Improved Preparations of Molybdenum Coordination Compounds from Tetrachlorobis(diethyl ether)molybdenum(IV)

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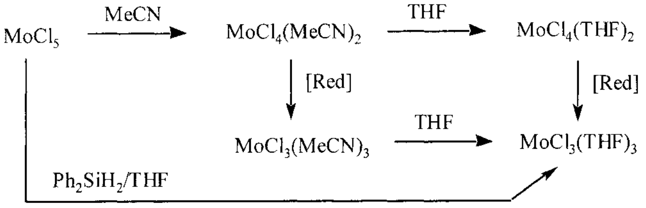
The reduction of $MoCl_5$ with metallic tin in diethyl ether provides a rapid and convenient entry to $[MoCl_4(OEt_2)_2]$ This compound can be transformed easily and in high yields into a variety of other useful synthons. The loss of ether in the solid state affords a new and reactive form of $MoCl_4$. Treatment with THF, PMe_3 or LiO*t*Bu affords $[MoCl_4(THF)_2]$, $[MoCl_4(PMe_3)_3]$ or $[Mo(OtBu)_4]$ in high isolated yields. Treatment with metallic tin in THF affords $[MoCl_3(THF)_3]$ All of these reactions can be carried out under simple experimental conditions and represent significant improvements relative to previously reported syntheses of the same compounds.

Introduction

The element molybdenum displays a very rich chemistry in low, intermediate and high oxidation states. Research with this metal is intense in the organometallic/catalysis, coordination, bioinorganic, cluster, and solid state/materials fields. However, all this activity stems from a very limited amount of commercially available Mo-containing starting materials, the most convenient ones being elemental Mo, $Mo(CO)_6$, MoS_2, MoO_3 and $MoCl_5$. Some transformations require long, multiple-step procedures, resulting in a considerable investment of time and, perhaps more importantly, in considerable product losses due to the compounding of imperfect reaction yields. The improvement of known synthetic methods and the search for alternative procedures allowing a reduction of reaction times, the simplification of isolation and purification procedures, and an increase of overall yields are continuous goals of the synthetic chemist.

The situation is perhaps best illustrated by the example of $[MoCl_3(THF)_3]$, a useful intermediate for a wide variety of inorganic synthetic applications. Following the first reported preparation by a carbonyl route,[1] the compound was subsequently obtained by a reductive procedure starting from $MoCl_5$. This pentachloride compound is a strong Lewis acid and also a powerful oxidant and its direct reduction in THF is complicated by the acid-catalysed ring opening polymerization of THF, a problem which is circumvented by using other solvents. The most commonly employed synthetic procedure (Scheme 1) starts with the interaction of $MoCl_5$ with a nitrile RCN to afford $[MoCl_4(RCN)_2]$, followed by replacement of the nitrile with THF and final reduction to the Mo^{III} product. A variety of improvements of this procedure have been published over the years including three reports in Inorganic Synthesis, replacing propionitrile with acetonitrile, zinc with tin as the reducing agent, and modifying the reaction conditions and product separation procedures.[2−7] Nevertheless, this three-step procedure remains rather long and requires, in our hands, isolation of both $[MoCl_4(MeCN)_2]$ and $[MoCl_4(THF)_2]$ intermediates in order to obtain a product of sufficient quality. With individual step yields of 63−86%, the overall yield from $MoCl_5$ is 46% at best with a time investment of more than two days. Another variation on the same theme (Scheme 1) is the reduction of $[MoCl_4(MeCN)_2]$ to $[MoCl_3(MeCN)_3]$, followed by solvent exchange.[8] A direct and rapid one-step, high-yield (85%) procedure has been published more recently, but this requires the use of Ph_2SiH_2 as a reducing agent and a controlled, slow addition of the $MoCl_5$ solid to the silane-containing THF solution.[9] A reverse addition of the silane to $MoCl_5$ is possible only in pentane as solvent, prolonging the reaction time to 48 h.



Scheme 1

Our continued interest in the coordination and organometallic chemistry of middle-valent molybdenum continuously pushes us to improve the preparative procedures of our required synthetic intermediates. Our attention has been attracted by $[MoCl_4(OEt_2)_2]$, whose high yield synthesis was reported a few years ago from $MoCl_5$ and either norbornene[10] or allyltrimethylsilane[11] as reducing agents. However, only a limited use of this compound in sub-

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sequent synthetic work was described. In this contribution, we shall show that $[MoCl_4(OEt_2)_2]$ can also be conveniently prepared by tin reduction of $MoCl_5$, and that it is a versatile intermediate for the preparation of a variety of other molybdenum compounds. In particular, $[MoCl_3(THF)_3]$ is now accessible in a half-day, two-step, single-flask procedure (no isolation of intermediates is required) in greater than 80% overall yields from $MoCl_5$ and the common reagents ether, THF, and metallic tin.

Results and Discussion

While the high Lewis acidity of $MoCl_5$ makes this compound incompatible with the THF solvent, causing its cationic ring-opening polymerization, non-cyclic ethers do not suffer from this decomposition pathway. Ethereal solutions of $MoCl_5$ are stable and are rapidly reduced by metallic tin to yield a fine, orange, crystalline powder of $[MoCl_4(OEt_2)_2]$ [Equation (1)]. The reaction is fast but controlled at room temperature, and is usually complete within 0.5 h as evident from the visual appearance of the powdery orange precipitate. No wild exothermic behavior has been observed during this reductive process, which therefore does not require any special precautions. In addition, the tin chloride co-product is ether-soluble while $[MoCl_4(OEt_2)_2]$ is only sparingly soluble. Therefore, the Mo^{IV} product is easily purified by washing with ether with only minimal product loss. The yields of this preparation are consistently greater than 80% for quantities of product greater than a gram. These yields and the product purity are comparable with those of the previously reported syntheses, which used more exotic reducing agents such as allyltrimethylsilane or norbornene.[10,11] It should be noted that a possible by-product, $[MoOCl_3(Et_2O)_2]$,[12] may form when wet ether and/or partially hydrolyzed $MoCl_5$ starting compound are employed. This compound, however, is green and soluble in ether,[10] while the $[MoCl_4(Et_2O)_2]$ product is orange and sparingly soluble. Thus, minor impurities of the molybdenyl species may be easily eliminated. In our work, we found no evidence for the formation of this by-product.

$$2\,MoCl_5 + Sn \xrightarrow{Et_2O} 2\,MoCl_4(OEt_2)_2 + SnCl_2 \qquad (1)$$

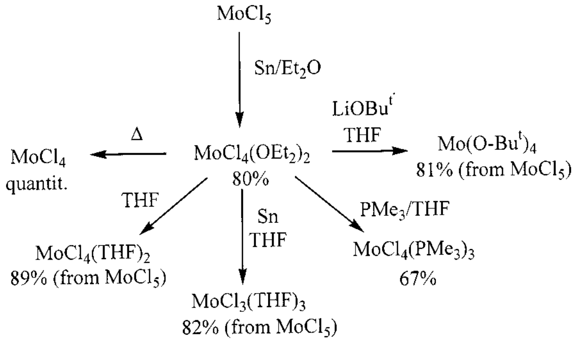
We have not investigated in detail the nature of the oxidized tin product. The literature reports that $SnCl_2$ is capable of reducing $[MoCl_4(THF)_2]$ in THF to afford $[MoCl_3(THF)_3]$ and $[SnCl_4(THF)_2]$.[9] Metallic tin is equally capable of carrying out the same reduction and to even over-reduce the metal below the +3 level. In ether, however, any further reduction by Sn (which may be used in excess) must be extremely slow since we found no NMR evidence for the formation of Mo^{III}, after isolation of the solid material and exchange with THF (vide infra). On the basis of this observation, we assume that $SnCl_2$ is probably also a poorer reductant in ether than in THF. Thus, the tin/ether combination seems ideal, giving rise to a rapid, controlled and selective reduction.

Although $[MoCl_4(OEt_2)_2]$ is only sparingly soluble in ether, it is readily soluble in aromatic hydrocarbons. In this respect, it resembles its sulfur congener $[MoCl_4(SEt_2)_2]$.[13] Besides elemental analysis and IR, no additional characterization was shown in the previous reports. The magnetic moment ($\mu_{eff} = 2.33\ \mu_B$) is significantly lower than the spin-only value for two unpaired electrons because of the expected spin-orbit coupling for the triplet ground state derived from the pseudo-t_{2g}^2 configuration. This value is in the range observed for other $[MoCl_4L_2]$ complexes (L = THF, MeCN, PPh_3, etc.), namely 2.2–2.5 μ_B.[14] The ^1H NMR spectrum in C_6D_6 shows only one resonance for the methyl and one for the methylene protons. These resonances are broad as may be expected for a paramagnetic complex. However, they are not significantly contact-shifted from the position of free ether (cf. the highly shifted resonances of the bis-THF adduct, vide infra, or those of the sulfur congener $[MoCl_4(SEt_2)_2]$[13]). We attribute this behavior to the rapid dissociation equilibrium of Equation (2), as proposed previously.[10] Thus, the broad lines would be the time-averaged signals of the methylene and methyl protons of the diamagnetic free ether and the paramagnetic complexes, at the fast exchange limit. In comparison with the related bis-SEt_2 complex, the NMR spectrum shows that diethyl ether is a much more labile ligand than the sulfur congener, as might be expected.

$$MoCl_4(OEt_2)_2 \rightleftharpoons MoCl_4(OEt_2) + Et_2O \qquad (2)$$

The only available crystal structure for a $[Mo^{IV}X_4L_2]$ complex with monodentate ligands appears to be that of $[MoCl_4(SEt_2)_2]$ which is trans.[13] $[MoCl_4(CH_3OCH_2CH_2OCH_3)]$ has a cis arrangement enforced by the chelating dimethoxyethane ligand.[15] For this reason, it is likely that $[MoCl_4(OEt_2)_2]$ also adopts a trans configuration. Most related Mo^{III} anions $[Mo^{III}X_4L_2]^-$ also adopt a trans arrangement,[16–18] although examples having a cis configuration are also known.[19,20] In spite of numerous attempts under a variety of conditions, we have not been able to grow single crystals of this compound.

The synthetic utility of $[MoCl_4(OEt_2)_2]$ has been investigated in some detail and the results are summarized in Scheme 2. Because of the facile ether loss shown by the NMR study above, it is best to use a freshly prepared sample for the purpose of further synthetic applications. Heating the isolated $[MoCl_4(OEt_2)_2]$ solid under vacuum leads to the complete loss of the ether ligands at a relatively low temperature, leaving amorphous (by X-ray powder diffraction) $MoCl_4$. Darkening of the solid already occurs at about 55 °C, while at 80 °C the powder is totally black. Samples of ether-free $MoCl_4$ have been obtained by operating at temperatures up to 130 °C. This procedure is considerably more practical and time efficient than the literature preparations (see below) and leads to a more chemically reactive material.



Scheme 2

Three different crystalline forms of $MoCl_4$ have been described in the literature, namely α-$MoCl_4$,[21] β-$MoCl_4$,[22,23] and γ-$MoCl_4$.[24] The α form was obtained from $MoCl_5$ by reflux with tetrachloroethylene in carbon tetrachloride; a reflux time shorter than two days is said to leave unchanged pentachloride.[21] The β form was obtained by comproportionation of $MoCl_5$ and $MoCl_3$ in a temperature gradient,[22] while the γ form was prepared by heating a mixture of MoO_2 and carbon with a nitrogen stream saturated with CCl_4 vapors.[24] The observed magnetic moment of 1.6 μ_B for our amorphous $MoCl_4$ does not compare with any of those reported for the three crystalline phases (i.e. 0.85 μ_B for α-$MoCl_4$,[21] 2.31−2.54 μ_B for β-$MoCl_4$,[22] and 1.91 μ_B for γ-$MoCl_4$ [24]), although it is closest to that of the γ phase. An additional and significant difference is observed in the temperature behavior. A disproportionation process occurs at temperatures above 140 °C to generate $MoCl_5$ and $MoCl_3$. This process is also observed for the β phase, but only at about 288 °C.[24] On the other hand, the γ phase was shown to transform at ca. 140 °C into the α phase, which in turn converts into the β phase at ca. 240 °C. Our evidence for the disproportionation of amorphous $MoCl_4$ at 140 °C is clear: volatile $MoCl_5$ sublimes and the solid residue transforms into a reddish material which is no longer soluble in ethanol, indicating the formation of lower chlorides. Furthermore, the signals of $MoCl_3$ in this material have been detected by powder X-ray diffraction. On the basis of this evidence, it seems obvious that amorphous $MoCl_4$ is a labile and reactive form, leading directly to the thermodynamic mixture of Mo^{III} and Mo^{V} chlorides at relatively low temperature, while the crystalline α, β and γ phases are more inert.

The lability of amorphous $MoCl_4$ is further shown by its high chemical reactivity. Addition of THF leads to the rapid and exothermic formation of $[MoCl_4(THF)_2]$, and treatment of the resulting mixture with other reagents (for instance, Li*Ot*Bu) affords the expected Mo^{IV} products in excellent yields (vide infra). The conversion of $MoCl_4$ to the bis-THF adduct is quantitative and is best accomplished by addition of THF to a pentane suspension of the tetrachloride, in order to evacuate the reaction heat.

$[MoCl_4(THF)_2]$, however, is more conveniently obtained by direct substitution of the ether in $[MoCl_4(OEt_2)_2]$, which may be obtained in situ from $MoCl_5$ (overall 89% isolated yields). This route appears to give a cleaner $[MoCl_4(THF)_2]$ product relative to the previously described synthesis from $[MoCl_4(MeCN)_2]$. It is possible that the ligand-exchange equilibrium is further shifted toward the bis-THF product when the less coordinating Et_2O ligand is bonded to the metal center. As for the bis-Et_2O analogue, no NMR spectroscopic data seem to be available in the literature for $[MoCl_4(THF)_2]$. The NMR spectrum in $CDCl_3$ shows highly shifted (12.5 and −32.8 ppm) but relatively sharp ($w_{1/2}$ = 12 and 15 Hz, respectively) resonances, indicating the presence of a single isomer in solution. These chemical shifts compare relatively well with those of the bis-thioether complex $[MoCl_4(SEt_2)_2]$.[13] As for the bis-Et_2O analogue, we were unable to grow single crystals of this compound. Substitution of the ether in $[MoCl_4(OEt_2)_2]$ with PMe_3 leads to the previously reported compound $[MoCl_4(PMe_3)_3]$.[25]

Besides substitution reactions of the ether ligand, the chlorides can also be easily replaced. This metathesis process provides a convenient entry to the tetrakis(*tert*-butoxy) derivative $[Mo(OtBu)_4]$. The previous synthesis of this compound involves metathesis from $[Mo(NMe_2)_4]$,[26] a compound that is available only in low yields from $MoCl_5$.[27] After its first report, this compound does not appear to have been used for further investigations, possibly because of the laborious and low-yield synthetic procedure. It is now available, however, in a practical half-day procedure in greater than 80% yields from $MoCl_5$. As such, it may constitute a new useful synthon for Mo^{IV} chemistry. Previous physical characterization of $[Mo(OtBu)_4]$ comprised IR, UV/Visible and mass spectra, and magnetic susceptibility. The compound was reported as having an intermediate magnetic moment between those expected for a magnetically diluted compound with two unpaired electrons and a diamagnetic compound (μ_{eff} = 1.38 μ_B in toluene or 1.37−1.40 μ_B in the solid state).[26] In our hands, the compound is diamagnetic by solid-state magnetic susceptibility and by NMR and EPR spectroscopy. In this respect, it appears perfectly homologous to the corresponding thiolato derivative $[Mo(StBu)_4]$.[28] Other MoX_4 compounds with π-donor X ligands, namely $[Mo(NMe_2)_4]$,[29] $[Mo(2\text{-}MeC_6H_4)_4]$,[30] and other mixed amido-phosphido derivatives[31] are mononuclear and diamagnetic, while compounds with π-neutral X ligands such as $[Mo(2\text{-}MeC_6H_4)_4]$[32] and $[Mo(norbornyl)_4]$[33] are paramagnetic with two unpaired electrons.

When $[MoCl_4(OEt_2)_2]$ was exposed to THF in the presence of metallic tin, a smooth reduction to $[MoCl_3(THF)_3]$ occurred. This is not surprising as the transformation of $[MoCl_4(OEt_2)_2]$ to $[MoCl_4(THF)_2]$ in a THF slurry has been established above, and the reduction of the latter to $[MoCl_3(THF)_3]$ by tin in THF is a well-established process. However, we found that this reaction gives excellent results without the need to isolate either the $[MoCl_4(OEt_2)_2]$ product after the first reductive step or the second $[MoCl_4(THF)_2]$ intermediate. Thus, it suffices to use enough tin reagent to reduce Mo^{V} to Mo^{III} and to replace the solvent after completion of the first reduction step, in order to achieve a convenient high-yield synthesis of [$MoCl_3(THF)_3$], in half a day, from $MoCl_5$.

Conclusion

In conclusion, we have developed a new, simple and time-efficient preparation of [$MoCl_4(OEt_2)_2$], and demonstrated its synthetic utility with the improved preparation of a few key materials such as [$MoCl_4(THF)_2$], [$MoCl_3(THF)_3$], [$Mo(O\textit{t}Bu)_4$], and a new and reactive form of $MoCl_4$.

Experimental Section

General: All manipulations were carried out under an atmosphere of dry and oxygen-free argon with standard Schlenk techniques. Solvents were dried and deoxygenated by refluxing over suitable reagents (THF and ether over sodium benzophenone ketyl, toluene over sodium) and distilled under argon before use. ^1H NMR measurements were carried out on a Bruker AC 200 spectrometer. The peak positions are reported with positive shifts in ppm downfield of TMS as calculated from residual solvent peaks. The magnetic susceptibility measurements were carried out with a Johnson−Matthey magnetic balance, which operates by a modified Gouy method. The molar susceptibilities for the calculation of the magnetic moments were corrected for the diamagnetism of the ligands by using Pascal's constants. Elemental analyses were performed with a Fisons EA 1108 apparatus. $MoCl_5$, PMe_3 (1 M in THF) and Sn (fine grains, 20 mesh) were purchased from Aldrich Chemical Co. and used as received.

Synthesis of [$MoCl_4(Et_2O)_2$]: $MoCl_5$ (1.20 g, 4.39 mmol) and coarse tin powder (1.04 g, 8.76 mmol) were suspended in 30 mL of Et_2O at room temperature. The mixture was then stirred for 30 min. to form an orange solution and orange solid. The latter was separated mechanically from the excess tin taking advantage of the large difference in density between the two solids. Under gentle stirring with a magnetic stirring bar, the metallic tin remained at the bottom of the flask and the supernatant suspension of the [$MoCl_4(Et_2O)_2$] product was transferred into a new flask through a medium size (G15) cannula. The product was then collected by filtration, washed with Et_2O (5 × 5 mL) and dried under vacuum. Yield: 1.36 g, 80%. The compound has a marked tendency to lose diethyl ether (see Results and Discussion) and samples dried without special precautions systematically gave low C,H analyses; a freshly prepared sample which was dried at −20 °C gave a correct analysis ($C_8H_{20}Cl_4MoO_2$: calcd. C 24.89, H 5.22; found C 25.31, H 5.23). The IR spectrum (Nujol mull) is identical with that reported in the literature.[11] ^1H NMR (C_6D_6, 25 °C): $\delta = 1.1$ (broad, $w_{1/2} = 23$ Hz, CH_3) ca. 3.5 ppm (broad, $w_{1/2} = 200$ Hz, CH_2). $\mu_{eff} = 2.33\ \mu_B$ (diamagnetic correction: $\chi = -196.22 \cdot 10^{-6}$ c.g.s. units).

Synthesis of $MoCl_4$: In a typical reaction, orange [$MoCl_4(Et_2O)_2$] was placed in a dry, air-free Schlenk tube and slowly heated under vacuum in an oil bath. First darkening occurred at about 55 °C. At 80 °C the powder was totally black. The yield of $MoCl_4$ produced is quantitative. Two experiments, carried out at 120° for 5 h and at 130° for 2 h gave materials with the same properties. Elemental analysis of the black material confirmed the absence of C and H. $\mu_{eff} = 1.60\ \mu_B$ and $1.61\ \mu_B$, respectively (diamagnetic correction: $\chi = -80.4 \cdot 10^{-6}$ c.g.s. units). The product dissolves completely in ethanol. When the reaction temperature is raised above 140 °C, sublimation of $MoCl_5$ is observed and the resulting reddish solid residue ($MoCl_3$) is no longer soluble in ethanol. This decomposition process is also observed for isolated $MoCl_4$ in vacuum and under an argon atmosphere in a sealed ampoule.

Synthesis of [$MoCl_4(THF)_2$]. (a) From Isolated [$MoCl_4(Et_2O)_2$]: Compound [$MoCl_4(Et_2O)_2$] (1.26 g, ca. 3.26 mmol) was suspended in 15 mL of THF. The mixture was then stirred for 3 h at room temperature to form an orange-yellow solid. The supernatant liquid was decanted off and the solid was washed with THF (10 mL), then ether (10 mL), and finally dried under vacuum. Yield: 0.99 g (79%). − $C_8H_{16}Cl_4MoO_2$ (381.96): calcd. C 25.16, H 4.22; found C 24.99, H 4.76. − ^1H NMR ($CDCl_3$, 25 °C): $\delta = 12.5$ ($w_{1/2} = 12$ Hz), -32.8 ($w_{1/2} = 15$ Hz) (intensity ratio: 1.1).

(b) From $MoCl_5$: $MoCl_5$ (1.156 g, 4.23 mmol) and coarse tin powder (1 g, 8.42 mmol) were suspended in 20 mL of Et_2O at room temperature. The mixture was stirred for 30 min. to form [$MoCl_4(Et_2O)_2$]. Then, the excess metallic tin was eliminated by transferring the supernatant suspension of [$MoCl_4(Et_2O)_2$] into a new flask through a medium-sized cannula. The solid was washed with Et_2O (3 × 10 mL) and 20 mL of THF was subsequently added. The mixture was then stirred for 3 h at room temperature to form an orange-yellow solid. The supernatant liquid was then decanted off and the residue was washed with 10 mL of THF and then with 10 mL of ether, and finally dried under vacuum. Yield: 1.438 g, 89%. The color and ^1H NMR spectrum of this material are identical with the analyzed product obtained as described in the previous section.

(c) From $MoCl_4$: Black $MoCl_4$ (553 mg, 2.33 mmol) was suspended in 5 mL of pentane. After addition of 5 mL THF on top of the pentane layer the mixture was allowed to stir for two minutes. The reaction occurred very rapidly to produce an orange precipitate. The colorless supernatant liquid was removed by cannula and the residue was dried in vacuo leaving 890 mg of [$MoCl_4(THF)_2$] (quantitative yield).

Synthesis of [$MoCl_3(THF)_3$]: $MoCl_5$ (3.18 g, 11.64 mmol) and coarse tin powder (2.77 g, 23.33 mmol) were suspended in 30 mL of Et_2O. The mixture was then stirred for 30 min. at room temperature to form an orange solution and orange solid. The supernatant liquid was decanted off and 30 mL of THF was added. The mixture was then stirred for 3 h at room temperature. The pale orange-brown crystalline product [$MoCl_3(THF)_3$] was separated from excess tin as described above for the synthesis of [$MoCl_4(Et_2O)_2$]. The product was then washed with Et_2O (2 × 15 mL) and dried under vacuum. Yield: 3.99 g, 82%. − $C_{12}H_{24}Cl_3MoO_3$ (418.62): calcd. C 34.43, H 5.78; found C 34.04, H 5.51. The ^1H NMR properties of this material correspond with those previously described for [$MoCl_3(THF)_3$].[34]

Synthesis of [$MoCl_4(PMe_3)_3$]: A THF solution of PMe_3 (1 M, 8 mL, 8 mmol) was slowly added to a magnetically stirred suspension of [$MoCl_4(Et_2O)_2$] (0.96 g, ca. 2.5 mmol) in THF (10 mL). The orange suspension rapidly transformed into a deep violet suspension. The mixture was stirred for 4 h at room temperature, then the supernatant liquid was decanted off and the solid was washed with THF (2 × 5 mL) and dried under vacuum. Yield: 0.78 g, 67%. − $C_9H_{27}Cl_4MoP_3$ (465.99): calcd. C 23.20, H 5.84; found C 23.04, H 5.62. The ^1H NMR spectrum [broad band at $\delta = -17$ ($w_{1/2} = 130$ Hz) in $CDCl_3$ at 25 °C] corresponds to that reported in the literature.[25]

Synthesis of [$Mo(O\textit{t}Bu)_4$]. (a) From $MoCl_4$: THF (15 mL) was added to 330 mg (1.39 mmol) of black $MoCl_4$ causing a slight warming and precipitation of the orange THF adduct. The suspension was cooled in an ice bath and a 1 M LiO*t*Bu solution in THF/hexane (5.55 mL, 5.55 mmol) was added with a syringe. The reaction mixture was stirred for one hour at 0 °C, then slowly warmed to room temperature and stirred overnight to complete the reaction. The THF was removed in vacuo from the dark brown solution. The brown solid was extracted with 20 mL of pentane, then with 10 mL of CH_2Cl_2. After filtration, the combined extracts were evaporated in vacuo to dryness, leaving crude [Mo(O*t*Bu)$_4$] as a brown solid (540 mg, quantitative yield). The product can be recrystallized in low yields (ca. 25%) from cold pentane. − $C_{16}H_{36}MoO_4$ (388.40): calcd. C 49.48, H 9.34; found C 49.58, H 9.29. − ^{1}H NMR: $\delta = 1.55$ (s) in C_6D_6, 1.66 (s) in $C_6D_5CD_3$ and 1.12 (s) in [D$_6$]acetone. All these solutions are EPR-silent, but a strong signal rapidly develops upon exposure to air. $\mu_{eff} = 0.72\ \mu_B$ (diamagnetic correction: $\chi = -219.92 \cdot 10^{-6}$ c.g.s. units).

(b) From [MoCl$_4$(Et$_2$O)$_2$]: [MoCl$_4$(Et$_2$O)$_2$] was obtained in situ from $MoCl_5$ (3.06 g, 11.2 mmol) and tin as described above. After separation from the excess tin and the ether, it was suspended in 40 mL of THF and the suspension was cooled in an ice bath. After addition of LiO*t*Bu (40 mL of a 1 M solution in THF/hexane, 40 mmol) the reaction mixture was stirred at 0 °C for 2 h, then slowly warmed to room temperature and stirred overnight to complete the reaction. Removal of the solvent in vacuo left a brown residue which was extracted with 35 mL of CH_2Cl_2 and filtered. After total removal of the solvent in vacuo, a gummy brown-black residue was left which became an almost black powdery solid over a period of two days. The yield of crude [Mo(O*t*Bu)$_4$] was 3.517 g (81% from $MoCl_5$).

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