Synthesis of (Hexafluoro-*tert*-butyl)amine and Molybdenum(VI) (Hexafluoro-*tert*-butyl)imido Complexes

Michael Buchmeiser and Richard R. Schrock*

Department of Chemistry, 6-331, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139

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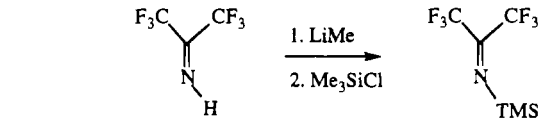
Introduction

The reactivity of well-defined transition metal alkylidene complexes of the type Mo(CHR)(NAr)(OR′)$_2$ (where Ar = 2,6-*i*-Pr$_2$C$_6$H$_3$, for example) toward olefins depends to an enormous degree on the nature of the OR′ group (OR′ = OCMe$_3$, OCMe(CF$_3$)$_2$, phenoxides, etc.).[1-3] Recently it was shown that the rate of interconversion of syn and anti alkylidene rotamers (which have significantly different reactivities) also depends dramatically on the nature of the OR′ group[4] and that the stereochemistry of polymerization can be linked to whether syn or anti rotamers are accessible on the polymerization time scale.[4-6] A qualitative correlation between olefin metathesis activity and the electron-withdrawing ability of phenoxides has also been noted.[7,8]

In contrast, the role of the imido group in reactions of Mo(CHR)(NAr)(OR′)$_2$ complexes has been explored to only a small degree. Part of the problem has been the fact that complexes that contain imido ligands other than substituted phenylimido ligands have not been readily accessible.[9-11] Complexes containing the ubiquitous *tert*-butylimido ligand,[12] for example, are not as stable as those containing arylimido ligands or are often oils that are difficult to purify.[13,14] Therefore we turned to adamantylimido analogs, which have tended to be more crystalline and readily synthesized than *tert*-butyl derivatives.[9] So far adamantylimido complexes have been shown to behave significantly differently from arylimido complexes.[4,15] In view of the vast difference between *tert*-butoxide and hexafluoro-*tert*-butoxide Mo(CHR)(NAr)(OR′)$_2$ complexes, we therefore became interested in the possibility of preparing (hexafluoro-*tert*-butyl)imido complexes in order to compare their reactivity with that of adamantylimido complexes. We were surprised to find that hexafluoro-*tert*-butylamine is not a known compound. In this paper we report its synthesis and the result of attempts to prepare Mo(CHR)(NR″)(OR′)$_2$ catalysts in which R″ is hexafluoro-*tert*-butyl.

Results and Discussion

(Hexafluoro-*tert*-butyl)amine can be prepared from the known hexafluoroisopropylidene (or hexafluoroacetone) imine.[16,17] Protection with TMS (eq 1), followed by addition of methyllithium and then trimethylchlorosilane, gave the bis(trimethylsilyl) derivative of the desired amine, all in one pot (eq 2).



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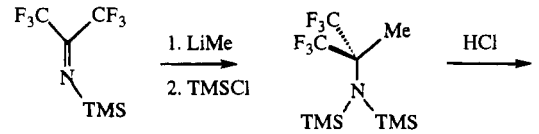

$(CF_3)_2MeCNH_3^+Cl^-$ (2)

Addition of excess HCl to the ether solution of (CF$_3$)$_2$MeCN(TMS)$_2$ precipitated the hydrochloride salt of the desired amine in an overall yield of 90−95%. The free amine, (CF$_3$)$_2$MeCNH$_2$, was prepared by treating a suspension of [(CF$_3$)$_2$MeCNH$_3$]$^+$Cl$^-$ in glycerol with KOH pellets at 60 °C. (Hexafluoro-*tert*-butyl)amine is a colorless, volatile liquid with a boiling point of 77 °C (uncorrected). KNHCMe(CF$_3$)$_2$, a white THF-soluble powder that does not readily sublime at 120 °C, can be prepared readily from [(CF$_3$)$_2$MeCNH$_3$]$^+$Cl$^-$ and KH in THF.

Many complexes of the type Mo(NR)$_2$Cl$_2$(1,2-dimethoxyethane) have been prepared from (NH$_4$)$_2$Mo$_2$O$_7$, trimethylchlorosilane, and triethylamine in dimethoxyethane.[10] Unfortunately, we have not been able to synthesize "Mo[NCMe(CF$_3$)$_2$]$_2$Cl$_2$(1,2-dimethoxyethane)" under a variety of conditions. (Evidence presented below suggests that this compound might be inherently unstable.) However, substitution of triethylamine by pyridine in the synthesis led to the isolation of Mo(O)[NCMe(CF$_3$)$_2$]Cl$_2$(pyridine)$_2$ in high yield.

Addition of excess *tert*-butylamine to Mo(O)[NCMe(CF$_3$)$_2$]Cl$_2$(pyridine)$_2$ led to the formation of Mo(N-*t*-Bu)$_2$Cl$_2$(py)$_2$[10] quantitatively. Evidently both the oxo and the (hexafluoro-*tert*-butyl)imido groups are readily protonated by (presumably coordinated) *tert*-butylamine. The ready displacement of the (hexafluoro-*tert*-butyl)imido group by proton transfer from *tert*-butylamine is disappointing but perhaps understandable in view of what must be a relatively poor ability of the electron pair in a (hexafluoro-*tert*-butyl)imido group to bind to the metal to give a pseudo triple bond compared to the ability of an electron pair in an ordinary *tert*-butylimido group to bind to the metal.

Addition of the less basic and more sterically demanding 2,6-diisopropylaniline to Mo(O)[NCMe(CF$_3$)$_2$]Cl$_2$(pyridine)$_2$ gave the "mixed imido" complex Mo[NCMe(CF$_3$)$_2$](NAr)Cl$_2$(py)$_2$ (Ar = 2,6-*i*-Pr$_2$C$_6$H$_5$), in high yield, which can be purified by recrystallization from a mixture of ether and pentane. It slowly disproportionates in C$_6$D$_6$ to yield known Mo(NAr)$_2$Cl$_2$(py)$_2$, but no trace of "Mo[NCMe(CF$_3$)$_2$]$_2$Cl$_2$(py)$_2$". Therefore we suspect that the latter may be unstable under the reaction conditions.

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We felt that there was an opportunity to selectively protonate the arylimido ligand in hypothetical $Mo(NAr)[NCMe(CF_3)_2](CH_2CMe_2Ph)_2$ with triflic acid in dimethoxyethane[11] in order to give $Mo(CHCMe_2Ph)[NCMe(CF_3)_2](OTf)_2(dme)$. Unfortunately, addition of $PhMe_2CCH_2MgCl$ to $Mo[NCMe(CF_3)_2](NAr)Cl_2(py)_2$ led only to the known $Mo(NAr)_2(CH_2CMe_2Ph)_2$ in moderate yield (<50%). There was no evidence for the formation of $Mo[NCMe(CF_3)_2]_2(CH_2CMe_2Ph)_2$. NMR spectra of crude reaction mixtures contain resonances that are consistent with the presence of $Mo(NAr)[NCMe(CF_3)_2](CH_2CMe_2Ph)_2$, but these are slowly replaced by those for $Mo(NAr)_2(CH_2CMe_2Ph)_2$. We conclude from these results that $Mo[NCMe(CF_3)_2]_2(CH_2CMe_2Ph)_2$, if it is indeed formed as a consequence of "disproportionation" of $Mo(NAr)[NCMe(CF_3)_2](CH_2CMe_2Ph)_2$, also is not stable under these conditions.

Conclusions

(Hexafluoro-*tert*-butyl)amine appears to be a relatively poor base and (hexafluoro-*tert*-butyl)imides (and probably also amides) bound to Mo(6+) therefore good leaving groups. Several molybdenum compounds that contain two (hexafluoro-*tert*-butyl)imido groups do not appear to be stable, and those that contain one (hexafluoro-*tert*-butyl)imido group and a more basic arylimido ligand are prone to disproportionation. On the basis of these results, the probability of preparing well-behaved molybdenum alkylidene complexes that contain the (hexafluoro-*tert*-butyl)imido group does not appear to be high. On the other hand, these experiments certainly do not rule out the possibility of synthesizing (hexafluoro-*tert*-butyl)amido or -imido complexes of more electropositive metals.

Experimental Section

General Procedures. All experiments were performed under a nitrogen atmosphere in a Vacuum Atmospheres drybox or by standard Schlenk techniques unless stated otherwise. Reaction solvents were purified by standard methods. All deuterated NMR solvents were passed through a column of activated alumina prior to use. $(NH_4)_2Mo_2O_7$ was purchased commercially and used as received. 2,6-Diisopropylaniline was distilled prior to use. Pyridine was dried over potassium hydroxide and distilled from CaH_2.

NMR data are listed in parts per million downfield from tetramethylsilane for proton and carbon and downfield from $CFCl_3$ (in toluene) for fluorine. Coupling constants are listed in hertz. Spectra were obtained in the indicated solvent at 25 °C unless otherwise noted. Elemental analyses (C, H, N) were performed by Oneida Research Services or in our laboratories using a Perkin-Elmer 2400 analyzer. NeophylMgCl was prepared by following the procedure described in the literature.[18] (Hexafluoroisopropylidene)imine was synthesized from hexafluoroacetone and ammonia as described in the literature.[16,17]

$[(CF_3)_2MeCNH_3]^+Cl^-$. Methyllithium (40.0 mL, 1.4 M in diethyl ether, 56 mmol) was added to a solution of (hexafluoroisopropylidene)-amine (8.84 g, 53.6 mmol) in 50 mL of diethyl ether at −70 °C. The solution was warmed to −40 °C and cooled again to −70 °C, and trimethylchlorosilane (6.8 mL, 53.6 mmol) was added.[19,20] After 5 min, methyllithium (38.5 mL, 53.9 mmol) was added. After a further 5 min, trimethylchlorosilane (6.8 mL, 53.6 mmol) was added and the solution was allowed to warm to room temperature. After a few minutes, a white precipitate (LiCl) formed, which was filtered off. The amine was collected as a hydrochloride salt by passing HCl through the ether layer at −70 °C until no more precipitate was formed: yield 10.85 g (93%); ^1H NMR (DMSO-d_6) δ 5.8 (br s, 3, NH_3), 1.40 (s, 3, CH_3); ^{13}C NMR (DMSO-d_6) δ 16.2 (CH_3); ^{19}F NMR (acetone-d_6) δ −68.0 (CF_3); LRMS calcd for $C_4H_6F_6N$ (M^+) 180, found (EI, 70 eV) 112 (100%, $M^{\bullet+}$ − 70(CF_3H)), 69 (18%, $CF_3^{\bullet+}$), 43 (60%, $CH_3CNH_2^{\bullet+}$).

$(CF_3)_2MeCNH_2$. KOH (500 mg, 8.9 mmol) was added to a suspension of $[(CF_3)_2MeCNH_3]^+Cl^-$ (1.0 g, 4.60 mmol) in 5 mL of glycerol. The mixture was heated to 60 °C, and the free amine was collected in a Schlenk tube that was held at −180 °C; yield 706 mg (85%). The amine thus obtained was pure by ^1H and ^{19}F NMR: ^1H NMR ($CDCl_3$) δ 1.70 (br s, 2, NH_2), 1.46 (s, 3, CH_3); ^1H NMR (CD_3CN) δ 2.1 (br s, 2, NH_2), 1.43 (s, 3, CH_3); ^{19}F NMR ($CDCl_3$) δ −78.5 (CF_3).

$KNHCMe(CF_3)_2$. $[(CF_3)_2MeCNH_3]^+Cl^-$ (1.68 g, 7.72 mmol) was dissolved in 50 mL of THF, and the solution was cooled to −40 °C. KH (740 mg, 18.4 mmol) was added, and the solution was stirred for 1 h. The solution was filtered, and the solvent was removed from the filtrate in vacuo to yield the product as a white powder: yield 1.61 g (95%); ^1H NMR (THF-d_8) δ 4.85 (br, 1, NH), 1.40 (s, 3, CH_3); ^{19}F NMR (THF-d_8) δ −80.4 (CF_3). The compound cannot be sublimed at <0.005 Torr (T = 120 °C).

$MoO[NCMe(CF_3)_2]Cl_2(pyridine)_2$. $(NH_4)_2Mo_2O_7$ (1.038 g, 3.05 mmol), trimethylchlorosilane (5.6 g, 51.55 mmol), pyridine (17 g, 215 mmol), DME (50 mL), and $[(CF_3)_2MeCNH_3]^+Cl^-$ (1.35 g, 6.25 mmol) were placed in a pressure tube. The tube was closed and heated to 60 °C for 18 h. After the tube was cooled to room temperature, the inorganic salts were filtered off and the volume of the filtrate was reduced in vacuo. A yellow solid was filtered off and recrystallized from a mixture of methylene chloride and pyridine (3:1); yield 3.0 g of bright yellow product (95%). The compound is slightly soluble in methylene chloride and THF and soluble in dimethoxyethane: ^1H NMR (CD_2Cl_2) δ 8.83 (br s, 4, H_o), 7.87 (br s, 2, H_p), 7.55 (br s, 4, H_m), 1.97 (s, 3, CH_3); ^{13}C NMR (CD_2Cl_2) δ 151.8 (C_o), 139.2 (C_p), 121.7 (C_m), 15.7 (CH_3); ^{19}F NMR (CD_2Cl_2) δ −70.4 (CF_3). Anal. Calcd for $C_{14}H_{13}Cl_2F_6MoN_3O$: C, 32.33; H, 2.52; N, 8.07; Cl, 13.63. Found: C, 32.26; H, 2.47; N, 8.03; Cl, 13.23.

$Mo(NAr)[NCMe(CF_3)_2]Cl_2(pyridine)_2$. $MoO[NCMe(CF_3)_2]Cl_2(pyridine)_2$ (392 mg, 0.75 mmol), 2,6-diisopropylaniline (132 mg, 0.75 mmol), (TMS)Cl (200 mg, 1.84 mmol), triethylamine (184 mg, 1.82 mmol), and pyridine (1.0 g, 12.7 mmol) were dissolved in 10 mL of methylene chloride. The mixture was stirred for 2 h and filtered, and the solvent was removed in vacuo from the filtrate. The residue was dissolved in diethyl ether, and approximately an equal volume of *n*-pentane was added to the resulting solution. The solution was cooled to −40 °C, and the resulting crystalline product was collected by filtration. Recrystallization from a mixture of diethyl ether and *n*-pentane yielded 400 mg (80%) of a deep red solid: ^1H NMR ($CDCl_3$) δ 8.85 (d, 4, $^3J_{HH}$ = 3.9, H_o), 7.76 (t, 2, J_{HH} = 7, H_p), 7.31 (t, 4, J_{HH} = 6, H_m), 7.1−6.9 (m, 3, H_m+ H_p), 3.90 (sept, 2, $^3J_{HH}$ = 7, $CHMe_2$), 1.85 (s, 3, CH_3), 1.05 (d, 6, J = 7, $CH(CH_3)_2$); ^{13}C NMR ($CDCl_3$) δ 151.5 (C_o), 145.8, 137.9, 126.3, 123.8, 123.0, 27.6 ($CHMe_2$), 24.5 (CH_3), 16.7 (CH_3); ^{19}F NMR ($CDCl_3$) δ −77.8 (CF_3). Anal. Calcd for $C_{26}H_{30}Cl_2F_6MoN_4$: C, 45.97; H, 4.45; N, 8.25. Found: C, 46.09; H, 4.82; N, 8.24.

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