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Synthesis of Molybdenum(VI) Monoimido Alkyl and Alkylidene Complexes

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In this paper we report the synthesis of several new Mo(NR)Cl₄(THF) species (R = C₆F₅, 3,5-(CF₃)₂C₆H₃, 1-adamantyl, CPh₃, and 2,6-*i*-Pr₂C₆H₃) via the treatment of MoCl₄(THF)₂ with azides and their reactions with neopentyl reagents. Addition of Mo(NR)Cl₄(THF) complexes in toluene to a cold solution of NpMgCl in ether gave Mo(NR)Np₃Cl species (R = C₆F₅, 3,5-(CF₃)₂C₆H₃, Ad, Ph₃C, and 2,6-*i*-Pr₂C₆H₃ (Ar); Np = CH₂-*t*-Bu) in poor (35%) to modest (51%) yields. Heating Mo(NAr)Np₃Cl in C₆D₆ to 50 °C results in α -hydrogen abstraction to give neopentane and a molecule whose NMR spectra are consistent with it being Mo(NAr)(CH-*t*-Bu)(CH₂-*t*-Bu)Cl; it decomposed bimolecularly upon attempted isolation. The other Mo(NR)Np₃Cl species were found to be more stable than Mo(NAr)Np₃Cl, but when they did decompose at elevated temperatures, no neopentylidene complex could be observed. Addition of neopentyllithium to Mo(NR)Np₃Cl species (R = Ar, CPh₃, or Ad) yielded Mo(NR)(CH-*t*-Bu)Np₂ species, the adamantylimido version of which is unstable toward bimolecular decomposition. Addition of neopentyllithium to Mo(NR)Np₃Cl complexes in which R = pentafluorophenyl or 3,5-trifluoromethylphenyl led to intractable mixtures. Addition of 1 equiv of 2,6-diisopropylphenol, 2,6-dimethylphenol, or 3,5-(2,4,6-*i*-Pr₃C₆H₂)₂C₆H₃OH (HIPTOH) to Mo(NCPh₃)(CH-*t*-Bu)Np₂ led to formation of Mo(NCPh₃)(CH-*t*-Bu)Np(OR) species, while treatment of Mo(NCPh₃)(CH-*t*-Bu)₂(CH₂-*t*-Bu) with C₆F₅OH gave Mo(NCPh₃)-Np₃(OC₆F₅). The three monophenoxide neopentylidene complexes showed poor to moderate metathesis activity for ring-closing a small selection of substrates. X-ray studies were completed for Mo[N-3,5-(CF₃)₂C₆H₃]Cl₄(THF), Mo[N-3,5-(CF₃)₂C₆H₃]Np₃Cl, Mo(NCPh₃)-Np₃Cl, and Mo(NCPh₃)(CH-*t*-Bu)(CH₂-*t*-Bu)(OHIPT).

Introduction

We recently reported complexes of the type M(NR)-(CH-*t*-Bu)(OR')(CH₂-*t*-Bu) where M is Mo¹ or W,² R is 2,6-*i*-Pr₂C₆H₃ (Ar) or 2,6-Me₂C₆H₃ (Ar'), and OR' is one of several alkoxides or phenoxides. The molybdenum complexes were prepared via a traditional route to bisalkoxide metathesis catalysts³ that centers around the reaction of Mo(NAr)₂(CH₂-*t*-Bu)₂ with triflic acid to yield Mo(NAr)(CH-*t*-Bu)(dme)(OTf)₂. In contrast, W(NAr)(CH-*t*-Bu)(CH₂-*t*-Bu)₂ could be prepared from W(NAr)Cl₄.² M(NR)(CH-*t*-Bu)(OR')(CH₂-*t*-Bu) species are being explored as olefin metathesis catalysts and have also been found to decompose to give unusual species of the type [M(NR)(OR')(CH₂-*t*-Bu)]₂ that contain unbridged M=M bonds.²

A potentially more direct route to Mo(NR)(CH-*t*-Bu)-(OR')(CH₂-*t*-Bu) complexes would involve a synthesis patterned after that for the W analogues, i.e., addition of neopentyl groups to Mo(NR)Cl₄(THF) complexes. However, few examples of Mo(NR)Cl₄ complexes have appeared in the literature. The first, Mo(*N-p*-tolyl)Cl₄(THF), was published in 1984 by Maatta.⁴ It was

prepared in high yield by adding *p*-tolyl azide to MoCl₄(THF)₂ and was crystallographically characterized. A dimeric version in which two imido nitrogens are linked with a *p*-phenylene group, (THF)₂Cl₄Mo=N-*p*-C₆H₄-N=MoCl₄(THF), was prepared in an analogous manner.⁵ Mo(NCH₂CH=CH₂)Cl₄(THF) was prepared in situ from allyl azide and MoCl₄(THF)₂; it was not isolated or characterized, but converted directly into a Mo(V) bisphosphine derivative.⁶ All published imido tetrachlorides are reduced readily by phosphines to yield Mo(V) species, e.g., Mo(Nallyl)Cl₃(PPh₃)₂.⁶

In this paper we report the synthesis of several new Mo(NR)Cl₄(THF) species and their reactions with neopentyl reagents. The object is to explore the general features of alkylation and α hydrogen abstraction in Mo(VI) monoimido species, and in particular to prepare new examples of Mo(NR)(CH-*t*-Bu)(OR')(CH₂-*t*-Bu) species more simply and directly.

Results

Synthesis of Imido Tetrachloride Complexes. We were interested in the possibility of preparing catalysts

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Table 1. Crystal Data and Structure Refinement for Mo[N-3,5-(CF₃)₂C₆H₃]Cl₄(THF), Mo[N-3,5-(CF₃)₂C₆H₃](CH₂-t-Bu)₃Cl, Mo[NC(C₆H₅)₃](CH₂-t-Bu)₃Cl, and Mo(NCPh₃)(CH-t-Bu)(CH₂-t-Bu)(OHIPT)^a

empirical formula	C ₁₂ H ₁₁ Cl ₄ F ₆ MoNO	C ₂₃ H ₃₆ ClF ₆ MoN	C ₃₄ H ₄₈ ClMoN	C ₆₅ H ₈₅ MoNO
fw	536.96	571.92	602.12	992.28
<i>T</i> (K)	193(2)	193(2)	193(2)	100(2)
cryst syst	triclinic	monoclinic	monoclinic	monoclinic
space group	<i>P</i> $\bar{1}$	<i>C</i> 2/ <i>c</i>	<i>P</i> 2(1)/ <i>n</i>	<i>P</i> 2(1)
unit cell dimens (Å, deg)	<i>a</i> = 9.0151(8) <i>b</i> = 10.3616(9) <i>c</i> = 11.0455(10) α = 63.349(2) β = 86.872(2) γ = 88.901(2)	17.3743(13) 9.8338(7) 32.380(2) 90 103.7330(10) 90	10.153(2) 18.451(4) 17.416(4) 90 103.55(3) 90	10.212(6) 40.85(3) 13.861(9) 90 102.618(12) 90
volume (Å ³)	920.76(14)	5374.2(7)	3171.7(11)	5642(6)
<i>Z</i>	2	8	4	4
density (calcd; Mg/m ³)	1.937	1.414	1.261	1.168
absorp coeff (mm ⁻¹)	1.351	0.639	0.519	0.273
<i>F</i> (000)	524	2352	1272	2128
cryst size (mm)	0.3 × 0.16 × 0.09	0.38 × 0.28 × 0.20	0.25 × 0.20 × 0.20	0.25 × 0.08 × 0.08
θ range (deg)	2.07 to 24.99	1.29 to 28.30	1.63 to 26.44	1.00 to 28.28
index ranges	−10 ≤ <i>h</i> ≤ 9 −7 ≤ <i>k</i> ≤ 12 −13 ≤ <i>l</i> ≤ 12	−22 ≤ <i>h</i> ≤ 23 −8 ≤ <i>k</i> ≤ 13 −32 ≤ <i>l</i> ≤ 42	−12 ≤ <i>h</i> ≤ 12 −23 ≤ <i>k</i> ≤ 23 −21 ≤ <i>l</i> ≤ 21	−13 ≤ <i>h</i> ≤ 13 −54 ≤ <i>k</i> ≤ 54 0 ≤ <i>l</i> ≤ 18
no. of reflns collected	5000	16 562	54 550	125 702
no. of indep reflns [<i>R</i> (int)]	3233 [0.0233]	6297 [0.0153]	6532 [0.0300]	27 827 [0.07980]
completeness (to θ =)	99.6% (24.99°)	94.1% (28.30°)	99.8% (26.44°)	99.7% (28.28°)
no. of data/restraints/params	3233/0/227	6297/0/290	6532/0/334	27 827/1374/1247
goodness-of-fit on <i>F</i> ²	1.076	1.114	1.097	1.091
final <i>R</i> indices [<i>I</i> > 2 σ (<i>I</i>)]	<i>R</i> 1 = 0.0360 w <i>R</i> 2 = 0.0883	<i>R</i> 1 = 0.0309 w <i>R</i> 2 = 0.0755	<i>R</i> 1 = 0.0265 w <i>R</i> 2 = 0.0669	<i>R</i> 1 = 0.0685 w <i>R</i> 2 = 0.1461
<i>R</i> indices (all data)	<i>R</i> 1 = 0.0524 w <i>R</i> 2 = 0.0929	<i>R</i> 1 = 0.0321 w <i>R</i> 2 = 0.0762	<i>R</i> 1 = 0.0313 w <i>R</i> 2 = 0.0706	<i>R</i> 1 = 0.0875 w <i>R</i> 2 = 0.1562
largest diff. peak and hole (e Å ⁻³)	0.518 and −0.486	0.800 and −0.608	0.816 and −0.257	1.268 and −1.101

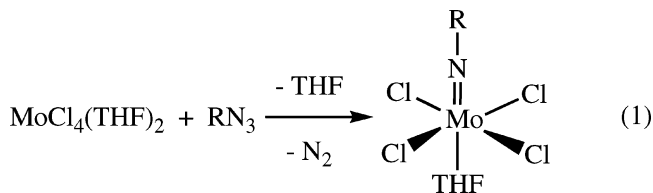
^a In each case the wavelength was 0.71073 Å, the refinement method was full-matrix least-squares on *F*², and the absorption correction was semiempirical.

that contain an electron-withdrawing imido group and therefore chose to attempt to prepare pentafluorophenylimido and 3,5-bis(trifluoromethyl)phenylimido Mo(NR)Cl₄(THF) complexes. We also were interested in preparing alkylimido complexes and, for this reason, chose 1-adamantylimido (AdN) and tritylimido (triphenylmethylimido). Finally, we chose to prepare Mo(NAr)Cl₄(THF) (Ar = 2,6-*i*-Pr₂C₆H₃), since molybdenum alkylidene complexes that contain the NAr group are the most numerous and stable.^{7,8}

Pentafluorophenyl azide,⁹ 3,5-bis(trifluoromethyl)phenyl azide,¹⁰ 1-adamantyl azide,¹¹ triphenylmethyl azide,¹² and 2,6-diisopropylphenyl azide¹³ were all prepared readily in good yields by published methods or slight variations thereof. Adamantyl azide and trityl azide are white crystalline compounds; the others are oils.

The azides react with MoCl₄(THF)₂¹⁴ to give complexes of the type Mo(NR)Cl₄(THF) in good (66%) to excellent (96%) yields (eq 1). Reactions can be carried

out in 1,2-dichloroethane or toluene. The lowest yield was obtained for Mo(NAr)Cl₄(THF), in which the imido group is the most demanding sterically.



Single crystals of Mo[N-3,5-(CF₃)₂C₆H₃]Cl₄(THF) were grown from pentane, and an X-ray determination was carried out (Tables 1 and 2). The structure of Mo[N-3,5-(CF₃)₂C₆H₃]Cl₄(THF) (Figure 1) is closely analogous to that of Mo(N-*p*-tolyl)Cl₄(THF).⁴ The Mo–N(1) distance (1.715(3) Å) and Mo–N(1)–C(1) angle (171.2(3)°) are typical of imido complexes of Mo(IV). The chlorides are all bent away from the imido group, as judged from the N(1)–Mo–Cl angles, which vary from ~92° to ~98°. The Mo–O(1) bond length (2.230(2) Å) is normal, even though it is *trans* to the pseudo triply bound imido ligand.

Synthesis of Imido Trineopentyl Complexes.

Osborn reported in 1987 that Mo(N-t-Bu)(O)Cl₂(MeCN)₃ could be alkylated with MgNp₂(dioxane) (Np = CH₂-t-Bu) in diethyl ether to yield Mo(N-t-Bu)Np₃Cl in 35% yield as a colorless crystalline solid.¹⁵ On the basis of proton NMR spectra he proposed that this compound has a trigonal bipyramidal structure with the

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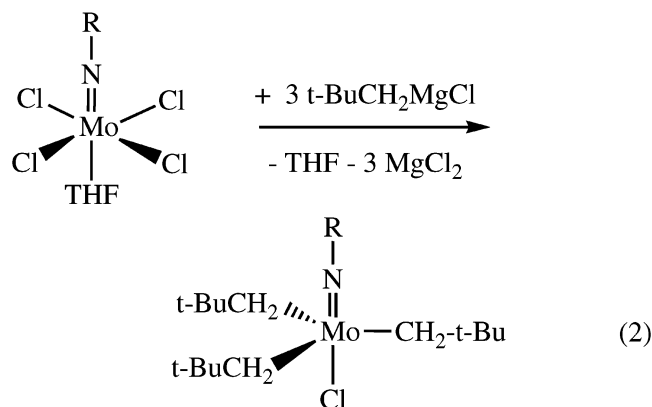
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Table 2. Selected Bond Lengths (Å) and Angles (deg) in Mo[N-3,5-(CF₃)₂C₆H₃]Cl₄(THF), Mo[N-3,5-(CF₃)₂C₆H₃](CH₂-*t*-Bu)₃Cl, and Mo(NCPh₃)(CH₂-*t*-Bu)₃Cl

Mo[N-3,5-(CF ₃) ₂ C ₆ H ₃]Cl ₄ (THF)		Mo[N-3,5-(CF ₃) ₂ C ₆ H ₃]Np ₃ Cl		Mo(NCPh ₃)Np ₃ Cl	
Mo–N(1)	1.711(3)	Mo–N(1)	1.7471(17)	Mo–N(1)	1.7509(15)
Mo–Cl(1)	2.3271(12)	Mo–C(10)	2.1473(19)	Mo–C(10)	2.1507(18)
Mo–Cl(2)	2.3137(11)	Mo–C(20)	2.151(2)	Mo–C(20)	2.1430(19)
Mo–Cl(3)	2.3311(11)	Mo–C(30)	2.1281(19)	Mo–C(30)	2.1475(18)
Mo–Cl(4)	2.3459(11)	Mo–Cl(1)	2.3944(5)	Mo–Cl(1)	2.4268(7)
Mo–O(1)	2.230(2)	N(1)–Mo–C(10)	90.24(8)	N(1)–Mo–C(10)	93.83(7)
N(1)–Mo–Cl(1)	95.39(12)	N(1)–Mo–C(20)	91.69(8)	N(1)–Mo–C(20)	94.03(7)
N(1)–Mo–Cl(2)	98.03(12)	N(1)–Mo–C(30)	93.06(8)	N(1)–Mo–C(30)	93.03(7)
N(1)–Mo–Cl(3)	95.69(12)	C(10)–Mo–C(20)	120.17(8)	C(10)–Mo–C(20)	117.89(7)
N(1)–Mo–Cl(4)	92.20(12)	C(10)–Mo–C(30)	120.34(7)	C(10)–Mo–C(30)	121.13(7)
N(1)–Mo–O(1)	176.09(13)	C(20)–Mo–C(30)	119.23(8)	C(20)–Mo–C(30)	119.80(7)
C(1)–N(1)–Mo	171.4(3)	N(1)–Mo–Cl(1)	177.39(6)	N(1)–Mo–Cl(1)	178.25(5)
O(1)–Mo–Cl(1)	84.51(7)	C(1)–N(1)–Mo	174.94(15)	C(40)–N(1)–Mo	178.16(12)
O(1)–Mo–Cl(2)	85.88(7)	C(10)–Mo–Cl(1)	87.55(6)	C(10)–Mo–Cl(1)	86.77(5)
O(1)–Mo–Cl(3)	84.39(7)	C(20)–Mo–Cl(1)	88.24(6)	C(20)–Mo–Cl(1)	87.14(5)
O(1)–Mo–Cl(4)	83.89(7)	C(30)–Mo–Cl(1)	89.24(6)	C(30)–Mo–Cl(1)	85.26(5)
Cl(2)–Mo–Cl(1)	89.42(4)	C(11)–C(10)–Mo	120.42(13)	C(11)–C(10)–Mo	123.86(12)
Cl(2)–Mo–Cl(3)	89.73(4)	C(21)–C(20)–Mo	121.25(14)	C(21)–C(20)–Mo	121.10(12)
Cl(2)–Mo–Cl(4)	169.77(4)	C(31)–C(30)–Mo	121.71(13)	C(31)–C(30)–Mo	122.69(12)
Cl(1)–Mo–Cl(3)	168.89(4)				
Cl(1)–Mo–Cl(4)	89.61(5)				
Cl(3)–Mo–Cl(4)	89.26(4)				

neopentyl groups in equatorial positions. We have found that addition of Mo(NR)Cl₄(THF) complexes in toluene to a cold solution of NpMgCl in ether gave analogous Mo(NR)Np₃Cl species (R = C₆F₅, 3,5-(CF₃)₂-C₆H₃, Ad, Ph₃C, and 2,6-*i*-Pr₂C₆H₃) in poor (35%) to modest (51%) yields (eq 2). NMR data at room temperature are all in accord with 3-fold symmetric species. Varying the order of addition, time, and temperature (down to –78 °C) so far has not led to an increase in the yields. We suspect that a susceptibility of Mo to reduction is limiting the yields under the conditions and with the reagents employed so far. The trineopentyl species tend to be quite soluble and therefore relatively difficult to crystallize, especially in small quantities.



An X-ray structural determination of Mo[N-3,5-(CF₃)₂C₆H₃]Np₃Cl (Tables 1 and 2) confirmed that it is approximately a trigonal bipyramid with neopentyl groups in equatorial positions (Figure 2). The neopentyl groups are all turned in one direction with their β carbon atoms approximately in the equatorial plane and with Mo–C_α–C_β angles of ~121° and Mo–C_α bond distances of ~2.13 Å. These Mo–C_α–C_β angles and Mo–C_α bond distances are typical for neopentyl ligands in Mo(VI) and W(VI) complexes. There is no evidence that the neopentyl ligands are distorted for steric reasons or that any α hydrogen is activated toward

abstraction. The only notable feature of the structure is a somewhat long Mo–Cl distance of 2.3944(5) Å that

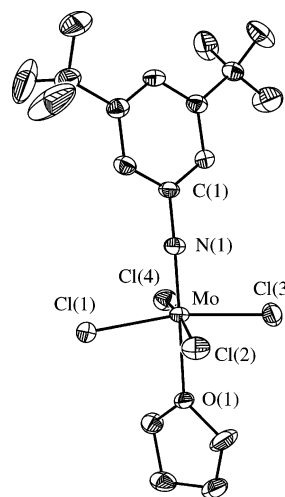
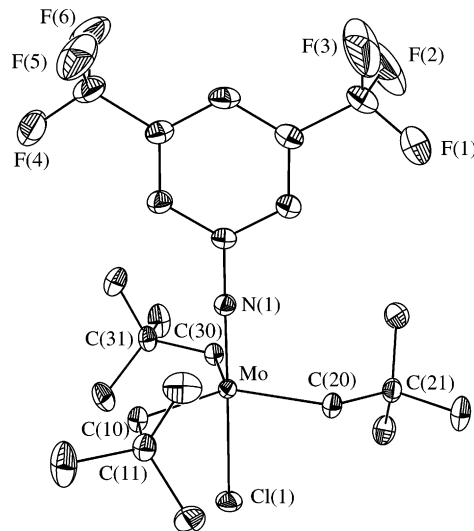
**Figure 1.** Thermal ellipsoid drawing of Mo[N-3,5-(CF₃)₂C₆H₃]Cl₄(THF).**Figure 2.** Thermal ellipsoid drawing of Mo[N-3,5-(CF₃)₂C₆H₃](CH₂-*t*-Bu)₃Cl.

Table 3. Selected Bond Lengths (Å) and Angles (deg) in the Two Molecules of Mo(NCPh₃)(CH-*t*-Bu)(CH₂-*t*-Bu)(OHIPT)

Mo(1)–N(1)	1.725(4)	Mo(2)–N(2)	1.725(4)
Mo(1)–C(171)	1.886(5)	Mo(2)–C(271)	1.855(5)
Mo(1)–O(1)	1.928(4)	Mo(2)–O(2)	1.926(4)
Mo(1)–C(161)	2.154(5)	Mo(2)–C(261)	2.107(6)
N(1)–Mo(1)–C(171)	105.4(2)	N(2)–Mo(2)–C(271)	106.7(2)
N(1)–Mo(1)–O(1)	123.97(15)	N(2)–Mo(2)–O(2)	125.29(16)
C(171)–Mo(1)–O(1)	111.0(2)	C(271)–Mo(2)–O(2)	109.7(2)
N(1)–Mo(1)–C(161)	105.0(2)	N(2)–Mo(2)–C(261)	107.7(2)
C(171)–Mo(1)–C(161)	92.9(2)	C(271)–Mo(2)–C(261)	106.5(3)
O(1)–Mo(1)–C(161)	113.9(2)	O(2)–Mo(2)–C(261)	99.4(2)
C(162)–C(161)–Mo(1)	122.3(4)	C(262)–C(261)–Mo(2)	131.9(4)
C(172)–C(171)–Mo(1)	146.9(4)	C(272)–C(271)–Mo(2)	148.5(4)
C(101)–O(1)–Mo(1)	133.4(3)	C(201)–O(2)–Mo(2)	126.0(4)
C(140)–N(1)–Mo(1)	164.1(3)	C(240)–N(2)–Mo(2)	161.2(3)

could be ascribed to the combined steric effect of the three equatorial neopentyl groups on the apical chloride ligand, plus the *trans* effect of the imido ligand.

Synthesis of Imido Neopentylidene Complexes. Heating Mo(NAr)Np₃Cl in C₆D₆ to 50 °C results in α -hydrogen abstraction to give neopentane and a molecule that we propose to be Mo(NAr)(CH-*t*-Bu)(CH₂-*t*-Bu)Cl. The decomposition takes place in a unimolecular fashion in C₆D₆ with a rate constant of $k_{50} = 9.0 \times 10^{-5} \text{ s}^{-1}$ at an initial concentration of 0.1 M, and $k_{50} = 9.5 \times 10^{-5} \text{ s}^{-1}$ at an initial concentration of 0.2 M. At 60 °C $k_{60} = 3.0 \times 10^{-4} \text{ s}^{-1}$. This rate constant should be compared with that found for decomposition of Mo(NAr)Np₃(OC₆F₅) to Mo(NAr)(CH-*t*-Bu)(CH₂-*t*-Bu)(OC₆F₅) in C₆D₆ at 60 °C ($1.0 \times 10^{-4} \text{ s}^{-1}$).¹ A resonance for the alkylidene proton in Mo(NAr)(CH-*t*-Bu)(CH₂-*t*-Bu)Cl is found at 11.70 ppm and for the alkylidene carbon atom at 283 ppm ($J_{\text{CH}} = 109 \text{ Hz}$). Unfortunately this species is not stable toward bimolecular decomposition to yield di-*tert*-butylethylene, and so far all attempts to isolate it have failed. The nature of the metal-containing decomposition product or products is not known. The other Mo(NR)Np₃Cl species were found to be more stable than Mo(NAr)Np₃Cl, but when they did decompose (after several hours at 70 °C or higher temperatures), no neopentylidene complex could be observed. If neopentylidene complexes are formed, they presumably decompose too readily under these conditions to be observed.

Addition of neopentyllithium to Mo(NAr)Np₃Cl at –30 °C led to formation of Mo(NAr)(CH-*t*-Bu)Np₂ in 90% yield ($\delta \text{H}_\alpha = 9.50$ in C₆D₆, $\delta \text{C}_\alpha = 255 \text{ ppm}$ in C₆D₆, $J_{\text{CH}} = 108 \text{ Hz}$). This compound is identical in all respects to the relatively stable crystalline solid prepared by alkylation of Mo(NAr)(CH-*t*-Bu)(OTf)₂(dme).¹ The low J_{CH} value is typical of imido alkylidenes that have a *syn* orientation with respect to the imido group.⁷

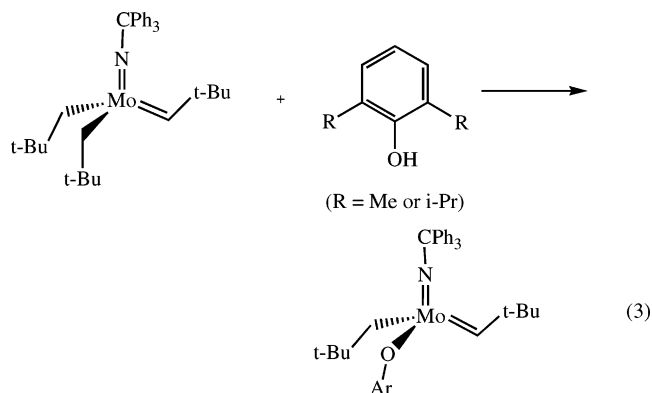
Addition of neopentyllithium to Mo(NCPh₃)Np₃Cl led to formation of Mo(NCPh₃)(CH-*t*-Bu)Np₂ as a pentane-soluble ivory powder in 96% yield. The proton NMR spectrum of Mo(NCPh₃)(CH-*t*-Bu)Np₂ in C₆D₆ shows the neopentylidene H _{α} resonance at 8.95 ppm and the C _{α} resonance at 250.1 ppm with $J_{\text{CH}} = 109 \text{ Hz}$. It should be noted that although Mo(N-*t*-Bu)(CH-*t*-Bu)Np₂ could be prepared in 75% yield, it could be isolated only as a brown oil ($\delta \text{H}_\alpha = 9.22$, $\delta \text{C}_\alpha = 249.5$ in C₆D₆).¹⁵

Addition of neopentyllithium to Mo(NAd)Np₃Cl led to formation of what is believed to be Mo(NAd)(CH-*t*-Bu)Np₂ with $\delta \text{H}_\alpha = 9.22 \text{ ppm}$ in C₆D₆. This species is

not stable in solution at 22 °C, judging from the appearance of olefinic resonances at 5.38 and 5.42 ppm, which are characteristic of *cis*- and *trans*-(*t*-Bu)CH=CH-(*t*-Bu), the product of bimolecular coupling of neopentylidenes. Mo(NAd)(CH-*t*-Bu)Np₂ prepared from Mo(NAd)(CH-*t*-Bu)(OTf)₂(dme)¹⁶ on a multigram scale also was found to be unstable at room temperature in solution and could be isolated only as a partially decomposed red oil. These results suggest that Mo(N-*t*-Bu)(CH-*t*-Bu)Np₂¹⁵ also may not be completely stable with respect to decomposition to give di-*tert*-butylethylene.

Addition of neopentyllithium to Mo(NR)Np₃Cl complexes in which R = pentafluorophenyl or 3,5-trifluoromethylphenyl led to intractable mixtures.

Synthesis of Monoalkoxide Complexes. Addition of 1 equiv of 2,6-diisopropylphenol or 2,6-dimethylphenol to Mo(NCPh₃)(CH-*t*-Bu)Np₂ leads to formation of Mo(NCPh₃)(CH-*t*-Bu)Np(OAr) species as a consequence of addition of the alcohol across a Mo–C single bond in a manner similar to reactions reported for Mo(NAr)(CH-*t*-Bu)(CH₂-*t*-Bu)₂¹ (eq 3). The 2,6-dimethylphenox-



ide derivative is a colorless powder, while the extremely soluble 2,6-diisopropylphenoxide derivative could be obtained only as a brown oil. Reaction of 1 equiv of 3,5-(2,4,6-*i*-Pr₃C₆H₂)₂C₆H₃OH (HIPTOH), which was prepared in 75% yield from 3,5-(2,4,6-*i*-Pr₃C₆H₂)₂-C₆H₃Br,^{17,18} with Mo(NCPh₃)(CH-*t*-Bu)(CH₂-*t*-Bu)₂ gives

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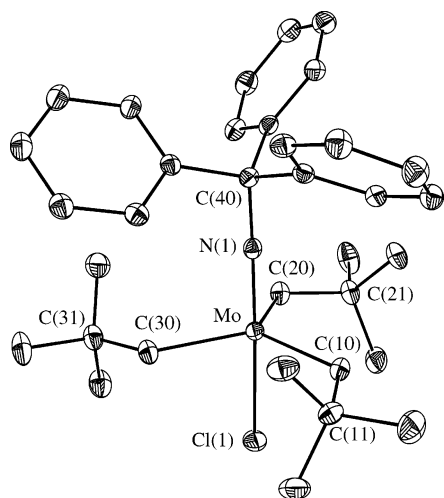


Figure 3. Thermal ellipsoid drawing of $\text{Mo}(\text{NCPh}_3)(\text{CH}_2\text{-t-Bu})_3\text{Cl}$.

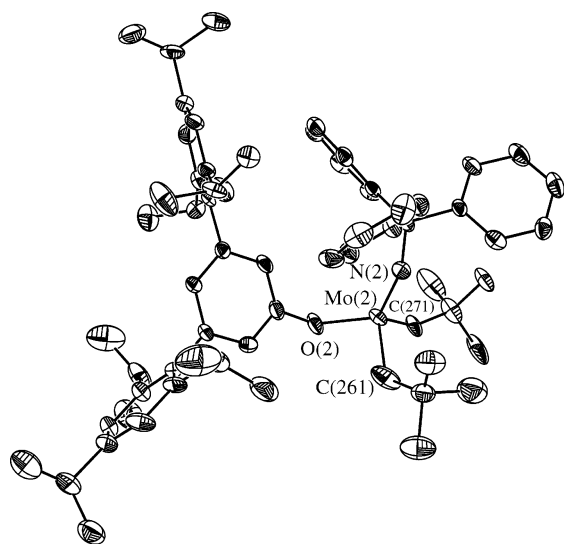
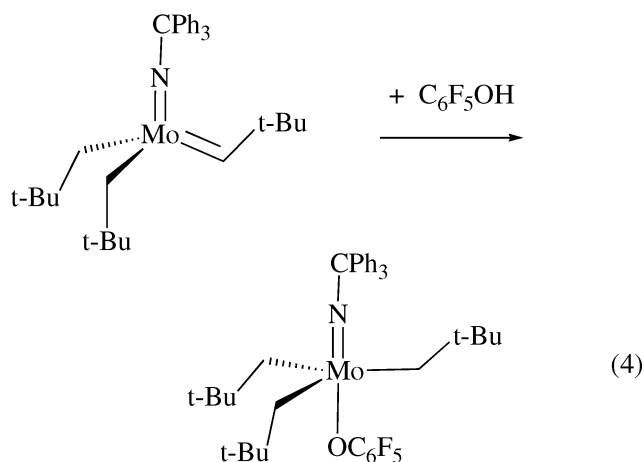


Figure 4. Thermal ellipsoid drawing of $\text{Mo}(\text{NCPh}_3)(\text{CH-t-Bu})(\text{CH}_2\text{-t-Bu})(\text{OHIPT})$.

$\text{Mo}(\text{NCPh}_3)(\text{CH-t-Bu})\text{Np}(\text{OHIPT})$ as a yellow-golden powder in 95% yield.

The X-ray structure of $\text{Mo}(\text{NCPh}_3)(\text{CH-t-Bu})(\text{CH}_2\text{-t-Bu})(\text{OHIPT})$ (Tables 1 and 3; Figure 4) shows it to be a monomeric species with a *syn* neopentylidene ligand. The two molecules in the unit cell are enantiomers in terms of the arrangement of the four ligands around the metal; only one of the two molecules (containing Mo(2); Table 3) is shown in Figure 4. The bond lengths and angles are typical of four-coordinate alkylidene imido compounds, although this is actually the first published structural determination of a compound of this mononeopentyl monoalkoxide type.¹ Several bond lengths and angles differ significantly in the two molecules, including (for example) the Mo–N–C angles ($164.1(3)^\circ$ in Mo(1) and $161.2(3)^\circ$ in Mo(2)). Both are at the lower end of the range of angles typically found in “linear” imido alkylidene complexes. Since several other bond lengths and angles differ significantly from one another in the two molecules (Table 3), we believe that packing forces may play a significant role in determining the detailed structures of the two molecules of $\text{Mo}(\text{NCPh}_3)(\text{CH-t-Bu})(\text{CH}_2\text{-t-Bu})(\text{OHIPT})$.

A reaction between $\text{Mo}(\text{NCPh}_3)(\text{CH-t-Bu})_2(\text{CH}_2\text{-t-Bu})$ and $\text{C}_6\text{F}_5\text{OH}$ gives $\text{Mo}(\text{NCPh}_3)\text{Np}_3(\text{OC}_6\text{F}_5)$ as an off-white powder in 93% yield (eq 4). The difference in behavior between the phenols described above and pentafluorophenol in the manner in which they react with a dineopentyl neopentylidene complex is analogous to that reported for reactions of phenols and various other alcohols with $\text{Mo}(\text{NAr})(\text{CH-t-Bu})_2(\text{CH}_2\text{-t-Bu})$; that is, pentafluorophenol adds across the $\text{Mo}=\text{C}$ bond instead of the $\text{Mo}-\text{C}$ bond. $\text{Mo}(\text{NCPh}_3)\text{Np}_3(\text{OC}_6\text{F}_5)$ does not undergo α -hydrogen abstraction upon heating in C_6D_6 to 60°C for 2 days. In contrast, when benzene- d_6 solutions of $\text{Mo}(\text{NAr})\text{Np}_3(\text{OC}_6\text{F}_5)$ are heated to 60°C , neopentane evolves smoothly and $\text{Mo}(\text{NAr})(\text{CH-t-Bu})(\text{CH}_2\text{-t-Bu})(\text{OC}_6\text{F}_5)$ is formed in a unimolecular manner with $k = 1.0 \times 10^{-4} \text{ s}^{-1}$.¹ It is not clear whether the more rapid decomposition of $\text{Mo}(\text{NAr})\text{Np}_3(\text{OC}_6\text{F}_5)$ can be ascribed to steric or electronic differences between the imido groups, or both.



The three monophenoxide neopentylidene complexes showed poor to moderate metathesis activity for ring-closing a small selection of substrates shown in Table 4.⁸ It is worth noting that in the case of $\text{Mo}(\text{NCPh}_3)(\text{CH-t-Bu})\text{Np}(\text{OAr}')$ and $\text{Mo}(\text{NCPh}_3)(\text{CH-t-Bu})\text{Np}(\text{OAr})$ the majority of the initial species can be observed throughout the reaction; that is, no alkylidene resonance ascribed to an intermediate could be observed. $\text{Mo}(\text{NCPh}_3)(\text{CH-t-Bu})\text{Np}(\text{OHIPT})$, on the other hand, was completely consumed in the initial reaction with an olefin. However, no intermediate alkylidene could be observed in this case either. No improvement in the metathesis conversions could be detected after the first hour of the experiment. Therefore we suspect that although the metal in $\text{Mo}(\text{NCPh}_3)(\text{CH-t-Bu})\text{Np}(\text{OHIPT})$ is sterically more accessible toward olefin substrates, for the same reason some intermediate alkylidenes, especially $\text{Mo}(\text{NCPh}_3)(\text{CH}_2)\text{Np}(\text{OHIPT})$, are unstable toward bimolecular decomposition, while in $\text{Mo}(\text{NCPh}_3)(\text{CH-t-Bu})\text{Np}(\text{OAr}')$ and $\text{Mo}(\text{NCPh}_3)(\text{CH-t-Bu})\text{Np}(\text{OAr})$ the ortho methyl and isopropyl groups sterically prevent ready reaction of the initial neopentylidene complex with olefin substrate. Therefore only a small fraction of any initial neopentylidene complex is consumed.

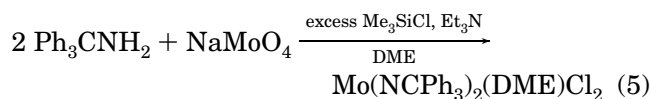
Attempted Synthesis of Tritylimido Neopentylidene Bisalkoxide Complexes. We were interested in whether $\text{Mo}(\text{NCPh}_3)(\text{CH-t-Bu})(\text{OR})_2$ catalysts could be prepared via the “bistriflate” route,³ which currently

Table 4. Catalytic Ring-Closing Metathesis Reactions

Substrate	Product	Catalyst ^a	time (h)	conv (%)
		Mo(Ph ₃ CN)(CH-t-Bu)(Np)(OAr)	0.3	4
			12	100
		Mo(Ph ₃ CN)(CH-t-Bu)(Np)(OAr')	1	85
			12	100
		Mo(Ph ₃ CN)(CH-t-Bu)(Np)(OHIPT)	1	40
			24	40
		Mo(Ph ₃ CN)(CH-t-Bu)(Np)(OAr)	12	54
			30	78 ^b
		Mo(Ph ₃ CN)(CH-t-Bu)(Np)(OAr')	1	89
		Mo(Ph ₃ CN)(CH-t-Bu)(Np)(OHIPT)	1	30
			24	36
		Mo(Ph ₃ CN)(CH-t-Bu)(Np)(OAr)	12	54
			30	75 ^b
		Mo(Ph ₃ CN)(CH-t-Bu)(Np)(OAr')	1	40
			24	89
		Mo(Ph ₃ CN)(CH-t-Bu)(Np)(OHIPT)	1	34
			24	34

^a Catalyst loading 5%, C₆D₆, rt. ^b The reaction mixture was heated to 65 °C for 18 h after 12 h at rt.

is the only route to bisalkoxide complexes of this general type. That would require the synthesis of Mo(NCPh₃)₂(DME)Cl₂ and Mo(NCPh₃)₂(CH₂-t-Bu)₂ and reaction of the latter with triflic acid to yield Mo(NCPh₃)(CH-t-Bu)(OTf)₂(DME). Mo(NCPh₃)₂(DME)Cl₂ was prepared as shown in eq 5 as a yellow powder in 66% yield. Alkylation of Mo(NCPh₃)₂(DME)Cl₂ with 2 equiv of PhMe₂CCH₂MgCl at -78 °C in ether gave Mo(NCPh₃)₂(CH₂CMe₂Ph)₂ in 60% yield as yellow crystals. However, addition of 3 equiv of triflic acid to Mo(NCPh₃)₂(CH₂CMe₂Ph)₂ yielded an orange oil whose ¹H NMR spectrum showed it to be a complex mixture of unidentifiable species, only a minor component of which could be the desired Mo(NCPh₃)(CHCMe₂Ph)(OTf)₂(DME). Varying the reaction conditions so far has not changed the outcome of this reaction. We suspect that the trityl group is cleaved from the imido nitrogen, although at this stage we have no proof. In any case, we must turn to alternative methods of preparing what we believe should be relatively stable Mo(NCPh₃)(CHCMe₂Ph)(OR)₂ complexes.



Conclusions

A variety of Mo(NR)Cl₄(THF) complexes can be prepared readily from azides and MoCl₄(THF)₂. Alkylation of Mo(NR)Cl₄(THF) is a viable route to Mo(NR)(CH-t-Bu)Np₂ species when R is trityl or 2,6-diisopropylphenyl. However, it is necessary to isolate intermediate Mo(NR)-Np₃Cl complexes, and these are formed in only modest yield. The stability of Mo(NCPh₃)(CH-t-Bu)Np₂ compared to Mo(NAd)(CH-t-Bu)Np₂ suggests that the stability of Mo=NR complexes (where R contains a quaternary carbon bound to Mo) will depend sensitively upon the steric bulk of R. Mo(NCPh₃)(CH-t-Bu)Np₂ reacts cleanly with certain alcohols to yield Mo(NCPh₃)-

(CH-t-Bu)(OR)Np complexes, which are potentially valuable variations of known Mo(NAr)(CH-t-Bu)(OR)Np complexes. We still consider syntheses of Mo(NR')(CH-t-Bu)(OR)₂ species in which R' is an alkyl group other than adamantyl a worthwhile goal, although alternative methods must be devised when R' is a CPh₃ group.

Experimental Section

General Details. All reactions were conducted in oven-dried (135 °C) and flame-dried glassware under an inert atmosphere of dry nitrogen employing standard Schlenk and glovebox techniques. Toluene, diethyl ether, and THF were degassed and then passed through a column of activated alumina. DME was distilled from sodium/benzophenone under nitrogen atmosphere. *n*-Pentane was washed with H₂SO₄ and water, dried over CaCl₂, degassed, and then passed through a column of activated alumina. MoCl₄(THF)₂,¹⁴ C₆F₅N₃,⁹ 3,5-(CF₃)₂C₆H₃N₃,¹⁰ 1-AdN₃,¹¹ Ph₃CN₃,¹² and 3,5-(2,4,6-*i*-Pr₃C₆H₂)₂-C₆H₃Br¹⁸ were prepared according to literature procedures.

¹H, ¹⁹F, and ¹³C NMR spectra were recorded on Varian spectrometers. Chemical shifts in ¹H and ¹³C NMR spectra are reported in ppm from tetramethylsilane with the solvent as an internal standard. ¹⁹F NMR spectra were referenced externally using C₆F₆ as a standard. Elemental analyses were performed by H. Kolbe Laboratories, Mülheim an der Ruhr, Germany.

2,6-*i*-Pr₂C₆H₃N₃.¹³ 2,6-Diisopropyl aniline (8.81 g, 0.049 mol) was dissolved in a mixture of concentrated HCl and H₂O (10/30 mL) and 30 g of ice. The mixture was stirred vigorously with a mechanical stirrer, and a solution of NaNO₂ (3.80 g, 0.055 mol) in 20 mL of water was added slowly over a period of 5 min. The mixture was stirred for 20 min, and then a saturated solution of NaHCO₃ (30 mL) was added. NaN₃ (3.71 g, 0.057 mol) in 30 mL of water was added. After 30 min the reaction mixture was warmed to room temperature and the organic layer was extracted with diethyl ether (3 × 50 mL). The ethereal fractions were combined and washed with a saturated solution of NaHCO₃ (50 mL) and water (2 × 50 mL) and dried over MgSO₄. The solvent was removed from the ether solution in vacuo, and the oily residue was chromatographed on silica gel with hexane as an eluent to yield the

product as a pale yellow, light-sensitive oil; yield 6.51 g (0.032 mol, 65%): ^1H NMR (C_6D_6) δ (ppm) 7.07–6.94 (m, 3H), 3.33 (septet, $J_{\text{HH}} = 6.9$ Hz, 2H), 1.12 (d, $J_{\text{HH}} = 6.9$ Hz, 12H); $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6) δ (ppm) 143.31 (s, 2C), 135.52 (s, 1C), 127.02 (s, 1C), 124.14 (s, 1C), 29.01 (s, 1C), 23.73 (s, 2C); IR (neat, KBr, cm^{-1}) 2125 (azide). These NMR data match those for the published material.¹³

$\text{Mo}(\text{NC}_6\text{F}_5)\text{Cl}_4(\text{THF})$. A 200 mL Schlenk vessel was loaded with $\text{MoCl}_4(\text{THF})_2$ (5.48 g, 14.3 mmol), pentafluorophenyl azide (6.00 g, 28.7 mmol), and 50 mL of toluene. The reaction mixture was heated to 50 °C and stirred under a flow of dinitrogen for 30 h. The reaction mixture was filtered, and the solvent was removed from the filtrate in vacuo to give a dark red solid. The solid was washed with cold pentane and dried to yield a red crystalline product; yield 6.16 g (12.0 mmol, 88%): ^1H NMR (C_6D_6 , ppm) δ 4.50 (m, 4H), 1.31 (m, 4H); ^{19}F NMR (C_6D_6 , ppm) δ -151.84 (m, 2F), -160.81 (m, 1F), -162.37 (m, 2F). Anal. Calcd for $\text{C}_{10}\text{H}_8\text{NOCl}_4\text{F}_5\text{Mo}$: C, 24.47; H, 1.64; N, 2.85; Cl, 28.99. Found: C, 24.51; H, 1.58; N, 2.79; Cl, 28.70.

$\text{Mo}(\text{N}[\text{3,5-(CF}_3)_2\text{C}_6\text{H}_3])\text{Cl}_4(\text{THF})$. A 200 mL Schlenk vessel was loaded with $\text{MoCl}_4(\text{THF})_2$ (4.68 g, 12.3 mmol), 3,5-bis-(trifluoromethyl)phenyl azide (3.75 g, 14.7 mmol), and 30 mL of toluene. The reaction mixture was heated to 60 °C and stirred under a flow of dinitrogen for 10 h. The reaction mixture was filtered, and the solvent was removed in vacuo to give a dark red solid. The solid was washed with cold pentane and dried to yield a red crystalline product; yield 4.93 g (9.2 mmol, 75%): ^1H NMR (C_6D_6 , ppm) δ 7.77 (s, 2H), 7.10 (s, 1H), 4.49 (m, 4H), 1.32 (m, 4H); ^{19}F NMR (C_6D_6 , ppm) δ -62.66 (s, 6F); ^{13}C NMR (C_6D_6 , ppm) δ 152.8 (s), 132.8 (q, $J_{\text{C-F}} = 34.6$ Hz), 129.9 (s), 127.4 (s), 122.6 (q, $J_{\text{C-F}} = 274.1$ Hz), 74.7 (s), 25.9 (s). Anal. Calcd for $\text{C}_{12}\text{H}_{11}\text{NOCl}_4\text{F}_6\text{Mo}$: C, 26.84; H, 2.06; N, 2.61; Cl, 26.41. Found: C, 26.73; H, 2.11; N, 2.55; Cl, 26.58.

Single crystals for the X-ray study were grown from a pentane solution at -30 °C.

$\text{Mo}(\text{Nad})\text{Cl}_4(\text{THF})$. A 300 mL Schlenk vessel was loaded with $\text{MoCl}_4(\text{THF})_2$ (7.52 g, 19.7 mmol), 1-adamantyl azide (3.49 g, 19.7 mmol), and 100 mL of toluene. The reaction mixture was heated to 55 °C and stirred under a flow of nitrogen for 17 h. The reaction mixture was filtered, and the solvent was removed under vacuum to give a dark red solid. The solid was triturated with pentane for 10 h, and the mixture was filtered and the red crystalline product thereby isolated; yield 8.34 g (18.3 mol, 93%): ^1H NMR (C_6D_6 , ppm) δ 4.55 (br s, 4H), 2.25 (d, $J_{\text{HH}} = 3$ Hz, 6H), 1.74 (br s, 3H), 1.35 (br s, 4H), 1.14 (t, $J_{\text{HH}} = 3$ Hz, 6H). Anal. Calcd for $\text{C}_{14}\text{H}_{23}\text{NOCl}_4\text{Mo}$: C, 36.63; H, 5.05; N, 3.05; Cl, 30.89. Found: C, 36.54; H, 5.12; N, 2.72; Cl, 30.75.

$\text{Mo}(\text{NAr})\text{Cl}_4(\text{THF})$. ArN_3 (3.35 g, 16.4 mmol) was added to a suspension of $\text{MoCl}_4(\text{THF})_2$ (6.28 g, 16.4 mmol) in 50 mL of toluene, and the mixture was heated to 50 °C for 12 h under a flow of dinitrogen. The dark red reaction mixture was then cooled to room temperature and filtered, and the solvent was removed from the filtrate under vacuum to give dark red solid. The solid was stirred in pentane for 24 h, and the mixture was filtered and the product dried to give a red powder (5.30 g, 10.9 mmol, 66%): ^1H NMR (C_6D_6 , ppm) δ 6.91 (d, $J_{\text{HH}} = 7.6$ Hz, 2H), 6.44 (t, $J_{\text{HH}} = 7.6$ Hz, 1H), 5.08 (septet, $J_{\text{HH}} = 6.4$ Hz, 2H), 4.53 (s, 4H), 1.23 (d, $J_{\text{HH}} = 6.7$ Hz, 16H). Anal. Calcd for $\text{C}_{16}\text{H}_{25}\text{NOCl}_4\text{Mo}$: C, 39.61; H, 5.19; Cl, 29.23; N, 2.89. Found: C, 39.73; H, 5.25; Cl, 29.82; N, 2.84.

$\text{Mo}(\text{NCPH}_3)\text{Cl}_4(\text{THF})$. Ph_3CN_3 (7.12 g, 25 mmol) was added to a suspension of $\text{MoCl}_4(\text{THF})_2$ (9.54 g, 25 mmol) in 100 mL of toluene, and the mixture was stirred for 12 h at room temperature under a flow of N_2 . The dark red reaction mixture was filtered, and the solvent was removed in vacuo. The dark red solid residue was triturated with pentane for 24 h, and the product was filtered off and dried in vacuo; yield 13.69 g (24 mmol, 96%): ^1H NMR (C_6D_6 , ppm) δ 7.75–7.72 (m, 6H), 7.17–7.00 (m, 9H), 4.42 (s, 4H), 1.26 (s, 4H). Anal. Calcd for

$\text{C}_{23}\text{H}_{23}\text{NOCl}_4\text{Mo}$: C, 48.70; H, 4.09; Cl, 25.00; N, 2.47. Found: C, 48.86; H, 4.03; Cl, 24.82; N, 2.39.

$\text{Mo}(\text{NC}_6\text{F}_5)(\text{CH}_2\text{-t-Bu})_3\text{Cl}$. A solution of $\text{t-BuCH}_2\text{MgCl}$ (25.0 mmol) in 20 mL of ether was cooled to -78 °C, and a solution of $\text{Mo}(\text{NC}_6\text{F}_5)\text{Cl}_4(\text{THF})$ (4.09 g, 8.3 mmol) in 20 mL of toluene was added to it dropwise with stirring. The reaction mixture was stirred at -78 °C for 20 min, then warmed to 20 °C and stirred for 2 h. The solvents were removed in vacuo, the solid residue was extracted with 70 mL of pentane, and the mixture was filtered. The pentane was removed in vacuo to give the pale yellow crystalline product; yield 1.84 g (3.7 mmol, 45%): ^1H NMR (C_6D_6 , ppm) δ 3.275 (s, 6H), 1.155 (s, 27H); ^{19}F NMR (C_6D_6 , ppm) δ -141.27 (d, $J_{\text{FF}} = 22.2$ Hz, 2F), -151.55 (m, F), -160.31 (m, 2F). Anal. Calcd for $\text{C}_{21}\text{H}_{33}\text{NClF}_5\text{Mo}$: C, 47.96; H, 6.33; N, 2.66; Cl, 6.74. Found: C, 47.81; H, 6.27; N, 2.56; Cl, 6.63.

$\text{Mo}(\text{N}[\text{3,5-(CF}_3)_2\text{C}_6\text{H}_3])(\text{CH}_2\text{-t-Bu})_3\text{Cl}$. A solution of $\text{t-BuCH}_2\text{MgCl}$ (37.4 mmol) in 25 mL of diethyl ether was cooled to -78 °C, and a solution of $\text{Mo}[\text{3,5-(CF}_3)_2\text{C}_6\text{H}_3\text{N}]\text{Cl}_4(\text{THF})$ (7.13 g, 12.5 mmol) in 35 mL of ether was added to it dropwise while the mixture was stirred. The reaction mixture was stirred at -78 °C for 1 h, then it was warmed to 20 °C and stirred for 2 h. Ether was removed in vacuo, and the solid residue was extracted with 400 mL of pentane for 2 h. The mixture was filtered and pentane was removed from the filtrate in vacuo to give the yellow crystalline product; yield 2.52 g (4.4 mmol, 35%): ^1H NMR (C_6D_6 , ppm) δ 8.16 (s, 2H), 7.52 (s, 1H), 3.09 (s, 6H), 1.05 (s, 27H); ^{19}F NMR (C_6D_6 , ppm) δ -62.49 (s, 6F); ^{13}C NMR (C_6D_6 , ppm) δ 154.3 (quintet, $J_{\text{CF}} = 4$ Hz), 133.3 (q, $J_{\text{CF}} = 34.6$ Hz), 129.0 (s), 126.6 (s), 122.6 (q, $J_{\text{CF}} = 274.1$ Hz), 86.7 (s), 36.1 (s), 33.7 (s). Anal. Calcd for $\text{C}_{23}\text{H}_{36}\text{NClF}_6\text{Mo}$: C, 48.30; H, 6.34; N, 2.45; Cl, 6.20. Found: C, 48.16; H, 6.29; N, 2.40; Cl, 6.30.

Single crystals for the X-ray study were grown from a pentane solution at -30 °C.

$\text{Mo}(\text{Nad})(\text{CH}_2\text{-t-Bu})_3\text{Cl}$. A solution of $\text{t-BuCH}_2\text{MgCl}$ (4.00 mmol) in 15 mL of diethyl ether was cooled to -78 °C, and a solution of $\text{Mo}(\text{Nad})\text{Cl}_4(\text{THF})$ (608 mg, 1.33 mmol) in 15 mL of toluene was added to it dropwise with stirring. The reaction mixture was warmed to 20 °C and stirred for 2 h. The solvents were removed in vacuo, and the solid residue was extracted with 100 mL of pentane. The mixture was filtered and the pentane was removed in vacuo to give a brown crystalline product; yield 193 mg (0.68 mmol, 51%): ^1H NMR (C_6D_6 , ppm) δ 2.92 (s, 6H), 2.21 (d, $J_{\text{HH}} = 2.8$ Hz, 6H), 1.59 (s, 3H), 1.41 (br s, 6H), 1.24 (s, 27H). Anal. Calcd for $\text{C}_{25}\text{H}_{48}\text{NClMo}$: C, 60.78; H, 9.79; N, 2.84; Cl, 7.18. Found: C, 60.65; H, 9.85; N, 2.73; Cl, 7.14.

$\text{Mo}(\text{NAr})(\text{CH}_2\text{-t-Bu})_3\text{Cl}$. $\text{Mo}(\text{NAr})\text{Cl}_4(\text{THF})$ (915 mg, 1.89 mmol) was dissolved in 10 mL of toluene. The solution was cooled to -30 °C and added dropwise to a -30 °C solution of $\text{t-BuCH}_2\text{MgCl}$ (5.66 mmol) in 5 mL of diethyl ether. The mixture was stirred at room temperature for 18 h. The solvents were removed in vacuo, and the resulting brown residue was extracted with pentane. The mixture was filtered and the solvent was removed in vacuo to give yellow powder; yield 414 mg (0.0796 mmol, 42%): ^1H NMR (C_6D_6 , ppm) δ 6.97 (s, 3H), 4.07 (septet, $J_{\text{HH}} = 6.6$ Hz, 2H), 3.04 (s, 6H), 1.25 (s, 27H), 1.22 (d, $J_{\text{HH}} = 6.6$ Hz, 12H). Anal. Calcd for $\text{C}_{27}\text{H}_{50}\text{NClMo}$: C, 62.35; H, 9.69; Cl, 6.82; N, 2.69. Found: C, 62.31; H, 9.56; Cl, 6.74; N, 2.71.

$\text{Mo}(\text{NCPH}_3)(\text{CH}_2\text{-t-Bu})_3\text{Cl}$. $\text{Mo}(\text{NCPH}_3)\text{Cl}_4(\text{THF})$ (13.6 g, 24 mmol) was dissolved in 50 mL of toluene. The solution was cooled to -78 °C and added dropwise to a solution of $\text{t-BuCH}_2\text{MgCl}$ (77 mmol) in 100 mL of diethyl ether. The mixture was stirred at room temperature for 3 h. The solvents were removed in vacuo, and the resulting brown residue was extracted with 400 mL of pentane. The extract was filtered, and the solution was reduced in volume in vacuo to 100 mL and left at -30 °C for 12 h. The first crop of off-white crystals was collected, and the remaining solution was reduced in

volume to 20 mL and left at $-30\text{ }^{\circ}\text{C}$ for 1 day. Three additional crops were collected over a period of 3 days; yield 6.28 g (10 mmol, 42%): ^1H NMR (C_6D_6 , ppm) δ 7.44–7.41 (m, 6H), 7.16–7.05 (m, 9H), 3.12 (s, 6H), 1.03 (s, 27H). Anal. Calcd for $\text{C}_{34}\text{H}_{48}\text{NClMo}$: C, 67.82; H, 8.03; Cl, 5.89; N, 2.33. Found: C, 68.48; H, 8.26; Cl, 5.69; N, 2.17.

Single crystals for the X-ray study were grown from a pentane solution at $-30\text{ }^{\circ}\text{C}$.

Mo(NAr)(CH-t-Bu)(CH₂-t-Bu)₂. Mo(NAr)(CH₂-t-Bu)₃Cl (465 mg, 0.89 mmol) and LiCH₂-t-Bu (69.4 mg, 0.89 mmol) were dissolved in 5 mL of pentane in separate vials, and each solution was cooled to $-30\text{ }^{\circ}\text{C}$. The solution of Mo(NAr)(CH₂-t-Bu)₃Cl was added to the solution of LiCH₂-t-Bu, and the mixture was stirred at room temperature for 12 h. The LiCl was removed by filtration. The filtrate was stirred with dry activated charcoal and filtered, and the solvent was removed to give a brown powder; yield 389 mg (0.80 mmol, 90%). The NMR spectral data for this compound match those reported.¹

Mo(NCPh₃)(CH-t-Bu)(CH₂-t-Bu)₂. Mo(NCPh₃)(CH₂-t-Bu)₃-Cl (600 mg, 0.95 mmol) was dissolved in 6 mL of toluene, and the solution was cooled to $-30\text{ }^{\circ}\text{C}$. Solid LiCH₂-t-Bu (81.7 mg, 1.05 mmol) was added to the solution, and the reaction mixture was stirred for 24 h at room temperature. Activated charcoal was added to the reaction mixture, and the mixture was stirred for 1 h. Toluene was removed in vacuo. The mixture was redissolved in pentane, and the solution was filtered. The pentane was removed in vacuo to yield an ivory powder; yield 539 mg (0.91 mmol, 96%): ^1H NMR (C_6D_6 , ppm) δ 8.95 (s, $J_{\text{CH}} = 108.5\text{ Hz}$, 1H), 7.61–7.58 (m, 6H), 7.15–7.02 (m, 9H), 2.45 (d, $J_{\text{HH}} = 11.7\text{ Hz}$, 2H), 1.10 (s, 18H), 1.06 (s, 9H), 0.98 (d, $J_{\text{HH}} = 11.7\text{ Hz}$, 2H). Anal. Calcd for $\text{C}_{34}\text{H}_{47}\text{NMo}$: C, 72.19; H, 8.37; N, 2.48. Found: C, 72.28; H, 8.24; N, 2.39.

Conversion of Mo(NAr)(CH₂-t-Bu)₃Cl to Mo(NAr)(CH-t-Bu)(CH₂-t-Bu)₂Cl. Mo(NAr)(CH₂-t-Bu)₃Cl (32.1 mg, 0.062 mmol) was dissolved in 0.6 mL of C_6D_6 in a J. Young tube to give a 0.1 N solution, and the solution was heated to $50\text{ }^{\circ}\text{C}$ for 8 h. The ^1H NMR spectrum showed that Mo(NAr)(CH₂-t-Bu)₃-Cl had been converted quantitatively to Mo(NAr)(CH-t-Bu)(CH₂-t-Bu)₂Cl in a reaction that was unimolecular with $k = 9.0 \times 10^{-5}\text{ s}^{-1}$: ^1H NMR (C_6D_6 , ppm) δ 11.71 (s, $J_{\text{CH}} = 109\text{ Hz}$, 1H), 6.97 (s, 3H), 3.82 (septet, $J_{\text{HH}} = 6.9\text{ Hz}$, 2H), 2.63 (d, $J_{\text{HH}} = 13.2\text{ Hz}$, 1H), 1.91 (d, $J_{\text{HH}} = 13.2\text{ Hz}$, 1H), 1.22 (s, 3H), 1.20 (s, 3H), 1.19 (s, 3H), 1.17 (s, 3H), 1.14 (s, 9H), 1.01 (s, 9H).

A 0.2 N solution of Mo(NAr)(CH₂-t-Bu)₃Cl (72.8 mg, 0.14 mmol) in 0.7 mL of C_6D_6 was heated to $50\text{ }^{\circ}\text{C}$ for 8 h. The reaction was unimolecular with $k = 9.5 \times 10^{-5}\text{ s}^{-1}$. At an initial concentration of 0.1 M $k_{50} = 9.0 \times 10^{-5}\text{ s}^{-1}$.

A 0.1 N solution of Mo(NAr)(CH₂-t-Bu)₃Cl (35 mg, 0.07 mmol) in 0.7 mL of C_6D_6 was heated to $60\text{ }^{\circ}\text{C}$ for 4 h. The reaction was unimolecular with $k = 3.0 \times 10^{-4}\text{ s}^{-1}$.

Mo(NCPh₃)Np₃(OC₆F₅). Mo(NCPh₃)(CH-t-Bu)(CH₂-t-Bu)₂ (244 mg, 0.41 mmol) was dissolved in 4 mL of benzene, and solid $\text{C}_6\text{F}_5\text{OH}$ (75.6 mg, 0.41 mmol) was added. The mixture was stirred for 24 h, then benzene was removed and the solid residue was redissolved in 5 mL of pentane and stirred with dry activated charcoal for 1 h. The solution was filtered, and the solvent was removed from the filtrate to give off-white powder; yield 293 mg (0.38 mmol, 93%): ^1H NMR (C_6D_6 , ppm) δ 7.50–7.47 (m, 6H), 7.17–7.06 (m, 9H), 2.76 (s, 6H), 0.93 (s, 27H); ^{19}F NMR (C_6D_6 , ppm) δ -156.08 (m, 2F), -165.46 (m, 2F), -175.42 (m, 1F). Anal. Calcd for $\text{C}_{41}\text{H}_{56}\text{NOF}_5\text{Mo}$: C, 63.97; H, 7.33; N, 1.82. Found: C, 64.14; H, 7.24; N, 1.76.

3,5-(2,4,6-i-Pr₃C₆H₂)₂C₆H₃OH (HIPTOH).¹⁷ Li-n-Bu (0.85 mmol) was added to a solution of 3,5-(2,4,6-i-Pr₃C₆H₂)₂-C₆H₃Br (400 mg, 0.71 mmol) in 20 mL of dry THF that had been cooled to $-78\text{ }^{\circ}\text{C}$. In 15 min B(OMe)₃ (0.24 mL, 2.13 mmol) was added to the mixture. The mixture was allowed to warm to room temperature and was stirred for 2 h. Anhydrous *N*-methylmorpholine *N*-oxide (250 mg, 2.13 mmol) was added to the reaction mixture, and the mixture was refluxed for 5 h. The mixture was diluted with 50 mL of diethyl ether and

washed with water ($5 \times 50\text{ mL}$). The aqueous washes were extracted with ether, and the ethereal fractions were combined and dried with MgSO_4 . The solvents were removed in vacuo, and the oily residue was transferred to a silica gel column and eluted with hexanes, then a 5:1 hexanes/ether mixture and then a 1:1 hexanes/ether mixture. The second collected fraction upon solvent removal gave a white powder; yield 260 mg (0.52 mmol, 73%): ^1H NMR (C_6D_6 , ppm) δ 7.20 (s, 4H), 7.13 (s, 2H), 6.53 (s, 1H), 3.91 (s, 1H), 3.03 (septet, $J_{\text{HH}} = 11.3\text{ Hz}$, 4H), 2.87 (septet, $J_{\text{HH}} = 11.1\text{ Hz}$, 2H), 1.28 (d, $J_{\text{HH}} = 11.3\text{ Hz}$, 24H), 1.22 (septet, $J_{\text{HH}} = 11.1\text{ Hz}$, 12H).

Mo(NCPh₃)(CH-t-Bu)Np(OAr). Mo(NCPh₃)(CH-t-Bu)(CH₂-t-Bu)₂ (228 mg, 0.38 mmol) was dissolved in 2 mL of pentane, and 2,6-diisopropyl phenol (68.5 mg, 0.38 mmol) was added. The solution was stirred for 24 h. Activated charcoal was added, and the mixture was stirred for 1 h. The solution was filtered, and the solvent was removed to give a brown oil; yield 235 mg (0.35 mmol, 92%): ^1H NMR (C_6D_6 , ppm) δ 11.81 (s, 1H), 7.53–7.50 (m, 6H), 7.14–6.93 (m, 12H), 3.44 (quintet, $J_{\text{HH}} = 6.9\text{ Hz}$, 2H), 2.82 (d, $J_{\text{HH}} = 12.5\text{ Hz}$, 1H), 2.29 (d, $J_{\text{HH}} = 12.5\text{ Hz}$, 1H), 1.19 (s, 9H), 1.19 (d, $J_{\text{HH}} = 6.6\text{ Hz}$, 12H), 1.10 (s, 9H); ^{13}C NMR (C_6D_6 , ppm) δ 278.38 (d, $J_{\text{CH}} = 111.7\text{ Hz}$). Anal. Calcd for $\text{C}_{41}\text{H}_{53}\text{NOMo}$: C, 73.30; H, 7.95; N, 2.08. Found: C, 73.15; H, 7.90; N, 1.96.

Mo(NCPh₃)(CH-t-Bu)Np(OAr'). Mo(NCPh₃)(CH-t-Bu)(CH₂-t-Bu)₂ (486 mg, 0.76 mmol) was dissolved in 2 mL of pentane, and 2,6-dimethyl phenol (92.5 mg, 0.82 mmol) was added. The solution was stirred for 24 h. Activated charcoal was added, and the mixture was stirred for 1 h. The solution was filtered, and the solvent was removed in vacuo to give the product as a yellow powder; yield 434 mg (0.71 mmol, 93%): ^1H NMR (C_6D_6 , ppm) δ 11.69 (s, 1H), 7.54–7.16 (m, 6H), 7.10–6.93 (m, 9H), 6.88–6.74 (m, 3H), 2.73 (d, $J_{\text{HH}} = 12.4\text{ Hz}$, 1H), 2.34 (d, $J_{\text{HH}} = 12.4\text{ Hz}$, 1H), 2.16 (s, 6H), 1.16 (s, 9H), 1.08 (s, 9H). ^{13}C NMR (C_6D_6 , ppm): δ 277.52 (d, $J_{\text{CH}} = 109.4\text{ Hz}$). Anal. Calcd for $\text{C}_{37}\text{H}_{45}\text{NOMo}$: C, 72.18; H, 7.37; N, 2.27. Found: C, 72.06; H, 7.41; N, 2.19.

Mo(NCPh₃)(CH-t-Bu)Np(OHIPT). Mo(NCPh₃)(CH-t-Bu)(CH₂-t-Bu)₂ (159 mg, 0.32 mmol) was dissolved in 2 mL of pentane, and 2 mL of ether and solid HIPTOH (189 mg, 0.32 mmol) was added. The solution was stirred for 24 h. Activated charcoal was added, and the mixture was stirred for 1 h. The solution was filtered and the solvent was removed to give the product as a golden yellow powder; yield 299 mg (0.30 mmol, 95%): ^1H NMR (C_6D_6 , ppm) δ 11.45 (s, 1H), 7.57–7.42 (m, 8H), 7.32–6.90 (m, 13H), 6.72 (s, 1H), 3.08 (septet, $J_{\text{HH}} = 11.3\text{ Hz}$, 4H), 2.88 (septet, $J_{\text{HH}} = 11.1\text{ Hz}$, 2H), 2.53 (d, $J_{\text{HH}} = 13\text{ Hz}$, 1H), 2.26 (d, $J_{\text{HH}} = 13\text{ Hz}$, 1H), 1.30 (d, $J_{\text{HH}} = 11.3\text{ Hz}$, 24H), 1.22 (s, 9H), 1.19 (d, $J_{\text{HH}} = 11.1\text{ Hz}$, 12H), 1.03 (s, 9H); ^{13}C NMR (C_6D_6 , ppm): δ 278.00 (d, $J_{\text{CH}} = 112.8\text{ Hz}$). Anal. Calcd for $\text{C}_{65}\text{H}_{85}\text{NOMo}$: C, 78.67; H, 8.63; N, 1.41. Found: C, 78.58; H, 8.57; N, 1.37.

Single crystals for the X-ray study were grown from a pentane solution at $-30\text{ }^{\circ}\text{C}$.

Mo(NCPh₃)₂Cl₂(dme). Ph₃CNH₂ (11.53 g, 0.044 mol), Na₂MoO₄ (4.53 g, 0.022 mol), Et₃N (8.90 g, 12.3 mL, 0.088 mol), and trimethylsilyl chloride (23.9 g, 27.9 mL, 0.22 mol) were dissolved in 150 mL of dry DME. Upon stirring at $65\text{ }^{\circ}\text{C}$ for 12 h the mixture became bright yellow. The solids were filtered off and the solvent was removed from the filtrate in vacuo to give a yellow powder. The yellow powder was triturated with 100 mL of pentane, filtered off, and dried in vacuo. The pentane washes were reduced to 20 mL in volume in vacuo, and an additional crop of the product was crystallized from this solution; yield 11.27 g (0.015 mol, 66%): ^1H NMR (C_6D_6 , ppm) δ 7.57–7.53 (m, 12H), 7.03–7.01 (m, 18H), 3.05 (s, 4H), 3.01 (s, 6H). Anal. Calcd for $\text{C}_{42}\text{H}_{40}\text{N}_2\text{O}_2\text{Cl}_2\text{Mo}$: C, 65.37; H, 5.23; N, 3.63; Cl, 9.19. Found: C, 65.47; H, 5.20; N, 3.51; Cl, 9.23.

Mo(NCPh₃)₂(CH₂CMe₃)₂. A solution of Mo(Ph₃CN)₂Cl₂-(dme) (2.06 g, 3.63 mmol) dissolved in 30 mL of toluene was

cooled to $-78\text{ }^{\circ}\text{C}$. A solution of $(\text{PhCMe}_2\text{CH}_2)\text{MgCl}$ (7.25 mmol) in 15 mL of ether was added dropwise to the reaction mixture. The mixture was allowed to warm to room temperature and was stirred for 12 h. The solvents were removed in vacuo, and the solid residue was redissolved in 20 mL of toluene. After addition of 4 mL of 1,4-dioxane the mixture was stirred for 1 h and the white precipitate was removed by filtration. The solvents were removed in vacuo, and the solid was triturated with pentane overnight. The product was filtered off, and the pentane washes were reduced to 5 mL and left at $-35\text{ }^{\circ}\text{C}$ for 12 h. The material that crystallized from pentane was collected and combined with the solid obtained from trituration to give a tan powdery product; yield 1.84 g (2.1 mmol, 58%): ^1H NMR (C_6D_6 , ppm) δ 7.26–7.12 (m, 16H), 7.10–7.01 (m, 24H), 2.13 (s, 4H), 1.34 (s, 12H). Anal. Calcd for $\text{C}_{58}\text{H}_{56}\text{N}_2\text{Mo}$: C, 79.43; H, 6.44; N, 3.19. Found: C, 79.57; H, 6.41; N, 3.11.

Representative Olefin Metathesis with $\text{Mo}(\text{NCPH}_3)(\text{CH-t-Bu})\text{Np}(\text{OR})$ Complexes. Diallyl ether (10.6 mg, 0.108 mmol) was dissolved in 1 mL of C_6D_6 in a 20 mL vial, and $\text{Mo}(\text{NCPH}_3)(\text{CH-t-Bu})\text{Np}(\text{OHIPt})$ (5.4 mg, 5.5×10^{-3} mmol) was added. The reaction mixture was stirred for 1 h and then transferred to a J. Young tube. Conversion of the ring-closing metathesis reaction with time was judged by analysis of the ^1H NMR spectrum. The amine substrates shown in Table 4 were prepared as described in the literature.¹⁹

Crystallography. Low-temperature diffraction data were collected on a Siemens Platform three-circle diffractometer coupled to a Bruker-AXS Smart 1K CCD detector (for the structures of $\text{Mo}[\text{N-3,5-(CF}_3)_2\text{C}_6\text{H}_3](\text{CH}_2\text{-t-Bu})_3\text{Cl}$ and $\text{Mo}(\text{Ph}_3\text{CN})(\text{CH}_2\text{-t-Bu})_3\text{Cl}$) or a Bruker-AXS Apex CCD detector (for the structures of $\text{Mo}[\text{N-3,5-(CF}_3)_2\text{C}_6\text{H}_3]\text{Cl}_4(\text{THF})$ and $\text{Mo}(\text{NCPH}_3)(\text{CH-t-Bu})\text{Np}(\text{OHIPt})$) with graphite-monochromated Mo $\text{K}\alpha$ radiation ($\lambda = 0.71073\text{ \AA}$), performing ϕ and ω scans. All four structures were solved by direct methods using SHELXS²⁰ and refined against F^2 on all data by full-matrix least squares with SHELXL-97 (Sheldrick, G. M. *SHELXL 97*; Universität Göttingen: Göttingen, Germany, 1997). All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were included in the model at geometrically calculated positions and refined using a riding model. The isotropic displacement parameters of the hydrogen atoms were fixed to 1.2 times the U value of the atoms they are linked to (1.5 times for methyl groups).

The space group determination for $\text{Mo}(\text{NCPH}_3)(\text{CH-t-Bu})\text{Np}(\text{OHIPt})$ was problematic. The data intensity statistics suggests a non-centrosymmetric space group, and no system-

atic absences were found. However, a closer look suggested the presence of both a 2-fold screw axis along b and a glide plane, compatible only with the space group $P2_1/c$. Even though all systematic absences were somewhat violated, a solution could be found in this space group. The refinement, however, was not stable, and practically all carbon atoms seemed to be involved in disorders. The structure can also be solved in the triclinic space group $P1$ with four crystallographically independent molecules. Analysis of the coordinates in this solution with the program PLATON²¹ resulted in 100% equivalence with $P2_1$ and only 90% equivalence with $P2_1/c$. Therefore the structure was solved and refined in the monoclinic space group $P2_1$ with two crystallographically independent molecules in the asymmetric unit. The two crystallographically independent molecules are basically a pair of enantiomers. In addition to the pseudo-inversion, the two molecules differ from one another significantly in several bond lengths and angles, thereby avoiding the higher symmetric space group $P2_1/c$. This explains the problems described above. The structure was refined as a racemic twin (twin law $-1\ 0\ 0\ 0\ -1\ 0\ 0\ 0\ -1$); the twin ratio refined to 0.43(3). To break the parameter correlation arising from the pseudo-symmetry, similarity restraints as well as rigid bond restraints for anisotropic displacement parameters were applied to all atoms. Three disordered $i\text{-Pr}$ groups were refined with the help of similarity restraints on 1–2 and 1–3 distances and constraining the anisotropic displacement parameters of equivalent atoms to be identical. The occupancies for the disordered components were refined freely.

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Supporting Information Available: Experimental details, fully labeled thermal ellipsoid drawing, crystal data and structure refinement, atomic coordinates, bond lengths and angles, anisotropic displacement parameters, hydrogen coordinates, isotropic displacement parameters, and torsion angles for $\text{Mo}[\text{N-3,5-(CF}_3)_2\text{C}_6\text{H}_3]\text{Cl}_4(\text{THF})$, $\text{Mo}[\text{N-3,5-(CF}_3)_2\text{C}_6\text{H}_3](\text{CH}_2\text{-t-Bu})_3\text{Cl}$, $\text{Mo}(\text{NCPH}_3)(\text{CH}_2\text{-t-Bu})_3\text{Cl}$, and $\text{Mo}(\text{NCPH}_3)(\text{CH-t-Bu})(\text{CH}_2\text{-t-Bu})(\text{OHIPt})$. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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