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Siloxymethylamines as Aminomethylation Reagents for Amines Leading to Labile Diaminomethanes That can be Trapped as Their $[Mo(CO)_4]$ Complexes

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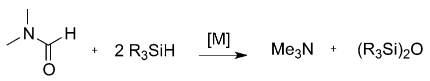
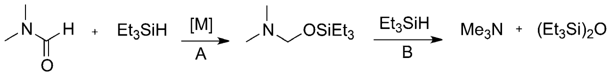
Abstract: Compound $Et_3SiOCH_2NMe_2$ transfers Me_2NCH_2 to R_2NH ($R_2 = Et_2$, PhMe, $[Cr(\eta^6\text{-}C_6H_5)(CO)_3]Me$, PhH) to form previously unknown diaminomethanes, $Me_2NCH_2NR_2$ and, in the case of $R_2 = PhH$, the triamine $Me_2NCH_2N(Ph)CH_2NMe_2$. The diaminomethanes exhibit an unreported disproportionation to a mixture of $(R_2N)_2CH_2$, $(Me_2N)_2CH_2$, and $Me_2NCH_2NR_2$, which can be trapped as their $[Mo(CO)_4(\text{diamine})]$ complexes. Whereas $PhMeNCH_2NMe_2$ is a labile material, the metal-substituted $([(\eta^6\text{-}C_6H_5)Cr(CO)_3]MeNCH_2NMe_2$ is a stable material. The triamine $Me_2NCH_2N(Ph)CH_2NMe_2$ is unstable with respect to transformation to 1,3,5-triphenyltriazine, but is readily trapped as the bidentate-triamine$Mo(CO)_4$. All metal complexes were characterized by single-crystal X-ray diffraction.

The organometallic-catalyzed organosilane ($R_{4-n}SiH_n$) reduction of organic functional groups has developed into a major area of academic and industrial chemistry.[1] In a largely ignored 1985 article, the Voronkov group first described the metal-catalyzed reaction between a silane and *N*,*N*-dimethylformamide (DMF) leading to the formation of Me_3N and the corresponding disiloxane [Eq. (1)].[2]



(1)

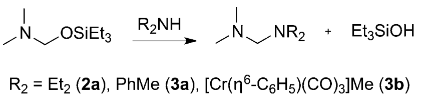
Since this seminal report, the generalized reduction of amides to form amines has become a popular "green" procedure due to the low energy requirement of the reaction and its regioselectivity.[3] We proposed and proved that by using Mo and Pt catalysts, the initial step A in the process involved a hydrosilylation of the amide carbonyl group to produce the intermediacy of readily isolated siloxymethyl dimethylamines obtained in high yield, for example, $R_3SiOCH_2NMe_2$ (**1**, $R_3 = Et_3$ (**1 a**); $PhMe_2$ (**1 b**); Ph_2Me (**1 c**); Eq. (2) for **1 a**, M = catalyst).[4] The second step B, that is, the reduction of **1** by the silane, led us to propose that **1** can be used as a masked analogue of Eschenmoser's salt,[5] and thereby act as a dimethylamino transfer agent (Mannich reagent) in the appropriate environment.



(2)

Indeed, we[6] and earlier the Mironov group[7] demonstrated that **1 d** ($Me_3SiOCH_2NMe_2$, formed from the reaction of Me_3SiNMe_2 and formaldehyde) reacted with R_3ECl ($R_3E^{\delta+}\text{–}Cl^{\delta-}$, $E = Si^{4,6,7}$, Ge^4 and Sn^4) behaving appropriately to form R_3SiOER_3 and $ClCH_2NMe_2$. Furthermore, the Mironov group illustrated the reaction of **1 d** with trimethylsilylamines, Me_3SiAm, led to the formation of hexamethyldisiloxane and $AmCH_2NMe_2$.[7b] We now report an initial study concerning the reactions of **1** with a series of N–H bonds, more readily available and more general than silylamines, which illustrates that **1** is a reliable $[CH_2NMe_2]$ transfer reagent to amines, and more fundamentally, illustrate previously unreported chemistry of the newly formed diaminomethanes.

The reactions of **1 a** with secondary amines, Et_2NH, PhMeNH and $[Cr(\eta^6\text{-}C_6H_5)(CO)_3]MeNH$ rapidly resulted in the formation of the corresponding, unreported, (dimethylaminomethyl) amines, $Me_2NCH_2NR_2$ [Eq. (3)].



(3)

Although tetraethyl and tetramethyl diaminomethane, **2 b** and **c**, respectively, are commercially available materials, **2 a** is unreported and simple unsymmetrical aryl/alkyl, alkyl/alkyl diaminomethanes are very rare in the literature. A few stable mixed 1,3-diaryl diamines have been reported, for example, $ArNH\text{–}CH_2\text{–}NHAr'$,[8a] and several indole-[8b] and imidazole-[8c] dialkylamino-methanes are also known. Symmetrical methylene-bridged diamines are more common and are useful re-

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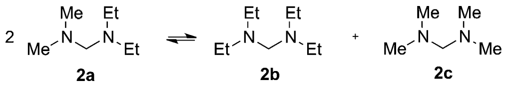
agents.[8d] The new reagents **1** could be particularly useful in unsymmetrical diamine synthesis; however, our attempts to purify the diaminomethane materials by distillation and/or column chromatography showed their significant lability. In all such attempts, the unsymmetrical diamines **2** and **3** exhibited unexpected lability. In the case of **2a**, an equilibrium mixture of all three isomeric diaminomethanes has been discovered [Eq. (4)]:



$$2\,\underset{\textbf{2a}}{Me(Me)N{-}CH_2{-}N(Et)Et} \rightleftharpoons \underset{\textbf{2b}}{Et(Et)N{-}CH_2{-}N(Et)Et} + \underset{\textbf{2c}}{Me(Me)N{-}CH_2{-}N(Me)Me} \qquad (4)$$

This previously unreported chemistry is outside the immediate scope of the present article; however, we are actively studying the scope and details of this chemistry and our results will be the subject of future publications involving $R_2NCH_2NR_2\leftrightarrow[R_2N]^-\ [CH_2{=}NR_2]^+$ dissociations. At this stage, we simply illustrate this simple equilibrium process studied by ^{1}H and ^{13}C NMR spectroscopy, in which a 1:1 mixture of **2b** and **c** eventually transform to an approximately 2:1:1 mixture of **2a**, **b**, and **c**, at 30 °C (Figure 1).

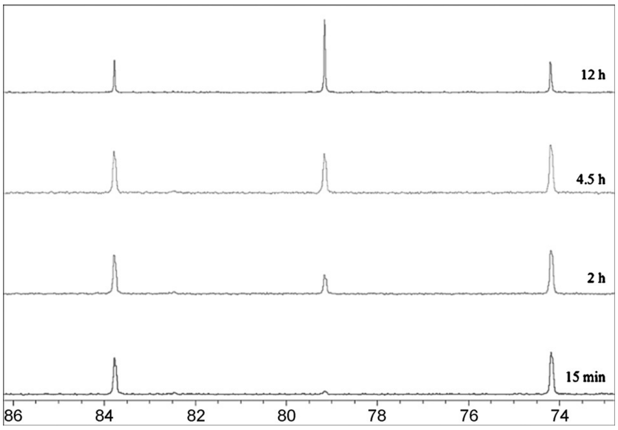


Figure 1. ^{13}C NMR spectrum of the methylene region ($N{-}CH_2{-}N$) for the reaction of **2b** and **c** (1:1) in C_6D_6 at 30 °C: **2c** 74.18 ppm; **2b** 83.77 ppm; and **2a** 79.16 ppm.

To unambiguously prove the formation of the unsymmetrical diamine, $Me_2N{-}CH_2{-}NEt_2$ (**2a**), the immediately formed crude reaction product from the reaction outlined in Equation (3) was reacted with $[Mo(CO)_4(norbornadiene)]$.[9] Such treatment led to replacement of norbornadiene with diamine and the formation of $[Mo(CO)_4(Me_2NCH_2NEt_2)]$ (**4a**) in reasonable yield, a rare example of a small-bite angle diaminomethane metal complex.[10] The structure of this complex is illustrated in Figure 2, and selected bond lengths and angles are presented in the caption. We also report the related structures of the tetraethyl- and tetramethyl diaminomethane $[Mo(CO)_4]$ complexes **4b** and **c** (Figures 3 and 4).

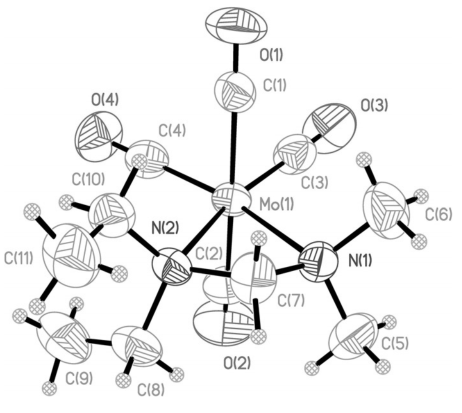


Figure 2. Structure of **4a**. Selected bond lengths [Å] and angles [°]: Mo1–C1 2.024(4), Mo1–C2 2.028(5), Mo1–C3 1.935(5), Mo1–C4 1.939(5), Mo1–N1 2.318(3), Mo1–N2 2.329(3); N1-Mo-N2 62.3(1), C1-Mo1-C2 (ax) 167.3(2), C3-Mo1-C4 (eq) 88.4(2), C7-N1-Mo1 93.1(2), C7-N2-Mo1 92.3(2).

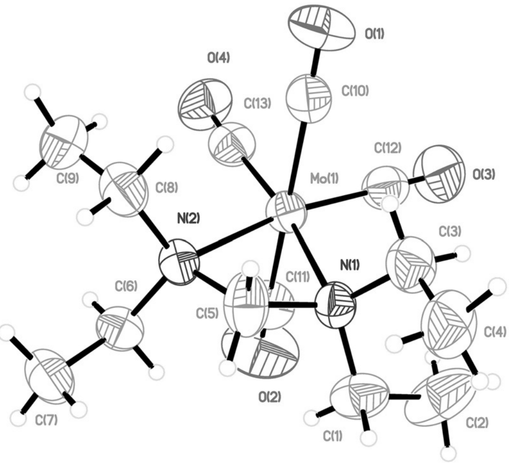


Figure 3. Structure of **4b**. Selected bond lengths [Å] and angles [°]: Mo1–C10 2.027(5), Mo1–C11 2.025(5), Mo1–C12 1.954(5), Mo1–C13 1.939(5), Mo1–N1 2.339(3), Mo1–N2 2.349(3); N1-Mo1-N2 62.1(1), C10-Mo1-C11 (ax) 170.6(2), C12-Mo1-C13 (eq) 84.7(2), C5-N1-Mo1 93.3(2), C5-N2-Mo1 93.0(2).

As may be expected on progressing in the order tetramethyl/dimethyldiethyl/tetraethyl, there is an increase in the cell volume (1285.0(2)→1460(2)→1674.5(9) Å^3). The angle N-Mo-N is not affected by the substituent changes on the nitrogen (average 62.4(1)°), but the angle between the axial CO groups for the tetraethyl is expanded compared to the corresponding angles for the dimethyldiethyl and tetramethyl derivatives, 170.6(2)°, see also, 167.3(2) and 166.4(2)°, respectively. All the other parameters are statistically the same. Related Re, Mo, and W complexes, with a range of differing N substituents exhibit N-W-N bond angle comparable to ours showing that the bite angle in this class of complex is independent of the substituent on the nitrogen and the metal atom.[10]

The reaction of the **1a** with PhMeNH led to the formation of $PhMeNCH_2NMe_2$, (**3a**), as was showed by NMR spectroscopy. However, this material was also too labile to be isolated, and attempts to form the $[Mo(CO)_4]$ complex were unsuccessful, possibly due to the steric bulk of the phenyl group, and/or re-

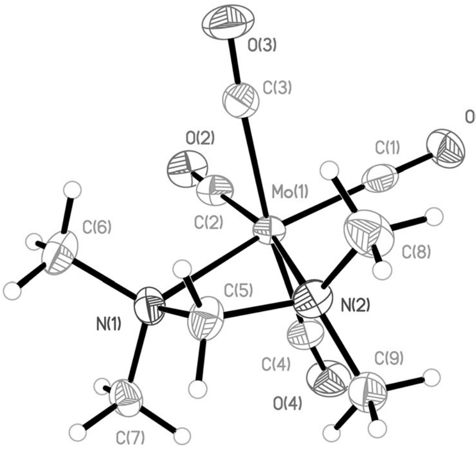


Figure 4. Structure of **4c**. Selected bond lengths [Å] and angles [°]: Mo1–C3 2.040(5), Mo1–C4 2.041(5), Mo1–C1 1.945(5), Mo1–C2 1.955(6), Mo1–N1 2.330(4), Mo1–N2 2.313(4); N1-Mo1-N2 62.8(1), C3-Mo1-C4 (ax) 166.4(2), C1-Mo1-C2 (eq) 89.0(2), C5-N1-Mo1 93.8(3), C5-N2-Mo1 94.1(3).

duced basicity of the ligand. However, the reaction of **1a** with $[Cr(\eta^6\text{-}C_6H_5)(CO)_3]MeNH$[11] formed the corresponding diaminomethane (**3b**) in good yield as a stable material [Eq. (3)]. Complex **3b** was readily purified, and we managed to obtain crystals of this complex, and its structure is illustrated in Figure 5.

The geometry around Cr exhibits the usual piano-stool arrangement, with an η^6 interaction with the aromatic ring. The arylamino group is not coplanar with the aromatic ring by 16° although it is planar (sum of the angles at N is 358.3°); however, the C_{ar}–N distance of 1.368(3) Å shows that there is a conjugation of the nitrogen with the aryl π system. The related complex, (η^6-*N*,*N*-dimethylaniline)-tricarbonyl-chromium, in which the N is coplanar with the aromatic ring, has a C_{ar}–N distance of 1.361 Å,[12] whereas (η^6-*N*-*tert*-utyldimethylsilyl-*N*-methylaniline)-tricarbonylchromium and bis-(η^6-*N*,*N*,-dimethylaniline) chromium with similar non-planar N-aryl arrangements exhibit C_{ar}–N distances of 1.387 and 1.390 Å, respectively.[13] When all conjugation is lost, as in the case of (bis(μ_2-1,1′-bis(η^6-*N*-methylanilino)(bromo)boryl)-ferrocene)-bis(tricarbonyl-chromium), the C_{ar}–N distance is 1.431 Å.[14]

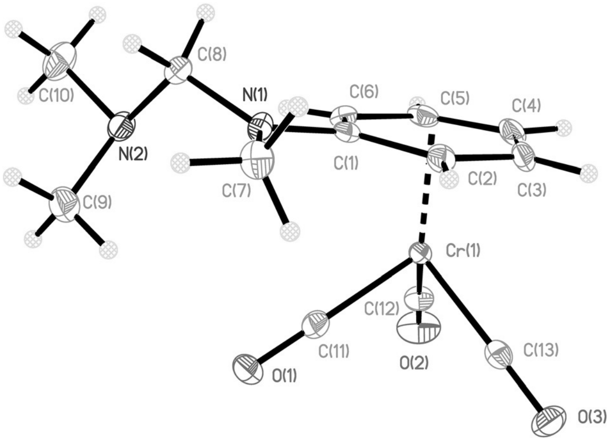
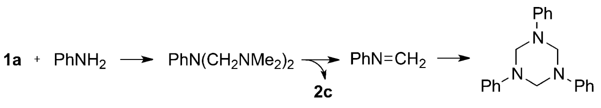


Figure 5. Structure of $[Cr(\eta^6\text{-}C_6H_5)(CO)_3]MeNCH_2NMe_2$ (**3b**). Selected bond lengths [Å] and angles [°]: Cr1–Ph_{center} 1.751(2); Cr1-C11 1.840(2), Cr1-C12 1.832(2), Cr1-C13 1.840(2), C7-N1-C1-C2 4.8(2), C8-N1-C1-C2 159.7(2), C1-N1-C8-N2 86.4(2). C7-N1-C8-N2 −109.0(2).

The out-of-the plane feature of the amino group in **3b** could be due to the presence of an intramolecular hydrogen bond N···H–C_{ar} of 2.603 Å. It is also possible that in solution, the amino group is co-planar with the aromatic ring, therefore, influencing in the increased stability we have found. Furthermore, the $[Cr(CO)_3]$ substituent is strongly electron withdrawing, and thus the reduced basicity of the amine is also a potential factor. Together with our studies on the disproportionation of the other diamines noted above, this is the subject of further experimental and theoretical studies.

The reaction of an excess of **1a** with the primary amine $PhNH_2$, as was monitored by ^1H and ^{13}C NMR spectroscopy, resulted in the formation of the "expected", but previously unreported, triamine Me_2NCH_2–NPh–CH_2NMe_2 (**5**). However, as with the attempted work-up of Me_2N–CH_2–NEt_2, we have been unable to obtain the new triamine in a purified form due to secondary chemistry. In this case, there appears to be an elimination of **2c**, and the transient formation of an imine, $C_6H_5N{=}CH_2$, which rapidly trimerizes to form 1,3,5-triphenyltriazine. Such trimerization reactions of imines are reported in the literature (Scheme 1).[15]



Scheme 1. Formation of 1,3,5-triphenyl-1,3,5-triazine.

However, the $[Mo(CO)_4(norbornadiene)]$ complex was used for isolation of the triamine **5** as the Mo complex **6**. The triamine acts as a bidentate ligand by coordination of the two terminal dimethylamino groups, as illustrated in Figure 6, with selected parameters noted in the caption.

The heteronuclear six-membered ring adopts a chair conformation, and the distances Mo–N, 2.376(3) and 2.389(3) Å, are longer than those for the diaminomethane complexes reported above. The 3D lattice structure is held together by hydrogen bonds of the type CH···OC ranging from 2.593(5) to 2.827(5) Å. This structure is similar to three triamine complexes described in the literature, that is, $CoCl_2[(Me_2NCH_2)_2NMe]$,[10c] and $[Co(CO)_4CuNMe_2)_2NR$ (R = H and propyl),[16a] together with a similar biuret iridium complex, Ir(NH–CO–NH–CO–NH), both involving bidentate structural motif.[16b]

Overall, siloxymethylamines reagents are produced in high yield, are stable indefinitely in dry O_2-free environments, and perform facile (low-energy) transfer of the dimethylamino group to NH-containing compounds. Previously unreported rearrangements of the simple new diaminomethanes have been noted, and their isomers were trapped by metal coordination.[17]

Experimental Section

All reactions were performed under N_2 or Ar atmospheres by using Schlenk techniques. A typical reaction of **1a** is outlined below, and

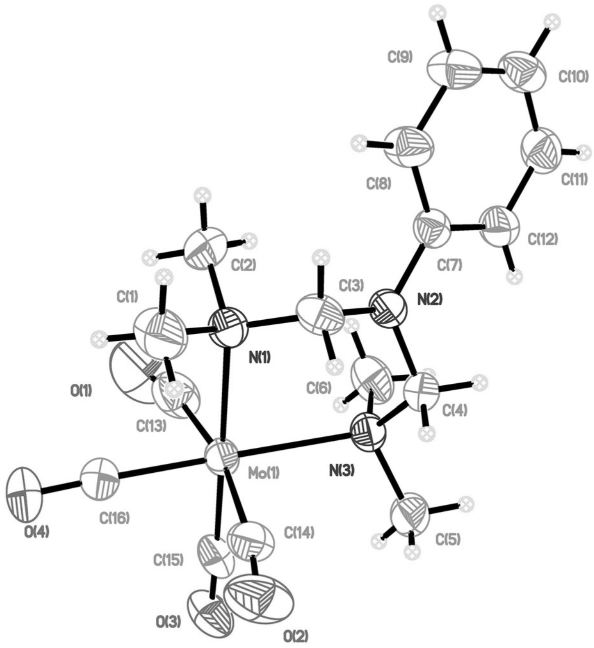


Figure 6. Structure of $[Mo(CO)_4(Me_2NCH_2)_2NPh]$ (**6**). Selected bond lengths [Å] and angles [°]: Mo1—C13 2.025(5), Mo1—C14 2.018(4), Mo1—C15 1.934(4), Mo1—C16 1.927(4), Mo1—N1 2.376(3), Mo1—N3 2.389(3), N1-Mo1-N2 87.8(9), C13-Mo1-C14 (ax) 168.7(2), C15-Mo1-C16 (eq) 86.5(2), C3-N1-Mo1 111.7(2), C5-N2-Mo1 112.0(2).

full details of all procedures, spectral data, etc. are provided in the Supporting Information.

CCDC 1428936 (4a), 1428934 (4b), 1428931 (4c),1428930 (3b), and 1428935 (6) contain the supplementary crystallographic data for this paper. These data are provided free of charge by The Cambridge Crystallographic Data Centre.

Reaction of $Et_3SiOCH_2NMe_2$ with $[Cr(\eta^6\text{-}C_6H_5)(CO)_3]MeNH$; formation of 3b: A 20 mL round-bottomed flask was charged with $Et_3SiOCH_2NMe_2$ (0.29 g, 1.5 mol) in benzene (5 mL). To this mixture, benzene solution (5 mL) of $[Cr(\eta^6\text{-}C_6H_5)(CO)_3]MeNH$ (0.37 g, 1.5 mmol) was added. The reaction mixture was stirred for 5 min at room temperature, the solvent was removed in vacuo; hexanes/CH_2Cl_2 (1:1; 10 mL) mixture was added. The solution was concentrated and left in the refrigerator to give yellow crystals of $[Cr(\eta^6\text{-}C_6H_5)(CO)_3]MeNCH_2NMe_2$ (**3b**). Solvents and Et_3SiOH were decanted, and crystals were washed with cold hexanes and dried in vacuum. Yield: 0.38 g (84%).

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Keywords: diaminomethane · disproportionation · molybdenum · silanes · siloxymethylamine

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[17] Note added in proof: Solutions of **4a** also exhibited a capacity to disproportionate to a mixture of **4a**, **b**, and **c**.

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