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Synthesis and Reactivity of Magnesium Complexes Supported by Tris(2-dimethylaminoethyl)amine (Me_6tren)

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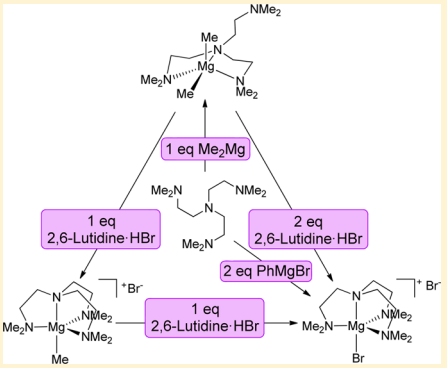
Supporting Information

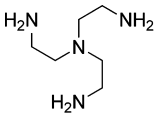
ABSTRACT: The reaction of tris(2-dimethylaminoethyl)amine (Me_6tren) with Grignard reagents and related Mg precursors has been investigated. Treating Me_6tren with 2 equiv of PhMgBr in diethyl ether resulted in the formation of [(Me_6tren)MgBr]Br (**1**), in which Me_6tren is bound in a κ^4 fashion. This is the first example of a Mg complex containing Me_6tren or a related tris(aminoethyl)amine ligand. In contrast, when MeMgBr was treated with either 1 or 2 equiv of Me_6tren, a mixture containing **1** and the alkyl species [(Me_6tren)MgMe]Br (**3**) was produced. It was not possible to separate the two compounds to generate a pure sample of **3**. Reaction between Me_6tren and greater than 4 equiv of MeMgBr formed [(Me_6tren)MgBr]$_2$[$MgBr_4$] (**4**), an analogue of **1** with a different counterion. The highly unusual dialkyl Mg compound (Me_6tren)$MgMe_2$ (**5**), which features a κ^3-bound Me_6tren ligand, was synthesized through the reaction of Me_2Mg with Me_6tren. The reaction of **5** with excess phenylacetylene or carbon dioxide yielded (Me_6tren)Mg(CCPh)$_2$ (**6**) and Mg(OAc)$_2$, respectively, while treatment with benzylalcohol, benzylamine, 4-*tert*-butylcatechol, 4-*tert*-butylphenol, and aniline all resulted in decomposition. The addition of 1 equiv of 2,6-lutidine·HBAr^F (BAr^F = tetrakis(3,5-bis(trifluoromethyl)phenyl)borate) to **5** formed [(Me_6tren)MgMe]BAr^F (**7**), a rare example of a neutral ancillary ligand supported cationic monoalkyl Mg species. Compounds **1**, **4**, and **5** have been crystallographically characterized.



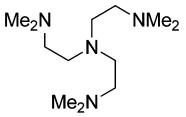
INTRODUCTION

Tren (tris(2-aminoethyl)amine, H_6tren) was the first tripodal tetraamine ligand to be reported,[1] and since its initial preparation in 1896, more than 50 derivatives have been synthesized.[2] It has been demonstrated that tren and related ligands will coordinate to almost all transition metals,[3−5] and a variety of different properties of H_6tren-containing complexes have been explored. These include in-depth studies of the thermodynamics and kinetics of H_6tren binding,[6] magnetism and conductivity measurements,[4] and structural studies on how the H_6tren ligand affects crystal field splitting and geometry.[4,5] Furthermore, H_6tren-containing compounds have found utility as catalysts for a number of processes, such as C−O bond formation,[7] the living radical polymerization of vinyl chlorides,[8] and the synthesis of thioesters from thiols and aryl halides.[9] A H_6tren-containing complex has even been used as a structure-directing agent in the synthesis of zeolites.[10] A common derivative of H_6tren is tris(2-dimethylaminoethyl)amine (Me_6tren), which provides reactive metal centers with increased steric protection and also results in complexes with greater solubility in organic solvents. Transition-metal complexes incorporating the Me_6tren ligand have been used for the reduction of nitrile ions,[11] for the modeling of cytochrome *c* oxidase,[12,13] as catalysts for atom transfer radical addition reactions,[14] and in aliphatic C−H bond activation.[15]

Although very frequently used to support transition metals,[2] tren and its derivatives have rarely been used to stabilize s-block



H_6tren



Me_6tren

compounds. The only H_6tren compounds were reported by White et al., who prepared and structurally characterized complexes of the type [(H_6tren)M]$^+$ (M = Li, Na).[16] Using the Me_6tren ligand, Davidson and co-workers synthesized the amido complex (Me_6tren)Li(HMDS) (HMDS = hexamethyldisilazide) and the alkoxide species (Me_6tren)Na(OR)(HOR) (R = 2,4,6-trimethylphenoxide) and (Me_6tren)Na(OR′) (R′ = 2,6-di-*tert*-butyl-4-methylphenoxide).[17] Subsequently, in collaboration with Mulvey and Robertson, Davidson reported (Me_6tren)M($PhCH_2$) (M = Li, Na, K), where the benzyl ligand was found to bind in a different mode, depending on the metal. These are the only examples of s-block *organometallic* compounds supported by tren or a related ligand.[18] Overall, group 1 compounds supported by tren or its derivatives are far more prevalent than group 2 species. In fact, to date the only reported X-ray crystal structure of tren or a derivative bound to a group 2 element was described by Koo and co-workers, who prepared (H_6tren)Sr(thd)$_2$ (thd = 2,2,6,6-tetramethyl-3,5-heptanedionate).[19]

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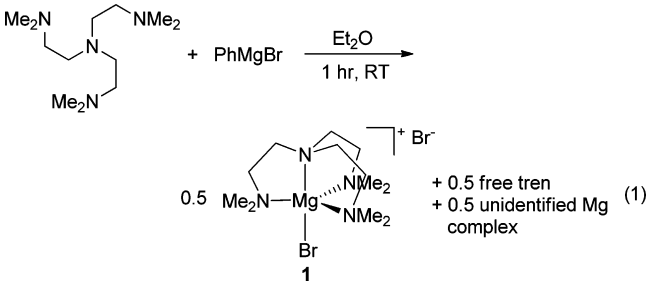
Organometallic s-block compounds (in particular those of Li and Mg) have been used extensively in organic synthesis in both carbon−carbon bond forming reactions and a number of different carbon−heteroatom bond forming processes.[20,21] However, at this stage our knowledge about the reactivity of organometallic Mg containing species is limited, in part due to the complex speciation of Grignard reagents in solution,[22] and the synthesis of well-defined monomeric organometallic Mg complexes could assist in increasing our mechanistic understanding of organic reaction pathways. As a result, our group recently attempted to prepare organometallic Mg complexes supported by the 2,2′:6,2″-terpyridine (terpy) ligand.[23] Unfortunately, we were only able to isolate complexes of the type (terpy)MgX_2 (X = Br, Cl), and when we attempted to explore the additional reactivity of these compounds, we found ligand decoordination to be a major problem. We postulated that using a κ^4 tripodal ligand instead of the κ^3 terpy ligand could result in more stable complexes, which would be more amenable to further experimentation and allow the isolation of organometallic complexes. Here, we report the synthesis of both coordination and organometallic complexes of Mg, supported by Me_6tren, which we believe are the first Mg complexes containing any form of the tren ligand. In particular, using Me_6tren, we have isolated rare examples of monomethyl and dimethyl Mg species supported by the same ligand set. Preliminary reactivity studies of the dimethyl Mg species are described.

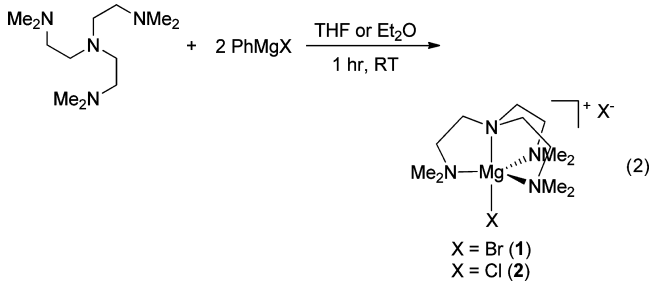
RESULTS AND DISCUSSION

The reaction of Me_6tren with 1 equiv of PhMgBr in diethyl ether resulted in the instant formation of a precipitate. The solid was isolated by filtration, and NMR spectroscopy and X-ray crystallography (vide infra) were used to establish that it was [(Me_6tren)MgBr]Br (**1**), which had formed in approximately 50% yield based on Me_6tren (eq 1). The filtrate from



the reaction mixture contained 0.5 equiv of unreacted Me_6tren and presumably 0.5 equiv of Ph_2Mg or a related decomposition product, which had formed through the disproportionation of PhMgBr. There was no evidence to indicate that the diphenyl species (Me_6tren)$MgPh_2$ or the monophenyl monohalide species [(Me_6tren)MgPh]Br formed in the reaction.

The reaction of Me_6tren with 2 equiv of PhMgBr afforded **1** in near-quantitative yield, with no unreacted ligand (eq 2). The analogous reaction between 2 equiv of PhMgCl and Me_6tren generated [(Me_6tren)MgCl]Cl (**2**) in 84% yield. The parent ions corresponding to both **1** and **2** were observed using ESI-MS, although in the case of **1** the parent ion was also accompanied by a small ion corresponding to **2**, which forms due to the reaction of **1** with dichloromethane (the solvent for the ESI-MS experiment). Both **1** and **2** are indefinitely stable when stored as solids in a nitrogen-filled glovebox but slowly



decompose in dichloromethane and acetonitrile solutions at room temperature. Our results for the reaction of PhMgX (X = Cl, Br) with the tetradentate Me_6tren ligand are consistent with those we recently reported for the reaction of PhMgX with tridentate terpy ligands, where we also only observed dihalide species.[23] To the best of our knowledge **1** and **2** represent the first time the tren ligand or any other neutral tetradentate nonplanar nitrogen ligand has been coordinated to Mg.

Compound **1** was characterized by X-ray crystallography (Figure 1), which clearly indicates that the coordination

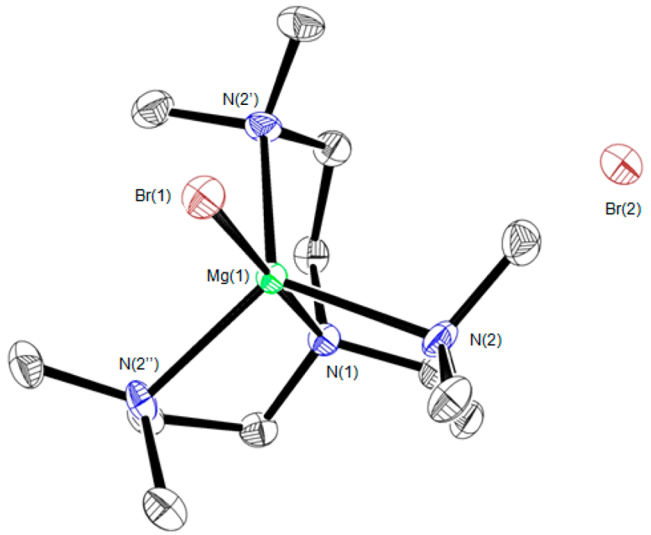


Figure 1. ORTEP[28] drawing of **1** at the 30% probability level (hydrogen atoms have been omitted for clarity). A C_3 axis is present along the N(1)−Mg(1)−Br(1) bond. Selected bond lengths (Å) and angles (deg): Mg(1)−N(1) = 2.193(8), Mg(1)−N(2) = 2.193(5), Mg(1)−Br(1) = 2.503(4); N(1)−Mg(1)−N(2) = 81.75(12), N(1)−Mg(1)−Br(1) = 180.00(11), N(2)−Mg(1)−Br(1) = 98.25(12), N(2)−Mg(1)−N(2′) = 117.98(6).

number around Mg is 5, with an outer-sphere bromide counterion. Presumably, steric factors prevent the outer-sphere bromide from coordinating and forming a six-coordinate Mg center. The geometry around Mg is trigonal bipyramidal, with the tren ligand occupying three equatorial sites and one axial site and the coordinated bromide occupying the second axial site. There is a C_3 rotation axis along the N(1)−Mg(1)−Br(1) bond, and the angle formed among any of the equatorial nitrogens, the Mg center, and the bromide ligand (for example, N(2)−Mg(1)−Br(1) is 98.25(12)°) is larger than the expected 90° for an idealized trigonal-bipyramidal structure. This distortion occurs because the Mg atom sits slightly out of the plane (0.316 Å) formed by the three equatorial nitrogen atoms. As a result, the bond angles among any two of the equatorial nitrogen atoms and Mg (for example, N(2)−Mg(1)−N(2′) is

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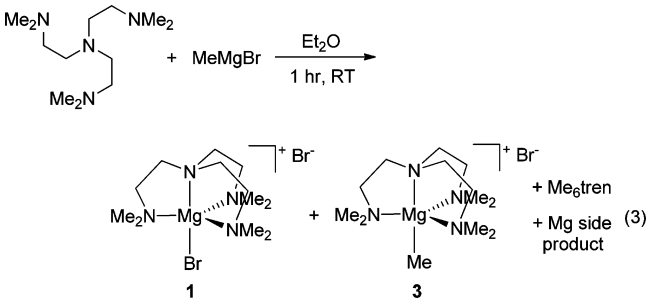
117.98(6)°) are not 120°. The distances between the Mg center and the axial and equatorial nitrogens are 2.193(8) and 2.193(5) Å, respectively, both unremarkable for Mg−N bonds.[24] Previously, transition-metal compounds of the type [(Me$_6$tren)MBr]Br (M = Co,[25] Cu,[26] Ni,[26] Mn,[27] Fe,[27] Zn[27]) were prepared and crystallized by Orioli and co-workers. The bond lengths and angles around the metal centers in those species are comparable to those observed in **1**.

In contrast to the reaction between Me$_6$tren and PhMgBr, a mixture containing two products was isolated when 1 equiv of MeMgBr was treated with Me$_6$tren (eq 3). One of these



products was compound **1**, while the second product contained a peak integrating to three protons (relative to the Me$_6$tren ligand) at −1.69 ppm in the ^{1}H NMR spectrum at 25 °C. This second product was too unstable to record a ^{13}C{^{1}H} NMR spectrum at room temperature, but at −40 °C, a peak at −19.2 ppm was visible in the ^{13}C{^{1}H} NMR spectrum. On the basis of the ^{1}H and ^{13}C{^{1}H} NMR data the second product is assigned as [(Me$_6$tren)MgMe]Br (**3**). We believe that the bromide ligand is outer sphere, by analogy to compound **1**. In order to balance the stoichiometry in eq 3, a third product is required. Although there was no evidence for the formation of (Me$_6$tren)MgMe$_2$, a significant amount of free Me$_6$tren and a small Mg side product were observed. These could be separated from **1** and **3** by filtration, as **1** and **3** precipitated from the reaction mixture. The relative ratio of **1** to **3** was 1.4:1. The addition of 2,6-lutidene·HBr to a CD_2Cl_2 solution of a mixture of **1** and **3** resulted in the quantitative conversion of **3** to **1**. Furthermore, the evolution of methane (identified by ^{1}H NMR spectroscopy) in a quantity consistent with the initial amount of **3** present in solution was observed. This provides further evidence for the assignment of **3** as the second component of the mixture. Unfortunately, **3** could not be separated from **1**, as the solubilities of both compounds were similar in solvents in which they were stable (THF) and **3** was unstable when dissolved in dichloromethane or acetonitrile for periods of time greater than 5 min. To the best of our knowledge the only other examples of Me$_6$tren-supported organometallic complexes were reported by Vacca and co-workers, who prepared [(Me$_6$tren)HgR][CF_3SO_3] (R = Me, Ph),[29] though only the latter was characterized by X-ray crystallography, and Mulvey, Robertson, and Davidson, who synthesized (Me$_6$tren)M(PhCH$_2$) (M = Li, Na, K).[17]

The relative ratio of **1** and **3** could be changed by varying the number of equivalents of MeMgBr used, and though neither could be formed exclusively, 1 equiv of MeMgBr produced a higher proportion of **3** (1.4:1 ratio of **1** to **3**) in comparison with 2 equiv (3:1 ratio of **1** to **3**). A similar trend was observed when MeMgCl was used as the Grignard reagent. Again, the two components could not be separated, as their solubilities in a range of common solvents were similar. The results from the reaction of Me$_6$tren and MeMgBr or MeMgCl are different from those observed in reactions between terpy and the same Grignard reagents. In the terpy systems we did not see any evidence for the formation of a ligated mixed Mg methyl/halide species and only observed the ligated Mg dihalide, free Me$_2$Mg, and an unidentified terpy-containing species after disproportionation of the Grignard reagent.[23] We believe that the κ^4 Me$_6$tren ligand assists in thermodynamically stabilizing the mixed methyl/halide species toward disproportionation in comparison with terpy. Previously, we have demonstrated that disproportionation is more favorable for phenyl species in

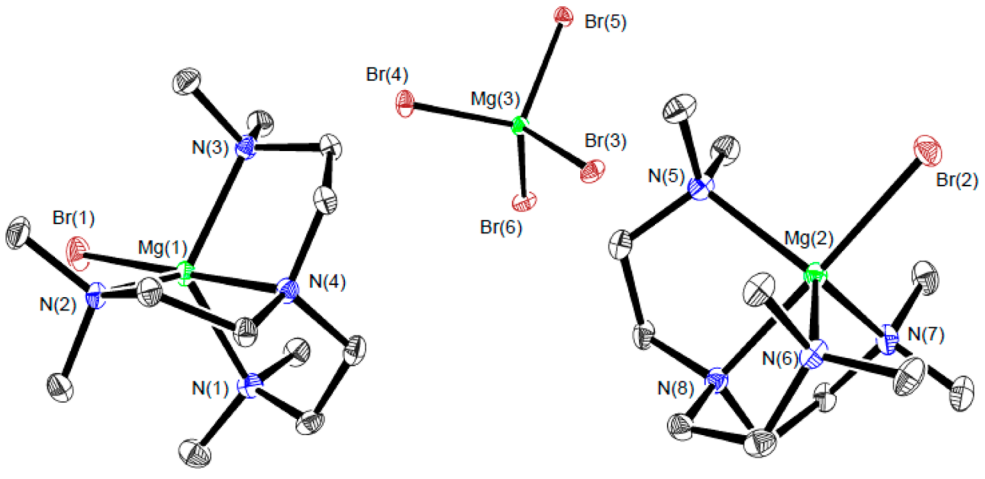


Figure 2. ORTEP[28] drawing of **4** at the 30% probability level (hydrogen atoms and toluene of crystallization have been omitted for clarity). Selected bond lengths (Å) and angles (deg) for molecule A (left): Mg(1)−N(1) = 2.197(2), Mg(1)−N(2) = 2.177(2), Mg(1)−N(3) = 2.182(2), Mg(1)−N(4) = 2.197(2), Mg(1)−Br(1) = 2.4970(9); N(1)−Mg(1)−N(2) = 117.42(9), N(1)−Mg(1)−N(3) = 118.98(9), N(1)−Mg(1)−Br(1) = 98.55(7), N(2)−Mg(1)−N(3) = 117.11(9), N(2)−Mg(1)−Br(1) = 99.39(7), N(3)−Mg(1)−Br(1) = 97.68(7), N(4)−Mg(1)−Br(1) = 179.06(7). Selected bond lengths (Å) and angles (deg) for molecule B (right): Mg(2)−N(5) = 2.213(2), Mg(2)−N(6) = 2.193(3), Mg(2)−N(7) = 2.196(2), Mg(2)−N(8) = 2.205(2), Mg(2)−Br(2) = 2.4787(9); N(5)−Mg(2)−N(6) = 118.72(9), N(6)−Mg(2)−N(7) = 115.89(10), N(5)−Mg(2)−Br(2) = 97.20(7), N(7)−Mg(2)−N(5) = 118.38(10), N(6)−Mg(2)−Br(2) = 100.28(7), N(7)−Mg(2)−Br(2) = 99.19(7), N(8)−Mg(2)−Br(2) = 178.37(7).

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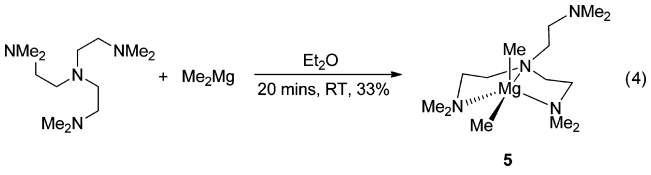
comparison with methyl species, and our results for the reactions of MeMgX and PhMgX with Me_6tren are consistent with this trend.[23]

The reaction of Me_6tren with 4 equiv or greater of MeMgBr resulted in the formation of a new tren-containing product. X-ray crystallography revealed that the new product was $[(Me_6tren)MgBr]_2[MgBr_4]$ (**4**) (Figure 2), an analogue of **1** with a different counterion. This was also confirmed by ESI-MS, where the single peak observed was attributed to the cationic fragment of **4**. The change in counterion caused a very slight perturbation in the ^{1}H NMR shifts. In **4** the most downfield triplet from the methylene protons appears at 3.06 ppm, whereas in **1** it is seen at 3.08 ppm. Similarly, the NMe_2 protons are at 2.56 ppm in **1** and 2.53 ppm in **4**. X-ray crystallography demonstrates that both cations in the structure are slightly distorted trigonal bipyramids with lengths and angles comparable to those in **1**. As in **1**, the metal center is positioned just below the plane formed by the three terminal nitrogen atoms; N(1)−Mg(1)−Br(1) is 98.55(7)°, and N(5)−Mg(2)−Br(2) is 97.20(7)°. The ligand is bound in a κ^4 manner, which is supported by the distances between the tripodal nitrogen and Mg (Mg(1)−N(4) is 2.197(2) Å, and Mg(2)−N(8) is 2.205(2) Å). A product analogous to **4** was observed from a reaction using MeMgI by ^{1}H NMR spectroscopy, though the corresponding chloride product has not been observed, even when 10 equiv of MeMgCl was used. Crystallization of **4** by layering of toluene onto a saturated solution of dichloromethane yielded the same cationic unit, but with an alternative chloride-containing counterion: $[(Me_6tren)MgBr]_2[Br_2Mg(\mu\text{-}Cl)]_2$ (see the Supporting Information for more details). This is the first time the $[Br_2Mg(\mu\text{-}Cl)]_2^{2-}$ counterion has been described in the literature, although a similar compound, $[Cd(Me_6tren)I]_2[Cd_2I_6]$, was previously reported by Ciampolini and co-workers.[30]

In an attempt to isolate a pure sample of an organometallic Mg complex, Me_6tren was treated with dimethylmagnesium (Me_2Mg) in diethyl ether. Over a period of 24 h, a solid precipitated from the reaction mixture at −80 °C. The solid was isolated and characterized as $(Me_6tren)MgMe_2$ (**5**) by NMR spectroscopy and X-ray crystallography (eq 4 and Figure 3). Compound **5** is thermally unstable and needed to be stored at −30 °C in a nitrogen-filled glovebox. This thermal instability is presumably why **5** was not observed as a disproportionation product in the reaction between MeMgBr and Me_6tren (eq 3).



(4)

Interestingly, the solid-state structure of **5** displays an unusual binding mode of Me_6tren, where the third arm of the ligand is free and is not coordinated to Mg. In addition, the bond length between the axial nitrogen of Me_6tren and the Mg center is extremely long (the Mg(1)−N(2) bond distance is 2.4814(13) Å). A survey of all Mg−N bonds in the Cambridge Structural Database[24,31] revealed that this distance is significantly longer than the mean Mg−N distance, which is 2.120 Å. The sum of van der Waals radii of Mg and N is 3.28 Å,[32] and this suggests that a bonding interaction between the central nitrogen in Me_6tren and the Mg center is present but weak.

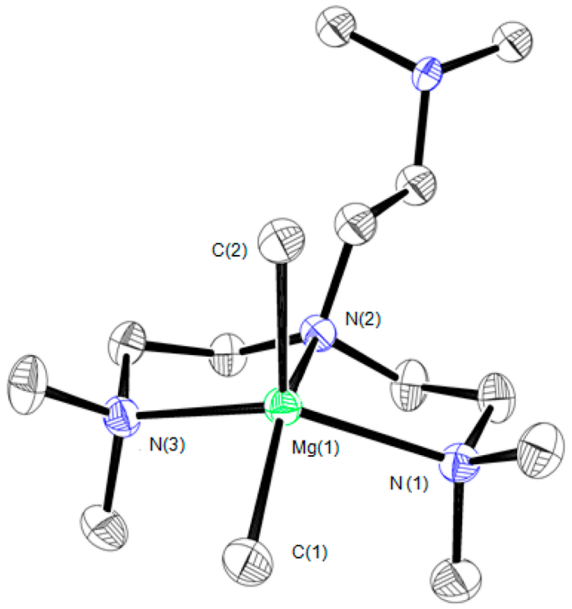


Figure 3. ORTEP[28] drawing of **5** at the 30% probability level (hydrogen atoms have been omitted for clarity; only one site of disordered Me_6tren arm is shown). Selected bond lengths (Å) and angles (deg): Mg(1)−N(1) = 2.3148(11), Mg(1)−N(2) = 2.4814(11), Mg(1)−N(3) = 2.2959(12), Mg(1)−C(1) = 2.2042(14), Mg(1)−C(2) = 2.1710(13); N(1)−Mg(1)−N(2) = 73.98(4), N(1)−Mg(1)−N(3) = 131.76(4), N(1)−Mg(1)−C(1) = 94.14(5), N(1)−Mg(1)−C(2) = 112.64(5), N(2)−Mg(1)−N(3) = 74.27(4), N(2)−Mg(1)−C(1) = 149.33(5), N(2)−Mg(1)−C(2) = 97.84(4), N(3)−Mg(1)−C(1) = 95.09(5), N(3)−Mg(1)−C(2) = 106.87(5), C(1)−Mg(1)−C(2) = 112.82(6).

Previously, κ^3 coordination of Me_6tren has been observed in transition-metal complexes containing Pd,[33] Ru,[34] and Cu,[14] while the only other example for an s-block element was reported by Davidson et al., who prepared $(Me_6tren)Li(HMDS)$.[17] Though it was not crystallographically confirmed, Macbeth and co-workers also postulated that $[(Me_6tren)Cu(CO)]PF_6$ featured a κ^3-bound ligand on the basis of IR spectroscopy.[35] More recently, the Me_6tren ligand has been observed to bind in a κ^2 fashion to zinc and bridge three gallium centers, with each metal bound to one arm.[36]

A comparison of the structure of **5** with that of $(PMDTA)MgMe_2$ (PMDTA = *N*,*N*,*N*′,*N*′,*N*″-pentamethyldiethylenetriamine), one of only three other crystallographically characterized monomers to feature two terminal methyl groups bound to Mg,[37−39] reveals significant lengthening of the Mg(1)−N(2) bond of **5**. In $(PMDTA)MgMe_2$, which features a κ^3 PMDTA ligand, the corresponding Mg−N bond length is 2.424(2) Å.[38] This suggests stronger binding for the tridentate PMDTA ligand, than for Me_6tren, once one arm of the Me_6tren is no longer coordinated. The overall geometry around Mg in **5** is square pyramidal. One of the methyl groups is trans to the apical nitrogen of the Me_6tren ligand, and the strong *trans* influence of the methyl ligand is presumably partially responsible for the elongated Mg(1)−N(2) bond distance. The other methyl ligand is *trans* to a vacant site, and as a result this Mg−C bond distance is significantly shorter (the Mg(1)−C(2) bond distance is 2.1710(13) Å compared to the Mg(1)−C(1) bond distance, which is 2.2042(14) Å). The bond distances between Mg and the Me_6tren ligands are significantly longer in **5** in comparison to those observed in **1**. For example,

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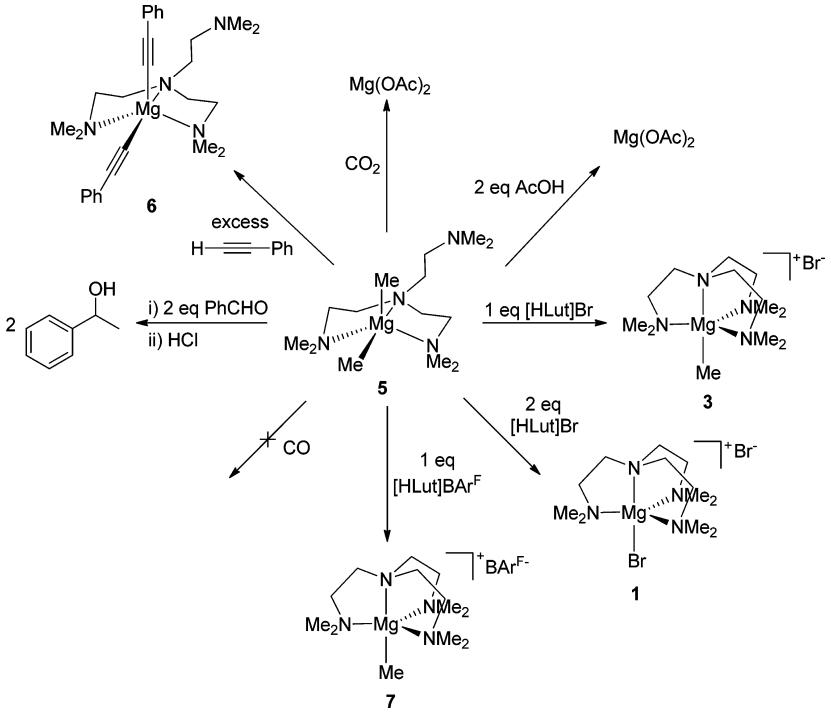
Scheme 1



the Mg(1)−N(1) and Mg(1)−N(3) bond distances in **5** are 2.3148(11) and 2.2959(12) Å, respectively, while the corresponding distance in **1** is 2.193(5) Å (due to symmetry requirements, the two Mg−N distances are identical). The longer distances in **5** probably occur because the compound is neutral, whereas **1** is cationic.

Although the solid-state structure of **5** shows one of the ligand arms to be chemically nonequivalent, the ^{1}H NMR spectrum in toluene-d_8 displays only one environment for the ligand methylene protons between −90 and +25 °C. This NMR behavior is comparable to that observed in transition-metal complexes containing κ^3-coordinated tren, which also only show one signal for the methylene protons at low temperature.[14,17] Consistent with the observation of only one methylene environment, only one Mg−Me resonance (at −0.99 ppm), which integrates to six protons, is observed in the ^{1}H NMR spectrum of **5**, even at low temperature. The ^{13}C{^{1}H} NMR spectrum of **5** features a resonance at −12.53 ppm, which is assigned to the Mg-bound Me groups.

Given the relative paucity of ligated bis(alkyl) Mg species, we were interested in exploring the reactivity of **5**. The reaction of **5** in C_6D_6 with a variety of substrates with O−H and N−H bonds such as aniline, benzylamine, 4-*tert*-butylcatechol, benzylalcohol, and 4-*tert*-butylphenol all resulted in the formation of Me_6tren, and no Mg-containing products were isolated. In all cases a precipitate formed which could not be easily dissolved. The observation of free Me_6tren suggests that even the tetradentate Me_6tren ligand is not tightly bound to Mg. The addition of 10 equiv of phenylacetylene to a solution of **5** in benzene formed (Me_6tren)Mg(CCPh)$_2$ (**6**), which was thermally unstable (Scheme 1). In a fashion analogous to that for **5**, **6** displays a signal pattern in its ^{1}H NMR spectrum different from that of **1**−**4**. In **6**, a resonance associated with one of the methylene proton triplets appears furthest upfield, while in **1**−**4**, the signal associated with the nitrogen methyl groups appears the furthest upfield. In lieu of an X-ray crystal structure, this could indicate that **6** also features a κ^3-bound Me_6tren.

The reaction of **5** with carbon dioxide in C_6D_6 led to the instant formation of a white precipitate, and free Me_6tren was present in the ^{1}H NMR spectrum. The same white precipitate was formed when 2 equiv of acetic acid was added to a solution of **5** in C_6D_6. In this experiment 2 equiv of methane was also observed by ^{1}H NMR spectroscopy. On this basis and by comparison with an authentic sample, we believe that the white precipitate is Mg(OAc)$_2$. It is probable that this reaction occurs by nucleophilic attack of the methyl group on electrophilic carbon dioxide, but other mechanisms cannot be ruled out at this stage. Further evidence of the nucleophilic character of the methyl was provided by the reaction of **5** with 2 equiv of benzaldehyde, which yielded 2 equiv of 1-phenylethanol, the product of nucleophilic attack, after an acidic workup. Compound **5** did not react with carbon monoxide. The inability of the Me_6tren ligand to remain coordinated after reactions of **5** is in dramatic contrast with the findings of Parkin and co-workers, who were able to isolate a wide range of ligated Mg products from the reactions of {tris(pyrazolyl)-hydroborato}Mg alkyl derivatives with substrates such as carbon dioxide, alcohols, terminal alkynes, and ketones, among others.[40−42] It appears that the use of an anionic ligand vastly improves the stability of Mg complexes supported by nitrogen-based ligands in comparison with our tripodal neutral nitrogen donor set.

The addition of 2 equiv of 2,6-lutidine·HBr in CD_2Cl_2 to **5** formed **1**, while reaction with 1 equiv generated the monomethyl species **3**, which was observed by ^{1}H NMR spectroscopy, though the previously mentioned instability led to swift decomposition. In an attempt to isolate a solution-stable Me_6tren-ligated Mg monomethyl species, **5** was reacted with 2,6-lutidine·HBAr^F (BAr^F = tetrakis(3,5-bis-(trifluoromethyl)phenyl)borate) in diethyl ether. The resulting product, **7**, is proposed to be [(Me_6tren)MgMe]BAr^F on the

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basis of NMR spectroscopy and ESI-MS. The shifts corresponding to the ligand are nearly identical with those observed for **3**, and Mg−Me resonances were observed at −1.65 and −19.38 ppm in the ^{1}H and $^{13}C\{^{1}H\}$ spectra, respectively. A single peak at 62.86 ppm in the ^{19}F NMR spectrum confirms the presence of the BAr^{F} counterion in **7**. The compound is stable for at least 1 h in CD_2Cl_2 at room temperature, which is in vast contrast to the case for **3**, where decomposition is observed almost instantly. Addition of 2,6-lutidine·HBr to a solution of **7** in CD_2Cl_2 results in the liberation of methane (detected by ^{1}H NMR spectroscopy) and the formation of a new tren-containing product. The more downfield ^{1}H NMR shifts associated with the new compound in comparison to the shifts for **7** and the disappearance of the Mg−Me peak are consistent with the formation of $[(Me_6tren)MgBr]BAr^{F}$. Though Mg monomethyls ligated by anionic nitrogen ligands are comparatively plentiful,[43−46] **7** is only the second example of a compound containing a Mg−Me group supported only by a neutral nitrogen donor set. The other example, [MeMg(14N4)]Cp (14N4 = 1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane; Cp = $C_5H_5^-$), features a planar nitrogen-containing macrocycle.[47] Compound **7** is considerably less stable than either [MeMg(14N4)]Cp or examples of monomethyls with anionic ligands.

CONCLUSIONS

The reaction of various Grignard reagents with Me_6tren has been shown to yield a series of Mg compounds where the type and quantity of the Grignard has a pronounced affect on the identity of the product. For RMgX (R = Ph, X = Cl, Br) only $[(Me_6tren)MgX]X$ was isolated, whereas when R = Me, a mixture containing both $[(Me_6tren)MgMe]X$ and $[(Me_6tren)MgX]X$ was observed. These compounds represent the first time Mg has been coordinated to any type of tren. The tren ligand was also able to support the unusual Mg dimethyl species $(Me_6tren)MgMe_2$, which was formed through the reaction of Me_6tren with Me_2Mg. $(Me_6tren)MgMe_2$ has an atypical structure in the solid state, where one of the ligand arms is not coordinated to the Mg center. When $(Me_6tren)MgMe_2$ and phenylacetylene were mixed, $(Me_6tren)Mg(CCPh)_2$ formed, but the use of aniline, benzylalcohol, benzylamine, 4-*tert*-butylphenol, and 4-*tert*-butylcatechol all resulted in decomposition. Insertion into both Mg−Me bonds was observed when $(Me_6tren)MgMe_2$ was placed under 1 atm of carbon dioxide, though no reaction was observed with CO. Reaction with benzaldehyde produced 1-phenylethanol after acidic workup, confirming the nucleophilic nature of the methyl group in this complex. The reaction of $(Me_6tren)MgMe_2$ with 1 equiv of 2,6-lutidine·$HBAr^{F}$ forms $[(Me_6tren)MgMe]BAr^{F}$, which is more stable in solution than the analogous compound with a halide counterion. Our previous work on the binding of κ^3 terpy to Mg was hindered by both ligand dissociation and an inability to observe any organometallic products. The use of a κ^4 ligand appears to have stabilized organometallic compounds and allowed us to prepare relatively rare examples of well-defined Mg methyl species.

EXPERIMENTAL SECTION

General Methods. Experiments were performed under a dinitrogen atmosphere in an M. Braun drybox or using standard Schlenk techniques, unless otherwise noted. (Under standard glovebox conditions, purging was not performed between uses of pentane, diethyl ether, benzene, toluene and THF; thus, when any of these solvents were used, traces of all these solvents were in the atmosphere and could be found intermixed in the solvent bottles.) Moisture- and air-sensitive liquids were transferred by stainless steel cannula on a Schlenk line or in a drybox. Solvents were dried by passage through a column of activated alumina followed by storage under dinitrogen. All commercial chemicals were used as received, except where noted. MeMgBr, MeMgCl, PhMgCl (all in THF), MeMgI in diethyl ether, and PhMgBr in both diethyl ether and THF were purchased from Acros Organics and titrated using salicylaldehyde phenylhydrazone.[48] 2,2′,2″-Triaminotriethylamine (tren) was purchased from Strem Chemicals. Trimethoxybenzene and 1-phenylethanol were purchased from Sigma Aldrich, as were phenylacetylene, aniline, benzaldehyde, benzylalcohol, and benzylamine, which were all distilled prior to use. 4-*tert*-Butylphenol and 4-*tert*-butylcatechol were sublimed before use and were purchased from Sigma Aldrich and Acros Organics, respectively. Deuterated solvents were obtained from Cambridge Isotope Laboratories. CD_2Cl_2 and CD_3CN were dried using CaH_2 and C_6D_6, and toluene-d_8 was dried using sodium metal. All deuterated solvents were vacuum-transferred prior to use. NMR spectra were recorded on Bruker AMX-400 and -500 and Varian-300 spectrometers at ambient probe temperatures unless otherwise stated. Chemical shifts are reported in ppm with respect to residual internal protio solvent for ^{1}H and $^{13}C\{^{1}H\}$ NMR spectra and to an external standard for $^{19}F\{^{1}H\}$ spectra ($CFCl_3$ at 0.0 ppm). NMR coupling constants (J) are given in Hz. IR spectra were measured using a diamond Smart Orbit ATR on a Nicolet 6700 FT-IR instrument. Elemental analysis was not performed, due to the extreme instability of almost all compounds studied in this work; however ^{1}H and $^{13}C\{^{1}H\}$ NMR spectra are provided in the Supporting Information. Literature procedures were utilized to synthesize Me_2Mg,[38] 2,6-lutidine·HCl,[49] and Me_6tren,[50] while 2,6-lutidine·HBr and 2,6-lutidine·$HBAr^{F}$ were prepared via an adapted literature procedure.[49]

X-ray Crystallography. X-ray diffraction experiments were carried out on a Rigaku Mercury 275R CCD (SCX mini) diffractometer using graphite-monochromated Mo Kα radiation (λ = 0.71073 Å) at −50 °C, a Rigaku R-AXIS RAPID diffractometer coupled to a R-AXIS RAPID imaging plate detector with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å) at −180 °C, or a Rigaku MicroMax-007HF diffractometer coupled to a Saturn994+ CCD detector with Cu Kα radiation (λ = 1.54178 Å) at −180 °C. The crystals were mounted on MiTeGen polyimide loops with immersion oil. The data frames were processed using Rigaku CrystalClear and corrected for Lorentz and polarization effects. Using Olex2,[51] the structure was solved with the XS[52] structure solution program by direct methods and refined with the XL[52] refinement package using least-squares minimization. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were refined using the riding model. Details of the crystal structure and refinement data for **1**, **4**, and **5** are given in the Supporting Information.

ESI-MS. Mass spectra were collected using the home-built cryogenic ion mass spectrometer of Johnson and co-workers.[53,54] Briefly, millimolar solutions of each species were prepared and drawn into the electrospray syringe under an inert atmosphere. The syringe was then quickly transported into a nitrogen-purged enclosure attached to the inlet capillary of the mass spectrometer, and the solutions were electrosprayed through a 30 μm fused silica capillary tip. The generated ions were guided through four differentially pumped stages using two RF-only quadrupole guides and an octupole guide. The ions were then directed 90° with a DC quadroupole bender through a second octupole and einzel lens, which guide the ions into a Paul trap (Jordan) cooled to 10 K with a closed-cycle helium cryostat. He buffer gas was introduced into the trap with a pulsed valve, allowing for collisional cooling of the ions. After equilibrating in the trap for about 90 ms, the ions were extracted by applying ±90 V push/pull to the entrance and exit lenses of the trap, respectively. The ejected ions next entered the extraction region of a Wiley−McLaren TOF mass spectrometer, accelerating the ions through a field-free flight tube, and finally detected with an MCP detector.

Synthesis and Characterization of Compounds. *[(Me$_6$tren)MgBr]Br (1).* A 15 mL portion of diethyl ether was transferred by

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cannula to a Schlenk flask containing PhMgBr (2.71 M in diethyl ether, 0.64 mL, 1.74 mmol) and subsequently added to a solution of Me_6tren in toluene (50 mg/mL, 4.00 mL, 0.87 mmol) diluted with 15 mL of diethyl ether. The immediate formation of a light brown precipitate was observed, and the mixture was stirred for 1 h at room temperature. The reaction mixture was filtered and the off-white solid collected. The crude product was washed with 2 × 15 mL of toluene and dried under reduced pressure to give **1** as a white powder. Yield: 0.35 g (97%). X-ray diffraction quality crystals were grown by layering toluene on a saturated acetonitrile solution of **1** at −30 °C.

^{1}H NMR (CD_2Cl_2, 400.0 MHz): δ 3.08 (6H, t, CH_2, J = 5.51 Hz), 2.88 (6H, t, CH_2, J = 5.20 Hz), 2.56 (18 H, s, N(CH_3)$_2$). ^{13}C{^{1}H} NMR (CD_2Cl_2, 100 MHz): δ 56.48, 50.20, 46.53. ESI-MS (CH_2Cl_2): 334 (M^+). IR (ATR, Smart Orbit diamond plate, cm^{-1}): 2979.3, 2874.6, 1642.0, 1590.7, 1484.0, 1474.7, 1457.5, 1293.9, 1170.8, 1096.7, 1018.7, 1000.2, 938.2, 930.7, 904.7, 798.5, 769.3, 698.1.

[(Me_6tren)MgCl]Cl (**2**). Me_6tren in toluene (50 mg/mL, 3.00 mL, 0.65 mmol) was diluted with 20 mL of diethyl ether and added to a Schlenk flask containing PhMgCl (1.73 M in THF, 753 μL, 1.30 mmol) in 20 mL of diethyl ether at room temperature. A white precipitate formed instantly, and the mixture was stirred for 1 h. The crude product was isolated by filtration and purified by addition of pentane to a concentrated THF solution to give **2** as a white powder. Yield: 0.18 g (84%).

^{1}H NMR (CD_2Cl_2, 300.0 MHz): δ 3.06 (6H, t, CH_2, J = 4.92 Hz), 2.82 (6H, t, CH_2, J = 4.69 Hz), 2.51 (18 H, s, N(CH_3)$_2$).^{13}C{^{1}H} NMR CD_2Cl_2, 75 MHz): δ 56.44, 50.15, 46.27. ESI-MS (CH_2Cl_2): 290 (M^+). IR (ATR, Smart Orbit diamond plate, cm^{-1}): 2968.0, 2845.0, 1472.9, 1293.9, 1173.3, 1101.6, 1039.9, 1023.1, 1010.4, 945.0, 933.2, 904.5, 801.9, 771.8.

[(Me_6tren)MgMe]Br (**3**). Me_6tren in toluene (50 mg/mL, 3.00 mL, 0.65 mmol) was diluted with 30 mL of diethyl ether, and MeMgBr (1.24 M in diethyl ether, 525 μL, 0.65 mmol) was added. A white precipitate formed instantly, and the mixture was stirred for 1 h at room temperature. Filtration of the reaction mixture yielded a white powder containing a mixture of **1** and **3** in a ratio of 1:0.7. The combined yield was 253 mg. Although both crystallization and extraction were attempted to separate **1** and **3**, these attempts were unsuccessful due to the similar solubilities of the compounds and the thermal instability of **3** in solution. The ^{1}H and ^{13}C{^{1}H} NMR spectra of the mixtures are shown in the Supporting Information. The NMR line listing for **3** is given below.

^{1}H NMR (CD_2Cl_2, 400.0 MHz): δ 2.85 (6H, t, CH_2, J = 5.51 Hz), 2.67 (6H, t, CH_2, J = 4.54 Hz), 2.33 (18 H, s, N(CH_3)$_2$), −1.76 (3H, s, MgCH_3). ^{13}C{^{1}H} NMR (CD_2Cl_2, 125 MHz, 233 K): δ 55.10, 49.48, 47.50, 42.66, −19.19.

[(Me_6tren)MgBr]$_2$[$MgBr_4$] (**4**). Me_6tren in toluene (50 mg/mL, 2.00 mL, 0.44 mmol) was placed in a Schlenk flask containing 30 mL of diethyl ether. MeMgBr (1.36 M in diethyl ether, 6.40 mL, 8.72 mmol) was added, and a white precipitate formed. The mixture was stirred for 80 min and then filtered. The resulting precipitate was purified by dissolution in THF and precipitation by addition of pentane. The solid was collected and dried under reduced pressure to give **4** as a white powder. Yield: 189 mg (86%). Diffraction-quality crystals were grown by layering toluene onto a saturated acetonitrile solution of **4** at −30 °C.

^{1}H NMR (CD_2Cl_2, 300.0 MHz): δ 3.05 (6H, t, CH_2, J = 5.64 Hz), 2.86 (6H, t, CH_2, J = 5.86 Hz), 2.53 (18 H, s, N(CH_3)$_2$). ^{13}C{^{1}H} NMR (CD_2Cl_2, 75 MHz): δ 56.52, 50.26, 46.52. ESI-MS (CH_2Cl_2): 334 (M^+). IR (ATR, Smart Orbit diamond plate, cm^{-1}): 2972.5, 2874.0, 1471.5, 1457.5, 1354.8, 1293.6, 1171.1, 1097.8, 1019.5, 1000.8, 931.4, 903.8, 873.3, 799.4, 770.3.

(Me_6tren)$MgMe_2$ (**5**). Me_6tren in toluene (45 mg/mL, 5 mL, 0.98 mmol) was placed in a Schlenk flask and the toluene removed *in vacuo*. To the resulting yellow oil were added diethyl ether (30 mL) and Me_2Mg (53 mg, 0.98 mmol), and a cloudy solution with an off-white precipitate formed. The mixture was stirred for 20 min and then filtered into a Schlenk flask in a −78 °C bath. The volume of the filtrate was reduced to ∼4 mL and placed in a −80 °C freezer. After 24 h, a white precipitate was present, which was separated from the solvent by filtration. After the precipitate was washed with pentane (2 × 5 mL), **5** was isolated as a thermally sensitive white powder, which was stored in a −30 °C freezer in a nitrogen-filled glovebox. Yield: 91 mg (33%). Diffraction-quality crystals were grown by layering diethyl ether and pentane at −30 °C.

^{1}H NMR (C_6D_6, 400.0 MHz): δ 2.41 (6H, t, NCH_2CH$_2$N, J = 5.66 Hz), 2.06 (6H, t, NCH$_2$CH_2N, J = 5.67 Hz), 1.98 (18H, s, N(CH_3)$_2$), −0.99 (6H, s, MgCH_3). ^{13}C{^{1}H} NMR (C_6D_6, 100 MHz): δ 55.29, 49.73, 46.88, −12.53.

(Me_6tren)Mg(CCPh)$_2$ (**6**). Compound **5** (20 mg, 0.07 mmol) was weighed into a vial, and 2 mL of benzene was added. Phenylacetylene (77 μL, 0.70 mmol) was added to the solution. The mixture was agitated for 3 min, and all the volatiles were removed under reduced pressure to give **6** as a white powder. Compound **6** is thermally unstable and was stored in a −30 °C freezer in a nitrogen-filled glovebox. Yield: 31 mg (97%).

^{1}H NMR (C_6D_6, 400.0 MHz): δ 7.76 (4H, app. d, ArH, J = 8.28 Hz), 7.14 (4H, t, ArH, J = 7.77 Hz), 7.00 (2H, tt, ArH, J = 7.41, 1.21 Hz), 2.45 (6H, t, NCH_2CH$_2$N, J = 5.41 Hz), 2.25 (18H, s, N(CH_3)$_2$), 1.97 (6H, t, NCH$_2$CH_2N, J = 5.63 Hz). ^{13}C{^{1}H} NMR (C_6D_6, 125 MHz): δ 131.90, 130.04, 129.83, 128.35, 125.11, 110.10, 54.98, 49.98, 46.15.

Reaction between **5** *and* CO_2 *or CO.* Compound **5** (5 mg, 0.02 mmol) was dissolved in C_6D_6 in a J. Young NMR tube. The mixture was degassed using three freeze−pump−thaw cycles and carbon dioxide introduced into the tube using a dual-manifold Schlenk line at room temperature. A ^{1}H NMR spectrum recorded less than 10 min after carbon dioxide addition showed that free Me_6tren was present in solution along with a precipitate. The solvent was removed under vacuum and the resulting white precipitate dissolved in D_2O. The ^{1}H NMR spectrum of the precipitate was consistent with an authentic sample of Mg(OAc)$_2$. The reaction with CO was carried out in an analogous fashion, but only **5** was observed in the ^{1}H NMR spectrum after mixing.

Reaction between **5** *and Acetic Acid.* Compound **5** (5 mg, 0.02 mmol) was dissolved in C_6D_6 in a screw-cap NMR tube. Acetic acid (0.083 M in THF, 500 μL, 0.042 mmol) was then added via a micro pipet and the tube quickly capped. Both Me_6tren and methane were visible in the ^{1}H NMR spectrum. The solvent was removed under reduced pressure and the residue dissolved in D_2O. The ^{1}H NMR spectrum indicated the formation of Mg(OAc)$_2$, which, as above, was compared with a spectrum of an authentic sample.

Reaction of **5** *with 2,6-Lutidine·HBr.* 2,6-Lutidine·HBr (3.3 mg, 0.02 mmol) was dissolved in CD_2Cl_2 in a screw-cap NMR tube containing **5** (5 mg, 0.02 mmol) and the sample frozen in liquid nitrogen. A ^{1}H NMR spectrum recorded at room temperature indicated that the sample contained 92% **3** and 8% **1**. The same procedure was followed for the reaction with 2 equiv of 2,6-lutidine·HBr (6.6 mg, 0.04 mmol). In this case only **1** was observed in the ^{1}H NMR spectrum.

Reaction of **5** *with Benzaldehyde.* Compound **5** (5 mg, 0.02 mmol) was weighed into a vial and dissolved in 1 mL of benzene to form a colorless solution. Benzaldehyde (3.6 μL, 0.04 mmol) was added by micropipet, with no visible change in the appearance of the solution. After the solution was agitated for 2 min, HCl (0.147 M in diethyl ether, 238 μL, 0.04 mmol) was added, resulting in the formation of a white precipitate. The reaction mixture was filtered and the solvent removed from the filtrate by the passage of dinitrogen over the reaction vessel. A ^{1}H NMR spectrum of the residue in $CDCl_3$ showed 1-phenylethanol to be the major product. This assignment was confirmed by comparison with an authentic sample.

[(Me_6tren)MgMe]BAr^F (**7**). 2,6-Lutidine·HBAr^F (12.2 mg, 0.01 mmol) was dissolved in 2 mL of diethyl ether and added dropwise to an agitated solution of **5** (4 mg, 0.01 mmol) in 3 mL of diethyl ether. The colorless solution was stirred for 1 min, and all volatiles were removed *in vacuo*. The residue was washed with 2 mL of toluene and dried to give **7** as a white solid. Yield: 14 mg (98%).

^{1}H NMR (CD_2Cl_2, 400.0 MHz): δ 7.72 (8H, app t, ArH, J = 2.37), 7.56 (4H, br s, ArH), 2.72 (6H, t, CH_2, J = 5.26 Hz), 2.62 (6H, t, CH_2, J = 6.34 Hz), 2.38 (18 H, s, N(CH_3)$_2$), −1.65 (3H, s, MgCH_3).

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$^{13}C\{^{1}H\}$ NMR (CD_2Cl_2, 125 MHz, 233 K): δ 161.73 (q, J = 49.9), 134.62, 128.61 (q, J = 31.1), 124.42 (q, J = 272.6), 117.52, 54.91, 49.50, 47.58, 42.45, −19.38. $^{19}F\{^{1}H\}$ NMR (CD_2Cl_2, 376 MHz): δ 62.86. ESI-MS (CH_2Cl_2): 270 (M^+).

■ ASSOCIATED CONTENT

Supporting Information

CIF files, tables, and figures giving X-ray information for **1**, **4**, and **5** and ^{1}H and $^{13}C\{^{1}H\}$ NMR spectra for all compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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