, W=CH), 7.71 (d, 2H, H³ or H⁴, ³JₚₚH = 2.4 Hz), 7.41-7.34 (m, 4H, Aromatic-CH), 7.25 (d, 2H, H⁵ or H⁶, ³JₚₚH = 2.3 Hz), 7.23-7.17 (m, 3H, Aromatic-CH), 7.14-7.08 (m, 4H, Aromatic-CH), 7.05-6.98 (m, 6H, Aromatic-CH), 6.93 (t, 1H, H⁷, ³JₚₚH = 7.9 Hz), 1.75 (s, 6H, CH₃), 1.70 (s, 6H, CH₃), 1.39 (s, 9H, CH₃), and 1.23 (s, 3H, P-CH₃) ppm; ³¹P NMR (162 MHz, C₆D₆) δ -14.70 (s) ppm; ¹³C NMR (125 MHz, C₆D₆) δ 264.02 (br s, W=CH), 162.00 (s, Aromatic-C), 155.62 (s, Aromatic-C), 153.58 (s, Aromatic-C), 141.82 (s, Aromatic-C), 139.78 (d, P-C, ¹JₚₚC = 7.3 Hz), 139.13 (s, Aromatic-C), 139.09 (s, Aromatic-C), 132.56 (d, Aromatic-CH, ³JₚₚC = 17.0 Hz), 128.58 (s, Aromatic-CH), 128.51 (d, Aromatic-CH, ¹JₚₚC = 6.7 Hz), 127.03 (s, Aromatic-C), 126.63 (s, Aromatic-CH), 125.91 (s, Aromatic-CH), 125.75 (s, Aromatic-CH), 123.72 (s, Aromatic-CH), 123.06 (s, Aromatic-CH), 49.00 (s, C(CH₃)₂Ph), 35.80 (s, C(CH₃)₃), 34.58 (s, C(CH₃)₃), 32.46 (s, CH₃), 31.83 (s, CH₃), 30.28 (s, CH₃), and 12.25 (d, P-CH₃, ¹JₚₚC = 10.6 Hz) ppm. Anal. Calc'd for C₁₅₆H₃₁₂NO₅PW: C, 66.07; H, 6.73; N, 1.38. Found: C, 66.22; H, 6.80; N, 1.24.

**W(O)(CHCMe₂Ph)(ONO)(PPh₂Me) (4(PPh₂Me)).** A solution of 0.200 g W(O)(CHCMe₂Ph)(PPh₂Me)₂Cl₂ (1 equiv, 0.249 mmol) in 20 mL benzene was added to 0.255 g Li₂ONO·(THF)₄ (1 equiv, 0.294 mmol) and the mixture was heated to 60 °C for 2 h. The orange solution was filtered through Celite and the solvent was removed in vacuo. The resulting residue was dissolved in ~10 mL CH₂CN and the solution was filtered through a 0.45 μm micropore frit. The solvent was removed under reduced pressure and the resulting residue stirred in ~5 mL pentane for 30 min. The product was isolated by filtration, washed with pentane, and dried under high vacuum to yield an orange powder; yield 0.230 g (81.5%): ¹H NMR (500 MHz, C₆D₆) δ 8.28 (s, 1H, W=CH), 7.70 (d, 2H, H³ or H⁴, ³JₚₚH = 2.3 Hz), 7.28-7.19 (m, 6H, Aromatic-CH), 7.15-7.09 (m, 4H, Aromatic-CH), 7.03-6.90 (m, 5H, Aromatic-CH), 1.75 (s, 9H, CH₃), 1.73 (s, 6H, CH₃), 1.39 (s, 9H, CH₃), and 1.03 (br s, 6H, P-CH₃) ppm; ³¹P NMR (162 MHz, C₆D₆) δ -27.94 (br s) ppm; ¹³C NMR (125 MHz, C₆D₆) δ 273.38 (br s, W=CH), 164.62 (s, Aromatic-C), 156.15 (s, Aromatic-C), 155.15 (s, Aromatic-C), 140.92 (s, Aromatic-C), 139.03 (s, Aromatic-C), 138.80 (s, Aromatic-
(CH), 138.52 (d, P-C, $J_{PC} = 3.0$ Hz), 130.65 (d, Aromatic-CH, $2J_{PC} = 13.0$ Hz), 128.55 (s, Aromatic-CH), 126.91 (s, Aromatic-C), 126.46 (s, Aromatic-CH), 126.36 (s, Aromatic-CH), 125.62 (s, Aromatic-CH), 124.23 (s, Aromatic-CH), 122.89 (s, Aromatic-CH), 48.47 (s, C(CH$_3$)$_2$Ph), 35.80 (s, C(CH$_3$)$_3$), 34.52 (s, C(CH$_3$)$_3$), 32.62 (s, CH$_3$), 31.89 (s, CH$_3$), 30.27 (s, CH$_3$), and 12.81 (br s, P-CH$_3$) ppm. Anal. Calcd for C$_3$H$_6$NO$_2$PW: C, 64.08; H, 6.96; N, 1.47. Found: C, 64.09; H, 6.85; N, 1.42.

$W$(O)(CHCMe$_2$Ph)(ONO)(PMe$_3$) (4(PMe$_3$)). A solution of 0.200 g $W$(O)(CHC(CH$_3$)$_2$Ph)(PMe$_3$)$_2$Cl$_2$ (1 equiv, 0.360 mmol) in 20 mL DCM was added to 0.284 g Li$_2$ONO-(THF)$_2$ (1 equiv, 0.360 mmol) and heated to 60 °C for 2 h. The orange solution was filtered through Celite and the solvent removed from the filtrate in vacuo. The resulting residue was dissolved in ~10 mL DCM and the solution was filtered through a 0.45 μm micropore frit. The product was isolated by filtration, washed with pentane, and dried under high vacuum to yield a pale yellow solid; yield 0.0514 g (77%).

$W$(O)(CH$_2$CH$_2$CH$_2$)(ONO) (5). A suspension of 0.100 g 4(PPh$_2$Me) (0.098 mmol) in 10 mL pentane was placed under an ethylene atmosphere using one freeze-pump-thaw cycle and the vessel was sealed. The mixture was stirred overnight and then the volume of solvent was reduced to ~2 mL. The resulting suspension was stored at -30 °C overnight, and the product isolated by filtration, washed with cold pentane, and dried under high vacuum to yield a pale yellow solid; yield 0.0514 g (77%).
**1-Hexene Coupling.** A solution of 1-hexene (20 equiv) in 0.5 mL C₆D₆ was added to 5.0 mg of catalyst (1 equiv) and loaded into a J-Young tube. The J-Young tube was attached to a Schlenk-line and exposed to a flow of N₂ gas. The progress of the reaction at both room temperature and 50 °C was followed by ¹H NMR spectroscopy.

**C₂D₄ Exchange Experiments.** A solution of 2 (6.21 μmol) or 5 (6.87 μmol) in 0.5 mL C₆D₆ with 1 μL mesitylene as an internal standard was transferred to a J-Young tube and put under a pressure of C₂D₄ using one freeze-pump-thaw cycle. The pressure of C₂D₄ was measured using a mercury manometer, and all pressures were measured while the C₆D₆ was frozen, but not submerged in liquid N₂. The solvent was thawed, the J-Young tube was shaken, and the disappearance of the beta metallacycle proton resonances were followed by NMR spectroscopy.

For both 2 and 5, the loss of ethylene at 20 °C was found to be first order in the metal complex and zero order in ethylene pressure. The rate constant for ethylene loss from 2 was approximately 8.2x10⁻⁵ s⁻¹, which corresponds to a half life of t₁/₂ = 2.35 h (see Figures S2 and S3). The rate constant for ethylene loss from 5 was an order of magnitude slower than in 2, approximately 9.2x10⁻⁶ s⁻¹, which corresponds to a half life of t₁/₂ = 21.0 h (see Figures S4 and S5).

![Figure S2. Log plot of the loss of H. resonance in the metallacycle in 2 over time under 760 mm Hg partial pressure of C₂D₄.](image-url)
**Figure S3.** Log plot of the loss of H. resonance in the metallacycle in 2 over time under 380 mm Hg partial pressure of C₂D₄.

**Figure S4.** Log plot of the loss of H. resonance in the metallacycle in 5 over time under 760 mm Hg partial pressure of C₂D₄.
Figure S5. Log plot following the loss of the H, resonance in the metallacycle in 5 over time under 380 mmHg partial pressure of C₂D₄.

Experimental details for X-ray studies

Low-temperature diffraction data were collected on a Bruker-AXS X8 Kappa Duo diffractometer coupled to a SMART Apex2 CCD detector with Mo Kα radiation (λ = 0.71073 Å) from an IµS micro-source, performing φ- and ω-scans. The structures were solved by direct methods using SHELXT⁵ and refined against F² on all data by full-matrix least squares with SHELXL-2015⁶ following established refinement strategies.⁷ All non-hydrogen atoms were refined anisotropically. Except when noted otherwise below, all hydrogen atoms were included in the model at geometrically calculated positions and refined using a riding model. The isotropic displacement parameters of all hydrogen atoms were fixed to 1.2 times the U value of the atoms they are linked to (1.5 times for methyl groups). Coordinates for those hydrogen atoms on the carbon binding directly to the metal (carbon atom C1 in all three structures) were taken from the difference Fourier Synthesis. Those hydrogen atoms were subsequently refined semi-free with the help of distance restraints (target C1—H1 distance 0.95(2) Å), while constraining their Uiso values as described above. Details of the data quality and a summary of the residual values of the refinements are listed in tables below.

Compound 1 crystallizes in the monoclinic space group C2/c with one molecule of 1 and one half a molecule of pentane per asymmetric unit. The second half of the pentane is generated from the first half by the crystallographic two-fold axis. The odd number of pentane molecules in the asymmetric unit leads to a non-integer number for element carbon in the empirical formula. Except for the C1—H1 distance restraint, no further restraints were applied.

Compound 1LiOTf crystallizes in the monoclinic space group P2₁/c with one molecule of 1LiOTf and one molecule of pentane in the asymmetric unit. The solvent molecule was refined as being disordered over two positions.
This disorder was refined with the help of similarity restraints on 1-2 and 1-3 distances and displacement parameters as well as rigid bond restraints for anisotropic displacement parameters. The disorder ratio was refined freely and converged at 0.773(6).

Compound 2 crystallizes in the triclinic space group $P\overline{1}$ with one molecule of 2 and 1.5 molecules of pentane in the asymmetric unit. The odd number of pentane molecules in the asymmetric unit leads to a non-integer number for carbon in the empirical formula. The half occupied solvent molecule was refined as disordered over four positions, two of which are crystallographically independent. The fully occupied pentane was refined as disordered over three independent positions. All disorders were refined with the help of similarity restraints on 1-2 and 1-3 distances and displacement parameters as well as rigid bond restraints for anisotropic displacement parameters. In addition, the thermal parameters of the atoms of the fourfold disordered pentane were pairwise constrained to be equal.

**Table S1.** Crystal data and structure refinement for 1.

| Identification code | X8_15136 |
|---------------------|----------|
| Empirical formula   | $C_{51.50}H_{61}F_5MoN_2O_2$ |
| Formula weight      | 930.96   |
| Temperature         | 100(2) K |
| Wavelength          | 0.71073 Å |
| Crystal system      | Monoclinic |
| Space group         | $C2/c$   |
| Unit cell dimensions| $a = 34.326(11)$ Å , $b = 16.556(6)$ Å , $c = 17.670(6)$ Å , $\alpha = 90^\circ$ , $\beta = 114.468(5)^\circ$ , $\gamma = 90^\circ$ |
| Volume              | 9140(5) Å³ |
| $Z$                 | 8        |
| Density (calculated)| 1.353 Mg/m³ |
| Absorption coefficient | 0.349 mm⁻¹ |
| $F(000)$            | 3896     |
| Crystal size        | $0.260 \times 0.250 \times 0.015$ mm³ |
| Theta range for data collection | 1.304 to 29.574° |
| Index ranges        | $-47 \leq h \leq 47$, $-22 \leq k \leq 22$, $-22 \leq l \leq 24$ |
| Reflections collected| 148096   |
| Independent reflections | 12817 [ $R_{int} = 0.0645$ ] |
| Completeness to theta $= 25.242^\circ$ | 100.0 % |
| Absorption correction | Semi-empirical from equivalents |
| Refinement method   | Full-matrix least-squares on $F^2$ |
| Data / restraints / parameters | 12817 / 1 / 573 |
| Goodness-of-fit on $F^2$ | 1.044 |
| Final $R$ indices [$I>2\sigma(I)$] | $R1 = 0.0396$, $wR2 = 0.0973$ |
| $R$ indices (all data) | $R1 = 0.0556$, $wR2 = 0.1069$ |
| Largest diff. peak and hole | 1.179 and -0.854 e.Å⁻³ |
Table S2. Bond lengths [Å] and angles [°] for 1.

| Mo(01)-N(1) | 1.7414(18) | C(32)-C(33) | 1.402(3) |
| Mo(01)-C(1) | 1.859(2)   | C(33)-C(34) | 1.386(3) |
| Mo(01)-O(1) | 2.0098(14) | C(33)-H(33) | 0.9500   |
| Mo(01)-O(2) | 2.0223(16) | C(34)-C(35) | 1.399(3) |
| Mo(01)-N(2) | 2.1948(16) | C(34)-C(37) | 1.529(3) |
| Mo(01)-H(1) | 2.18(2)    | C(35)-C(36) | 1.389(3) |
| C(1)-C(2)   | 1.502(3)   | C(35)-H(35) | 0.9500   |
| C(1)-H(1)   | 0.951(16)  | C(36)-C(41) | 1.530(3) |
| C(2)-C(4)   | 1.530(3)   | C(37)-C(39) | 1.525(3) |
| C(2)-C(5)   | 1.533(3)   | C(37)-C(40) | 1.525(3) |
| C(2)-C(3)   | 1.534(3)   | C(37)-C(38) | 1.531(3) |
| C(3)-H(3A)  | 0.9800     | C(38)-H(38A)| 0.9800   |
| C(3)-H(3B)  | 0.9800     | C(38)-H(38B)| 0.9800   |
| C(3)-H(3C)  | 0.9800     | C(38)-H(38C)| 0.9800   |
| C(4)-H(4A)  | 0.9800     | C(39)-H(39A)| 0.9800   |
| C(4)-H(4B)  | 0.9800     | C(39)-H(39B)| 0.9800   |
| C(4)-H(4C)  | 0.9800     | C(39)-H(39C)| 0.9800   |
| C(5)-C(10)  | 1.382(3)   | C(40)-H(40A)| 0.9800   |
| C(5)-C(6)   | 1.389(3)   | C(40)-H(40B)| 0.9800   |
| C(6)-C(7)   | 1.386(3)   | C(40)-H(40C)| 0.9800   |
| C(6)-H(6)   | 0.9500     | C(41)-C(44) | 1.531(3) |
| C(7)-C(8)   | 1.371(3)   | C(41)-C(42) | 1.533(3) |
| C(7)-H(7)   | 0.9500     | C(41)-C(43) | 1.539(3) |
| C(8)-C(9)   | 1.381(3)   | C(42)-H(42A)| 0.9800   |
| C(8)-H(8)   | 0.9500     | C(42)-H(42B)| 0.9800   |
| C(9)-C(10)  | 1.389(3)   | C(42)-H(42C)| 0.9800   |
| C(9)-H(9)   | 0.9500     | C(43)-H(43A)| 0.9800   |
| C(10)-H(10) | 0.9500     | C(43)-H(43B)| 0.9800   |
| N(1)-C(11)  | 1.371(3)   | C(43)-H(43C)| 0.9800   |
| C(11)-C(12) | 1.392(3)   | C(44)-H(44A)| 0.9800   |
| C(11)-C(16) | 1.395(3)   | C(44)-H(44B)| 0.9800   |
| C(12)-F(1)  | 1.334(2)   | C(44)-H(44C)| 0.9800   |
| C(12)-C(13) | 1.375(3)   | O(2)-C(51)  | 1.347(2) |
| C(13)-F(2)  | 1.333(2)   | C(51)-C(52) | 1.403(3) |
| C(13)-C(14) | 1.374(3)   | C(51)-C(56) | 1.423(3) |
| C(14)-F(3)  | 1.333(2)   | C(52)-C(53) | 1.403(3) |
| C(14)-C(15) | 1.377(3)   | C(53)-C(54) | 1.381(3) |
| C(15)-F(4)  | 1.334(3)   | C(53)-H(53) | 0.9500   |
| C(15)-C(16) | 1.382(3)   | C(54)-C(55) | 1.402(3) |
| C(16)-F(5)  | 1.333(2)   | C(54)-C(57) | 1.524(3) |
| N(2)-C(25)  | 1.358(2)   | C(55)-C(56) | 1.377(3) |
| N(2)-C(21)  | 1.360(2)   | C(55)-H(55) | 0.9500   |
| C(21)-C(22) | 1.386(3)   | C(56)-C(61) | 1.534(3) |
| C(21)-C(32) | 1.475(3)   | C(57)-C(59) | 1.526(3) |
| C(22)-C(23) | 1.381(3)   | C(57)-C(58) | 1.534(3) |
| C(22)-H(22) | 0.9500     | C(57)-C(60) | 1.535(3) |
| C(23)-C(24) | 1.387(3)   | C(58)-H(58A)| 0.9800   |
| C(23)-H(23) | 0.9500     | C(58)-H(58B)| 0.9800   |
| C(24)-C(25) | 1.387(3)   | C(58)-H(58C)| 0.9800   |
| C(24)-H(24) | 0.9500     | C(59)-H(59A)| 0.9800   |
| C(25)-C(52) | 1.479(3)   | C(59)-H(59B)| 0.9800   |
| O(1)-C(31)  | 1.342(2)   | C(59)-H(59C)| 0.9800   |
| C(31)-C(36) | 1.406(3)   | C(60)-H(60A)| 0.9800   |
| C(31)-C(32) | 1.411(3)   | C(60)-H(60B)| 0.9800   |
C(60)-H(60C)  0.9800  H(4A)-C(4)-H(4B)  109.5
C(61)-C(63)  1.530(3)  C(2)-C(4)-H(4C)  109.5
C(61)-C(64)  1.532(3)  H(4A)-C(4)-H(4C)  109.5
C(61)-C(62)  1.535(3)  H(4B)-C(4)-H(4C)  109.5
C(62)-H(62A)  0.9800  C(10)-C(5)-C(6)  117.7(2)
C(62)-H(62B)  0.9800  C(10)-C(5)-C(2)  122.66(19)
C(62)-H(62C)  0.9800  C(6)-C(5)-C(2)  119.60(18)
C(63)-H(63A)  0.9800  C(7)-C(6)-C(5)  121.4(2)
C(63)-H(63B)  0.9800  C(7)-C(6)-H(6)  119.3
C(63)-H(63C)  0.9800  C(5)-C(6)-H(6)  119.3
C(64)-H(64A)  0.9800  C(8)-C(7)-C(6)  120.3(2)
C(64)-H(64B)  0.9800  C(8)-C(7)-H(7)  119.8
C(64)-H(64C)  0.9800  C(6)-C(7)-H(7)  119.8
C(1X)-C(2X)  1.517(4)  C(7)-C(8)-C(9)  119.1(2)
C(1X)-H(1X1)  0.9800  C(7)-C(8)-H(8)  120.4
C(1X)-H(1X2)  0.9800  C(9)-C(8)-H(8)  120.4
C(1X)-H(1X3)  0.9800  C(8)-C(9)-C(10)  120.5(2)
C(2X)-C(3X)  1.516(3)  C(8)-C(9)-H(9)  119.7
C(2X)-H(2X1)  0.9900  C(10)-C(9)-H(9)  119.7
C(2X)-H(2X2)  0.9900  C(5)-C(10)-C(9)  120.9(2)
C(3X)-C(2X)#1  1.516(3)  C(5)-C(10)-H(10)  119.5
C(3X)-H(3X1)  0.9900  C(9)-C(10)-H(10)  119.5
C(3X)-H(3X2)  0.9900  C(11)-N(1)-Mo(01)  159.10(16)
N(1)-Mo(01)-C(1)  107.62(8)  N(1)-C(11)-C(12)  122.1(2)
N(1)-Mo(01)-O(1)  96.97(7)  N(1)-C(11)-C(16)  121.32(18)
C(1)-Mo(01)-O(1)  100.8(7)  C(12)-C(11)-C(16)  116.55(18)
N(1)-Mo(01)-O(2)  99.00(7)  F(1)-C(12)-C(13)  118.84(18)
C(1)-Mo(01)-O(2)  94.49(7)  F(1)-C(12)-C(11)  119.26(18)
O(1)-Mo(01)-O(2)  153.38(5)  C(13)-C(12)-C(11)  121.9(2)
N(1)-Mo(01)-N(2)  140.86(7)  F(2)-C(13)-C(14)  119.93(19)
C(1)-Mo(01)-N(2)  111.52(7)  F(2)-C(13)-C(12)  119.9(2)
O(1)-Mo(01)-N(2)  75.96(6)  C(14)-C(13)-C(12)  120.19(19)
O(2)-Mo(01)-N(2)  78.20(6)  C(3)-C(14)-C(13)  119.98(19)
N(1)-Mo(01)-H(1)  133.4(5)  F(3)-C(14)-C(15)  120.3(2)
C(1)-Mo(01)-H(1)  25.8(5)  C(13)-C(14)-C(15)  119.7(2)
O(1)-Mo(01)-H(1)  93.9(6)  F(4)-C(15)-C(14)  120.1(2)
O(2)-Mo(01)-H(1)  90.5(6)  F(4)-C(15)-C(16)  120.17(19)
N(2)-Mo(01)-H(1)  85.8(5)  C(14)-C(15)-C(16)  119.7(2)
C(2)-C(1)-Mo(01)  150.68(15)  F(5)-C(16)-C(15)  118.9(2)
C(2)-C(1)-H(1)  113.2(16)  F(5)-C(16)-C(11)  119.24(18)
Mo(01)-C(1)-H(1)  96.1(16)  C(15)-C(16)-C(11)  121.91(19)
C(1)-C(2)-C(4)  107.82(17)  C(25)-N(2)-C(21)  121.28(16)
C(1)-C(2)-C(5)  107.22(16)  C(25)-N(2)-Mo(01)  119.34(12)
C(4)-C(2)-C(5)  112.47(18)  C(25)-N(2)-Mo(01)  119.36(12)
C(1)-C(2)-C(3)  110.23(17)  N(2)-C(21)-C(22)  119.87(17)
C(4)-C(2)-C(3)  109.64(18)  N(2)-C(21)-C(22)  119.18(16)
C(5)-C(2)-C(3)  109.41(17)  C(22)-C(21)-C(22)  120.69(17)
C(2)-C(3)-H(3A)  109.5  C(23)-C(22)-C(21)  119.69(18)
C(2)-C(3)-H(3B)  109.5  C(23)-C(22)-H(22)  120.2
H(3A)-C(3)-H(3B)  109.5  C(21)-C(22)-H(22)  120.2
C(2)-C(3)-H(3C)  109.5  C(22)-C(23)-C(24)  119.57(18)
H(3A)-C(3)-H(3C)  109.5  C(22)-C(23)-H(23)  120.2
H(3B)-C(3)-H(3C)  109.5  C(24)-C(23)-H(23)  120.2
C(2)-C(4)-H(4A)  109.5  C(23)-C(24)-C(25)  119.76(18)
C(2)-C(4)-H(4B)  109.5  C(23)-C(24)-H(24)  120.1

H(60B)-C(60)-H(60C)  109.5  
C(63)-C(61)-C(64)  107.19(18)  
C(63)-C(61)-C(56)  110.90(17)  
C(64)-C(61)-C(56)  112.02(17)  
C(63)-C(61)-C(62)  110.68(18)  
C(64)-C(61)-C(62)  107.06(18)  
C(56)-C(61)-C(62)  108.93(17)  
C(61)-C(62)-H(62A)  109.5  
C(61)-C(62)-H(62B)  109.5  
H(62A)-C(62)-H(62B)  109.5  
C(61)-C(62)-H(62C)  109.5  
H(62A)-C(62)-H(62C)  109.5  
H(62B)-C(62)-H(62C)  109.5  
C(61)-C(63)-H(63A)  109.5  
C(61)-C(63)-H(63B)  109.5  
H(63A)-C(63)-H(63B)  109.5  
C(61)-C(63)-H(63C)  109.5  
H(63A)-C(63)-H(63C)  109.5  
H(63B)-C(63)-H(63C)  109.5  
C(61)-C(64)-H(64A)  109.5  
C(61)-C(64)-H(64B)  109.5  
H(64A)-C(64)-H(64B)  109.5  
C(61)-C(64)-H(64C)  109.5  
H(64A)-C(64)-H(64C)  109.5  
H(64B)-C(64)-H(64C)  109.5  
C(2X)-C(1X)-H(1X1)  109.5  
C(2X)-C(1X)-H(1X2)  109.5  
H(1X1)-C(1X)-H(1X2)  109.5  
C(2X)-C(1X)-H(1X3)  109.5  
H(1X1)-C(1X)-H(1X3)  109.5  
H(1X2)-C(1X)-H(1X3)  109.5  
C(3X)-C(2X)-C(1X)  112.7(2)  
C(3X)-C(2X)-H(2X1)  109.0  
C(1X)-C(2X)-H(2X1)  109.0  
C(3X)-C(2X)-H(2X2)  109.0  
C(1X)-C(2X)-H(2X2)  109.0  
H(2X1)-C(2X)-H(2X2)  107.8  
C(2X)#1-C(3X)-C(2X)  113.2(3)  
C(2X)#1-C(3X)-H(3X1)  108.9  
C(2X)-C(3X)-H(3X1)  108.9  
C(2X)#1-C(3X)-H(3X2)  108.9  
C(2X)-C(3X)-H(3X2)  108.9  
H(3X1)-C(3X)-H(3X2)  107.8  

Symmetry transformations used to generate equivalent atoms:  #1 -x+1,y,-z+5/2
Table S3. Crystal data and structure refinement for 1(LiOTf).

| Property                          | Value                                      |
|----------------------------------|--------------------------------------------|
| Identification code              | X8_15113                                   |
| Empirical formula                | C_{59}H_{77}F_{8}LiMoN_{2}O_{7}S           |
| Formula weight                   | 1213.16                                    |
| Temperature                      | 100(2) K                                   |
| Wavelength                       | 0.71073 Å                                  |
| Crystal system                   | Monoclinic                                 |
| Space group                      | P2_1/c                                     |
| Unit cell dimensions             |                                             |
| a                                | 16.5926(15) Å                             |
| α                                | 90°                                        |
| b                                | 12.4860(10) Å                             |
| β                                | 97.1486(17)°                              |
| c                                | 29.149(3) Å                               |
| γ                                | 90°                                        |
| Volume                           | 5992.0(9) Å                               |
| Z                                | 4                                          |
| Density (calculated)             | 1.345 Mg/m³                                |
| Absorption coefficient           | 0.330 mm⁻¹                                 |
| F(000)                           | 2536                                       |
| Crystal size                     | 0.220 x 0.180 x 0.130 mm³                  |
| Theta range for data collection  | 1.237 to 29.575°                           |
| Index ranges                     | -23 <= h <= 23, -16 <= k <= 17, -40 <= l <= 40 |
| Reflections collected            | 153852                                     |
| Independent reflections          | 16790 [Rint = 0.0485]                      |
| Completeness to theta            | 100.0 %                                    |
| Absorption correction            | Semi-empirical from equivalents            |
| Max. and min. transmission       | 0.7461 and 0.7053                          |
| Refinement method                | Full-matrix least-squares on F²            |
| Data / restraints / parameters    | 16790 / 182 / 777                          |
| Goodness-of-fit on F²            | 1.075                                      |
| Final R indices [I>2σ(I)]        | R1 = 0.0442, wR2 = 0.1091                  |
| R indices (all data)             | R1 = 0.0620, wR2 = 0.1219                  |
| Largest diff. peak and hole      | 0.793 and -0.423 e.Å⁻³                     |
Table S4. Bond lengths [Å] and angles [°] for **1(LiOTf)**.

| Bond                  | Length/Angle |
|-----------------------|--------------|
| C(1)-C(2)             | 1.527(3)     |
| C(1)-Mo(1)            | 1.927(2)     |
| C(1)-H(1)             | 0.960(16)    |
| C(2)-C(5)             | 1.526(3)     |
| C(2)-C(3)             | 1.534(3)     |
| C(2)-C(4)             | 1.539(3)     |
| C(3)-H(3A)            | 0.9800       |
| C(3)-H(3B)            | 0.9800       |
| C(3)-H(3C)            | 0.9800       |
| C(4)-H(4A)            | 0.9800       |
| C(4)-H(4B)            | 0.9800       |
| C(5)-C(10)            | 1.393(3)     |
| C(5)-C(6)             | 1.394(3)     |
| C(6)-H(6)             | 0.9500       |
| C(7)-C(8)             | 1.388(4)     |
| C(7)-H(7)             | 0.9500       |
| C(8)-C(9)             | 1.375(4)     |
| C(8)-H(8)             | 0.9500       |
| C(9)-C(10)            | 1.402(3)     |
| C(9)-H(9)             | 0.9500       |
| C(10)-H(10)           | 0.9500       |
| Mo(1)-N(2)            | 1.7407(18)   |
| Mo(1)-O(2)            | 2.1175(14)   |
| Mo(1)-O(3)            | 2.1271(16)   |
| Mo(1)-N(1)            | 2.1929(18)   |
| Mo(1)-O(1)            | 2.2442(15)   |
| Mo(1)-Li(1)           | 2.981(4)     |
| O(1)-C(21)            | 1.341(3)     |
| O(1)-Li(1)            | 1.881(4)     |
| C(21)-C(26)           | 1.413(3)     |
| C(21)-C(22)           | 1.432(3)     |
| C(22)-C(23)           | 1.392(3)     |
| C(22)-C(38)           | 1.533(3)     |
| C(23)-C(24)           | 1.396(3)     |
| C(23)-H(23)           | 0.9500       |
| C(24)-C(25)           | 1.384(3)     |
| C(24)-C(42)           | 1.542(3)     |
| C(25)-C(26)           | 1.405(3)     |
| C(25)-H(25)           | 0.9500       |
| C(26)-C(27)           | 1.475(3)     |
| C(27)-N(1)            | 1.367(3)     |
| C(27)-C(28)           | 1.390(3)     |
| C(28)-C(29)           | 1.386(3)     |
| C(28)-H(28)           | 0.9500       |
| C(29)-C(30)           | 1.378(3)     |
| C(29)-H(29)           | 0.9500       |
| C(30)-C(31)           | 1.397(3)     |
| C(30)-H(30)           | 0.9500       |
| C(31)-N(1)            | 1.369(3)     |
| C(31)-C(32)           | 1.478(3)     |
| C(32)-C(33)           | 1.403(3)     |
| C(32)-C(37)           | 1.414(3)     |
| Bond                    | Distance (Å) |
|-------------------------|--------------|
| C(42)-C(43)-H(43B)     | 109.5        |
| H(43A)-C(43)-H(43B)    | 109.5        |
| C(42)-C(43)-H(43C)     | 109.5        |
| H(43A)-C(43)-H(43C)    | 109.5        |
| H(43B)-C(43)-H(43C)    | 109.5        |
| C(42)-C(44)-H(44A)     | 109.5        |
| H(44A)-C(44)-H(44B)    | 109.5        |
| C(42)-C(44)-H(44B)     | 109.5        |
| C(50)-C(52)-H(52C)     | 109.5        |
| H(52A)-C(52)-H(52C)    | 109.5        |
| C(50)-C(52)-H(52C)     | 109.5        |
| C(50)-C(52)-H(52B)     | 109.5        |
| H(52A)-C(52)-H(52B)    | 109.5        |
Table S5. Crystal data and structure refinement for 2.

| Property                        | Value                          |
|---------------------------------|--------------------------------|
| Identification code             | X8_15138                       |
| Empirical formula               | C_{49.50} H_{67} F_{5} Mo N_{2} O_{2} |
| Formula weight                  | 912.99                         |
| Temperature                     | 100(2) K                       |
| Wavelength                      | 0.71073 Å                      |
| Crystal system                  | Triclinic                      |
| Space group                     | P̅1                            |
| Unit cell dimensions            |                                 |
| a                               | 10.9212(7) Å                   |
| α                               | 86.8869(15)°                   |
| b                               | 14.2236(9) Å                   |
| β                               | 72.7558(14)°                   |
| c                               | 16.8940(11) Å                  |
| γ                               | 73.8698(15)°                   |
| Volume                          | 2406.5(3) Å³                   |
| Z                               | 2                              |
| Density (calculated)            | 1.260 Mg/m³                    |
| Absorption coefficient          | 0.330 mm⁻¹                     |
| F(000)                          | 962                            |
| Crystal size                    | 0.250 x 0.150 x 0.050 mm³      |
| Theta range for data collection | 1.263 to 30.998°.              |
| Index ranges                    |                               |
| Reflections collected           | 115547                         |
| Independent reflections         | 15334 [R_{int} = 0.0372]       |
| Completeness to theta = 25.242° | 100.0 %                        |
| Absorption correction           | Semi-empirical from equivalents|
| Refinement method               | Full-matrix least-squares on F²|
| Data / restraints / parameters  | 15334 / 695 / 698              |
| Goodness-of-fit on F²           | 1.053                          |
| Final R indices [I>2σ(I)]       | R1 = 0.0338, wR2 = 0.0827      |
| R indices (all data)            | R1 = 0.0395, wR2 = 0.0865      |
| Largest diff. peak and hole     | 1.897 and -0.626 e.Å⁻³         |
Table S6. Bond lengths [Å] and angles [°] for 2.

| Bond          | Distance [Å] | Angle [°]  |
|---------------|--------------|-----------|
| Mo(1)-N(1)   | 1.7514(11)   |           |
| Mo(1)-O(1)   | 1.9412(10)   |           |
| Mo(1)-O(2)   | 1.9421(9)    |           |
| Mo(1)-C(3)   | 2.1948(14)   |           |
| Mo(1)-C(1)   | 2.2037(14)   |           |
| Mo(1)-N(2)   | 2.3769(11)   |           |
| C(1)-C(2)    | 1.519(2)     | 1.538(2)  |
| C(1)-H(1A)   | 0.994(14)    | 1.359(2)  |
| C(1)-H(1B)   | 0.973(14)    |           |
| C(2)-C(3)    | 1.517(2)     |           |
| C(2)-H(2A)   | 0.995(14)    |           |
| C(2)-H(2B)   | 0.985(14)    |           |
| C(3)-H(3A)   | 0.983(14)    |           |
| C(3)-H(3B)   | 0.976(14)    |           |
| N(1)-C(11)   | 1.370(4)     |           |
| N(11)-C(16)  | 1.398(5)     |           |
| N(11)-C(12)  | 1.401(5)     |           |
| C(12)-F(1)   | 1.334(1)     |           |
| C(12)-C(13)  | 1.379(1)     |           |
| C(13)-F(2)   | 1.340(1)     |           |
| C(13)-C(14)  | 1.380(2)     | 1.413(1)  |
| C(14)-F(3)   | 1.341(2)     | 1.401(1)  |
| C(14)-C(15)  | 1.380(2)     | 1.389(1)  |
| C(15)-F(4)   | 1.333(1)     | 0.950(1)  |
| C(15)-C(16)  | 1.384(2)     | 1.397(1)  |
| C(16)-F(5)   | 1.334(1)     | 1.531(1)  |
| N(2)-C(25)   | 1.370(1)     | 1.398(1)  |
| N(2)-C(21)   | 1.371(1)     | 0.950(1)  |
| C(21)-C(22)  | 1.400(1)     | 1.538(1)  |
| C(21)-C(32)  | 1.483(1)     | 1.533(1)  |
| C(22)-C(24)  | 1.377(1)     | 1.534(1)  |
| C(22)-H(22)  | 0.950(1)     |           |
| C(23)-C(24)  | 1.379(1)     | 0.980(1)  |
| C(23)-H(23)  | 0.950(1)     |           |
| C(24)-C(25)  | 1.402(1)     | 0.980(1)  |
| C(24)-H(24)  | 0.950(1)     |           |
| C(25)-C(52)  | 1.4883(1)    | 0.980(1)  |
| O(1)-C(31)   | 1.3473(15)   | 0.980(1)  |
| C(31)-C(32)  | 1.3979(18)   | 0.980(1)  |
| C(31)-C(36)  | 1.4184(18)   | 0.980(1)  |
| C(32)-C(33)  | 1.4076(17)   | 0.980(1)  |
| C(33)-C(34)  | 1.3853(18)   | 1.531(19) |
| C(33)-H(33)  | 0.950(1)     | 1.537(2)  |
| C(34)-C(35)  | 1.400(19)    | 1.538(2)  |
| C(34)-C(37)  | 1.533(19)    | 0.980(1)  |
| C(35)-C(36)  | 1.3915(19)   | 0.980(1)  |
| C(35)-H(35)  | 0.950(1)     |           |
| C(36)-C(41)  | 1.5373(19)   | 0.980(1)  |
| C(37)-C(38)  | 1.532(1)     | 0.980(1)  |
| C(37)-C(40)  | 1.535(1)     | 0.980(1)  |
| C(37)-C(39)  | 1.539(1)     | 0.980(1)  |
| C(38)-H(38A) | 0.980(1)     | 0.980(1)  |
| C(38)-H(38B) | 0.980(1)     |           |
| C(38)-H(38C) | 0.980(1)     |           |
| Bond | Length (Å) | Bond | Angle (°) |
|------|-----------|------|----------|
| C(54)-C(53)-C(52) | 121.93(12) | H(64A)-C(64)-H(64B) | 109.5 |
| C(54)-C(53)-H(53) | 119.0 | C(61)-C(64)-H(64C) | 109.5 |
| C(52)-C(53)-H(53) | 119.0 | H(64A)-C(64)-H(64C) | 109.5 |
| C(53)-C(54)-C(55) | 117.60(12) | H(64B)-C(64)-H(64C) | 109.5 |
| C(53)-C(54)-C(57) | 119.32(12) | C(2X)-C(1X)-H(1X1) | 109.5 |
| C(55)-C(54)-C(57) | 123.02(12) | C(2X)-C(1X)-H(1X2) | 109.5 |
| C(54)-C(55)-C(56) | 123.26(12) | H(1X1)-C(1X)-H(1X2) | 109.5 |
| C(54)-C(55)-H(55) | 118.4 | C(2X)-C(1X)-H(1X3) | 109.5 |
| C(56)-C(55)-H(55) | 118.4 | H(1X1)-C(1X)-H(1X3) | 109.5 |
| C(55)-C(56)-C(51) | 117.10(12) | H(1X2)-C(1X)-H(1X3) | 109.5 |
| C(55)-C(56)-C(61) | 121.44(11) | C(1X)-C(2X)-C(3X) | 123.2(9) |
| C(51)-C(56)-C(61) | 121.45(11) | C(1X)-C(2X)-H(2X1) | 106.5 |
| C(54)-C(57)-C(59) | 112.06(11) | C(3X)-C(2X)-H(2X1) | 106.5 |
| C(54)-C(57)-C(58) | 110.21(11) | C(1X)-C(2X)-H(2X2) | 106.5 |
| C(59)-C(57)-C(58) | 108.30(12) | C(3X)-C(2X)-H(2X2) | 106.5 |
| C(54)-C(57)-C(60) | 108.58(11) | H(2X1)-C(2X)-H(2X2) | 106.5 |
| C(59)-C(57)-C(60) | 108.29(12) | C(4X)-C(3X)-C(2X) | 118.5(10) |
| C(58)-C(57)-C(60) | 109.35(12) | C(4X)-C(3X)-H(3X1) | 107.7 |
| C(57)-C(58)-H(58A) | 109.5 | C(2X)-C(3X)-H(3X1) | 107.7 |
| C(57)-C(58)-H(58B) | 109.5 | C(2X)-C(3X)-H(3X2) | 107.7 |
| H(58A)-C(58)-H(58B) | 109.5 | C(2X)-C(3X)-H(3X2) | 107.7 |
| C(57)-C(58)-H(58C) | 109.5 | H(3X1)-C(3X)-H(3X2) | 107.1 |
| H(58A)-C(58)-H(58C) | 109.5 | C(5X)-C(4X)-C(3X) | 123.5(8) |
| H(58B)-C(58)-H(58C) | 109.5 | C(5X)-C(4X)-H(4X1) | 106.4 |
| C(57)-C(59)-H(59A) | 109.5 | C(3X)-C(4X)-H(4X1) | 106.4 |
| C(57)-C(59)-H(59B) | 109.5 | C(5X)-C(4X)-H(4X2) | 106.4 |
| H(59A)-C(59)-H(59B) | 109.5 | C(3X)-C(4X)-H(4X2) | 106.4 |
| C(57)-C(59)-H(59C) | 109.5 | H(4X1)-C(4X)-H(4X2) | 106.5 |
| H(59A)-C(59)-H(59C) | 109.5 | C(4X)-C(5X)-H(5X1) | 109.5 |
| H(59B)-C(59)-H(59C) | 109.5 | C(4X)-C(5X)-H(5X2) | 109.5 |
| C(57)-C(60)-H(60A) | 109.5 | H(5X1)-C(5X)-H(5X2) | 109.5 |
| C(57)-C(60)-H(60B) | 109.5 | H(5X1)-C(5X)-H(5X3) | 109.5 |
| H(60A)-C(60)-H(60B) | 109.5 | H(5X2)-C(5X)-H(5X3) | 109.5 |
| C(57)-C(60)-H(60C) | 109.5 | C(2Y)-C(1Y)-H(1Y1) | 109.5 |
| H(60A)-C(60)-H(60C) | 109.5 | C(2Y)-C(1Y)-H(1Y2) | 109.5 |
| H(60B)-C(60)-H(60C) | 109.5 | C(2Y)-C(1Y)-H(1Y2) | 109.5 |
| C(62)-C(61)-C(64) | 107.61(13) | H(1Y1)-C(1Y)-H(1Y2) | 109.5 |
| C(62)-C(61)-C(63) | 107.29(13) | C(2Y)-C(1Y)-H(1Y3) | 109.5 |
| C(64)-C(61)-C(63) | 110.15(12) | H(1Y1)-C(1Y)-H(1Y3) | 109.5 |
| C(62)-C(61)-C(56) | 112.04(11) | H(1Y2)-C(1Y)-H(1Y3) | 109.5 |
| C(64)-C(61)-C(56) | 109.57(12) | C(1Y)-C(2Y)-C(3Y) | 117.2(11) |
| C(63)-C(61)-C(56) | 110.13(12) | C(1Y)-C(2Y)-H(2Y1) | 108.0 |
| C(61)-C(62)-H(62A) | 109.5 | C(3Y)-C(2Y)-H(2Y1) | 108.0 |
| C(61)-C(62)-H(62B) | 109.5 | C(1Y)-C(2Y)-H(2Y2) | 108.0 |
| H(62A)-C(62)-H(62B) | 109.5 | C(3Y)-C(2Y)-H(2Y2) | 108.0 |
| C(61)-C(62)-H(62C) | 109.5 | H(2Y1)-C(2Y)-H(2Y2) | 107.2 |
| H(62A)-C(62)-H(62C) | 109.5 | H(2Y)-C(3Y)-C(4Y) | 120.4(10) |
| H(62B)-C(62)-H(62C) | 109.5 | C(2Y)-C(3Y)-H(3Y1) | 107.2 |
| C(61)-C(63)-H(63A) | 109.5 | C(4Y)-C(3Y)-H(3Y1) | 107.2 |
| C(61)-C(63)-H(63B) | 109.5 | C(2Y)-C(3Y)-H(3Y2) | 107.2 |
| H(63A)-C(63)-H(63B) | 109.5 | C(4Y)-C(3Y)-H(3Y2) | 107.2 |
| C(61)-C(63)-H(63C) | 109.5 | H(3Y1)-C(3Y)-H(3Y2) | 106.9 |
| H(63A)-C(63)-H(63C) | 109.5 | C(5Y)-C(4Y)-C(3Y) | 116.7(11) |
| H(63B)-C(63)-H(63C) | 109.5 | C(5Y)-C(4Y)-H(4Y1) | 108.1 |
| C(61)-C(64)-H(64A) | 109.5 | C(3Y)-C(4Y)-H(4Y1) | 108.1 |
| C(61)-C(64)-H(64B) | 109.5 | C(5Y)-C(4Y)-H(4Y2) | 108.1 |
C(3Y)-C(4Y)-H(4Y2) 108.1
H(4Y1)-C(4Y)-H(4Y2) 107.3
C(4Y)-C(5Y)-H(5Y1) 109.5
C(4Y)-C(5Y)-H(5Y2) 109.5
H(5Y1)-C(5Y)-H(5Y2) 109.5
C(4Y)-C(5Y)-H(5Y3) 109.5
H(5Y1)-C(5Y)-H(5Y3) 109.5
C(7X)-C(6X)-H(6X1) 109.5
C(7X)-C(6X)-H(6X2) 109.5
H(6X1)-C(6X)-H(6X2) 109.5
C(7X)-C(6X)-H(6X3) 109.5
H(6X1)-C(6X)-H(6X3) 109.5
C(6X)-C(7X)-C(8X) 114.2(7)
C(6X)-C(7X)-H(7X1) 108.7
C(8X)-C(7X)-H(7X1) 108.7
C(6X)-C(7X)-H(7X2) 108.7
C(8X)-C(7X)-H(7X2) 108.7
H(7X1)-C(7X)-H(7X2) 107.6
C(9X)-C(8X)-C(7X) 122.8(5)
C(9X)-C(8X)-H(8X1) 106.6
C(7X)-C(8X)-H(8X1) 106.6
C(9X)-C(8X)-H(8X2) 106.6
C(7X)-C(8X)-H(8X2) 106.6
H(8X1)-C(8X)-H(8X2) 106.6
C(10X)-C(9X)-C(8X) 119.8(8)
C(10X)-C(9X)-H(9X1) 107.4
C(8X)-C(9X)-H(9X1) 107.4
C(10X)-C(9X)-H(9X2) 107.4
C(8X)-C(9X)-H(9X2) 107.4
H(9X1)-C(9X)-H(9X2) 106.9
C(9X)-C(10X)-H(10A) 109.5
C(9X)-C(10X)-H(10B) 109.5
H(10A)-C(10X)-H(10B) 109.5
C(9X)-C(10X)-H(10C) 109.5
H(10A)-C(10X)-H(10C) 109.5
H(10B)-C(10X)-H(10C) 109.5
C(7Y)-C(6Y)-H(6Y1) 109.5
C(7Y)-C(6Y)-H(6Y2) 109.5
H(6Y1)-C(6Y)-H(6Y2) 109.5
C(7Y)-C(6Y)-H(6Y3) 109.5
H(6Y1)-C(6Y)-H(6Y3) 109.5
C(6Y)-C(7Y)-C(8Y) 127.1(11)
C(6Y)-C(7Y)-H(7Y1) 105.5
C(8Y)-C(7Y)-H(7Y1) 105.5
C(6Y)-C(7Y)-H(7Y2) 105.5
C(8Y)-C(7Y)-H(7Y2) 105.5
H(7Y1)-C(7Y)-H(7Y2) 106.1
C(7Y)-C(8Y)-C(9Y) 124.6(11)
C(7Y)-C(8Y)-H(8Y1) 106.2
C(9Y)-C(8Y)-H(8Y1) 106.2
C(7Y)-C(8Y)-H(8Y2) 106.2
C(9Y)-C(8Y)-H(8Y2) 106.2
H(8Y1)-C(8Y)-H(8Y2) 106.4
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