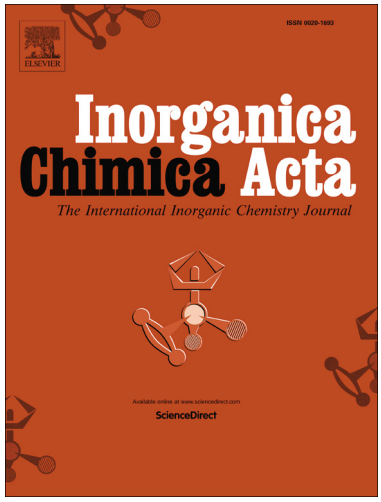

Research paper

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Reactivity of [Tism$^{Pr^iBenz}$]MgMe towards Secondary Amines and Terminal Alkynes: Catalytic Dehydrocoupling with Hydrosilanes to Afford Si–N and Si–C Bonds‡

Michael Rauch, Renee C. Roberts and Gerard Parkin,*

Department of Chemistry,

Columbia University,

New York, New York 10027, USA.

‡ In celebration of the distinguished and inspirational career of Malcolm L. H Green. Congratulations Malcolm!

Abstract: The magnesium hydride and methyl compounds, [Tism$^{Pr^iBenz}$]MgX (X = H, Me), react with diphenylamine (Ph_2NH) and pyrrolidine (C_4H_8NH) to afford the amide derivatives, [Tism$^{Pr^iBenz}$]MgNPh$_2$ and [Tism$^{Pr^iBenz}$]MgNC$_4$H$_8$, while reactions with the terminal alkynes, PhC≡CH and Bu^{n}C≡CH, afford the corresponding acetylide derivatives, [Tism$^{Pr^iBenz}$]MgC≡CPh and [Tism$^{Pr^iBenz}$]MgC≡CBu^n. The Mg–N bond of [Tism$^{Pr^iBenz}$]MgNR$_2$ may be cleaved by hydrosilanes, such that [Tism$^{Pr^iBenz}$]MgMe is an effective precatalyst for the dehydrocoupling of hydrosilanes and amines. For example, [Tism$^{Pr^iBenz}$]MgMe enables the conversion of a 1:1 mixture of Ph_2SiH_2 and C_4H_8NH at room temperature to the silazane, $Ph_2SiH(NC_4H_8)$. [Tism$^{Pr^iBenz}$]MgH and [Tism$^{Pr^iBenz}$]MgMe are also capable of dehydrocoupling PhC≡CH and $PhSiH_3$ to form $PhSiH_2C{\equiv}CPh$. In addition to dehydrocoupling of terminal alkynes, [Tism$^{Pr^iBenz}$]MgMe is also capable of achieving the isomerization 3-phenyl-1-propyne to phenylallene.

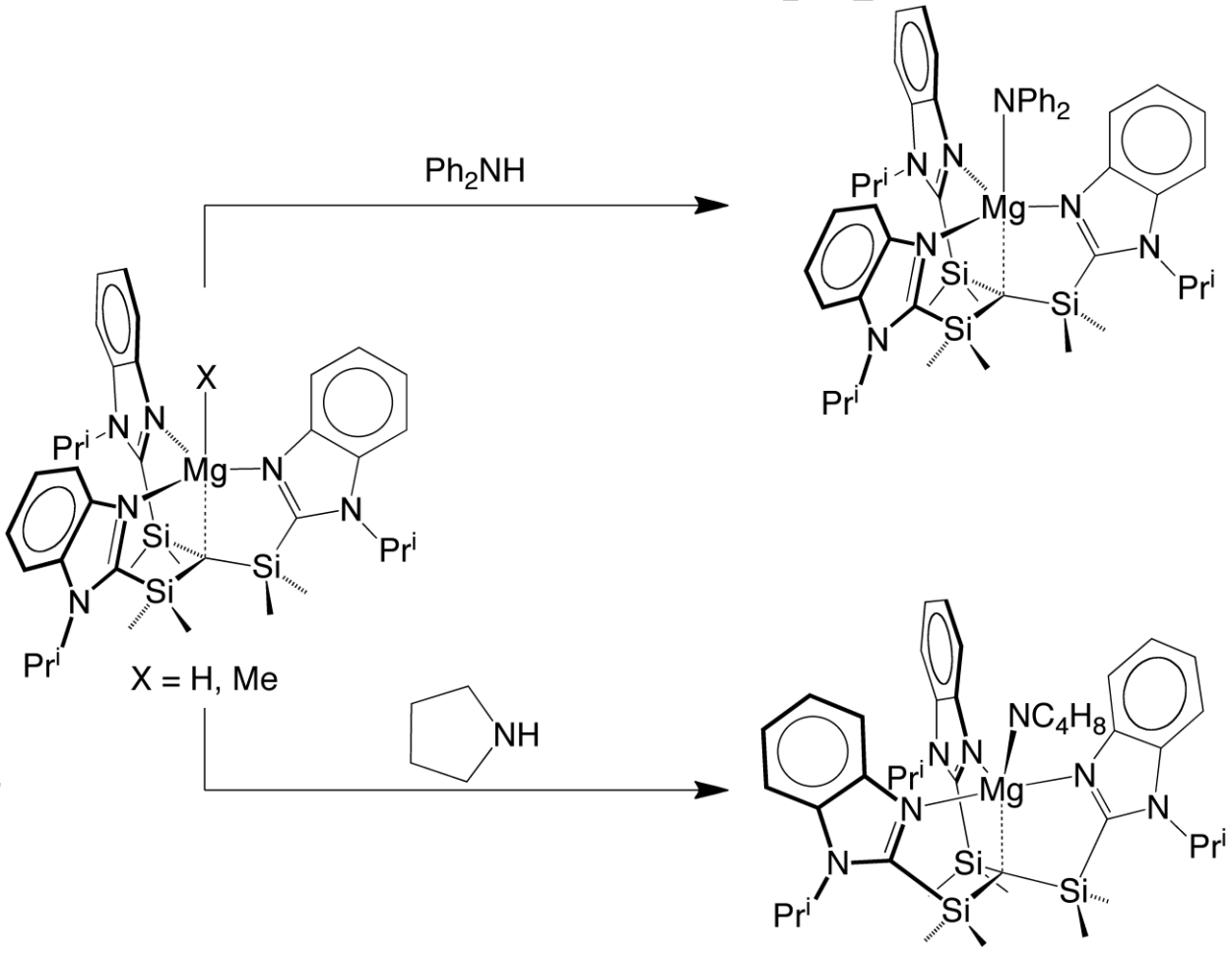
INTRODUCTION

Dehydrocoupling reactions involving molecules with Si–H and X–H bonds provide a valuable method for the synthesis of compounds with Si–X bonds,[1] which complements that of hydrosilylation in which Si–X bond formation is achieved by the addition of an Si–H bond across an X≈Y multiple bond.[2] For example, the formation of Si–N bonds by the dehydrocoupling of hydrosilanes with either primary or secondary amines is an important transformation for the synthesis of silazanes, which are a useful class of molecules with respect to their function as chemical reagents (*e.g.* bases and silylating agents).[3,4] Such compounds, however, are traditionally obtained by the net dehydrohalogenation of amines and halosilanes,[5] a transformation that is less appealing than one involving dehydrogenation, from the perspective of both functional group tolerance and the nature of the byproducts.[3] Likewise, alkynylsilanes are of use for the formation of C–C and C–X bonds, and are also traditionally obtained by employing halosilanes.[6] Efforts to obtain improved syntheses of alkynylsilanes have, therefore, also focused on the dehydrocoupling of terminal alkynes and hydrosilanes.[7] Despite these advances in the formation of Si–X bonds by dehydrocoupling, however, there is much current interest in developing catalytic systems that feature nonprecious metals.[3,8] Therefore, we report here the ability of the *tris*[(1-isopropylbenzimidazol-2-yl)dimethylsilyl]methyl magnesium compounds, [Tism$^{Pr^iBenz}$]MgMe[9] and [Tism$^{Pr^iBenz}$]MgH,[10] to enable the catalytic formation of Si–N and Si–C bonds.

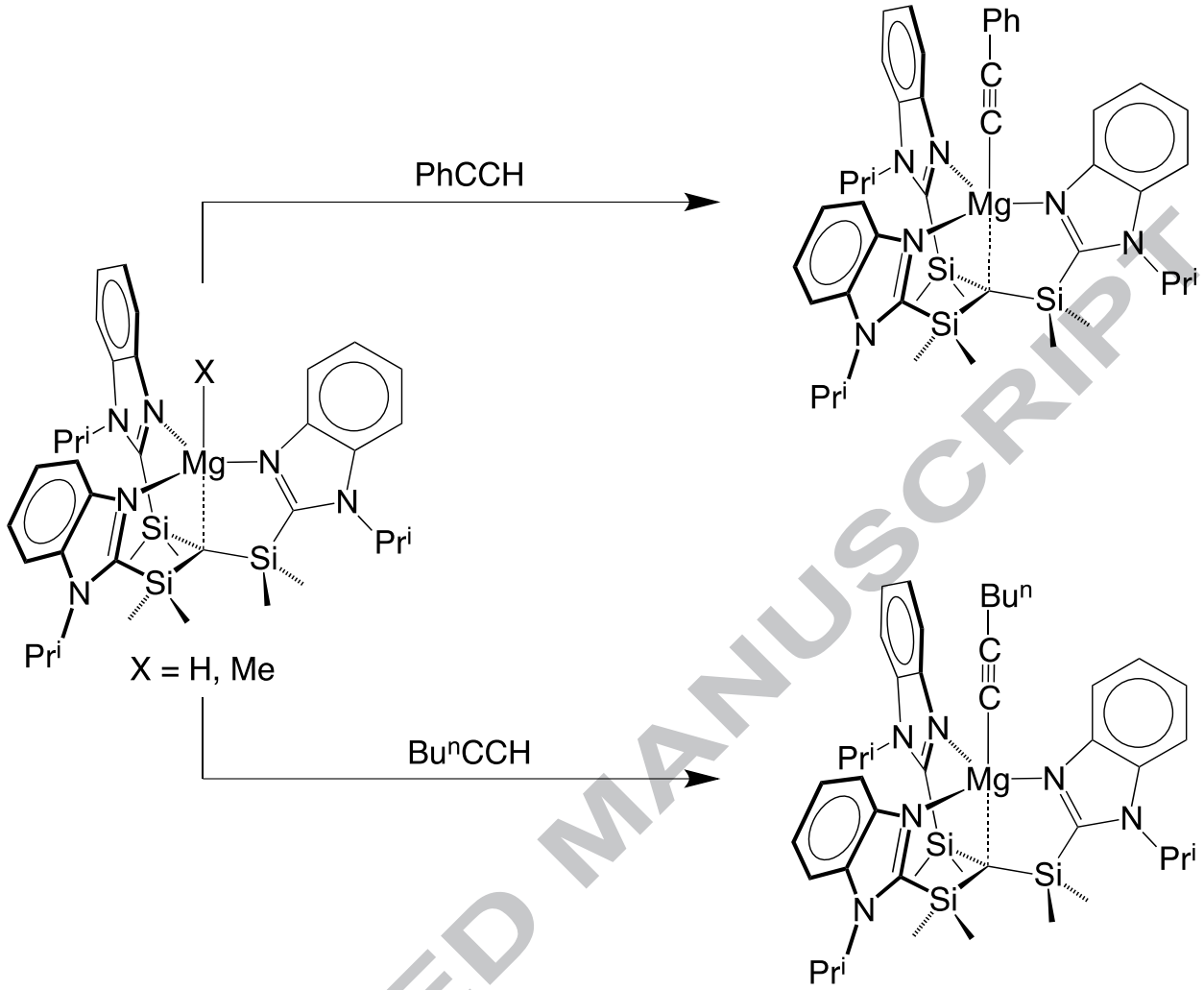
RESULTS AND DISCUSSION

We have recently demonstrated that the magnesium hydride and magnesium methyl compounds, [Tism$^{Pr^iBenz}$]MgH[10] and [Tism$^{Pr^iBenz}$]MgMe,[9] provide access to a series of [Tism$^{Pr^iBenz}$]MgX derivatives by either metathesis or insertion of X–Y into the Mg–H and Mg–Me bonds.[10,11,12] For example, protolytic cleavage of the Mg–Me bond by $PhNH_2$ and by H_2S affords [Tism$^{Pr^iBenz}$]MgN(H)Ph and [Tism$^{Pr^iBenz}$]MgSH, respectively. We now report that protolytic cleavage of the Mg–H and Mg–Me bonds can also be achieved by

secondary amines and terminal alkynes. Thus, [Tism$^{Pr^iBenz}$]MgMe reacts with diphenylamine (Ph_2NH) and pyrrolidine (C_4H_8NH) to form [Tism$^{Pr^iBenz}$]MgNPh$_2$ and [Tism$^{Pr^iBenz}$]MgNC$_4$H$_8$ (Scheme 1), while reactions with the terminal alkynes, PhC≡CH and Bu^{n}C≡CH, afford the corresponding magnesium acetylide derivatives, [Tism$^{Pr^iBenz}$]MgC≡CPh and [Tism$^{Pr^iBenz}$]MgC≡CBu^n (Scheme 2). The hydride complex, [Tism$^{Pr^iBenz}$]MgH, reacts similarly to [Tism$^{Pr^iBenz}$]MgMe, but with enhanced reactivity. For example, [Tism$^{Pr^iBenz}$]MgH reacts immediately with PhC≡CH at room temperature, whereas the corresponding reaction of [Tism$^{Pr^iBenz}$]MgMe occurs over a period of several hours under comparable conditions.



Scheme 1.



Scheme 2.

The molecular structures of [Tism$^{Pri Benz}$]MgNPh$_2$, [Tism$^{Pri Benz}$]MgNC$_4$H$_8$, [Tism$^{Pri Benz}$]MgC≡CPh and [Tism$^{Pri Benz}$]MgC≡CBu^n have been determined by X-ray diffraction, as illustrated in Figures 1–4. Interestingly, while [Tism$^{Pri Benz}$]MgX (X = NPh$_2$, C≡CPh and C≡CBu^n) exhibit a distorted trigonal bipyramidal geometry in which the X substituent resides in an axial site, the pyrrolidinide ligand of [Tism$^{Pri Benz}$]MgNC$_4$H$_8$ resides in an equatorial site.[13] In this regard, previous studies on other [Tism$^{Pri Benz}$]MgX derivatives indicate that H, Me, F, Cl, Br, N(H)Ph, and OC(H)OB(C$_6$F$_5$)$_3$ substituents reside in axial sites, whereas SH, I and C(H)(Me)Ph substituents reside in equatorial sites.[9,10,11]

Density functional theory (DFT) calculations indicate that there is a preference for the pyrrolidinide ligand to reside in an equatorial location as compared to an axial position (Figure 5), although the difference in energies is not large (2.4 kcal mol^{-1}). In contrast, DFT calculations indicate that the diphenylamide ligand prefers to occupy the axial site (Figure 6).

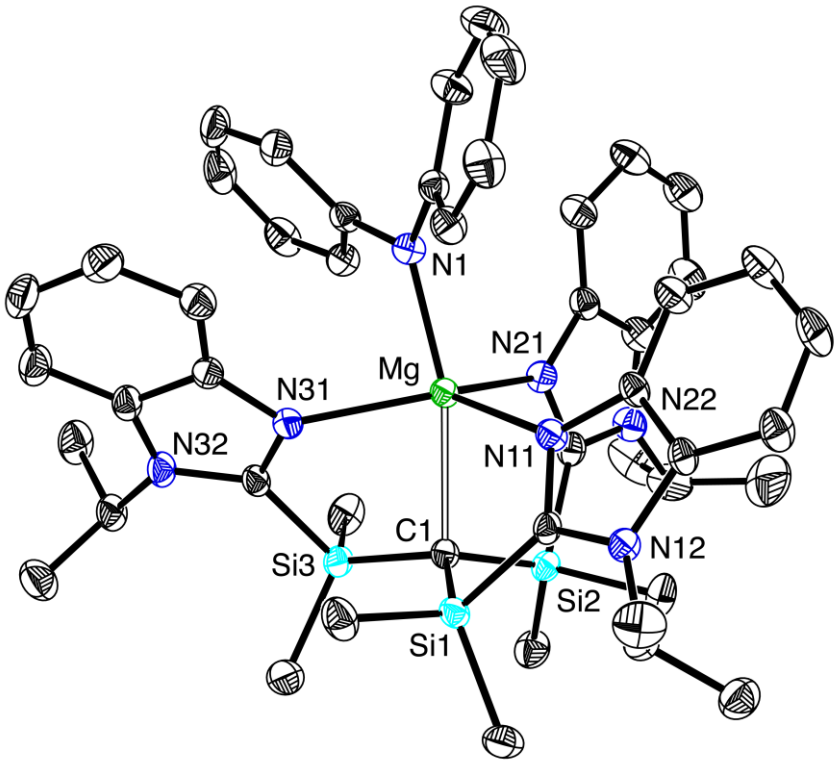


Figure 1. Molecular structure of [Tism$^{Pr^{i}Benz}$]MgNPh$_2$.

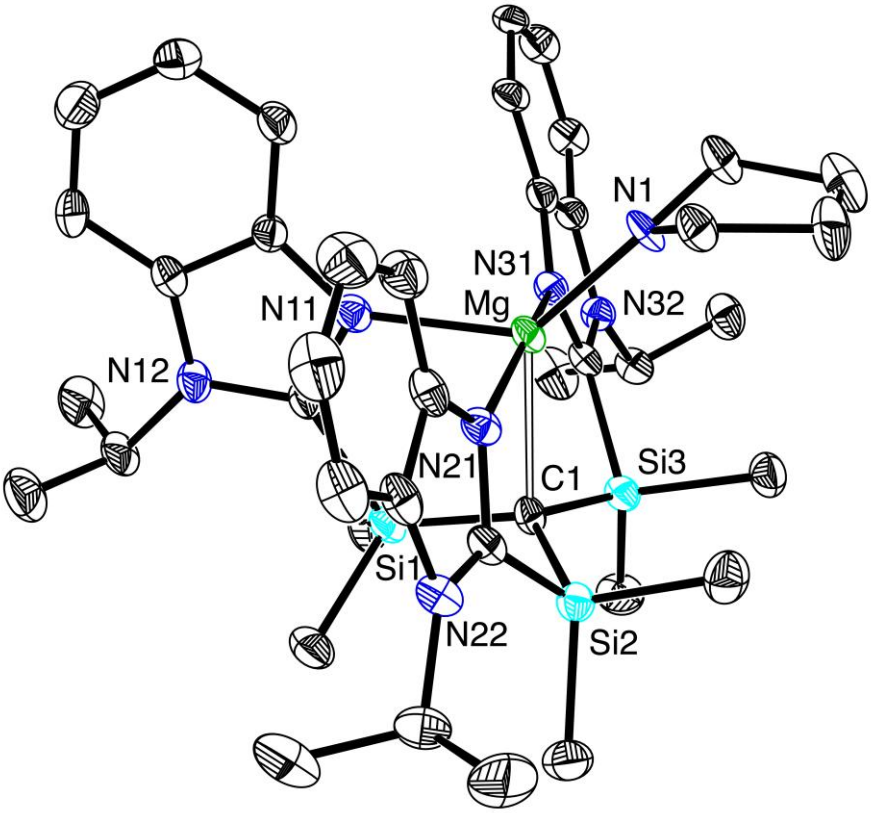


Figure 2. Molecular structure of [Tism$^{Pr^{i}Benz}$]MgNC$_4$H$_8$.

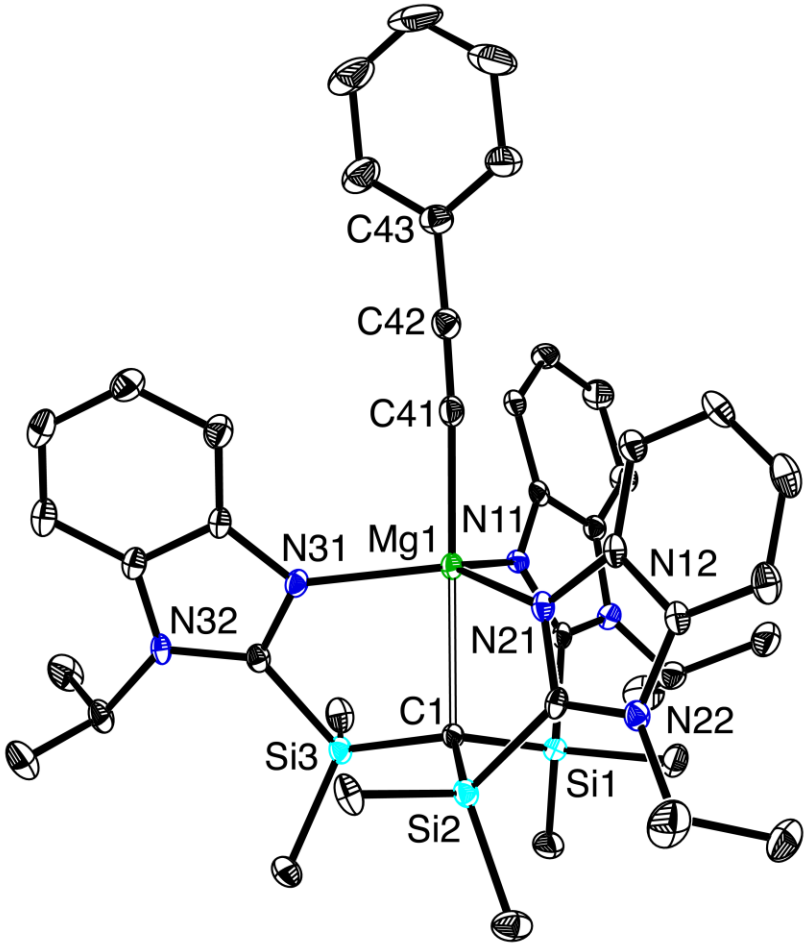


Figure 3. Molecular structure of [Tism$^{Pr^{i}Benz}$]MgC≡CPh (only one of the crystallographically independent molecules is shown).

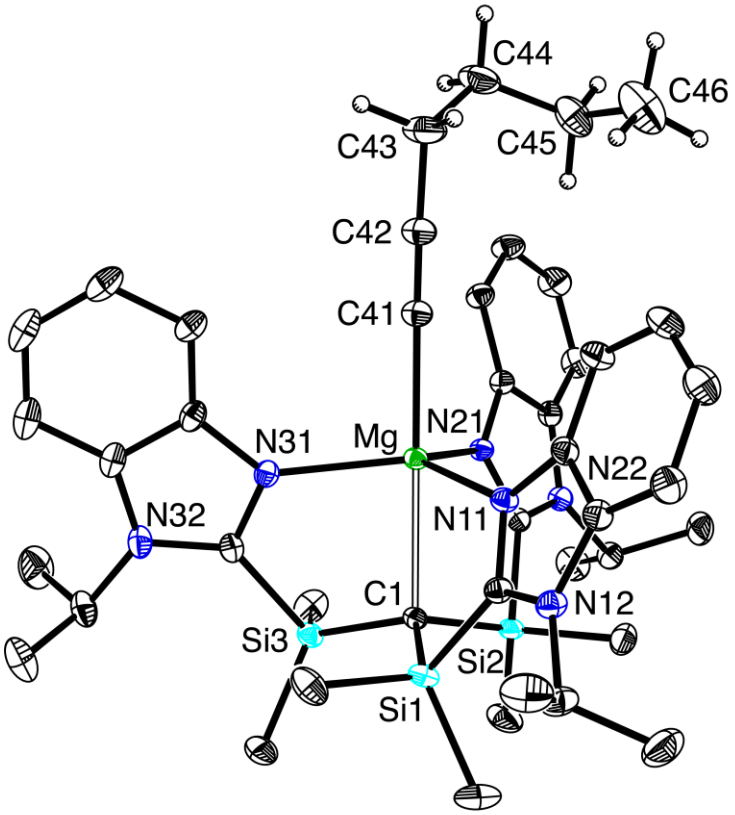
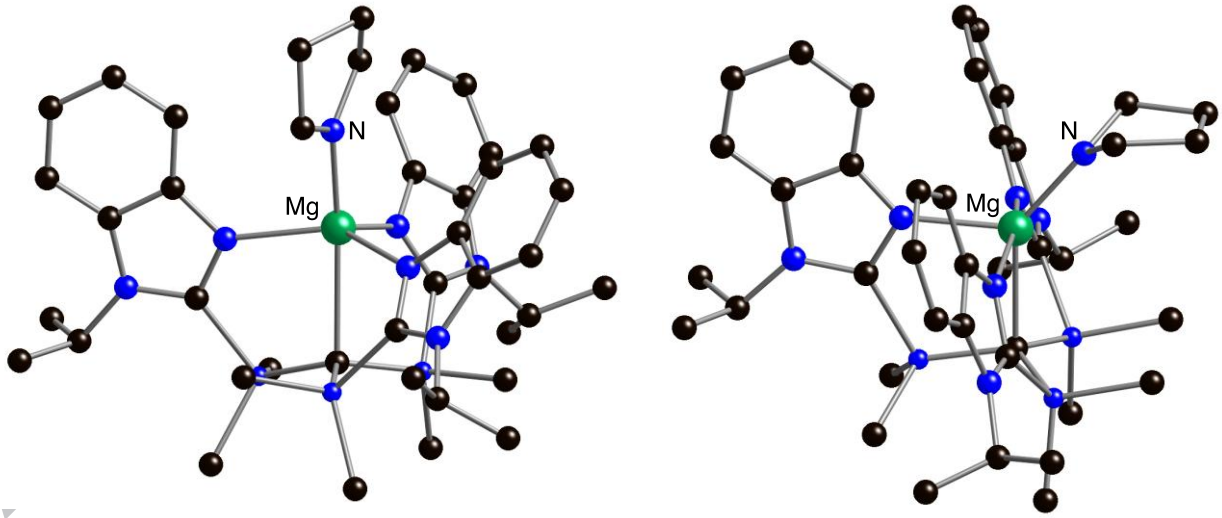


Figure 4. Molecular structure of [Tism$^{Pr^iBenz}$]MgC≡CBu^n.



E_{rel}(SCF) = 2.4 kcal mol^{-1} E_{rel}(SCF) = 0.0 kcal mol^{-1}

Figure 5. Geometry optimized structures of [Tism$^{Pr^iBenz}$]MgNC$_4$H$_8$ with axial (left) and equatorial (right) locations of the pyrrolidinide ligand. Hydrogen atoms are omitted for clarity.

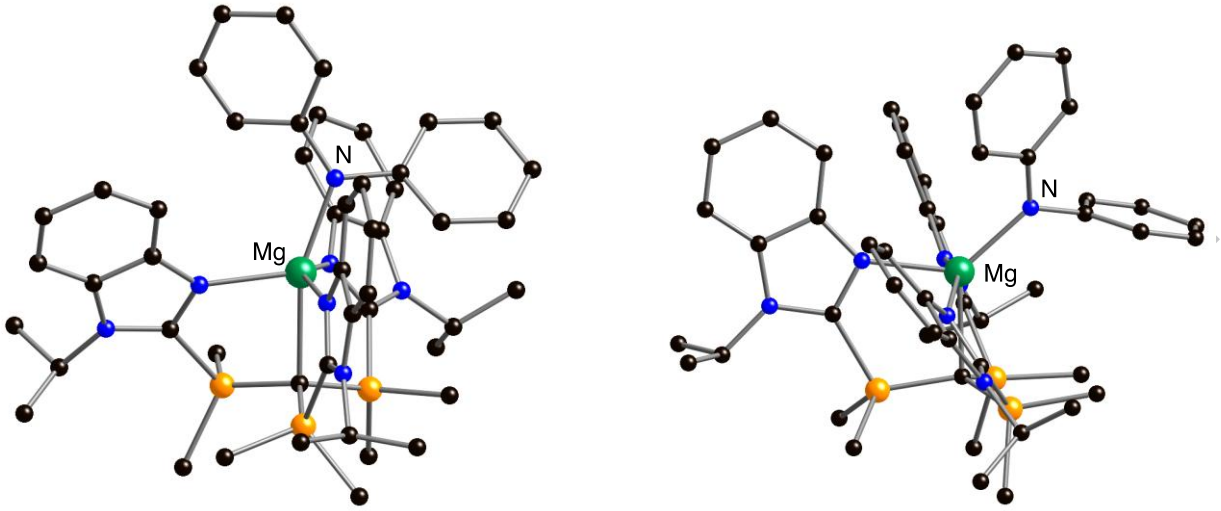


Figure 6. Geometry optimized structures of [Tism^{PriBenz}]MgNPh$_2$ with axial (left) and equatorial (right) locations of the diphenylamide ligand. Hydrogen atoms are omitted for clarity.

Although magnesium amide compounds are precedented,[14] there are relatively few examples of structurally characterized diphenylamide and pyrrolidinide derivatives listed in the Cambridge Structural Database (CSD),[15] of which a selection are presented in Table 1.[16-19] In particular, there is only one example of a magnesium pyrrolidinide complex, namely {[HC{C(Me)NAr}$_2$]Mg(μ–NC$_4$H$_8$)}$_2$ (Ar = 2,5-Pr$^i_2$C$_6$H$_3$),[14a] and the pyrrolidinide ligand in this complex bridges two magnesium centers rather than serve as a terminal ligand. Accordingly, the Mg–N bond length of [Tism^{PriBenz}]MgNC$_4$H$_8$ [1.970(5) Å] is shorter than those in {[HC{C(Me)NAr}$_2$]Mg(μ–NC$_4$H$_8$)}$_2$ [2.088(2) Å and 2.117(2) Å].[14a] It is also pertinent to note that the Mg–N bond length is shorter than the values observed for the pyrrolidine derivative, (dpp-bian)Mg(HNC$_4$H$_8$)$_3$ [2.090(2) Å, 2.196(2) Å and 2.221(2) Å],[20] a difference which is in accord with the L *versus* X nature of the ligands.[21]

Table 1. Bond lengths of terminal magnesium diphenylamido and related derivatives.

	d(Mg–N)/ Å	Mg-N-R_1/ °	Mg-N-R_2/ °	R_1-N-R_2/ °	Σ(X–N–Y)	Ref.
[Tism$^{Pr^iBenz}$]$MgNC_4H_8$	1.970	126.8	129.3	102.6	358.7	this work
[Tism$^{Pr^iBenz}$]$MgNPh_2$	2.100	115.1	125.7	118.5	359.3	this work
$(THF)_2Mg(NPh_2)_2$	2.013	113.4	124.3	119.3	357.0	16
	2.020	113.5	123.3	118.5	355.3	
$[(HMPA)_2Mg(NPh_2)_2]$	2.055	116.5	123.7	119.2	359.4	17
	2.056	117.9	123.4	118.7	360.0	
$EtMgNPh_2(THF)_2$	2.035	115.1	126.2	118.6	359.9	17
$Pr^iMgNPh_2(THF)_2$	2.037	115.6	125.7	118.7	360.0	17
$[Na(THF)_5][\{(CyN)_2C(NPh_2)\}_2Mg(NPh_2)]$	2.084	118.6	120.3[a]	121.0[a]	359.9	18
$[(PMDETA)K][Mg(THF)(NPh_2)_3]$[b]	2.043	113.2	128.4	118.3	359.9	19
	2.061	111.4	127.9	118.7	358.0	

(a) Average values for disordered structure.

(b) Two of the NPh_2 ligands interact with the [K(PMDETA)] moiety.

Magnesium diphenylamide compounds are more common than pyrrolidinide derivatives, and complexes that feature both terminal and bridging diphenylamide ligands have been reported. In this regard, the Mg–N bond length of [Tism$^{Pr^iBenz}$]MgNPh$_2$ [2.100(2) Å] is comparable to that of the pyrrolidinide derivative, [Tism$^{Pr^iBenz}$]MgNC$_4$H$_8$ [1.970(5) Å], and also [Tism$^{Pr^iBenz}$]MgN(H)Ph [2.058(4) Å and 2.049(4) Å for two crystallographically independent molecules],[10] but is distinctly longer than the values for the terminal diphenylamide compounds listed in Table 1, which range from 2.01 Å to 2.08 Å. Interestingly, the Mg–N bond length of [Tism$^{Pr^iBenz}$]MgNPh$_2$ is actually comparable to those in the bridging diphenylamide compounds, namely [(PhNpy)Mg(μ–NPh$_2$)]$_2$ [2.080(5) Å and 2.119(5) Å][22] and [CpMg(μ–NPh$_2$)]$_2$ [2.0934(16) Å, 2.1050(16) Å, 2.1092(17) Å and 2.1153(17) Å].[23] As such, it is evident that the Mg–N bond lengths in [Tism$^{Pr^iBenz}$]MgNR$_2$ are longer than anticipated. Also of note, the geometry about the nitrogen atom in each of the terminal amido compounds listed in Table 1 is close to planar, with the sum of bond angles at nitrogen being in the range 355.3˚ – 360.0˚.

With respect to the acetylide compounds, the Mg–C$_2$R bond lengths of [Tism$^{Pr^iBenz}$]MgC≡CPh [2.166(4) Å] and [Tism$^{Pr^iBenz}$]MgC≡CBu^n [2.1700(19) Å] are comparable to the Mg–Me bond length of [Tism$^{Pr^iBenz}$]MgMe [2.1781(13) Å],[9] but distinctly shorter than the corresponding Mg–C$_{alkyl}$ bond length of [Tism$^{Pr^iBenz}$]MgC(H)(Me)Ph [2.231(2) Å].[10] For further comparison, several other L$_n$MgC≡CPh derivatives have been structurally characterized (Table 2),[24-30] although there is only one other structurally characterized L$_n$MgC≡CBu^n derivative listed in the CSD, namely [HC{C(Me)NAr}$_2$]MgC≡CBu^n (Ar = 2,6-Ph$_2$CH-4-Me-C$_6$H$_2$).[31] Most magnesium acetylide compounds possess terminal ligands, but bridging derivatives are also known. For example, [{κ^2-Me$_2$NC$_2$H$_4$NHCH(Ph)CH$_2$Ph}Mg(C$_2$Ph)(μ–C$_2$Ph)]$_2$ possesses a symmetrically bridging phenylacetylide ligand with Mg–C bond lengths of 2.127(4) Å and 2.181(4) Å,[26,32] which are comparable to that for [Tism$^{Pr^iBenz}$]MgC≡CPh

and other terminal magnesium acetylide compounds, for which the mean value is 2.16 Å.

Spectroscopically, [Tism$^{Pri^{Benz}}$]MgC≡CPh and [Tism$^{Pri^{Benz}}$]MgC≡CBu^{n} are characterized by two signals in the $^{13}C\{^{1}H\}$ NMR spectrum attributable to the acetylide moiety. These values are within the range for other magnesium acetylide compounds that have been reported in the literature (Table 3).[24,31,33,34]

Table 2. Structural data for terminal magnesium phenylacetylide and n-butylacetylide compounds.

	***d*(Mg–C)/ Å**	***d*(C–C) / Å**	**Mg-C-C/ °**	**Ref**
[Tism$^{Pri Benz}$]MgCCPh[a]	2.166	1.216	175.0	this work
[Tism$^{Pri Benz}$]MgCCBu^{n}	2.170	1.215	177.7	this work
[F_{12}-Tp^{4Bo,3Ph}]MgCCPh[a]	2.045	1.213	175.0	24
[dpp-bian(H)]Mg(CCPh)$(THF)_2$	2.124	1.209	174.7	25
[{κ^2-$Me_2NC_2H_4NHCH(Ph)CH_2Ph$}Mg$(C_2Ph)]_2$	2.104	1.239	174.2	26
[(PhCC)Mg(μ-NPr$^{i}_2$)$(THF)]_2$	2.134	1.195	172.8	17
$(tmeda)_2Mg(CCPh)_2$[b]	2.176	1.219	180.0	27
	2.200	1.213	180.0	
$(THF)_4Mg(CCPh)_2$[b]	2.187	1.224	180.0	28
	2.191	1.220	180.0	
[{(dpp-mian)$(PhCCH_2)$}Mg$(CCPh)_2(THF)]_2$•(toluene)	2.151	1.223	168.8	29
[{(dpp-mian)$(PhCCH_2)$}Mg$(CCPh)_2(THF)]_2$•(THF)	2.138	1.210	168.4	29

(a) Average for crystallographically independent molecules in the asymmetric unit

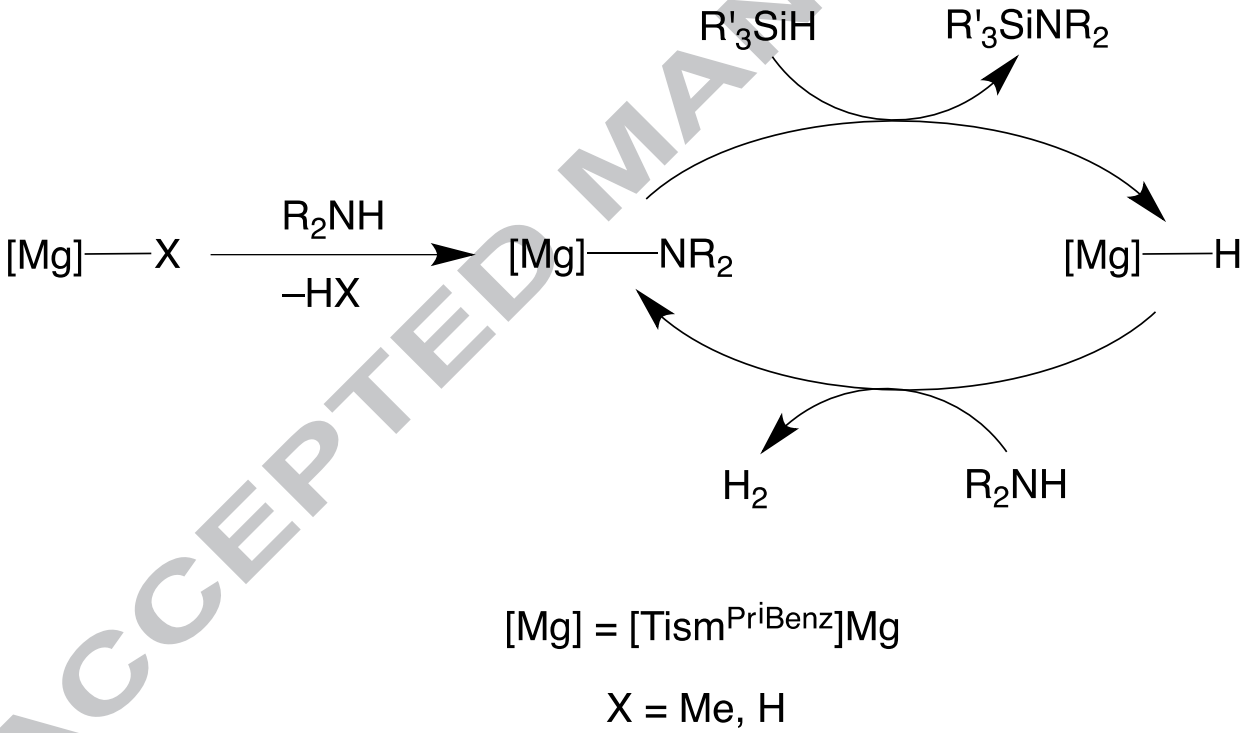
(b) Data for independent CCPh moieties in the same molecule

Table 3. ^{13}C NMR spectroscopic data for terminal magnesium acetylide compounds.

	δ ^{13}C/ ppm	Ref.
[Tism$^{Pr^iBenz}$]MgCCPh	112.2, 142.0	This work
[Tism$^{Pr^iBenz}$]MgCCBu^n	109.7, 126.0	This work
[Tp^{But}]MgCCPh	113.6, 121.8	33
[Tp^{But}]MgCCSiMe$_3$	120.0, 146.7	33
[F_{12}-Tp^{4Bo,3Ph}]MgCCPh	110.6, 117	24
[HC{C(Me)NAr}$_2$]MgCCBu^n (Ar = 2,6-Ph_2CH-4-Me-C_6H_2)	103.5, 111.9	31
{[HC{C(Me)NAr}$_2$]Mg(μ–CCBu^n)}$_2$ (Ar = 2,6-$Pr^i_2C_6H_3$)	112.2, 121.0	34
{[HC{C(Me)NAr}$_2$]Mg(μ–CCPh)}$_2$ (Ar = 2,6-$Pr^i_2C_6H_3$)	111.2, 122.0	34
{[HC{C(Me)NAr}$_2$]Mg(μ–CCBu^t)}$_2$ (Ar = 2,6-$Pr^i_2C_6H_3$)	103.5, 120.1	34

Significantly, the Mg–N bond of [Tism$^{Pr^iBenz}$]$MgNR_2$ may be cleaved by hydrosilanes, which provides a means to achieve catalytic Si–N bond formation by the dehydrocoupling of hydrosilanes and amines (Scheme 3). For example, [Tism$^{Pr^iBenz}$]MgMe is an effective precatalyst for the dehydrocoupling of a 1:1 mixture of Ph_2SiH_2 and C_4H_8NH at room temperature to afford the silazane, $Ph_2SiH(NC_4H_8)$, with a turnover frequency of 200 h^{-1}. [Tism$^{Pr^iBenz}$]MgMe also achieves the dehydrocoupling of a 1:1 mixture $PhSiH_3$ and C_4H_8NH, to afford a mixture of $PhSiH_2(NC_4H_8)$ and $PhSiH(NC_4H_8)_2$.[35] Although catalysts for the dehydrocoupling of silanes and amines are long known, it is only recently that they have become the subject of intense attention.[4]

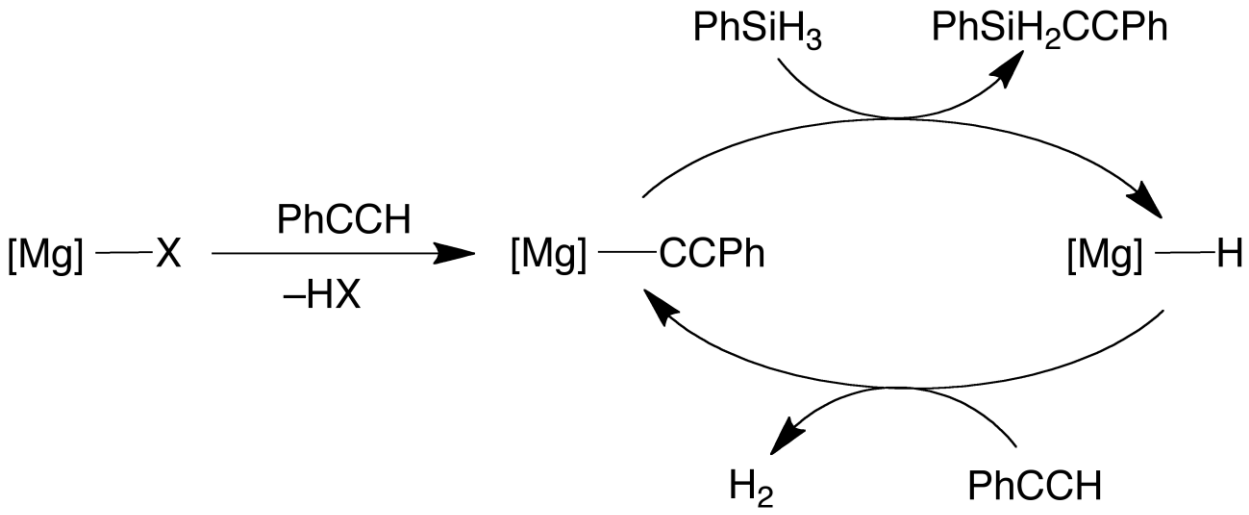
In this regard, there are very few magnesium systems,[3,36,37] of which the first reported employs the tris(4,4-dimethyl-2-oxazolinyl)phenylborate complex, [To^{M}]MgMe, as described by Sadow.[3] The proposed mechanism for the catalytic cycle is illustrated in Scheme 3 and is based on that suggested for [To^{M}]MgMe, which involves the intermediacy of the magnesium hydride complex [To^{M}]MgH, albeit not observed.[38,39] Support for the catalytic cycle presented in Scheme 3 is provided by the observations that (i) [Tism^{PriBenz}]MgH reacts with R_2NH to afford [Tism^{PriBenz}]MgNR_2 and (ii) [Tism^{PriBenz}]MgNC_4H_8 reacts with $PhSiH_3$ or Ph_2SiH_2 to regenerate [Tism^{PriBenz}]MgH. Furthermore, [Tism^{PriBenz}]MgNR_2 is observed as the resting state during the catalytic transformation.



Scheme 3.

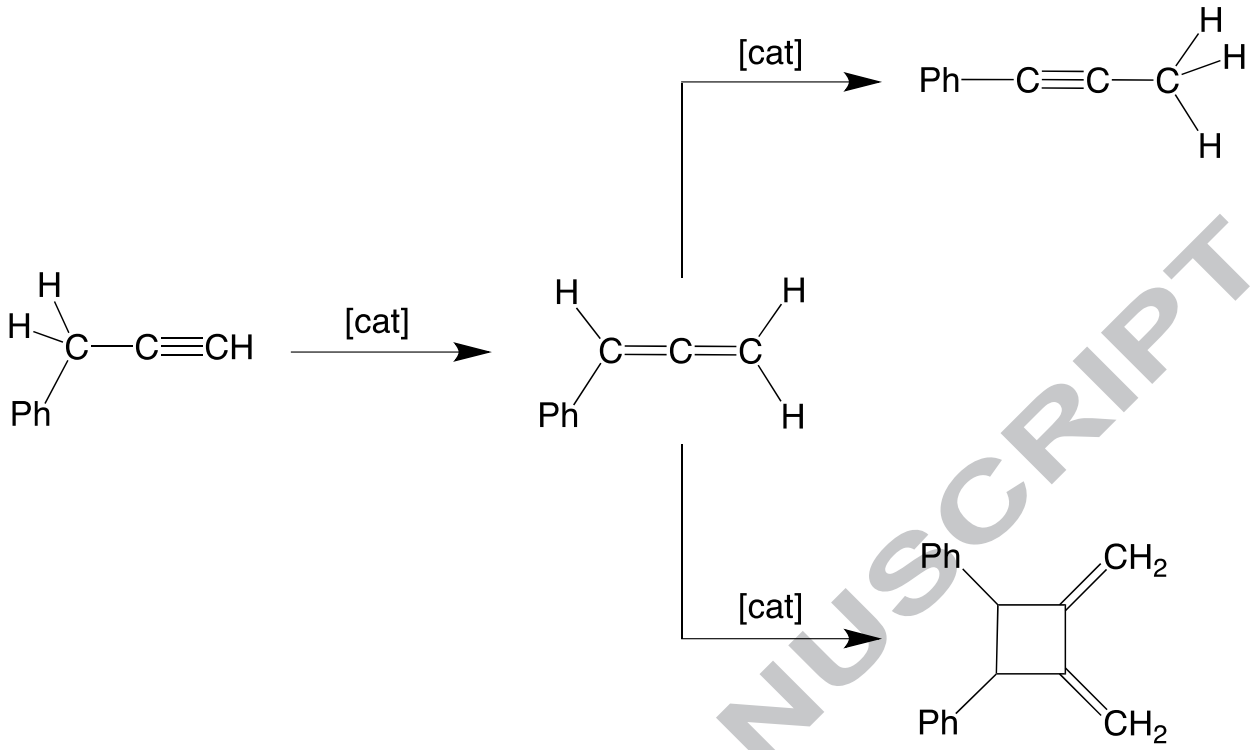
[Tism^{PriBenz}]MgH and [Tism^{PriBenz}]MgMe are also capable of dehydrocoupling PhC≡CH and $PhSiH_3$ at 130˚C to form $PhSiH_2C{\equiv}CPh$ (Scheme 4). Although the activity is lower than that for the dehydrocoupling of R_2NH and silanes, this transformation is,

nevertheless, of interest because there are no reports of well-defined mononuclear magnesium compounds that have been employed for this transformation.[40,41,42] The mechanism for the dehydrocoupling of PhC≡CH and $PhSiH_3$ is proposed to occur *via* a similar mechanism to that for R_2NH (Scheme 4), with the acetylide species being the resting state.



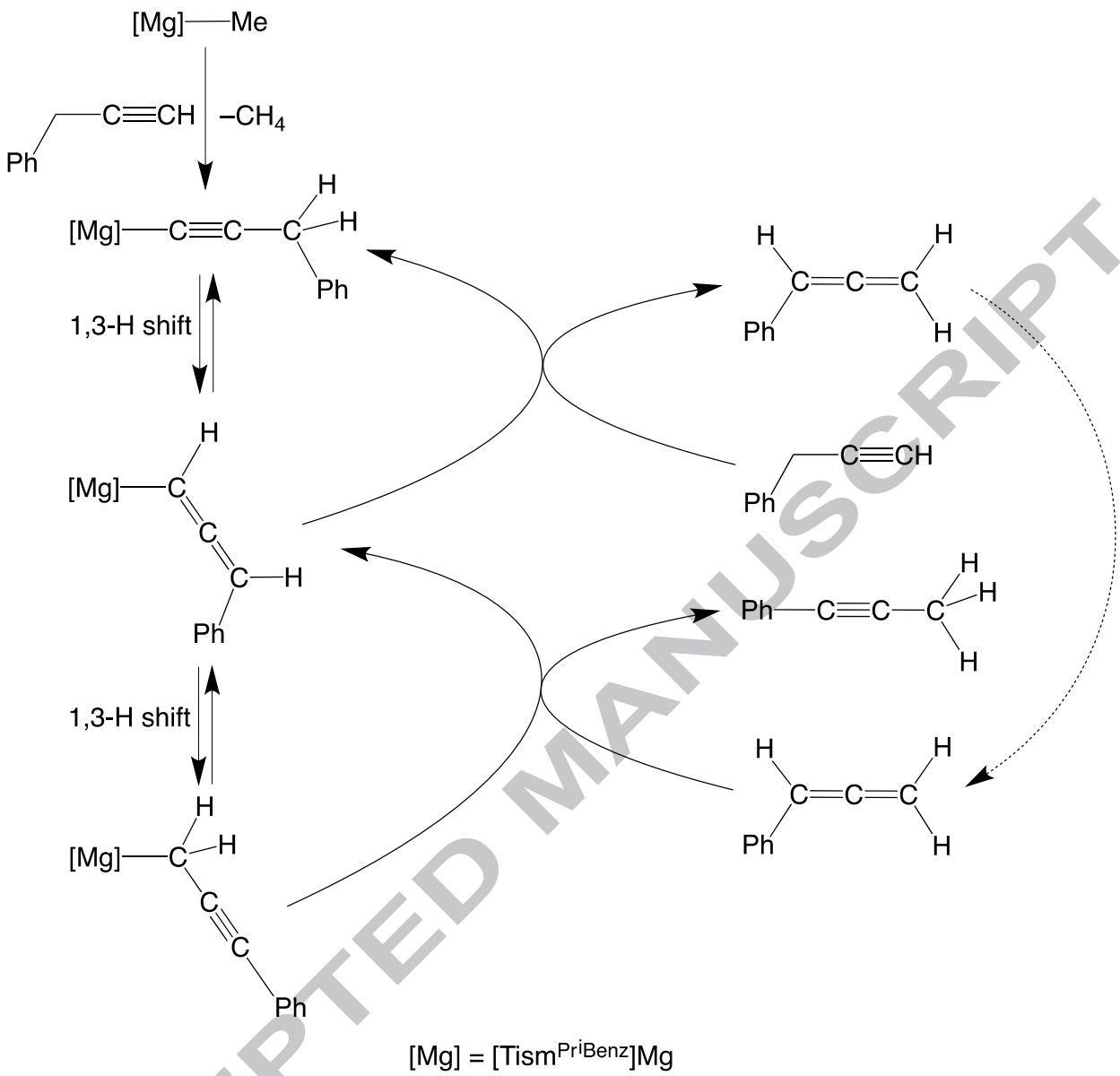
Scheme 4.

[$Tism^{PriBenz}$]MgMe is also capable of achieving the isomerization of a terminal alkyne to an allene. Specifically, 3-phenyl-1-propyne, $PhCH_2C{\equiv}CH$, isomerizes to phenylallene at elevated temperature (100 – 130˚C), as illustrated in Scheme 5. In addition, small quantities of 3-phenyl-2-propyne, PhC≡CMe, and a cyclobutane derivative resulting from the dimerization of phenylallene are also observed by NMR spectroscopy.



Scheme 5.

Metal catalyzed isomerization of terminal alkynes to allenes and 2-alkynes is precedented,[43] as illustrated by organomagnesium compounds that feature *N*,*N*-dialkylamineimine ligands.[26] On the basis of that proposed for the aforementioned magnesium system,[26] a potential mechanism for the isomerization is illustrated in Scheme 6. Specifically, key steps in this mechanism involve 1,3-hydrogen shifts to isomerize the acetylide [Tism$^{Pr^iBenz}$]MgC≡CCH$_2$Ph to [Tism$^{Pr^iBenz}$]MgCH=C=CHPh and [Tism$^{Pr^iBenz}$]MgCH$_2$C≡CPh. Sigma-bond metathesis[44] between [Tism$^{Pr^iBenz}$]MgCH=C=CHPh and PhCH$_2$C≡CH releases PhCH=C=CH$_2$ and regenerates [Tism$^{Pr^iBenz}$]MgC≡CCH$_2$Ph. Correspondingly, the metathesis between [Tism$^{Pr^iBenz}$]MgCH$_2$C≡CPh and PhCH=C=CH$_2$ releases PhC≡CCH$_3$,[26] but it is also possible that PhC≡CCH$_3$ is formed by reaction between [Tism$^{Pr^iBenz}$]MgCH$_2$C≡CPh and PhCH$_2$C≡CH (not shown).



Scheme 6.

CONCLUSIONS

In summary, the magnesium hydride and methyl compounds, [Tism$^{Pri Benz}$]MgX (X = H, Me), react with diphenylamine and pyrrolidine to afford the amide derivatives, [Tism$^{Pri Benz}$]MgNPh$_2$ and [Tism$^{Pri Benz}$]MgNC$_4$H$_8$, while reactions with the terminal alkynes, PhC≡CH and Bu^{n}C≡CH, form the corresponding magnesium acetylide derivatives, [Tism$^{Pri Benz}$]MgC≡CPh and [Tism$^{Pri Benz}$]MgC≡CBu^n. The molecular structures of [Tism$^{Pri Benz}$]MgX (X = NPh$_2$, NC$_4$H$_8$, C≡CPh, C≡CBu^n) have been determined by X-ray

diffraction, thereby demonstrating that each complex adopts a distorted trigonal bipyramidal geometry. However, while the X substituent of [Tism$^{Pr^iBenz}$]MgX (X = NPh_2, C≡CPh and C≡CBu^n) resides in an axial site, the pyrrolidinide ligand of [Tism$^{Pr^iBenz}$]MgNC_4H_8 resides in an equatorial site. The Mg–N bond of [Tism$^{Pr^iBenz}$]MgNR_2 may be cleaved by hydrosilanes, thereby providing a means to achieve catalytic Si–N bond formation by dehydrocoupling of hydrosilanes and amines. For example, [Tism$^{Pr^iBenz}$]MgMe is an effective precatalyst for the dehydrocoupling of a 1:1 mixture of Ph_2SiH_2 and C_4H_8NH at room temperature to afford the silazane, $Ph_2SiH(NC_4H_8)$. [Tism$^{Pr^iBenz}$]MgH and [Tism$^{Pr^iBenz}$]MgMe are also capable of dehydrocoupling PhC≡CH and $PhSiH_3$ to form $PhSiH_2C{\equiv}CPh$. In addition to dehydrocoupling of a terminal alkyne and hydrosilane, [Tism$^{Pr^iBenz}$]MgMe is also capable of achieving the isomerization of a terminal alkyne, namely, 3-phenyl-1-propyne to phenylallene.

EXPERIMENTAL SECTION

General considerations

All manipulations were performed using a combination of glovebox, high vacuum, and Schlenk techniques under an argon atmosphere.[45] Solvents were purified and degassed by standard procedures. NMR spectra were recorded on Bruker AVIII 300, Bruker AVIII 400SL and Bruker AVIII 500 spectrometers. ^{1}H NMR chemical shifts are reported in ppm relative to $SiMe_4$ (δ = 0), and were referenced with respect to the protio solvent impurity (δ = 7.16 for C_6D_5H).[46] ^{13}C NMR spectra are reported in ppm relative to $SiMe_4$ (δ = 0) and were referenced internally with respect to the solvent (δ = 128.06 for C_6D_5H). Coupling constants are given in hertz. NMR spectra are provided in the Supporting Information. Infrared spectra were recorded on a Perkin Elmer Spectrum Two spectrometer in attenuated total reflectance (ATR) mode and are reported in reciprocal centimeters. [Tism$^{Pr^iBenz}$]MgMe[9] and [Tism$^{Pr^iBenz}$]MgH[10] were obtained by literature

methods, and phenylsilane, diphenylsilane, phenylacetylene, 1-hexyne, pyrrolidine, diphenylamine, and 3-phenyl-1-propyne were obtained commercially and used as received.

X-ray Structure Determinations

X-ray diffraction data were collected on a Bruker Apex II diffractometer. The structures were solved by using direct methods and standard difference map techniques, and were refined by full-matrix least-squares procedures on F^2 with SHELXTL (Version 2014/7).[47] Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre (CCDC 1889843-1889846).

Computational Details

Calculations were carried out using DFT as implemented in the Jaguar 8.9 (release 15) suite of *ab initio* quantum chemistry programs.[48] Geometry optimizations were performed with the B3LYP density functional using the LACVP** basis sets and Cartesian coordinates are provided in the Supporting Information.

Synthesis of [Tism$^{Pri Benz}$]MgNPh$_2$

(i) A solution of [Tism$^{Pri Benz}$]MgMe (15 mg, 0.021 mmol) in C_6D_6 was added to a solution of diphenylamine (4.5 mg, 0.027 mmol) in C_6D_6 (0.7 mL total). The mixture was allowed to stand at room temperature for one hour and crystals suitable for X-ray diffraction were obtained *via* vapor diffusion of pentane into the benzene solution. The crystals were isolated and washed with pentane to afford [Tism$^{Pri Benz}$]MgNPh$_2$ as a white solid (8 mg, 44% yield). Anal. calcd. for [Tism$^{Pri Benz}$]MgNPh$_2$: C, 68.7%; H, 7.2%; N, 11.5%. Found: C, 66.8%; H, 7.3%; N, 11.0%. ^{1}H NMR (C_6D_6): 0.48 [s, 18H, Si(C$\underline{H}_3$)$_2$], 1.17 [d, J = 7, 18H, CH(C$\underline{H}_3$)$_2$], 4.61 [sep, J = 7, 3H, C$\underline{H}$(CH$_3$)$_2$], 6.43 [t, J = 7, 2H, MgN$\underline{Ph}_2$], 6.84 [t, J = 8, 4H, MgN$\underline{Ph}_2$], 6.90 [m, 6H, C$_6\underline{H}_4$], 7.07 [m, 3H, C$_6\underline{H}_4$], 7.33 [d, J = 8, 4H, MgN$\underline{Ph}_2$], 8.43 [m, 3H, C$_6\underline{H}_4$]. ^{13}C{^{1}H} NMR (C_6D_6): 4.92 [s, 6C, Si($\underline{C}$H$_3$)$_2$], 21.11 [s, 6C, CH($\underline{C}$H$_3$)$_2$], 50.27

[s, 3C, $\underline{C}H(CH_3)_2$], 111.97 [s, 3C, $\underline{C}_6H_4$], 115.04 [s, 2C, MgN$\underline{Ph}_2$], 121.58 [s, 4C, MgN$\underline{Ph}_2$], 122.53 [s, 3C, $\underline{C}_6H_4$], 122.91 [s, 3C, $\underline{C}_6H_4$], 122.94 [s, 3C, $\underline{C}_6H_4$], 128.66 [s, 4C, MgN$\underline{Ph}_2$], 134.07 [s, 3C, $\underline{C}_6H_4$], 143.86 [s, 3C, $\underline{C}_6H_4$], 157.22 [s, 2C, MgN$\underline{Ph}_2$], 166.42 [s, 3C, $N_2\underline{C}Si(CH_3)_2$], not observed [$\underline{C}$Mg]. IR Data (ATR, cm^{-1}): 3070 (w), 2973 (w), 2942 (w), 2898 (w), 2880 (w), 1576 (w), 1478 (m), 1463 (m), 1388 (w), 1357 (m), 1298 (m), 1253 (m), 1171 (w), 1064 (w), 989 (w), 950 (s), 929 (s), 824 (m), 791 (m), 738 (s), 693 (m), 648 (w), 558 (w), 527 (m), 502 (m), 438 (m).

(ii) A solution of [Tism$^{Pr^iBenz}$]MgH (5 mg, 0.007 mmol) in C_6D_6 was added to a solution of diphenylamine (1.5 mg, 0.009 mmol) in C_6D_6 (0.7 mL total). The sample was monitored by ^{1}H NMR spectroscopy, thereby indicating the immediate formation of [Tism$^{Pr^iBenz}$]MgNPh$_2$.

Synthesis of [Tism$^{Pr^iBenz}$]MgNC$_4$H$_8$

(i) A solution of [Tism$^{Pr^iBenz}$]MgMe (15 mg, 0.021 mmol) in C_6D_6 was added to a solution of pyrrolidine (2 mg, 0.028 mmol) in C_6D_6 (0.7 mL total). The mixture was allowed to stand at room temperature for one hour, during which time crystals suitable for X-ray diffraction were deposited. The crystals were isolated and washed with pentane to give [Tism$^{Pr^iBenz}$]MgNC$_4$H$_8$ as a white solid (8 mg, 49% yield). ^{1}H NMR (C_6D_6; due to low solubility following isolation, data is reported for the in situ generated compound): 0.65 [s, 18H, Si($\underline{CH}_3$)$_2$], 1.07 [d, J = 7, 18H, (CH($\underline{CH}_3$)$_2$], 1.91 [m, 4H, MgNC$_4\underline{H}_8$], 3.74 [m, 4H, MgNC$_4\underline{H}_8$], 4.64 [sep, J = 7, 3H, C$\underline{H}$(CH$_3$)$_2$], 6.91 [t, J = 8, 3H, C$_6\underline{H}_4$], 7.04 [d, J = 8, 3H, C$_6\underline{H}_4$], 7.14 [m, 3H, C$_6\underline{H}_4$], 8.51 [d, J = 8, 3H, C$_6\underline{H}_4$]. ^{13}C{^{1}H} NMR (C_6D_6): 6.42 [s, 6C, Si($\underline{C}H_3$)$_2$], 21.04 [s, 6C, CH($\underline{C}H_3$)$_2$], 28.19 [s, 2C, MgN$\underline{C}_4H_8$], 49.65 [s, 3C, $\underline{C}H(CH_3)_2$], 55.04 [s, 2C, MgN$\underline{C}_4H_8$], 112.50 [s, 3C, $\underline{C}_6H_4$], 120.91 [s, 3C, $\underline{C}_6H_4$], 122.34 [s, 3C, $\underline{C}_6H_4$], 122.44 [s, 3C, $\underline{C}_6H_4$], 133.83 [s, 3C, $\underline{C}_6H_4$], 144.05 [s, 3C, $\underline{C}_6H_4$], 165.66 [s, 3C, ($C_6H_4N_2CH(CH_3)_2\underline{C}Si(CH_3)_2)_3$CMgNC$_4H_8$], not observed [$\underline{C}$Mg]. IR Data (ATR, cm^{-1}): 3056 (w), 2973 (w), 2942 (w), 2902 (w), 2882 (w), 1462 (m), 1391 (w), 1340 (m), 1250 (m),

1158 (w), 1132 (w), 1061 (m), 1011 (m), 951 (m), 913 (m), 824 (s), 787 (m), 739 (vs), 686 (m), 531 (w), 430 (m).

(ii) A solution of [Tism$^{Pr^iBenz}$]MgH (5 mg, 0.007 mmol) in C_6D_6 was added to a solution of pyrrolidine (0.7 mg, 0.010 mmol) in C_6D_6 (0.7 mL total). The mixture was monitored by ^{1}H NMR spectroscopy, thereby indicating the immediate formation of [Tism$^{Pr^iBenz}$]MgNC$_4$H$_8$.

Synthesis of [Tism$^{Pr^iBenz}$]MgC≡CPh

(i) A solution of [Tism$^{Pr^iBenz}$]MgMe (15 mg, 0.021 mmol) in C_6D_6 was added to a solution of phenylacetylene (2.7 mg, 0.026 mmol) in C_6D_6 (0.7 mL total). The mixture was allowed to stand at room temperature for 16 hours, after which period, crystals of [Tism$^{Pr^iBenz}$]MgC≡CPh suitable for X-ray diffraction were deposited and isolated. Vapor diffusion of pentane into the remaining benzene solution resulted in a second crop of crystals. The samples were combined and washed with pentane to give [Tism$^{Pr^iBenz}$]MgC≡CPh as a white solid (9 mg, 53% yield). ^{1}H NMR (C_6D_6): 0.39 [s, 18H, Si(C$\underline{H}_3$)$_2$], 1.16 [d, J = 7, 18H, CH(C$\underline{H}_3$)$_2$], 4.63 [sep, J = 7, 3H, C$\underline{H}$(CH$_3$)$_2$], 7.04 [m, 4H, (C$_6\underline{H}_4$N$_2$CH(CH$_3$)$_2$CSi(CH$_3$)$_2$)$_3$CMgCC$\underline{Ph}$], 7.20 [m, 9H, (C$_6\underline{H}_4$N$_2$CH(CH$_3$)$_2$CSi(CH$_3$)$_2$)$_3$CMgCC$\underline{Ph}$], 7.96 [m, 2H, MgCC$\underline{Ph}$], 10.08 [d, J = 8, 3H, C$_6\underline{H}_4$]. ^{13}C{^{1}H} NMR (C_6D_6): 4.43 [s, 6C, Si($\underline{C}$H$_3$)$_2$], 21.03 [s, 6C, CH($\underline{C}$H$_3$)$_2$], 50.13 [s, 3C, $\underline{C}$H(CH$_3$)$_2$], 111.97 [s, 3C, $\underline{C}_6$H$_4$], 112.22 [s, 1C, MgC$\underline{C}$Ph], 122.58 [s, 3C, $\underline{C}_6$H$_4$], 122.92 [s, 3C, $\underline{C}_6$H$_4$], 124.11 [s, 3C, $\underline{C}_6$H$_4$], 124.67 [s, 2C, MgCC$\underline{Ph}$], 131.22 [s, 1C, MgCC$\underline{Ph}$], 131.63 [s, 2C, MgCC$\underline{Ph}$], 132.40 [s, 1C, MgCC$\underline{Ph}$], 134.39 [s, 3C, $\underline{C}_6$H$_4$], 142.03 [s, 1C, Mg$\underline{C}$CPh], 144.82 [s, 3C, $\underline{C}_6$H$_4$], 166.94 [s, 3C, N$_2\underline{C}$Si(CH$_3$)$_2$], not observed [$\underline{C}$MgCCPh]. IR Data (ATR, cm^{-1}): 3054 (w), 2973 (w), 2946 (w), 2904 (w), 2886 (w), 1462 (w), 1391 (w), 1341 (w), 1253 (w), 1160 (w), 1133 (w), 1062 (w), 1012 (w), 946 (m), 825 (s), 790 (m), 741 (s), 693 (w), 531 (w), 433 (w).

(ii) A solution of [Tism$^{Pr^iBenz}$]MgH (5 mg, 0.007 mmol) in C_6D_6 was added to a solution of phenylacetylene (1 mg, 0.010 mmol) in C_6D_6 (0.7 mL total). The mixture was monitored by ^{1}H NMR spectroscopy, indicating the immediate formation of [Tism$^{Pr^iBenz}$]MgC≡CPh.

Synthesis of [Tism$^{Pr^iBenz}$]MgC≡CBu^n

(i) A solution of [Tism$^{Pr^iBenz}$]MgMe (15 mg, 0.021 mmol) in C_6D_6 was added to a solution of 1-hexyne (2.3 mg, 0.027 mmol) in C_6D_6 (0.7 mL total). The mixture was heated at 60˚C for 16 hours, after which period, crystals suitable for X-ray diffraction were obtained *via* vapor diffusion of pentane into the benzene solution. The crystals were isolated and washed with pentane to afford [Tism$^{Pr^iBenz}$]MgC≡CBu^n as a white solid (4 mg, 24% yield). Anal. calcd. for [Tism$^{Pr^iBenz}$]MgC≡CBu^n: C, 67.1%; H, 7.9%; N, 10.9%. Found: C, 67.1%; H, 8.0%; N, 10.8%. ^{1}H NMR (C_6D_6): 0.38 [s, 18H, Si(C$\underline{H}_3$)$_2$)], 1.01 [t, J = 7, 3H, MgCC(C$_4\underline{H}_9$)], 1.14 [d, J = 7, 18H, CH(C$\underline{H}_3$)$_2$], 1.79 [m, 2H, MgCC(C$_4\underline{H}_9$)], 1.92 [m, 2H, MgCC(C$_4\underline{H}_9$)], 2.79 [t, J = 7, 2H, MgCC(C$_4\underline{H}_9$)], 4.61 [sep, J = 7, 3H, C$\underline{H}$(CH$_3$)$_2$], 7.10 [m, 3H, C$_6\underline{H}_4$], 7.19 [m, 3H, C$_6\underline{H}_4$], 7.34 [m, 3H, C$_6\underline{H}_4$], 10.23 [d, J = 8, 3H, C$_6\underline{H}_4$]. ^{13}C{^{1}H} NMR (C_6D_6): 4.45 [s, 6C, Si($\underline{C}$H$_3$)$_2$], 14.38 [s, 1C, MgCC($\underline{C}_4$H$_9$)], 21.01 [s, 6C, CH($\underline{C}$H$_3$)$_2$], 22.32 [s, 1C, MgCC($\underline{C}_4$H$_9$)], 22.82 [s, 1C, MgCC($\underline{C}_4$H$_9$)], 33.47 [s, 1C, MgCC($\underline{C}_4$H$_9$)], 50.05 [s, 3C, $\underline{C}$H(CH$_3$)$_2$], 109.73 [s, 1C, Mg$\underline{C}$C(C$_4$H$_9$)], 111.89 [s, 3C, MgC$\underline{C}$(C$_4$H$_9$)], 122.18 [s, 3C, MgC$\underline{C}$(C$_4$H$_9$)], 122.78 [s, 3C, MgC$\underline{C}$(C$_4$H$_9$)], 124.63 [s, 3C, $\underline{C}_6$H$_4$)], 126.04 [s, 1C, MgC$\underline{C}$(C$_4$H$_9$)], 134.41 [s, 3C, $\underline{C}_6$H$_4$], 144.97 [s, 3C, $\underline{C}_6$H$_4$], 166.93 [s, 3C, N$_2\underline{C}$Si(CH$_3$)$_2$], not observed [$\underline{C}$MgCC(C$_4$H$_9$)]. IR Data (ATR, cm^{-1}): 3066 (w), 2972 (w), 2946 (w), 2904 (w), 2892 (w), 1463 (w), 1391 (w), 1353 (w), 1252 (w), 1160 (w), 1133 (w), 1105 (w), 1063 (w), 1013 (w), 947 (s), 825 (s), 790 (m), 740 (vs), 695 (w), 559 (w), 530 (w), 460 (w), 436 (m).

(ii) A solution of [Tism$^{Pr^iBenz}$]MgH (5 mg, 0.007 mmol) in C_6D_6 was added to a solution of 1-hexyne (0.8 mg, 0.009 mmol) in C_6D_6 (0.7 mL total). The mixture was heated at 60˚C overnight, and monitored by ^{1}H NMR spectroscopy, indicating the formation of [Tism$^{Pr^iBenz}$]MgC≡CBu^n.

Dehydrocoupling of Ph_2SiH_2 and C_4H_8NH

A solution of Ph_2SiH_2 (0.284 mmol) and C_4H_8NH (0.284 mmol) in C_6D_6 (0.7 mL), containing mesitylene as an internal standard, was treated with [Tism^{PriBenz}]MgMe (2 mg, 0.003 mmol). The reaction was monitored by ^{1}H NMR spectroscopy, thereby indicating the formation of $Ph_2SiH(NC_4H_8)$[49] (TON[50] = 200) within a period of 30 minutes.

Dehydrocoupling of $PhSiH_3$ and C_4H_8NH

A solution of $PhSiH_3$ (0.085 mmol) and C_4H_8NH (0.085 mmol) in C_6D_6 (0.7 mL), containing mesitylene as an internal standard, was treated with [Tism^{PriBenz}]MgMe (3 mg, 0.004 mmol). The reaction was monitored by ^{1}H NMR spectroscopy, thereby indicating the formation of $PhSiH_2(NC_4H_8)$ and $PhSiH(NC_4H_8)_2$[49] (TON[50] = 20) within a period of 30 minutes.

Dehydrocoupling of $PhSiH_3$ and Ph_2NH

(a) A solution of $PhSiH_3$ (0.085 mmol) and Ph_2NH (0.085 mmol) in C_6D_6 (0.7 mL), containing mesitylene as an internal standard, was treated with [Tism^{PriBenz}]MgMe (3 mg, 0.004 mmol). The sample was heated at 100˚C and monitored by ^{1}H NMR spectroscopy, thereby indicating the formation of $PhSiH_2(NPh_2)$[51] (TON[50] = 4) after a period of 21 days.

(b) A solution of [Tism^{PriBenz}]MgH (2 mg, 0.003 mmol) was treated with diphenylamine (5 mg, 0.030 mmol) and phenylsilane (3 mg, 0.028 mmol). The reaction mixture was heated at 100˚C for 3 days, resulting in the formation of $PhH_2Si(NPh_2)$.

Reactivity of [Tism^{PriBenz}]$MgNC_4H_8$ towards Ph_2SiH_2

A solution of [Tism^{PriBenz}]$MgNC_4H_8$ (3 mg, 0.004 mmol) in C_6D_6 (*ca* 0.7 mL) was treated with Ph_2SiH_2 (*ca* 3 equivs) and monitored by ^{1}H NMR spectroscopy, thereby

demonstrating the formation of [Tism$^{Pri Benz}$]MgH as the major magnesium-containing species, together with $Ph_2SiH(NC_4H_8)$.

Reactivity of [Tism$^{Pri Benz}$]MgNC$_4$H$_8$ towards PhSiH$_3$

A solution of [Tism$^{Pri Benz}$]MgNC$_4$H$_8$ (3 mg, 0.004 mmol) in C_6D_6 (0.7 mL) was treated with $PhSiH_3$ (*ca* 3 equivs) and monitored by ^{1}H NMR spectroscopy, thereby demonstrating the formation of [Tism$^{Pri Benz}$]MgH as the major magnesium-containing species, together with $PhSiH_2(NC_4H_8)$ and $PhSiH(NC_4H_8)_2$.

Dehydrocoupling of PhSiH$_3$ and PhC≡CH

(a) A solution of $PhSiH_3$ (0.063 mmol) and PhC≡CH (0.021 mmol) in C_6D_6 (0.7 mL), containing mesitylene as an internal standard, was treated with [Tism$^{Pri Benz}$]MgMe (3 mg, 0.004 mmol). The sample was heated at 130˚C and was monitored by ^{1}H NMR spectroscopy, thereby demonstrating the formation of $PhSiH_2C{\equiv}CPh$[52] (TON[50] = 4.5) after a period of 21 days.

(b) A solution of [Tism$^{Pri Benz}$]MgH (2 mg, 0.003 mmol) in C_6D_6 (0.7 mL) was treated with PhCCH (3 mg, 0.020 mmol) and $PhSiH_3$ (3 mg, 0.028 mmol). The sample was heated at 130˚C for 7 days, resulting in the formation of $PhSiH_2C{\equiv}CPh$.

Isomerization of PhCH$_2$C≡CH

A solution of 3-phenyl-1-propyne (0.043 mmol) in C_6D_6 (*ca* 0.7 mL) was treated with [Tism$^{Pri Benz}$]MgMe (3 mg, 0.004 mmol). The mixture was heated at 100˚C for 4 days and monitored by ^{1}H NMR spectroscopy, thereby demonstrating 32% conversion and the formation of $PhCH{=}C{=}CH_2$, PhC≡CMe and $C_4H_2Ph_2(CH_2)_2$[53] in a 94:3:3 ratio. Subsequent heating at 130˚C for 9 days results in 90% conversion and the formation of $PhCH{=}C{=}CH_2$, PhC≡CMe and $C_4H_2Ph_2(CH_2)_2$ in a 81:8:11 ratio with an overall TON[50] = 9.

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APPENDIX A. Supplementary Data

Crystallographic data in CIF format (CCDC #1889843-1889846). These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at https://dx.doi.org/10.1016/j.ica.xxxxxx.

REFERENCES

(1) (a) Kucinski, K.; Hreczycho, G. *ChemCatChem* **2017**, *9*, 1868-1885.
(b) Leitao, E. M.; Jurca, T.; Manners, I. *Nat. Chem.* **2013**, *5*, 817-829.
(c) Melen, R. L. *Chem. Soc. Rev.* **2016**, *45*, 775-788.
(d) Waterman, R. *Chem. Soc. Rev.* **2013**, *42*, 5629-5641.

(2) *Hydrosilylation: A Comprehensive Review on Recent Advances*, Advances in Silicon Science, Marciniec B. (ed.), Springer (2009).

(3) Dunne, J. F.; Neal, S. R.; Engelkemier, J.; Ellern, A.; Sadow, A. D. *J. Am. Chem. Soc.* **2011**, *133*, 16782-16785.

(4) (a) Ríos, P.; Roselló-Merino, M.; Rivada-Wheelaghan, O.; Borge, J.; López-Serrano, J.; Conejero, S. *Chem. Commun.* **2018**, *54*, 619-622.
(b) Nako, A. E.; Chen, W.; White, A. J. P.; Crimmin, M. R. *Organometallics* **2015**, *34*, 4369-4375.
(c) Forosenko, N. V.; Basalov, I. V.; Cherkasov, A. V.; Fukin, G. K.; Shubina, E. S.; Trifonov, A. A. *Dalton Trans.* **2018**, *47*, 12570-12581.
(d) Erickson, K. A.; Cibuzar, M. P.; Mucha, N. T.; Waterman, R. *Dalton Trans.* **2018**, *47*, 2138-2142.
(e) Anga, S.; Sarazin, Y.; Carpentier, J.-F.; Panda, T. K. *ChemCatChem* **2016**, *8*, 1373-1378.
(f) Greb, L.; Tamke, S.; Paradies, J. *Chem. Commun.* **2014**, *50*, 2318-2320.

(5) (a) Neugebauer, P.; Jaschke, B.; Klingebiel, U. in *PATAI's Chemistry of Functional Groups*, John Wiley & Sons, Ltd, Wiley VCH, Weinheim. DOI: 10.1002/9780470682531.pat0240 (2009).
(b) Fessenden, R.; Fessenden, J. S. *Chem. Rev.* **1961**, *61*, 361-388.

(6) Larson, G. L. *Synthesis* **2018**, *50*, 2433-2462.

(7) (a) Yamaguchi, K.; Wang, Y.; Oishi, T.; Kuroda, Y.; Mizuno, N. *Angew. Chem.* **2013**, *52*, 5627-5630.

(b) Skrodzki, M.; Witomska, S.; Pawluć , P. *Dalton Trans.* **2018**, *47*, 5948-5951.

(c) Tsuchimoto, T.; Fujii, M.; Iketani, Y.; Sekine, M. *Adv. Synth. Catal.* **2012**, *354*, 2959-2964.

(d) Ishikawa, J.; Itoh, M. *J. Catal.* **1999**, *185*, 454-461.

(e) Toutov, A. A.; Betz, K. N.; Schuman, D. P.; Liu, W. B.; Fedorov, A.; Stoltz, B. M.; Grubbs, R. H. *J. Am. Chem. Soc.* **2017**, *139*, 1668-1674.

(f) Kahnes, M.; Görls, H.; Westerhausen, M. *Organometallics* **2010**, *29*, 3490-3499.

(g) Liu, H. Q.; Harrod, J. F. *Can. J. Chem.* **1990**, *68*, 1100-1105.

(h) Buch, F.; Harder, S. *Organometallics* **2007**, *26*, 5132-5135.

(8) (a) Chirik, P.; Morris, R. *Acc. Chem. Res.* **2015**, *48*, 2495.

(b) *Catalysis without Precious Metals* Bullock, R. M. (Ed), Wiley-VCH, Weinheim, Germany (2010)

(9) Ruccolo, S.; Rauch, M.; Parkin, G. *Chem. Sci.* **2017**, *8*, 4465-4474.

(10) Rauch, M.; Ruccolo, S.; Parkin, G. *J. Am. Chem. Soc.* **2017**, *139*, 13264-13267.

(11) Rauch, M.; Parkin, G. *J. Am. Chem. Soc.* **2017**, *139*, 18162−18165.

(12) Rauch, M.; Parkin, G. *Dalton Trans.* **2018**, *47*, 12596-12605.

(13) It should be noted that, in view of the constraints of the [Tism$^{Pr^{i}Benz}$] ligand, the angles in the equatorial plane deviate substantially from 120˚ such that the trigonal bipyramidal description is only approximate for the NC_4H_8, SH, I and C(H)(Me)Ph.

(14) See, for example, reference 3 and:

(a) Barrett, A. G. M.; Casely, I. J.; Crimmin, M. R.; Hill, M. S.; Lachs, J. R.; Mahon, M. F.; Procopiou, P. A. *Inorg. Chem.* **2009**, *48*, 4445-4453.

(b) Chisholm, M. H.; Gallucci, J.; Phomphrai, K. *Inorg. Chem.* **2002**, *41*, 2785-2794.

(15) Cambridge Structural Database (CSD version 5.39). Groom, C. R.; Bruno, I. J.; Lightfoot, M. P.; Ward, S. C. *Acta Cryst.* **2016**, *B72*, 171-179.

(16) Gärtner, M.; Fischer, R.; Langer, J.; Görls, H.; Walther, D.; Westerhausen, M. *Inorg. Chem.* **2007**, *46*, 5118-5124.

(17) Yang, K.-C.; Chang, C.-C.; Huang, J.-Y.; Lin, C.-C.; Lee, G.-H.; Wang, Y.; Chiang, M. Y. *J. Organomet. Chem.* **2002**, *648*, 176-187.

(18) De Tullio, M.; Hernán-Gómez, A.; Livingstone, Z.; Clegg, W.; Kennedy, A. R.; Harrington, R. W.; Antiñolo, A.; Martínez, A.; Carrillo-Hermosilla, F.; Hevia, E. *Chem. Eur. J.* **2016**, *22*, 17646-17656.

(19) Fleming, B. J.; García-Álvarez, P.; Keating, E.; Kennedy, A. R.; O'Hara, C. T. *Inorg. Chim. Acta* **2012**, *384*, 154-157.

(20) Yakub, A. M.; Moskalev, M. V.; Bazyakina, N. L.; Cherkasov, A. V.; Shavyrin, A. S.; Fedushkin, I. L. *Russ. Chem. Bull.* **2016**, *65*, 2887-2894.

(21) (a) Green, M. L. H.; Parkin, G. *J. Chem. Educ.* **2014**, *91*, 807-816.
(b) Green, M. L. H. *J. Organomet. Chem.* **1995**, *500*, 127-148.
(c) Parkin, G. *Comprehensive Organometallic Chemistry III*, Volume 1, Chapter 1; Crabtree, R. H. and Mingos, D. M. P. (Eds), Elsevier, Oxford, 2006.

(22) Henderson, K. W.; Mulvey, R. E.; Clegg, W.; O'Neil, P. A. *Polyhedron* **1993**, *12*, 2535-2538.

(23) Xia, A.; Heeg, M. J.; Winter, C. H. *Organometallics* **2002**, *21*, 4718-4725.

(24) Romero, N.; Dufrois, Q.; Vendier, L.; Dinoi, C.; Etienne, M. *Organometallics* **2017**, *36*, 564-571.

(25) Fedushkin, I. L.; Khvoinova, N. M.; Skatova, A. A.; Fukin, G. K. *Angew. Chem. Int. Ed.* **2003**, *42*, 5223-5226.

(26) Rochat, R.; Yamamoto, K.; Lopez, M. J.; Nagae, H.; Tsurugi, H.; Mashima, K. *Chem. Eur. J.* **2015**, *21*, 8112-8120.

(27) Schubert, B.; Behrens, U.; Weiss, E. *Chem. Ber.* **1981**, *114*, 2640-2643.

(28) Schwamm, R. J.; Coles, M. P. *Organometallics* **2013**, *32*, 5277-5280.

(29) Razborov, D. A.; Lukoyanov, A. N.; Baranov, E. V.; Fedushkin, I. L. *Dalton Trans.* **2015**, *44*, 20532-20541.

(30) Schubert, B.; Weiss, E. *Chem. Ber.* **1984**, *117*, 366-375.

(31) Arrowsmith, M.; Maitland, B.; Kociok-Kohn, G.; Stasch, A.; Jones, C.; Hill, M. S. *Inorg. Chem.* **2014**, *53*, 10543-10552.

(32) Asymmetric bridging is also known. See reference 17 and Stasch, A.; Sarish, S. P.; Roesky, H. W.; Meindl, K.; Dall'Antonia, F.; Schulz, T.; Stalke, D. *Chem.-Asian J.* **2009**, *4*, 1451-1457.

(33) Han, R.; Parkin, G. *J. Am. Chem. Soc.* **1992**, *114*, 748-757.

(34) Arrowsmith, M.; Crimmin, M. R.; Hill, M. S.; Lomas, S. L.; MacDougall, D. J.; Mahon, M. F. *Organomet.* **2013**, *32*, 4961−4972.

(35) [Tism^{PriBenz}]MgMe also achieves the dehydrocoupling of Ph_2NH with $PhSiH_3$ to afford $PhSiH_2(NPh_2)$, although it is slower than that for C_4H_8NH and requires a higher temperature (100˚C). Ph_2SiH_2 is, however, unreactive under these conditions.

(36) (a) MacDougall, D. J.; Mahon, M. F.; Robinson, T. P. *Chem. Sci.* **2013**, *4*, 4212−4222.

(b) Baishya, A.; Peddarao, T.; Nembenna, S. *Dalton Trans.* **2017**, *46*, 5880-5887.

(37) For catalysts that feature calcium, strontium and barium, see reference 7i, 36a and:

(a) Bellini, C.; Carpentier, J.-F.; Tobisch, S.; Sarazin, Y. *Angew. Chem., Int. Ed.* **2015**, *54*, 7679−7683.

(b) Bellini, C.; Roisnel, T.; Carpentier, J.-F.; Tobisch, S.; Sarazin, Y. *Chem. Eur. J.* **2016**, *22*, 15733-15743.

(c) Bellini, C.; Dorcet, V.; Carpentier, J.-F.; Tobisch, S.; Sarazin, Y. *Chem. Eur. J.* **2016**, *22*, 4564-4583.

(38) The overall metathesis reaction is not proposed to be a single step transformation but is proposed to involve initial nucleophilic attack of the amide nitrogen on silicon to form a five-coordinate silicon species which delivers the hydrogen to magnesium *via* a β–H elimination type process. See reference 3.

(39) For other mechanistic discussions pertaining to related Si–N bond formation transformations, see references 3, 4e, 7i, 36a, 37a and:

(a) Takaki, K.; Kamata, T.; Miura, Y.; Shishido, T.; Takehira, K. J. *Org. Chem.* **1999**, *64*, 3891−3895.

(b) Xie, W.; Hu, H.; Cui, C. *Angew. Chem., Int. Ed.* **2012**, *51*, 11141−11144.

(40) Bu^n_2Mg, Bu^nMgCl, and $Mg(OEt)_2$ have been reported to have almost no activity. See reference 7d.

(41) For studies employing MgO, see reference 7d and

(a) Itoh, M.; Mitsuzuka, M.; Utsumi, T.; Iwata, K.; Inoue, K. *J. Organomet. Chem.* **1994**, *476*, C30-C31.

(b) Itoh, M.; Mitsuzuka, M.; Iwata, K.; Inoue, K. *Macromolecules* **1994**, *27*, 7917-7919.

(42) For other examples of dehydrocoupling of silanes and alkynes using non-transition metal calatysts, see:

(a) Ma, Y.; Lou, S.-J.; Luo, G.; Luo, Y.; Zhan, G.; Nishiura, M.; Luo, Y.; Hou, Z. *Angew. Chem. Int. Ed.* **2018**, *57*, 15222-15226.

(b) Itoh, M.; Kobayashi, M.; Ishikawa, J. *Organometallics* **1997**, *16*, 3068-3070.

(43) Hasmi, A. S. K. in *Modern Allene Chemistry*, Krause, N.; Hashmi, A. S. K. eds, Wiley-VCH (2004), Chapter 1.

(44) Thompson, M. E.; Baxter, S. M.; Bulls, A. R.; Burger, B. J.; Nolan, M. C.; Santarsiero, B. D.; Schaefer, W. P.; Bercaw, J. E. *J. Am. Chem. Soc.* **1987**, *109*, 203-219.

(45) (a) McNally, J. P.; Leong, V. S.; Cooper, N. J. in *Experimental Organometallic*

Chemistry, Wayda, A. L.; Darensbourg, M. Y., Eds.; American Chemical Society: Washington, DC, 1987; Chapter 2, pp 6-23.

(b) Burger, B.J.; Bercaw, J. E. in *Experimental Organometallic Chemistry*; Wayda, A. L.; Darensbourg, M. Y., Eds.; American Chemical Society: Washington, DC, 1987; Chapter 4, pp 79-98.

(c) Shriver, D. F.; Drezdzon, M. A.; *The Manipulation of Air-Sensitive Compounds*, 2nd Edition; Wiley-Interscience: New York, 1986.

(46) (a) Gottlieb, H. E.; Kotlyar, V.; Nudelman, A. *J. Org. Chem*. **1997**, *62*, 7512-7515.

(b) Fulmer, G. R.; Miller, A. J. M.; Sherden, N. H.; Gottlieb, H. E.; Nudelman, A.; Stoltz, B. M.; Bercaw, J. E.; Goldberg, K. I. *Organometallics* **2010**, *29*, 2176-2179.

(47) (a) Sheldrick, G. M. SHELXTL, An Integrated System for Solving, Refining, and Displaying Crystal Structures from Diffraction Data; University of Göttingen, Göttingen, Federal Republic of Germany, 1981.

(b) Sheldrick, G. M. *Acta Cryst.* **2008**, *A64*, 112-122.

(c) Sheldrick, G. M. *Acta Cryst.* **2015**, *A71*, 3-8.

(48) (a) Jaguar, version 8.9, Schrodinger, Inc., New York, NY, 2015.

(b) Bochevarov, A. D.; Harder, E.; Hughes, T. F.; Greenwood, J. R.; Braden, D. A.; Philipp, D. M.; Rinaldo, D.; Halls, M. D.; Zhang, J.; Friesner, R. A. *Int. J. Quantum Chem*. **2013**, *113*, 2110–2142.

(49) $Ph_2SiH(NC_4H_8)$ and $PhSiH(N(C_4H_8)]_2$ were identified by comparison of the ^1H NMR spectra with those of authentic samples. See reference 4e.

(50) The turnover number (TON) is defined as the number of N–H or C–H bonds that react per molecule of catalyst.

(51) $PhSiH_2(NPh_2)$ was identified by comparison of the ^1H NMR data with the literature values. See reference 36b.

(52) $PhSiH_2C{\equiv}CPh$ was identified by comparison of the ^1H NMR data in $CDCl_3$ with the literature values on a sample obtained by lyophilization. See reference 7g.

(53) Formation of the products was confirmed by lyophilizing a sample prepared catalytically and redissolving in $CDCl_3$ to compare to the literature, although the stereochemistry associated with the cyclobutane substituents is not discussed. See reference 26.

Highlights

- [Tism$^{Pr^iBenz}$]MgX (X = H, Me) react with diphenylamine (Ph_2NH) and pyrrolidine (C_4H_8NH) to afford the amide derivatives, [Tism$^{Pr^iBenz}$]$MgNPh_2$ and [Tism$^{Pr^iBenz}$]$MgNC_4H_8$.

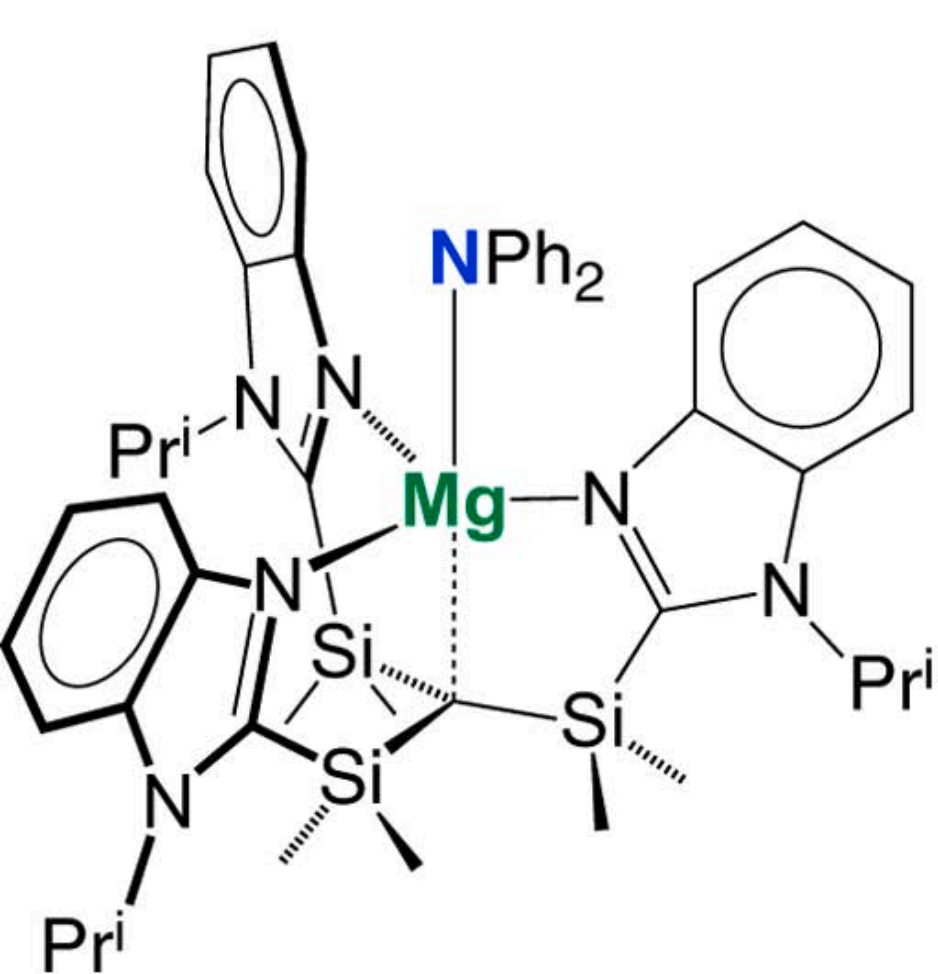
- [Tism$^{Pr^iBenz}$]MgX (X = H, Me) react with terminal alkynes, PhC≡CH and Bu^nC≡CH, to afford the acetylide derivatives, [Tism$^{Pr^iBenz}$]MgC≡CPh and [Tism$^{Pr^iBenz}$]MgC≡CBu^n.

- The molecular structures of [Tism$^{Pr^iBenz}$]$MgNPh_2$, [Tism$^{Pr^iBenz}$]$MgNC_4H_8$, [Tism$^{Pr^iBenz}$]MgC≡CPh and [Tism$^{Pr^iBenz}$]MgC≡CBu^n have been determined by single crystal X-ray diffraction.

- [Tism$^{Pr^iBenz}$]MgH and [Tism$^{Pr^iBenz}$]MgMe are capable of achieving catalytic dehydrocoupling reactions involving hydrosilanes.

Graphical Abstract

The magnesium hydride and methyl compounds, [Tism$^{Pr^iBenz}$]MgX (X = H, Me), react with diphenylamine (Ph_2NH) and pyrrolidine (C_4H_8NH) to afford the amide derivatives, [Tism$^{Pr^iBenz}$]MgNPh$_2$ and [Tism$^{Pr^iBenz}$]MgNC$_4$H$_8$, while reactions with the terminal alkynes, PhC≡CH and Bu^{n}C≡CH, afford the corresponding acetylide derivatives, [Tism$^{Pr^iBenz}$]MgC≡CPh and [Tism$^{Pr^iBenz}$]MgC≡CBu^n. The Mg–N and Mg–C≡CR bonds may be cleaved by hydrosilanes, thereby providing a catalytic system for dehydrocoupling.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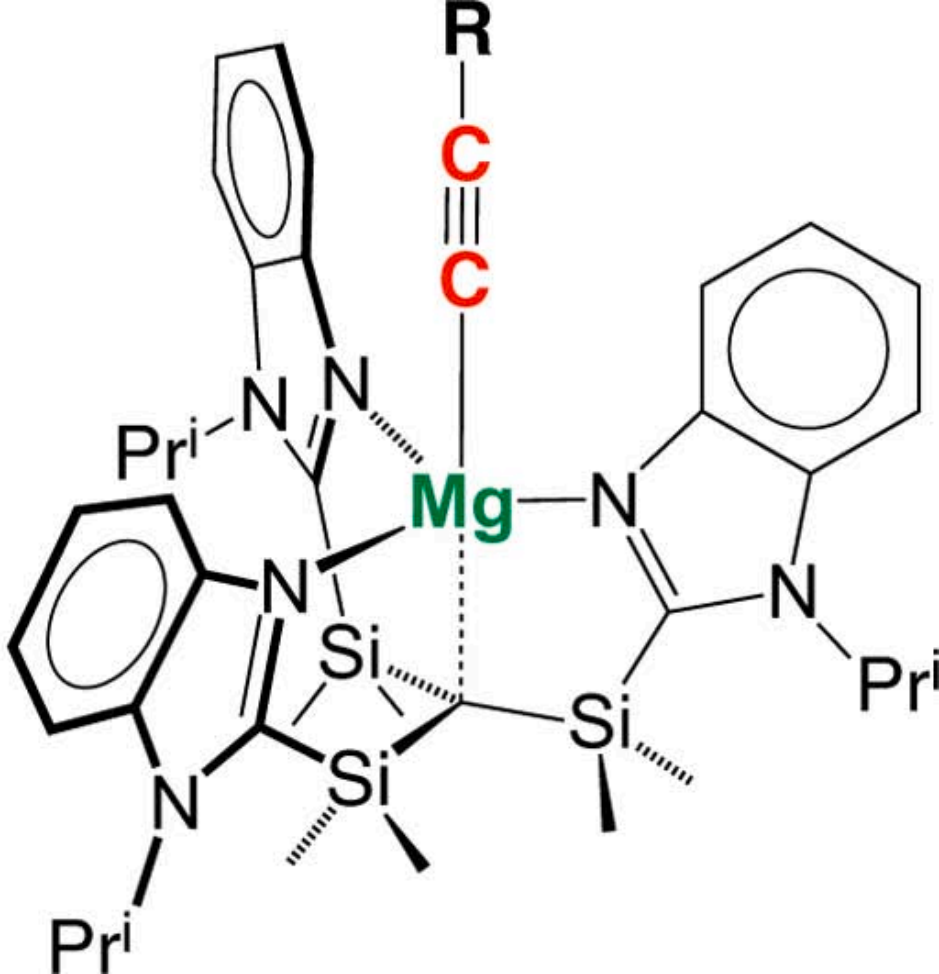
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