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Syntheses of Molybdenum(VI) Imido Alkylidene Complexes That Contain a Bidentate Dithiolate Ligand

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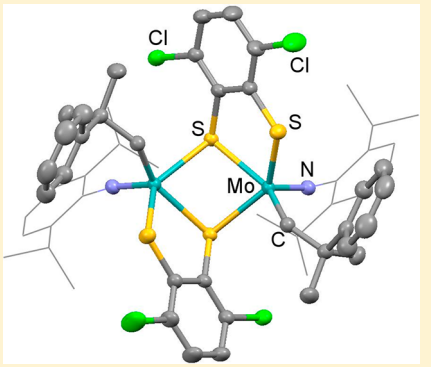
Supporting Information

ABSTRACT: Zn(DCTC) (DCTC = 3,6-dichlorodithiacatecholate) reacts with Mo(NAd)(CHCMe$_2$Ph)Cl$_2$(PPh$_2$Me) (Ad = 1-adamantyl) to give Mo(NAd)(CHCMe$_2$Ph)(DCTC)(PPh$_2$Me). The reactions between Zn(DCTC) and Mo(NAd)(CH-*t*-Bu)(OTf)$_2$(dme) or Mo(NAr)(CHCMe$_2$Ph)(OTf)$_2$(dme) (Ar = 2,6-*i*-Pr$_2$C$_6$H$_3$; OTf = triflate; dme = 1,2-dimethoxyethane) produce [Mo(NAd)(CH-*t*-Bu)(DCTC)]$_2$ and [Mo(NAr)(CHCMe$_2$Ph)(DCTC)]$_2$, respectively. Complexes that contain a 3,3′,5,5′-tetrasubstituted dithiabiphenolate were prepared in a reaction between Mo(NAr)(CHCMe$_2$Ph)(Me$_2$pyr)$_2$ (Me$_2$pyr = 2,5-dimethylpyrrolide) and the 3,3′,5,5′-tetrasubstituted dithiabiphenols, (3,3′,5,5′-tetrachlorodithiabiphenol (H$_2$Cl$_4$S$_2$), 3,3′,5,5′-tetrabromodithiabiphenol (H$_2$Br$_4$S$_2$), and 3,3′,5,5′-tetra-*t*-Bu-dithiabiphenol (H$_2$Bu$_4$S$_2$)). The isolated complexes include Mo(NAr)(CHCMe$_2$Ph)(Cl$_4$S$_2$)(pyridine), Mo(NAr)(CHCMe$_2$Ph)(Br$_4$S$_2$)(pyridine), Mo(NAr)(CHCMe$_2$Ph)(Bu$_4$S$_2$)(PMe$_3$), and [Mo(NAr)(CHCMe$_2$Ph)(Cl$_4$S$_2$)]$_2$. Only the dithiabiphenolate derivatives (in the presence of B(C$_6$F$_5$)$_3$) show activity for the metathesis of 1-decene, and although that reaction is limited by a sensitivity of the alkylidene complexes to ethylene, as suggested by the reaction between ethylene and Mo(NAr)(CHCMe$_2$Ph)(Bu$_4$S$_2$) to give the ethylene complex, Mo(NAr)(C$_2$H$_4$)(Bu$_4$S$_2$). Mo(NAr)(C$_2$H$_4$)(Bu$_4$S$_2$) was unstable with respect to loss of ethylene and formation of an ethylene-free dimer. Mo(NAd)(CHCMe$_2$Ph)(DCTC)(PPh$_2$Me), [Mo(NAr)(CHCMe$_2$Ph)(DCTC)]$_2$, and [Mo(NAr)(CHCMe$_2$Ph)(Cl$_4$S$_2$)]$_2$ were characterized crystallographically.

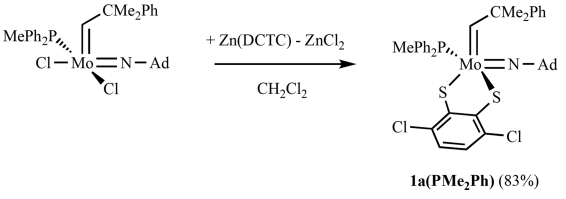


INTRODUCTION

The olefin metathesis chemistry of four-coordinate catalysts with the formula M(NR)(CHR′)(X)(Y) (M = Mo or W) has been dominated by compounds in which X and Y are monoanionic and oxygen-based (alkoxides, aryloxides, biphenolates, and binaphtholates)[1] or those in which X is oxygen-based and Y is a pyrrolide or (more recently[2]) a chloride. Analogous M(O)(CHR′)(X)(Y) complexes have been studied to a lesser degree because of synthetic challenges, but examples are now known for W[3] and even Mo.[4] It is generally agreed that high metathesis activity requires formation of a trigonal bipyramidal metallacyclobutane intermediate in which the metallacycle occupies equatorial positions;[1,5] square pyramidal metallacycles must convert to a TBP in order to lose an olefin readily. Metathesis activity has long been known to correlate directly with the electrophilicity of the metal center. In particular, the reduced metathesis activity of thiolate analogues of bisalkoxides or aryloxides[6] are relatively dramatic examples of what has been attributed to the greater degree of electron donation by a thiolate ligand to the metal relative to an alkoxide or aryloxide analogue. Alkylidene thiolate complexes of tantalum[7] and alkylidyne thiolate complexes of tungsten[8] also show greatly reduced reactivity toward olefins or internal acetylenes, respectively. This necessarily short history of thiolate complexes would suggest that further attempts to prepare metathesis-active thiolate complexes of Mo or W would not be productive. However, the relatively recent discovery of active and *Z*-selective 14e catecholate ruthenium catalysts[9] raises the question as to whether any 14e Mo or W complex that contains a catecholate or other bidentate dithiolate ligand, of which we could find no examples in the literature, might for some non-obvious reason be especially metathesis active. In this paper, we prepare several examples of Mo complexes that contain a bidentate dithiolate ligand and provide some answers to this question.

RESULTS AND DISCUSSION

Zn(DCTC) reacts with Mo(NAd)(CHCMe$_2$Ph)Cl$_2$(PPh$_2$Me) in dichloromethane to give **1a(PMePh$_2$)** (eq 1). NMR studies



(1)

1a(PMe$_2$Ph) (83%)

suggested that **1a** contains 1 equiv of coordinated PPh$_2$Me and an alkylidene in which the CMe$_2$Ph group points toward the

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imido ligand (the *syn* isomer) on the basis of the value for $^1J_{CH}$ ($^1J_{CH}$ = 118 Hz, $^3J_{HP}$ = 5.2 Hz).

An X-ray structural study (Figure 1) shows that the core geometry of **1a(PMePh$_2$)** is approximately halfway between a

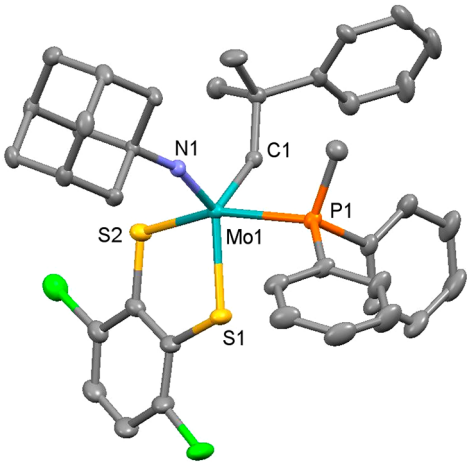
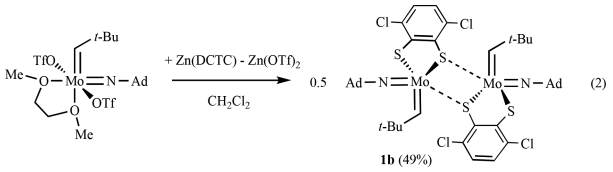
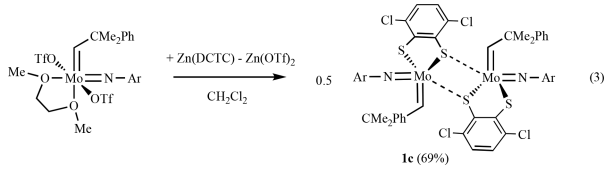


Figure 1. Thermal ellipsoid drawing of **1a(PMePh$_2$)**. Hydrogen atems have been omitted for clarity.

trigonal bipyramid (TBP) and a square pyramid (SP) according to the τ value[10] (0.54). The metal–ligand bond lengths (Table 1) are not unusual. The relatively long Mo1–P1 bond suggests that the phosphine may be labile, but so far, attempts to remove any dissociated phosphine through addition of $B(C_6F_5)_3$ (in CH_2Cl_2 or benzene) have led only to complex mixtures instead of the expected phosphine-free complex to be described immediately below.

Phosphine-free variations of **1a(PMePh$_2$)** were prepared in reactions between Mo(NAd)(CH-*t*-Bu)(OTf)$_2$(dme) or Mo(NAr)(CHCMe$_2$Ph)(OTf)$_2$(dme) (Ar = 2,6-*i*-Pr$_2$C$_6$H$_3$; OTf = triflate; dme = 1,2-dimethoxyethane) and Zn(DCTC) (eqs 2





and 3, respectively). NMR spectra of **1b** and **1c** are consistent with molecules that contain a *syn*-alkylidene but that do not have mirror symmetry; that is, the catecholate protons on C4 and C5 are inequivalent. Therefore, we proposed that **1b** and **1c** are both dimers in which one sulfur of one catecholate ligand is bridging two Mo centers, whereas the other sulfur of that DCTC ligand is bound to only one Mo, as shown in eqs 2 and 3.

An X-ray structural study of **1c** confirmed the above proposal (Figure 2). The overall structure at each Mo is closest

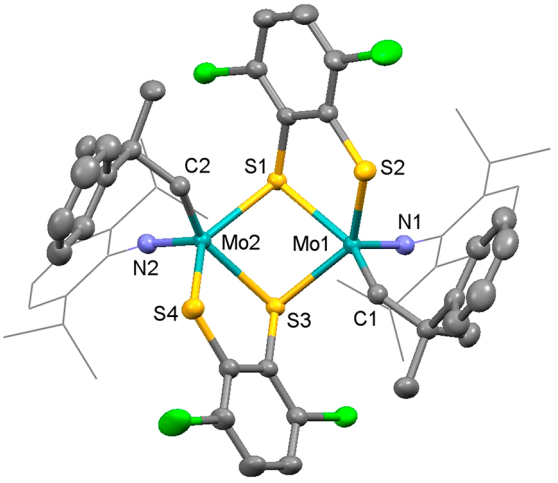
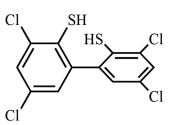


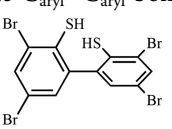
Figure 2. Thermal ellipsoid drawing of **1c** (τ = 0.17).

to a TBP (τ = 0.17), with the values for Mo1–S1 and Mo1–S3 being similar to the Mo–S values found in **1a(PMePh$_2$)**, whereas Mo1–S2 (2.366(6) Å) is understandably the shortest of the three Mo–S distancs in **1c**. Diffusion-ordered spectroscopy (DOSY) showed that the diffusion coefficient obtained for **1a(PMePh$_2$)** (6.90×10^{-10} m^2/s) is larger than that of **1b** (5.56×10^{-10} m^2/s), which supports the proposal that **1b** is a dimer rather than a monomer in solution. The hydrodynamic molecular radii obtained from the Stokes–Einstein equation for both complexes also were relatively close to radii calculated from the X-ray data (see the Supporting Information).

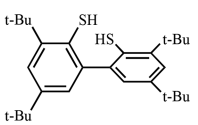
Dithiolate ligands derived from the three dithiols shown below ($H_2Cl_4S_2$, $H_2Br_4S_2$, $H_2Bu_4S_2$) are related to various biphenolate and binaphtholate complexes that have been used so successfully for ring-opening metathesis polymerization of norbornenes and norbornadienes to yield *cis,isotactic* polymers[11] or (in enantiomerically pure form) for asymmetric metathesis reactions.[1a,12] $H_2Cl_4S_2$ and $H_2Bu_4S_2$ are known, whereas $H_2Br_4S_2$ was synthesized in a manner that is nearly identical to that used to make $H_2Cl_4S_2$. In the metal-free or protonated forms, none of the four is likely to be resolvable into enantiomerically pure forms as a consequence of facile 180° rotation about the C_{aryl}–C_{aryl} bond.



$H_2Cl_4S_2$



$H_2Br_4S_2$



$H_2Bu_4S_2$

Table 1. Selected Bond Lengths (Å) in 1a(L) (L = PMePh$_2$) and 1c

	Mo1–C1	Mo1–N1	Mo1–S1	Mo1–S2	Mo1–P1	Mo1–S3
1a(L)	1.924(11)	1.731(9)	2.434(6)	2.436(10)	2.523(3)	na
1c	1.936(2)	1.730(19)	2.522(5)	2.366(6)	na	2.488(5)

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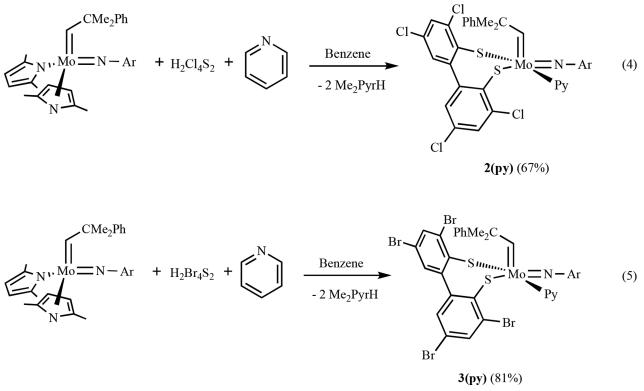
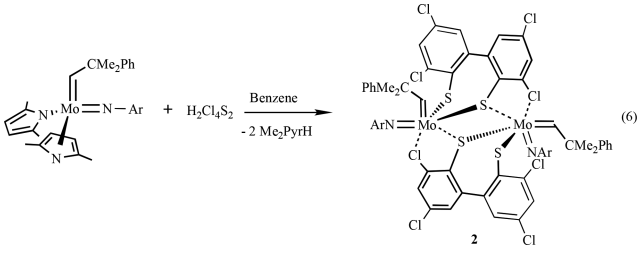
The tetrachloro- ($H_2Cl_4S_2$) and tetrabromodithiols ($H_2Br_4S_2$) react within 30 min in C_6D_6 with Mo(NAr)-($CHCMe_2Ph$)(Me_2pyr)$_2$ in the presence of pyridine to yield the five-coordinate complexes **2(py)** and **3(py)** (eqs 4 and 5).



Both **2(py)** and **3(py)** contain the *anti* isomer of the alkylidene according to the J_{CH} values (144 and 143 Hz). Proton NMR spectra of both complexes show broad isopropyl methyl and methine groups at room temperature. Pyridine that has been added to proton NMR samples of **2(py)** or **3(py)** does not exchange on the NMR time scale with coordinated pyridine, so pyridine exchange cannot be part of the process that leads to the broadening just described. Therefore, we attribute the broadening to internal restricted motion.

When pyridine is omitted in the reaction shown in eq 4, pyridine-free dimeric **2** is formed (eq 6). The proton NMR



spectrum of **2** contains contains two different *syn*-alkylidene proton resonances of equal intensity at 14.35 ppm (J_{CH} = 121 Hz) and 13.43 ppm (J_{CH} = 120 Hz) in CD_2Cl_2 (cf. 14.56 and 13.64 ppm in C_6D_6. An X-ray structural study of **2** (Figure 3) showed that two thiolate sulfur atoms (S2 and S4) bridge between two Mo centers, while two (S1 and S3) do not. One of the chlorides in each dithiolate ligand could be said to be weakly interacting with Mo (Mo1−Cl8 = 2.797 Å; Mo2−Cl4 = 2.839 Å). The arrangements of the "six" atoms in the primary coordination spheres of each metal are different, which leads to the two alkylidenes being inequivalent in the proton NMR spectrum on the NMR time scale. It may be relevant (see below) to note that the two dithiolate ligands have the same "chirality" with respect to the relative orientation of the two phenyl rings about the C−C bond connecting the two phenyl rings. Compound **2** reacts with pyridine (1−3 equiv) to give small amounts of **2(py)** only very slowly (days) at 22 °C.

Compound **2** also can be prepared through addition of one equivalent of $B(C_6F_5)_3$ to **2(py)** followed by removal of (py)$B(C_6F_5)_3$. As shown Figure 4, two alkylidene resonances with equal area at 15.44 and 14.74 ppm grow in initially and only after 12 h are replaced with the two alkylidene resonances for **2**. The complex formed initially upon removing pyridine

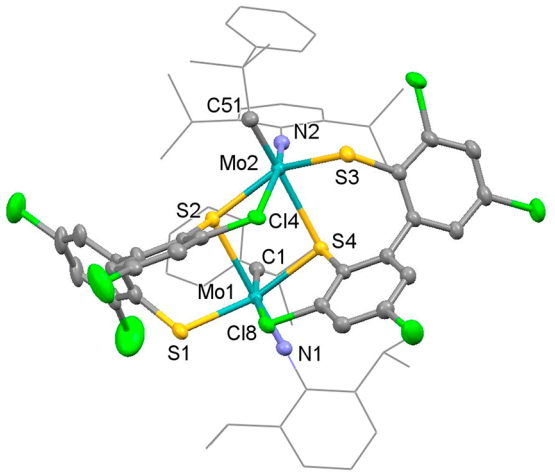


Figure 3. Thermal ellipsoid drawing of **2**.

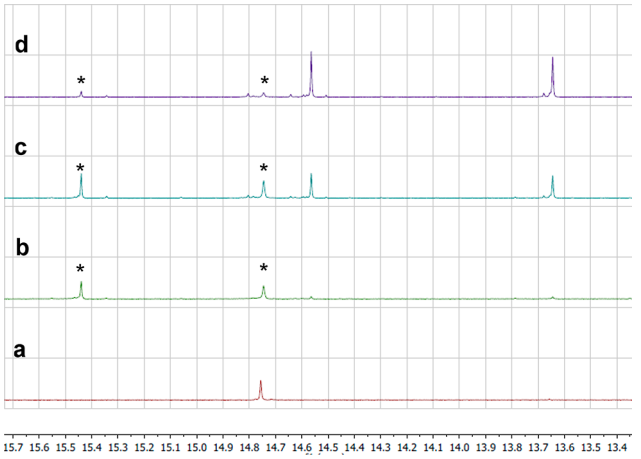
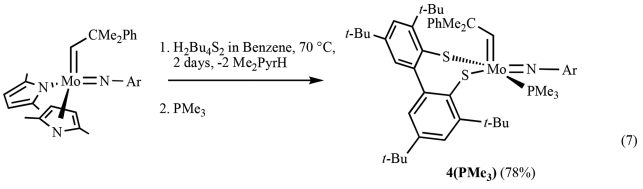


Figure 4. ^{1}H NMR spectra of (a) **2(py)** and **2(py)** + 1 equiv $B(C_6F_5)_3$ after (b) 15 min, (c) 2 h, and (d) 12 h (C_6D_6, 400 MHz) (*initially formed dimeric product).

from **2(py)** almost certainly is a slight variation of that observed for **2**, but we cannot say in detail what its structure is.

The reaction between Mo(NAr)($CHCMe_2Ph$)(Me_2pyr)$_2$ and $H_2Bu_4S_2$ in benzene requires 2 days at 70 °C to go to completion (eq 7). All volatiles were removed in vacuo to give



a brittle red solid that is extremely soluble in pentane, a property that suggests that it is a 14e monomer. No crystals or precipitate could be obtained from even highly concentrated solutions at −78 °C. However, a saturated solution of **4** in acetonitrile resulted in the formation of a brown powder upon standing the solution at −20 °C overnight. A ^{1}H NMR spectrum of the brown powder obtained upon filtration and drying it in vacuo is identical to that of **4**. Dissolution of **4** in 5 mL of pentane and addition of 2 equiv of PMe_3 followed by removal of all volatiles in vacuo gave orange crystals of the adduct, **4(PMe$_3$)**, which can be recrystallized from a saturated

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pentane solution at −20 °C. Addition of 1 equiv of $B(C_6F_5)_3$ to **4(PMe$_3$)** in C_6D_6 led to a precipitate of $(PMe_3)B(C_6F_5)_3$ and a proton NMR spectrum identical to that of **4** described above. The doublet *syn*-alkylidene α proton resonance for **4(PMe$_3$)** at 11.79 ppm ($^3J_{HP}$ = 3.8 Hz and $^1J_{CH}$ = 110 Hz) suggests that the phosphine is not dissociating from the metal rapidly enough to be decoupled from the alkylidene proton. However, PMe_3 is lost readily on the chemical time scale and therefore can be scavenged by $B(C_6F_5)_3$.

All complexes were tested for metathesis of 1-decene. No metathesis activity was observed in the presence of **1a-(PMePh$_2$)**, **1b**, or **1c**. The most likely explanation, in our opinion, is that 14e complexes simply are not formed in solution in significant amounts; $PMePh_2$ is bound too strongly to the metal in **1a(PMePh$_2$)**, and the bridging sulfurs are too strongly bound in **1b** and **1c** to allow them to break into 14e monomeric fragments. Some metathesis of 1-decene was observed in the presence of 5% **2(py)**, **3(py)**, or **4(PMe$_3$)** and 6 mol % of $B(C_6F_5)_3$ in C_6D_6 in a J-Young NMR tube. A moderate conversion (20−33%) to 9-octadecenes and ethylene was observed within the first 30 min, but the catalytic activity essentially stopped thereafter.

We suspected that sensitivity of an alkylidene complex to ethylene may be the reason why conversion of 1-decene to product is limited. Therefore, we explored the reaction of **2(py)** and **4(PMe$_3$)** with ethylene in the presence $B(C_6F_5)_3$. In both reactions, 3-methyl-3-phenyl-1-butene (from the reaction between the initial complex and ethylene) was observed along with less than 1 equiv of propylene. (The exact amount of propylene in solution could not be measured reliably in the proton NMR spectrum due to some propylene residing in the head space.) These data suggest that a methylene complex is formed when 3-methyl-3-phenyl-1-butene is formed and part or all of it reacts with ethylene to form an unsubstituted metallacyclobutane complex, which then rearranges to propylene; propylene then is displaced by ethylene.

The reaction of **4** with ethylene yields a single Mo product, which appears to be an ethylene complex, $Mo(NAr)(Bu_4S_2)(C_2H_4)$, on the basis of ethylene multiplets being observed at 2.92, 2.80, 2.36, and 1.95 ppm in proton NMR spectra (see Supporting Information Figure S33). Bisalkoxide Mo(IV) imido olefin complexes are known,[13] including monomeric ethylene complexes, but in general, Mo(IV) olefin complexes are relatively rare.[14] However, attempted isolation of "$Mo(NAr)(Bu_4S_2)(C_2H_4)$" led only to formation of a yellow crystalline product that lacks ethylene proton resonances and does not react with ethylene to yield "$Mo(NAr)(Bu_4S_2)(C_2H_4)$". We propose that this final product is $[Mo(NAr)(Bu_4S_2)]_2$. Formations of a variety of metal−metal bonded complexes are known modes of decomposition of Mo-,[15] W-,[14c,16] and Re-based[17] alkylidene complexes, and stepwise loss of ethylene to form a dimeric tungsten product has been documented.[14c] We had no interest in decomposition products that do not contain an alkylidene ligand and therefore did not isolate and characterize "$[Mo(NAr)(Bu_4S_2)]_2$". Because monomeric complexes that contain the $[Bu_4S_2]^{2-}$ ligand are the *least* likely to dimerize from a steric point of view, yet do ultimately, we did not investigate any other reactions of complexes reported here with ethylene. In view of formation of dimers through bimolecular coupling in Mo, W, and Re chemistry noted above, and the reaction of **4** with ethylene just described, we think that formation of bimolecular complexes is likely the reason why the metatheses of 1-decene noted earlier do not proceed to completion.

CONCLUSIONS

We conclude that the molybdenum imido alkylidene thiolato complexes we have prepared here are likely to be poor metathesis catalysts because 14e core four-coordinate complexes cannot be accessed readily; either a phosphine ligand is not labile enough, or sulfur ultimately bridges too strongly to give dimeric complexes that do not dissociate readily into 14e monomers to any significant degree. The ultimate problem continues to be bimolecular decomposition to give inactive alkylidene-free complexes. Although in rare cases even "alkylidene-free" complexes will metathesize some olefins slowly through re-formation of an alkylidene,[13,18] metathesis activities so far are miniscule as a consequence of very little alkylidene being re-formed. We had hoped that dimerization of **4** through sulfur bridges would be limited because of the steric demands of the *t*-butyl groups in the 3 and 3′ positions of the $[t\text{-}Bu_4S_2]^{2-}$ ligand, but the relatively large size of sulfur and its nucleophilic character continue to be damaging characteristics if monomer Mo and W d^0 alkylidene complexes are desired. In contrast, M(NR)(CHR′)(X)(Y) (M = Mo or W) complexes that contain two bulky alkoxides or one bulky 2,6-terphenoxide are relatively stable toward bimolecular decompositions. It should be pointed out that the imido groups in all complexes prepared here are not comparable in steric demand to the dimesityl NHC ligand found in monomeric ruthenium catecholate complexes.[9] Therefore, imido alkylidene catecholate complexes that contain 2,6-disubstituted phenylimido ligands (with the 2 and 6 substituents being 2,4,6-$Me_3C_6H_2$[19a] or 2,4,6-*i*-$Pr_3C_6H_2$[19b] groups) could be relatively stable toward bimolecular decomposition.

EXPERIMENTAL SECTION

General Procedures. All air- and moisture-sensitive compounds were manipulated under a nitrogen atmosphere in a vacuum atmosphere glovebox or on a Schlenk line. Glassware was oven-dried prior to use. Solvents were degassed and dried by passing through columns of activated alumina or 4 Å molecular sieves and stored over activated molecular sieves. Pentane was shaken with sulfuric acid and then water before use in the solvent purification system. Benzene-d_6 and toluene-d_8 were dried over Na/benzophenone, vacuum transferred onto molecular sieves, and stored in the glovebox. ^{1}H and ^{13}C{^{1}H} NMR spectra were referenced to the NMR solvent residual peak, and ^{31}P {^{1}H} spectra were referenced externally to H_3PO_4 in a D_2O standard. Pyridine was purchased from Alfa Aesar, degassed under vacuum, and kept over molecular sieves before use. $B(C_6F_5)_3$ was purchased from Strem and used as received. PMe_3 and PPh_2Me were purchased from Strem and degassed and stored over sieves prior to use. Ultra-high-purity ethylene was purchased from Airgas and used without further purification. H_2DCTC was purchased from Sigma-Aldrich and used as received. Syntheses of Zn(DCTC),[20] $H_2Cl_4S_2$ and $H_2Bu_4S_2$,[21] $Mo(NAd)(CHCMe_2Ph)Cl_2(PPh_2Me)$,[2b] $Mo(NAd)(CHCMe_3)(OTf)_2DME$,[22] $Mo(NAr)(CHCMe_2Ph)(OTf)_2DME$ (NAr = 2,6-diisopropylphenylimido),[23] and $Mo(NAr)(CHCMe_2Ph)(Me_2Pyr)_2$[24] have been prepared as described in the literature. Elemental analyses were performed at the Elemental Analysis facility at the University of Rochester, New York, Midwest Microlab, Indiana, and Atlantic Microlab, Georgia. In the descriptions below, any dimeric compounds are shown as monomers for simplicity.

*Mo(NAd)(CHCMe$_2$Ph)(Cl$_2$S$_2$)(PPh$_2$Me) (**1a(PMePh$_2$)**).* $Mo(NAd)(CHCMe_2Ph)Cl_2(PPh_2Me)$ (400 mg, 0.617 mmol, 1 equiv) and Zn(DCTC) (186 mg, 0.678 mmol, 1.1 equiv) were placed in separate vials, and 5 and 10 mL of CH_2Cl_2 was added, respectively, to each. The solution of $Mo(NAd)(CHCMe_2Ph)Cl_2(PPh_2Me)$ was trans-

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ferred to the slurry of Zn(DCTC), while the mixture was stirred. The vial was washed with another 5 mL of CH_2Cl_2 and transferred to the reaction mixture. The vial was capped, and the mixture was stirred for 4 h. (Completion of the reaction was confirmed by ^{1}H NMR analysis.) The mixture was filtered through a frit and the filtrate reduced to a yellow-green residue in vacuo. This residue was stirred in pentane until it became a yellow powder. The yellow powder was filtered off, and all solvent was removed in vacuo; yield 404 mg (69%). Two isomers were found (83% *syn* with $^1J_{CH}$ = 118 Hz and 17% *anti* with $^1J_{CH}$ = 137 Hz): ^{1}H NMR (*syn* isomer, CD_2Cl_2, 400 MHz) δ 12.09 (d, $^3J_{HP}$ = 5.2 Hz, $^1J_{CH}$ = 118 Hz, 1H), 7.50−7.44 (m, 9H), 7.20−6.99 (m, 8H), 2.12 (d, $^3J_{HP}$ = 8.8 Hz, 3H), 2.03 (m, 3H), 1.94 (m, 1H), 1.91 (m, 3H), 1.87 (m, 2H), 1.86 (s, 3H), 1.84 (m, 1H), 1.67 (s, 3H), 1.56 (m, 5H); ^{13}C{^{1}H} (CD_2Cl_2, 100.6 MHz, *syn*isomer) δ 323 (d, J_{CP} = 21.3 Hz), 147 (d, J_{CP} = 2.1 Hz), 133.7, 133.6, 133.19 (d, J_{CP} = 11.2 Hz), 133.14 (d, J_{CP} = 11.5 Hz), 132.0 (d, J_{CP} = 19.9 Hz), 131.3 (d, J_{CP} = 2.5 Hz), 131.2 (d, J_{CP} = 2.4 Hz), 129.1 (d, J_{CP} = 10.4 Hz), 129.03 (d, J_{CP} = 10.3 Hz), 129.02 (d, J_{CP} = 10.3 Hz), 128.7, 128.6, 126.6, 126.5, 126.4, 125, 123, 73, 54, 45 (d, J_{CP} = 0.8 Hz), 44 (d, J_{CP} = 1.3 Hz), 36, 31 (d, J_{CP} = 2.3 Hz), 30.1, 30.0, 19 (d, J_{CP} = 30.0 Hz); ^{31}P{^{1}H} NMR (CD_2Cl_2, 162.0 MHz) δ 25.3. Anal. Calcd for $C_{39}H_{42}Cl_2MoNPS_2\cdot 0.2CH_2Cl_2$: C, 58.58%; H, 5.32%; N, 1.74%. Found: C, 58.42%; H, 5.48%; N, 1.86%.

*Mo(NAd)(CHCMe$_3$)(Cl$_2$S$_2$) (**1b**).* A mixture of Mo(NAd)-(CHCMe$_3$)(OTf)$_2$DME (200 mg, 0.284 mmol, 1 equiv) and Zn(DCTC) (117 mg, 0.426 mmol, 1.5 equiv) in 10 mL of benzene was stirred for 2 h. The solvent was removed in vacuo to give a yellow solid. The solid was suspended in 4 mL of acetonitrile; the mixture was stirred for a few minutes, and the acetonitrile washed supernatant was discarded. This step was repeated a second time. The obtained yellow precipitate was dissolved in benzene; the solution was filtered through a frit, and the solvent was removed from the filtrate in vacuo to produce **1b** as a yellow powder; yield 73 mg (49%). Crystals of this complex can be obtained from a cold benzene/acetonitrile (or toluene/acetonitrile) solution: ^{1}H NMR (CD_2Cl_2, 400 MHz, *syn* isomer) δ 12.62 (s, $^1J_{CH}$ = 109.5 Hz, 2H), 7.21 (d, $^3J_{HH}$ = 8.3 Hz, 2H), 7.11 (d, $^3J_{HH}$ = 8.3 Hz, 2H), 2.06−1.97 (m, 20H), 1.61 (m, 10H), 0.94 (s, 18H); ^{13}C{^{1}H} (CD_2Cl_2, 100.6 MHz) δ 331, 152, 144.5, 134, 133, 129, 125, 76, 48, 45, 36, 30.3, 30.0. Anal. Calcd for $C_{42}H_{54}Cl_4Mo_2N_2S_4$: C, 48.10%; H, 5.19%; N, 2.67%. Found: C, 47.84%; H, 5.19%; N, 2.64%.

*Mo(NAr)(CHCMe$_2$Ph)(Cl$_2$S$_2$) (**1c**).* A mixture of Mo(NAr)-(CHCMe$_2$Ph)(OTf)$_2$DME (200 mg, 0.253 mmol, 1 equiv) and Zn(DCTC) (83 mg, 0.303 mmol, 1.2 equiv) was stirred in 10 mL of a mixture of toluene and acetonitrile (9:1) for 30 min. The reaction mixture was then filtered through a glass frit, and all volatiles were removed from the filtrate in vacuo. The residue was washed with acetonitrile (2×, 2 mL each) and dried in vacuo to give a yellow solid; yield 107 mg (69%). Crystals of this complex can be obtained from a cold benzene/acetonitrile (or toluene/acetonitrile) solution: ^{1}H NMR (CD_2Cl_2, 400 MHz, *syn* isomer) δ 13.26 (s, $^1J_{CH}$ = 122.8 Hz, 2H), 7.21−7.01 (m, 20H), 3.94 (septet, $^3J_{HH}$ = 6.7 Hz, 4H), 1.59 (s, 6H), 1.25 (d, $^3J_{HH}$ = 6.7 Hz, 12H), 1.22 (s, 6H), 0.93 (d, $^3J_{HH}$ = 6.7 Hz, 12H); ^{13}C{^{1}H} (CD_2Cl_2, 100.6 MHz) δ 332, 153, 152, 147.1, 146.7, 145, 134, 133, 130, 129, 128, 127, 126.6, 126.5, 123, 59, 31, 29, 27, 24, 23. Anal. Calcd for $C_{56}H_{62}Cl_4Mo_2N_2S_4\cdot C_6H_6$: C, 57.14%; H, 5.26%; N, 2.15%. Found: C, 56.95%; H, 5.56%; N, 2.15%.

*Mo(NAr)(CHCMe$_2$Ph)(Cl$_4$S$_2$) (**2**).* A solution of H_2DCTC (1 equiv, 0.169 mmol) in benzene (5 mL) was added dropwise to a solution of Mo(NAr)(CHCMe$_2$Ph)(Me$_2$pyr)$_2$ in benzene (3 mL), and the mixture was stirred for 6 h. All volatiles were removed in vacuo, and the residue was washed with cold pentane (2×, 4 mL each). The resulting orange solid was washed with 4 mL of acetonitrile and dried in vacuo; yield 103 mg (80%). Crystals of **2** were grown from an diethyl ether/acetonitrile solution at −20 °C: ^{1}H NMR (CD_2Cl_2, 400 MHz) δ 14.35 (s, $^1J_{CH}$ = 121 Hz, 1H), 13.43 (s, $^1J_{CH}$ = 120 Hz, 1H), 7.62 (d, $^4J_{HH}$ = 2.3 Hz, 1H), 7.48 (d, $^4J_{HH}$ = 2.3 Hz, 1H), 7.40−7.39 (m, 2H), 7.25 (d, $^4J_{HH}$ = 2.3 Hz, 1H), 7.20−7.18 (m, 3H), 7.16−7.10 (m, 5H), 7.07−6.99 (m, 9H), 6.77−6.74 (m, 2H), 6.62−6.60 (m, 1H), 4.5 (septet, $^3J_{HH}$ = 6.7 Hz, 1H), 3.68 (septet, $^3J_{HH}$ = 6.7 Hz, 1H), 3.60 (septet, $^3J_{HH}$ = 6.7 Hz, 1H), 3.26 (septet, $^3J_{HH}$ = 6.7 Hz, 1H), 1.69 (s, 3H), 1.43 (s, 3H), 1.40 (s, 3H), 1.28 (d, $^3J_{HH}$ = 6.7 Hz, 3H), 1.23 (d, $^3J_{HH}$ = 6.7 Hz, 3H), 1.18 (d, $^3J_{HH}$ = 6.7 Hz, 3H), 1.11 (d, $^3J_{HH}$ = 6.7 Hz, 3H), 0.66 (d, $^3J_{HH}$ = 6.7 Hz, 3H), 0.60 (s, 3H), 0.57 (d, $^3J_{HH}$ = 6.7 Hz, 3H), 0.42 (d, $^3J_{HH}$ = 6.7 Hz, 3H), 0.32 (d, $^3J_{HH}$ = 6.7 Hz, 3H); ^{13}C{^{1}H} (CD_2Cl_2, 100.6 MHz) δ 329, 318, 154, 153, 151, 149.9, 149.6, 148.9, 148.8, 148.6, 148.2, 147.72, 147.68, 143, 140.69, 140.67, 139.8, 139.6, 139.4, 135.8, 135.7, 133.1, 132.8, 132.6, 132.3, 130, 129.4, 129.3, 129.2, 128.8, 128.5, 128.3, 128.0, 127.1, 127.0, 126.7, 126.5, 126.1, 125, 124.3, 124.1, 123.8, 58.6, 58.4, 32, 31, 30.4, 30.0, 28.9, 28.82, 28.80, 27.8, 27.6, 26, 25, 24.8, 24.7, 24.5, 23.8, 23.0. Anal. Calcd for $C_{68}H_{66}Cl_8Mo_2N_2S_4\cdot 0.3Et_2O$: C, 54.07%; H, 4.52%; N, 1.82%. Found: C, 54.53%; H, 4.49%; N, 1.96%. (On the basis of the intensity of the ether resonances in the ^{1}H NMR spectrum of the analyzed sample, 0.3 equiv of diethyl was included in the calculated values.)

*Mo(NAr)(CHCMe$_2$Ph)(Cl$_4$S$_2$)(py) (**2(py)**).* A solution of H_2DCTC (1 equiv, 0.339 mmol) and pyridine (4 equiv, 1.36 mmol) in benzene (5 mL) was added dropwise to a solution of Mo(NAr)(CHCMe$_2$Ph)-(Me$_2$pyr)$_2$ in 10 mL of benzene. The solution was stirred for 4 h, and the solvent was removed in vacuo. The residue was washed twice with cold pentane, and the pentane wash was discarded. The resulting yellow solid was dried in vacuo; yield 189 mg (67%): ^{1}H NMR (CD_2Cl_2, 400 MHz, *anti* isomer) δ 14.55 (s, $^1J_{CH}$ = 144 Hz, 2H), 9.13 (dt, $^3J_{HH}$ = 5.0 Hz, $^4J_{HH}$ = 1.5 Hz, 2H), 7.84 (tt, $^3J_{HH}$ = 7.6 Hz, $^4J_{HH}$ = 1.5 Hz, 1H), 7.47 (d, $^4J_{HH}$ = 2.4 Hz, 1H), 7.40−7.36 (m, 2H), 7.22−7.05 (m, 6H), 7.16 (d, $^4J_{HH}$ = 2.4 Hz, 1H), 7.08 (d, $^4J_{HH}$ = 2.4 Hz, 1H), 7.08 (d, $^4J_{HH}$ = 0.9 Hz, 1H), 7.06 (d, $^4J_{HH}$ = 0.9 Hz, 1H), 6.90−6.87 (m, 2H), 3.75 (broad s, 2H), 1.60 (s, 3H), 1.59 (s, 3H), 1.16 (broad s, 12H); ^{13}C{^{1}H} (CD_2Cl_2, 100.6 MHz) δ 327, 156, 154, 149.1, 148.7, 147.9, 146.6, 144, 139.6, 139.4, 138.7, 131.7, 131.6, 128.7, 128.6, 128.3, 127.9, 127.8, 126.5, 126.0, 125.6, 123 (broad), 53, 30 (broad), 27, 24, 23 (broad). Anal. Calcd for $C_{39}H_{37}Cl_4MoN_2S_4$: C, 55.99%; H, 4.58%; N, 3.35%. Found: C, 56.01%; H, 4.58%; N, 3.18%.

3,3′,5,5′-Tetrabromo-[1,1′-biphenyl]-2,2′-dithiol. $H_2Br_4S_2$ was synthesized using the reported procedure described for $H_2Cl_4S_2$[20] and crystallized from hot ethanol as a white solid; yield 950 mg (12%) from 2.7 g of 2,2′-biphenol. 3,3′,5,5′-Tetrabromo-[1,1′-biphenyl]-2,2′-diol can be prepared in large scale through addition of slight excess neat bromine to a methanol solution of 2,2′-biphenol. After the reaction was stirred for 2 h, the white precipitate was collected on a frit and washed with cold methanol and finally dried in vacuo. This compound was converted to the dithiol as it was described for $H_2Cl_4S_2$, and intermediate compounds were only characterized by ^{1}H NMR spectroscopy due to similarity to the tetrachloro analogue. It is noteworthy to say that although the Miyazaki−Newman−Kwart rearrangement step does not proceed well, the crude messy mixture can be reduced by $LiAlH_4$ (without further purification) and the desired product will crystallize upon cooling a hot ethanol solution: ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.78 (d, $^4J_{HH}$ = 2.1 Hz, 2H), 7.25 (d, $^4J_{HH}$ = 2.1 Hz, 2H), 3.94 (s, 2H); ^{13}C{^{1}H} ($CDCl_3$, 100.6 MHz) δ 140, 136, 134, 132, 123, 119. Anal. Calcd for $C_{12}H_6Br_4S_2$: C, 27.00%; H, 1.13%. Found: C, 27.38%; H, 1.10%.

*Mo(NAr)(CHCMe$_2$Ph)(Br$_4$S$_2$)(py) (**3(py)**).* Complex **3(py)** was synthesized in a manner analogous to that used to prepare **2(py)**; yield 138 mg (81%): ^{1}H NMR (CD_2Cl_2, 400 MHz, *anti* isomer) δ 14.60 (s, $^1J_{CH}$ = 14 Hz), 9.2 (d, $^3J_{HH}$ = 5.3 Hz, 2H), 7.9−7.7 (m, 1H), 7.6 (d, $^4J_{HH}$ = 2.2 Hz, 1H), 7.5 (d, $^4J_{HH}$ = 2.2 Hz, 1H), 7.4 (t, $^3J_{HH}$ = 6.0 Hz, 2H), 7.3−7.1 (m, 6H), 7.0−6.9 (m, 2H), 4.3 (broad s, 1H), 3.2 (broad s, 1H), 1.7 (s, 3H), 1.6 (s, 3H), 1.5 (broad s, 12H); ^{13}C{^{1}H} (CD_2Cl_2, 100.6 MHz) δ 326, 155, 153, 152, 150, 149, 148.1, 147.7, 146, 139, 134, 133, 131.3, 130.9, 130.6, 130.3, 128.3, 128.2, 126.1, 125.8, 125.5, 125.2, 123, 119.2, 119.0, 53, 29 (broad), 26, 24 (broad), 22, 14. Anal. Calcd for $C_{39}H_{37}Br_4MoN_2S_2$: C, 46.22%; H, 3.68%; N, 2.76%. Found: C, 46.36%; H, 3.52%; N, 2.65%.

*Mo(NAr)(CHCMe$_2$Ph)(Bu$_4$S$_2$)(PMe$_3$) (**4(PMe$_3$)**).* Mo(NAr)-(CHCMe$_2$Ph)(Me$_2$pyr)$_2$ (1 equiv 0.338 mmol) and $H_2Bu_4S_2$ (tetra-*t*-butyldithiophenol, 1 equiv, 0.338 mmol) were dissolved in 15 mL of benzene, and the reaction mixture was stirred at 70 °C for 2 days. All

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volatiles were removed in vacuo with gentle heating (40 °C). The resulting red brittle solid was redissolved in pentane, and solvent was removed in vacuo at 40 °C. The obtained red solid was dissolved in 10 mL of pentane, and PMe_3 (2 equiv, 0.676 mmol) was added as a solution in 5 mL of pentane. The mixture was stirred for 10 min, and all volatiles were then removed in vacuo. Orange crystals of **4(PMe$_3$)** can be obtained after a few hours from a saturated pentane solution at −20 °C; yield 224 mg (78%): ^{1}H NMR (CD_2Cl_2, 400 MHz, *syn* isomer) δ 11.79 (d, $^1J_{CH}$ = 110.2 Hz, $^3J_{HP}$ = 3.8 Hz, 1H), 7.50−7.47 (m, 2H), 7.43 (d, $^4J_{HH}$ = 2.6 Hz, 1H), 7.36−7.32 (m, 2H), 7.23−7.20 (m, 1H), 7.13 (d, $^4J_{HH}$ = 2.4 Hz, 1H), 7.08−7.05 (m, 2H), 6.99 (d, $^4J_{HH}$ = 2.4 Hz, 1H), 6.97−6.94 (m, 1H), 6.65 (d, $^4J_{HH}$ = 2.6 Hz, 1H), 4.42 (septet, $^3J_{HH}$ = 6.8 Hz, 1H), 3.09 (septet, $^3J_{HH}$ = 6.6 Hz, 1H), 1.85 (s, 3H), 1.83 (s, 3H), 1.72 (s, 9H), 1.33 (s, 9H), 1.32 (s, 9H), 1.29 (s, 9H), 1.24 (d, $^2J_{HP}$ = 9.2 Hz, 9H), 1.22 (d, $^3J_{HH}$ = 6.8 Hz, 3H), 1.20 (d, $^3J_{HH}$ = 6.8 Hz, 3H), 1.04 (d, $^3J_{HH}$ = 6.6 Hz, 3H), 0.34 (d, $^3J_{HH}$ = 6.6 Hz, 3H); ^{13}C{^{1}H} (CD_2Cl_2, 100.6 MHz) δ 306 (d, $^2J_{HP}$ = 19.1 Hz), 152 (d, J_{HP} = 5.1 Hz), 151 (d, J_{HP} = 3.4 Hz), 149.1 (d, J_{HP} = 3.3 Hz), 148.8, 147.9, 146.9, 146.7, 146.6 (d, J_{HP} = 2.9 Hz), 146.5 (d, J_{HP} = 2.6 Hz), 143.3, 143.2, 142.4 (d, J_{HP} = 2.6 Hz), 142.2, 128.4, 128.0 (d, J_{HP} = 2.8, Hz), 126.6, 126.4, 126.2, 125.9, 125.6, 123.1, 122.9, 121.8, 121.7, 55.4, 38, 37, 34.4, 34.1, 31.3, 31.2, 31.0, 30.9, 27, 24.1, 24.0, 23.9, 23.8, 22.3, 16 (d, $^2J_{H-P}$ = 24.8 Hz), 14; ^{31}P{^{1}H} NMR (CD_2Cl_2, 162.0 MHz) −13.2. Anal. Calcd for $C_{53}H_{78}Cl_4MoNPS_2$: C, 69.17%; H, 8.54%; N, 1.52%. Found: C, 69.06%; H, 8.84%; N, 1.65%.

Synthesis of an Ethylene Complex from 4 in Situ. In a typical reaction, 10 mg of the complex and 1 equiv of $B(C_6F_5)_3$ were placed in a vial. C_6D_6 (0.5 mL) was added, and the resulting mixture was transferred to a J-Young NMR tube. On a Schlenk line, the mixture was freeze−pump−thawed two times and then exposed to ethylene. The NMR tube was shaken a few times, and proton NMR spectra were collected.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.organomet.8b00614.

NMR spectra for all compounds and details of the X-ray studies for three complexes (PDF)

X-ray data (XYZ)

Accession Codes

CCDC 1863871−1863873 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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H.T. performed all synthetic reactions, and C.T. and P.M. performed all X-ray structural studies.

Notes

The authors declare no competing financial interest.

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