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Insertion of CS_2 into the Mg–H Bond: Synthesis and Structural Characterization of the Magnesium Dithioformate Complex, $[\mathrm{Tism}^{\mathrm{Pr^iBenz}}]\mathrm{Mg}(\kappa^2\text{–}S_2CH)$

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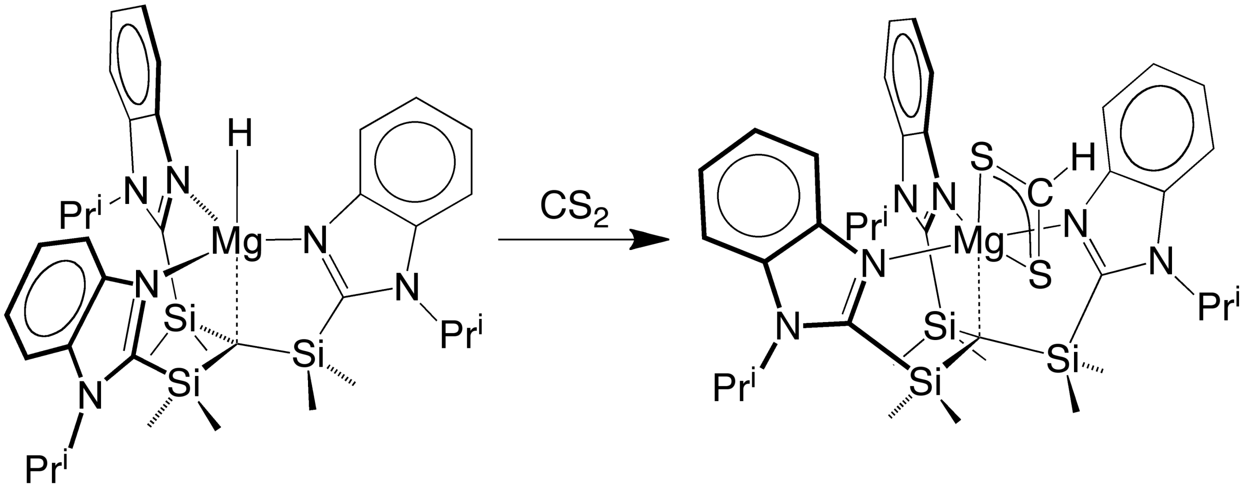
Abstract: The *tris*[(1-isopropylbenzimidazol-2-yl)dimethylsilyl]methyl magnesium hydride compound, $[\mathrm{Tism}^{\mathrm{Pr^iBenz}}]\mathrm{MgH}$, undergoes insertion of CS_2 into the Mg–H bond at room temperature to give $[\mathrm{Tism}^{\mathrm{Pr^iBenz}}]\mathrm{Mg}(\kappa^2\text{–}S_2CH)$, the first structurally characterized magnesium dithioformate compound. The dithioformate complex $[\mathrm{Tism}^{\mathrm{Pr^iBenz}}]\mathrm{Mg}(\kappa^2\text{–}S_2CH)$ reacts with *(i)* CO_2 at 80˚C to give, *inter alia*, the formate counterpart, $[\mathrm{Tism}^{\mathrm{Pr^iBenz}}]\mathrm{Mg}(\kappa^2\text{–}O_2CH)$, and *(ii)* Me_3SiX ($X = Cl, Br$), Me_3SnX ($X = F, Cl, Br$) and MeI to afford the halide derivatives, $[\mathrm{Tism}^{\mathrm{Pr^iBenz}}]\mathrm{MgX}$.

INTRODUCTION

By comparison to metal carboxylate complexes, dithiocarboxylate counterparts are uncommon. For example, there are only 65 structurally characterized $L_nM(S_2CR)$ (R = H, Me) derivatives listed in the Cambridge Structural Database (CSD),[1] a quantity which is less than 1 % of the number of $L_nM(O_2CR)$ (R = H, Me) derivatives. The paucity of metal dithiocarboxylates is a reflection of the fact that dithiocarboxylic acids are much less common and less stable than carboxylic acids.[2,3,4] Thus, rather than existing as hydrogen bonded dimers akin to carboxylic acids, dithiocarboxylic acids form oligomeric structures, $[RC(SH)S]_x$, with C–S–C single bonds; as such, the compounds do not actually possess the -C(S)SH functional group.[2] For example, dithioacetic acid has been structurally characterized by X-ray diffraction as a trimer $[MeC(SH)S]_3$ with a six-membered 1,3,5-trithiacyclohexane motif.[5,6,7,8] Likewise, mass spectrometric[9] and NMR spectroscopic[10] studies reveal that dithioformic acid is also oligomeric.[11,12] Here we report the synthesis and structural characterization of the first magnesium dithioformate complex.

RESULTS AND DISCUSSION

CS_2 is an important industrial chemical[13,14] that also plays roles in biological systems,[15] and has been extensively studied with respect to its reactivity towards metal centers.[14,16,17,18] For example, the insertion of CS_2 into a M–H bond provides a common method of synthesis for metal dithioformate compounds.[16,19,20] Metal formate compounds are likewise obtained by the insertion of CO_2 into a M–H bond, but the availability of formic acid provides a useful alternative method of synthesis[21] that is not readily accessible for dithioformate counterparts. As such, the absence of magnesium dithioformate complexes may be attributed to the relative paucity of magnesium hydride complexes. Indeed, terminal hydride derivatives of magnesium have been reported only relatively recently,[22,23] as illustrated by our use of the *tris*[(1-isopropylbenzimidazol-2-yl)dimethylsilyl]methyl ligand, $[\mathrm{Tism}^{\mathrm{Pr^iBenz}}]$,[24] to afford the terminal magnesium hydride derivative, $[\mathrm{Tism}^{\mathrm{Pr^iBenz}}]\mathrm{MgH}$.[25] The Mg–H bond of $[\mathrm{Tism}^{\mathrm{Pr^iBenz}}]\mathrm{MgH}$ is highly reactive, such that $[\mathrm{Tism}^{\mathrm{Pr^iBenz}}]\mathrm{MgH}$ undergoes a variety of metathesis and insertion reactions, as illustrated by the insertion of CO_2 and styrene to afford, respectively, $[\mathrm{Tism}^{\mathrm{Pr^iBenz}}]\mathrm{Mg}(\kappa^2\text{–}O_2CH)$[26] and $[\mathrm{Tism}^{\mathrm{Pr^iBenz}}]\mathrm{MgCH(Me)Ph}$.[25] In accord with this reactivity, we have now demonstrated that $[\mathrm{Tism}^{\mathrm{Pr^iBenz}}]\mathrm{MgH}$ reacts immediately with CS_2 to form $[\mathrm{Tism}^{\mathrm{Pr^iBenz}}]\mathrm{Mg}(\kappa^2\text{–}S_2CH)$ (Scheme 1).



Scheme 1.

The synthesis of $[\mathrm{Tism}^{\mathrm{Pr^iBenz}}]\mathrm{Mg}(\kappa^2\text{–}S_2CH)$ is noteworthy because it provides the first structurally characterized example of a magnesium dithioformate complex (Figure 1).[27] Furthermore, there are only three other structurally characterized dithioformate complexes of the main group metals, namely $[\mathrm{C(pz^{Me_2})_2(PPh_2NPh)}]\mathrm{Zn}(\kappa^1\text{–}S_2CH)$,[28] $[\mathrm{Tp^{Ph,Me}}]\mathrm{Zn}(\kappa^1\text{–}S_2CH)$,[29] and $[\mathrm{OC(Me)CHC(Me)NAr}]_2\mathrm{Al}(\kappa^1\text{–}S_2CH)$.[30,31]

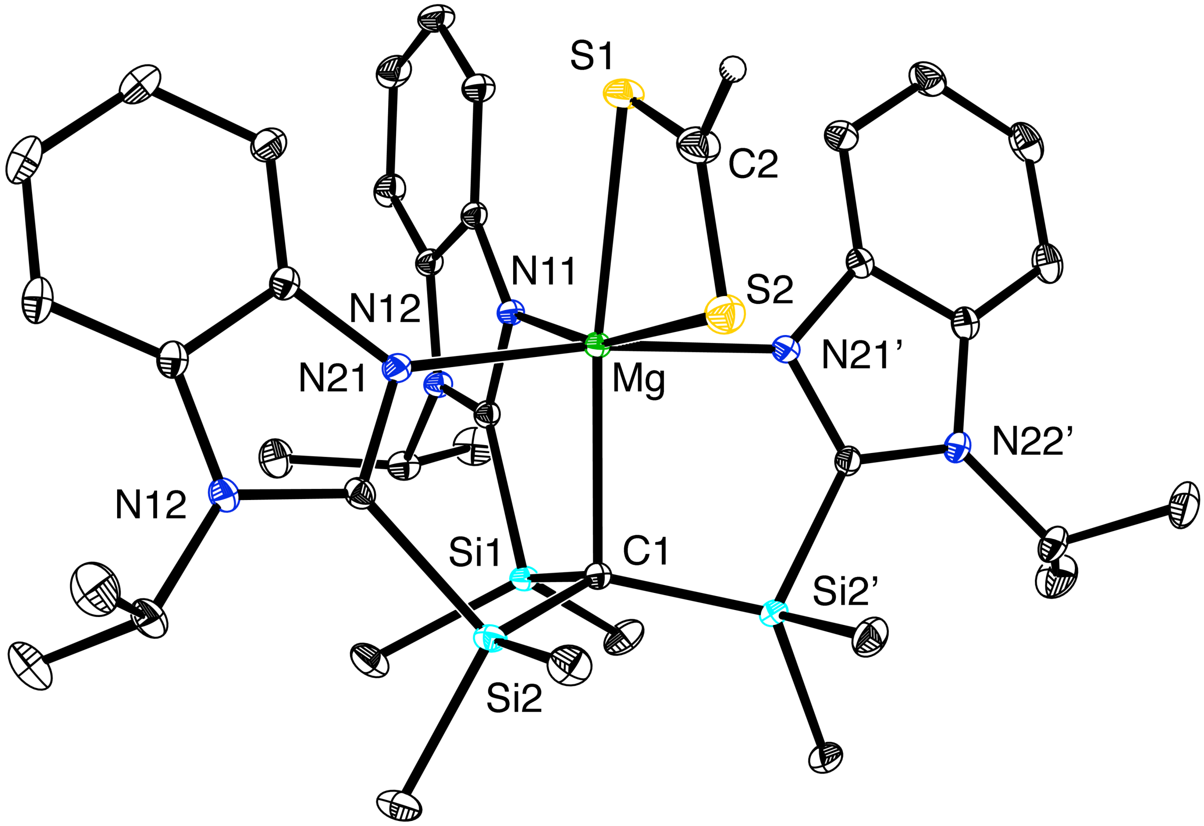


Figure 1. Molecular structure of $[\mathrm{Tism}^{\mathrm{Pr^iBenz}}]\mathrm{Mg}(\kappa^2\text{–}\mathrm{S_2CH})$.

The molecular structure of $[\mathrm{Tism}^{\mathrm{Pr^iBenz}}]\mathrm{Mg}(\kappa^2\text{–}\mathrm{S_2CH})$ is based on a distorted octahedral geometry with a bidentate dithioformate ligand. As such, the molecule possesses approximate molecular C_s symmetry in the solid state with a 2:1 set of benzimidazole groups. Despite this inequivalence, only one set of benzimidazole groups is observed by solution NMR spectroscopy, thereby demonstrating that the molecule is fluxional. The Mg–S bond lengths of $[\mathrm{Tism}^{\mathrm{Pr^iBenz}}]\mathrm{Mg}(\kappa^2\text{–}\mathrm{S_2CH})$ are 2.6219(7) Å and 2.8036(7) Å, with the longer value corresponding to the sulfur that is approximately trans to nitrogen. For comparison, the Mg–S bond length in $[\mathrm{Tism}^{\mathrm{Pr^iBenz}}]\mathrm{MgSH}$ is 2.412(1) Å,[25] and the mean value for structurally characterized compounds listed in the CSD is 2.54 Å.[1] The longer Mg–S bond distances for $[\mathrm{Tism}^{\mathrm{Pr^iBenz}}]\mathrm{Mg}(\kappa^2\text{–}\mathrm{S_2CH})$ are in accord with the fact that the bidentate dithioformate ligand is classified as an LX donor according to the Covalent Bond Classification;[32] as such, the magnesium-dithioformate interaction possesses a dative component, which is typically longer than that for a normal covalent bond.[33] While there are no other magnesium dithioformate compounds available for comparison, there are several structurally characterized magnesium dithiocarboxylate complexes and the Mg–S bond lengths in these complexes are comparable, although slightly shorter, than those in [Tism$^{\mathrm{Pr^iBenz}}$]Mg(κ^2–S_2CH), as summarized in Table 1.[34]

The C–S bond distances associated with the dithioformate moiety are 1.657(2) Å and 1.669(2) Å and, as expected, are intermediate between that for the C=S double bond in CS_2 (1.5549 Å)[35] and the mean value for compounds with C–S single bonds (1.77 Å) listed in the CSD.[1] The molecular structure of [Tism$^{\mathrm{Pr^iBenz}}$]Mg(κ^2–S_2CH) has also been determined by density functional theory geometry optimization calculations, and reproduces well the experimentally determined structure (see Supporting Information).

Table 1. Comparison of Mg–S bond lengths in magnesium dithiocarboxylate compounds.

Compound	***d*(Mg–S)/Å**	***d*(Mg–S)/Å**	**Ref.**
[Tism$^{\mathrm{Pr^iBenz}}$]Mg(κ^2–S_2CH)	2.6219(7)	2.8036(7)	this work
[Tism$^{\mathrm{Pr^iBenz}}$]Mg(κ^2–S_2CMe)	2.6271(11)	2.7273(11)	25
$(THF)_3Mg(\kappa^2\text{–}S_2CPh)Br^a$	2.596(3)	2.656(3)	34a
$(THF)_3Mg(\kappa^2\text{–}S_2CPh)Br^b$	2.578(2)	2.720(2)	34c
$(THF)_3Mg(\kappa^2\text{–}S_2CPr^i)Br$	2.574(3)	2.708(3)	34a
$(THF)_2Mg(\kappa^2\text{–}S_2CPh)_2$	2.5614(11) 2.5831(14)	2.6086(13) 2.5753(11)	34b

(a) 296 K. (b) 120 K.

With respect to the coordination mode of the dithioformate ligand, examination of the CSD demonstrates that dithioformate ligands can bind to either a single metal center or bridge two metals, of which the former is more common.[36] In terms of coordination to a single metal center, the dithioformate ligand can in principle bind with either bidentate, anisobidentate or unidentate coordination modes. Adopting criteria employed for carboxylate[37,38] and nitrate ligands,[39,40,41] the coordination modes for dithiocarboxylate ligands can be identified by the magnitude of the difference in M–S bond lengths (Δd), as illustrated in Figure 2 and Table 2. Examination of the data indicates that there is not a strong preference for either unidentate or bidentate coordination, although the latter is slightly more prevalent (65 %). It is also interesting to note that while the metal centers of bidentate metal dithioformate compounds reside close to the [S_2CH] plane, there is one example in which the metal is displaced considerably from the plane; as such the ligand coordinates in an η^3-manner, which is similar to that of an allyl ligand.[42]

In addition to these differences in coordination modes, unidentate metal dithioformate compounds can also adopt proximal and distal conformations in which the uncoordinated sulfur atom is respectively located in either a cis-like or trans-like relationship relative to the metal, similar to that reported for metal formate compounds.[38] The proximal and distal conformations are distinguished by respective M–S–C–S torsion angles of $|\tau| < 90^\circ$ and $|\tau| > 90^\circ$ (Figure 3), with the distal conformations also being identified by values of $\Delta d > 2$ Å. The distribution of metal dithoformate complexes according to these conformations is illustrated in Figure 4.

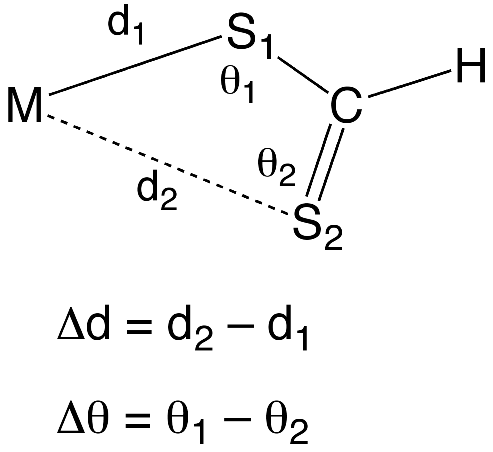


Figure 2. Parameters used for describing coordination of dithiocarboxylate ligands with a proximal conformation.

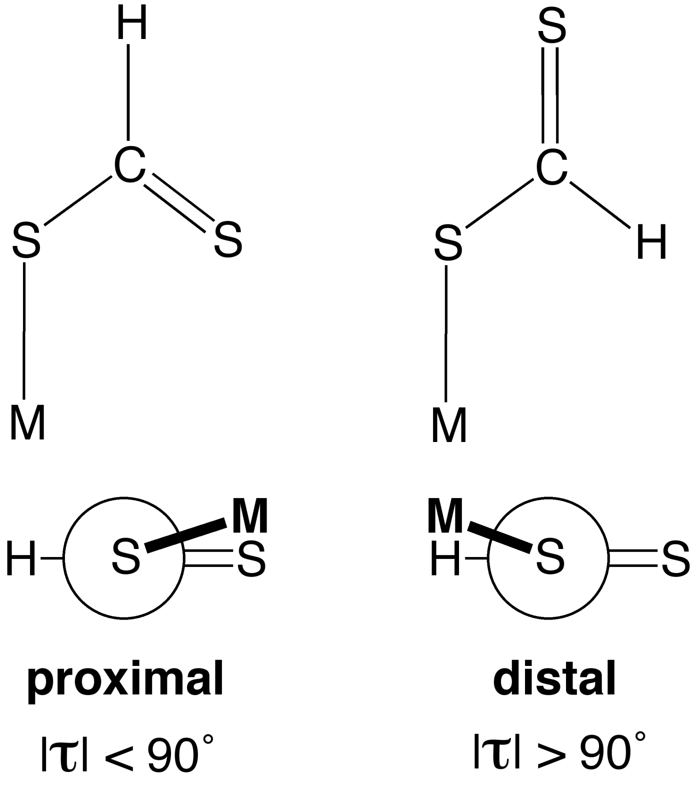


Figure 3. Proximal and distal conformations of unidentate dithioformate ligands.

Table 2. Criteria for assigning dithiocarboxylate coordination modes to a single metal center in which the secondary sulfur atom is proximal.[a]

Coordination mode	**Δ*d*/Å**
unidentate	> 0.6
anisobidentate	0.3 – 0.6
bidentate	< 0.3

(a) Based on the values for carboxylate ligands. See reference 37.

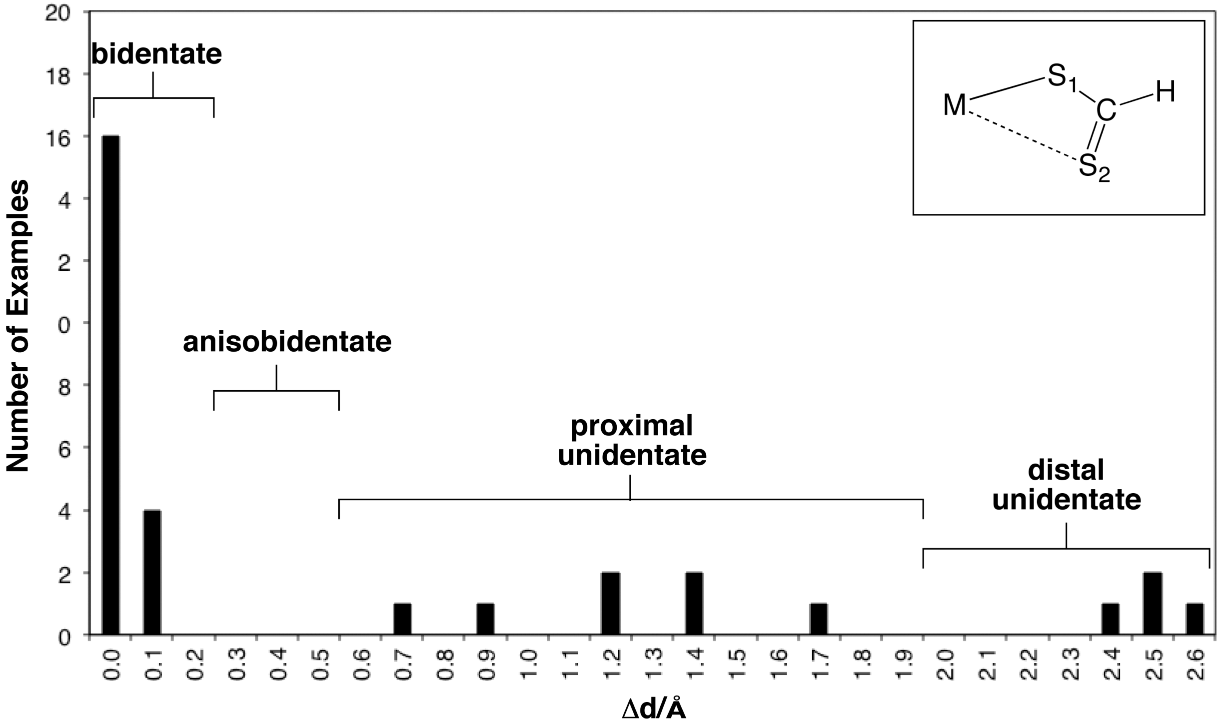


Figure 4. Distribution of dithioformate ligand coordination modes.

On the basis of the above criteria, [Tism$^{Pr^iBenz}$]Mg(κ^2–S_2CH) adopts a bidentate coordination mode since the difference in Mg–S bond lengths (0.182 Å) is less than 0.3 Å.[43] Significantly, this coordination mode is not observed for the other structurally characterized main group metal complexes (Table 3). Thus, the zinc complexes,

$[\mathrm{Tp}^{\mathrm{Ph,Me}}]\mathrm{Zn}(\kappa^1\text{–}\mathrm{S_2CH})$[29] and $[\mathrm{C}(\mathrm{pz}^{\mathrm{Me_2}})_2(\mathrm{PPh_2NPh})]\mathrm{Zn}(\kappa^1\text{–}\mathrm{S_2CH})$[28] exhibit unidentate coordination with a proximal conformation, whereas the aluminum complex $[\mathrm{OC(Me)CHC(Me)NAr}]_2\mathrm{Al}(\kappa^1\text{–}\mathrm{S_2CH})$[30] exhibits unidentate coordination with a distal conformation (Table 3). Distal conformations are not common for thioformates, but have been observed for transition metal complexes (Figure 4).[44,45]

Table 3. Selected metrical data for main group metal dithioformate compounds.

Compound	d_1/Å	d_2/Å	θ_1/°	θ_2/°	Δd/Å	$\Delta\theta$/°	$\lvert\tau\rvert$/°	**Conformation**	**Ref.**
$[\mathrm{Tism}^{\mathrm{Pr^iBenz}}]\mathrm{Mg}(\kappa^2\text{–}\mathrm{S_2CH})$	2.62	2.80	87.4	81.7	0.18	5.7	0	bidentate	This work
$[\mathrm{Tp}^{\mathrm{Ph,Me}}]\mathrm{Zn}(\kappa^1\text{–}\mathrm{S_2CH})$	2.29	3.02	94.6	72.2	0.73	22.4	1.8	proximal unidentate	29
$[\mathrm{C(pz^{Me_2})_2(PPh_2NPh)}]\mathrm{Zn}(\kappa^1\text{–}\mathrm{S_2CH})$	2.29	3.26	100.8	69.6	0.97	31.2	0.5	proximal unidentate	28
$(\mathrm{OCMeCHCMeNAr})_2\mathrm{Al}(\kappa^1\text{–}\mathrm{S_2CH})$	2.33	4.92	109.4	8.0	2.59	101.4	175.8	distal unidentate	30

In addition to X-ray diffraction, IR and ^{1}H NMR spectroscopies also provide diagnostic evidence for dithioformate complexes.[16] For example, with respect to IR spectroscopy, the [HCS$_2$] moiety is characterized by *(i)* an in-plane C–H deformation mode, δ(HCS$_2$), and *(ii)* antisymmetric and symmetric vibrations associated with the C–S bonds, namely ν_{as}(CS$_2$), and ν_s(CS$_2$). These vibrations are typically observed around 1200 cm^{-1}, 1000 cm^{-1} and 800 cm^{-1}, respectively. Of these, the signal due to ν_{as}(CS$_2$) is often the most distinctive because δ(HCS$_2$) and ν_s(CS$_2$) may be obscured by other vibrations of the molecules. In this regard, ν_{as}(CS$_2$) for [Tism$^{\text{Pr}^\text{i}\text{Benz}}$]Mg($\kappa^2$–S$_2$CH) is observed at 993 cm^{-1}, which compares favorably with the computed value of 1011 cm^{-1}; δ(HCS$_2$) and ν_{as}(CS$_2$) are calculated to have values of 1289 cm^{-1} and 815 cm^{-1}, respectively, but are experimentally masked by vibrations associated with the [Tism$^{\text{Pr}^\text{i}\text{Benz}}$] ligand. For comparison, ν(CS$_2$) data for other dithioformate metal complexes are summarized in Table 4,[46-58] thereby demonstrating that the value observed for [Tism$^{\text{Pr}^\text{i}\text{Benz}}$]Mg($\kappa^2$–S$_2$CH) is within the range observed for other metal dithioformate compounds.

Another distinctive feature of dithioformate complexes are signals at > 10 ppm in the ^{1}H NMR spectrum and > 220 ppm in the ^{13}C NMR spectrum (Table 4). Accordingly, the [HCS$_2$] moiety of [Tism$^{\text{Pr}^\text{i}\text{Benz}}$]Mg($\kappa^2$–S$_2$CH) is characterized by a signal at 11.80 ppm in the ^{1}H NMR spectrum, and a corresponding signal at 240.8 ppm in the ^{13}C NMR spectrum, with $^1J_{\text{C-H}} = 174$ Hz.

For comparison, these chemical shifts are downfield of the corresponding values for the formate counterpart, [Tism$^{\text{Pr}^\text{i}\text{Benz}}$]Mg($\kappa^2$–O$_2$CH) (9.06 ppm and 173.24 ppm),[26] which is in accord with the data for other systems. As an illustration, the ^{1}H and ^{13}C NMR chemical shifts of the dithioformate moiety of [(CO)$_5$Cr(κ^1–S$_2$CH)][K-crypt] (11.74 ppm and 239.3 ppm) are downfield of those of the formate counterpart (8.28 ppm and 167.9 ppm).[59] Likewise, the ^{1}H and ^{13}C NMR chemical shifts of trans-(dmpe)$_2$Fe(κ^1–S$_2$CH)H (11.66 ppm and 237.7 ppm) are downfield of those of the formate counterpart

(7.78 ppm and 168.1 ppm).[19a] It is also pertinent to note that $^{1}J_{C\text{-}H}$ for [Tism$^{\text{Pr}^{\text{i}}\text{Benz}}$]Mg($\kappa^2$–$S_2$CH) (174 Hz) is smaller than that for the formate complex [Tism$^{\text{Pr}^{\text{i}}\text{Benz}}$]Mg($\kappa^2$–$O_2$CH) (197 Hz), a trend which is in accord with literature reports, as illustrated by the values for $(CO)_5$Cr(κ^1–S_2CH)][K-crypt] (172 Hz) and $(CO)_5$Cr(κ^1–O_2CH)][K-crypt] (190 Hz).[59]

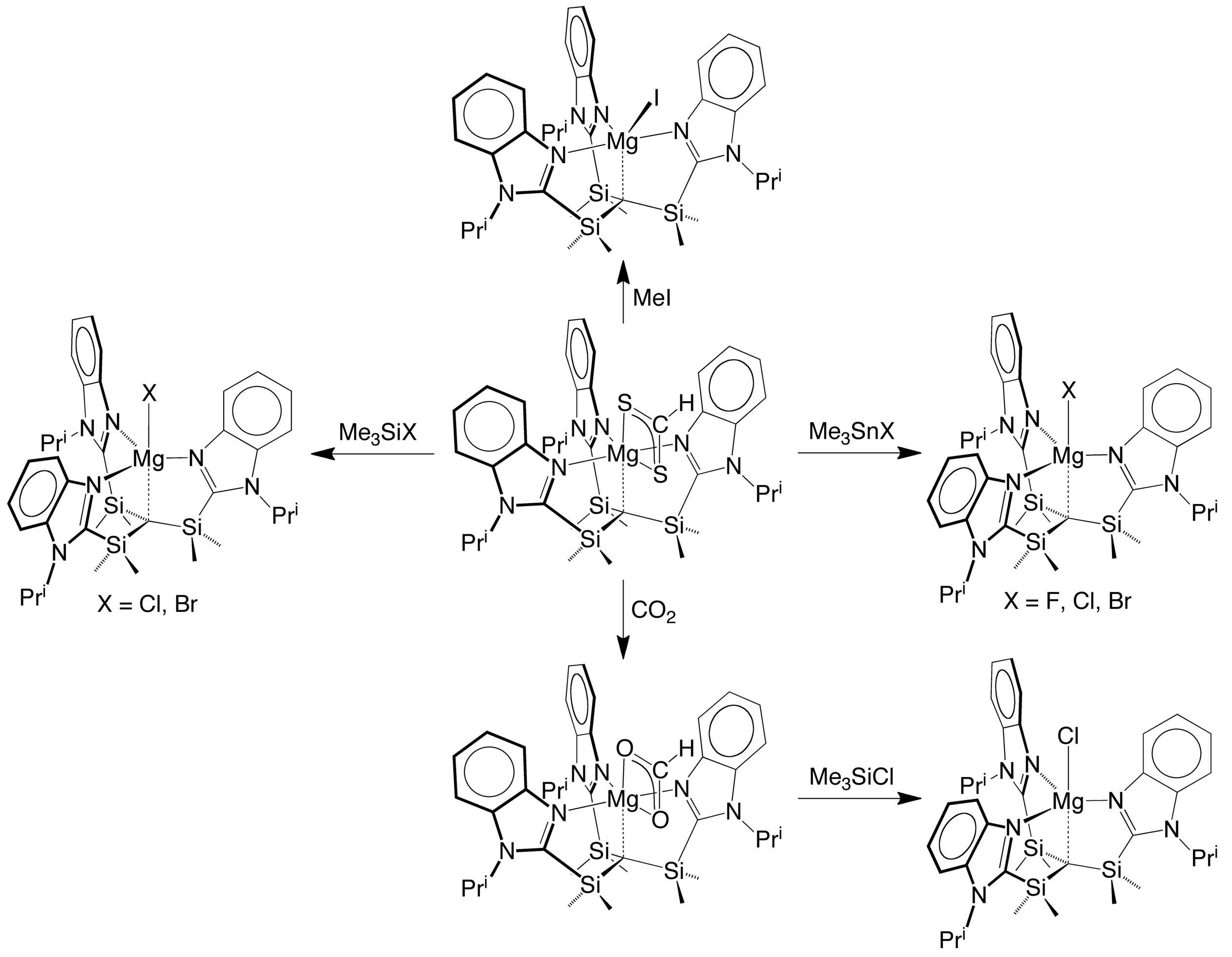
Table 4. IR and ^{1}H NMR spectroscopic data of $L_nM(S_2CH)$ Compounds.

Compound	**$\nu_{as}(CS_2)/cm^{-1}$**	**$\nu_s(CS_2)/cm^{-1}$**	**$\delta(^1H)/ppm$**	**$\delta(^{13}C)/ppm$**	**$^1J_{C-H}/Hz$**	**Ref.**
$K(S_2CH)$	980	786	12.22			9, 31e
$[Tism^{Pr^iBenz}]Mg(\kappa^2–S_2CH)$	993		11.80	240.8	174	this work
$[OC(Me)CHC(Me)NAr]Al(\kappa^1–S_2CH)$			11.66	240.5	178	30
$[(CO)_5Cr(\kappa^1–S_2CH)][PPN]$			11.80	239.2	173	59
$[(CO)_5Mo(\kappa^1–S_2CH)][PPN]$			11.85			59
$[(CO)_5W(\kappa^1–S_2CH)][PPN]$			11.70		173	59
fac-$(dppe)(CO)_3Mn(\kappa^1–S_2CH)$	1014 992	790 779	11.0	234.82		44a 46
fac-$(dppe)(CO)_3Re(\kappa^1–S_2CH)$	1011 1008	795 780	11.06	234.81		44a 46
trans-$(dmpe)_2Fe(\kappa^1–S_2CH)H$	984		11.66	237.6		19a
cis-$(PP_3)Fe(\kappa^1–S_2CH)H$			12.61	237.5		19a
$[(depe)_2Fe(\kappa^2–S_2CH)]^+$	910		10.94			47
$(Cyttp)Ru(\kappa^2–S_2CH)H$			11.85			49

$(Ph_3P)_2Ru(\kappa^2–S_2CH)_2$	915, 908	784, 775	11.5			50
cis-$(Ph_3P)_2(CO)Ru(\kappa^2–S_2CH)Cl$	930		11.88			51
	920		11.87			52
$(Ph_3P)_2(CO)Ru(\kappa^2–S_2CH)(ONO_2)$	920		9.5			19d
$(\kappa^1–P,O)_3Ru(\kappa^2–S_2CH)Cl$	907		10.29	230.3		53
$CpRu(PPh_3)_2(\kappa^1–S_2CH)$	970		11.63			54
$Cp(Ph_3As)_2Ru(\kappa^1–S_2CH)$	1020		11.6			55
$[(bpy)_2(Ph_3P)Ru(\kappa^1–S_2CH)]^+$	978		10.82			19b
$\{(C_6Me_6)(\kappa^1–P,O)Ru(\kappa^2–S_2CH)\}^+$			11.7	242.5		56
$(Ph_3P)_2Os(\kappa^2–S_2CH)_2$	910, 902		13.24			52
cis-$(Ph_3P)_2(CO)Os(\kappa^2–S_2CH)Cl$	920		13.65			52
trans-$(Ph_3P)_2(CO)Os(\kappa^2–S_2CH)Cl$	920		11.85			52
$(Ph_3P)_2Co(S_2CH)$	910	740				57
$(Ph_3P)_2Ir(\kappa^2–S_2CH)Cl_2$	915		13.20			52
$[2,6\text{-}(Pr^i{}_2PO)_2C_6H_3]Ni(\kappa^1–S_2CH)$			11.55	233.7		19c
$\{[(P(C_6H_3\text{-}3\text{-}SiMe_3\text{-}2\text{-}S)_3]Ni(\kappa^1–S_2CH)\}^-$	1007					44b
trans-$(Cy_3P)_2Pt(\kappa^1–S_2CH)H$	1005		12.12			58
$(Ph_3P)_2Cu(\kappa^2–S_2CH)$	960	820	11.27			20c

(triphos)Cu(κ^1–S$_2$CH)	1012	810	11.26			20c
[C(pz^{Me_2})$_2$(PPh$_2$NPh)]Zn(κ^1–S$_2$CH)			11.92			28
[Tp^{Ph,Me}]Zn(κ^1–S$_2$CH)			10.24			29

The facile insertion of CS_2 into the Mg–H bond is in accord with density functional theory calculations, which predict a thermodynamically favorable transformation ($\Delta E_{SCF} = -41.4$ kcal mol^{-1}), as is also observed for the insertion of CO_2 ($\Delta E_{SCF} = -53.3$ kcal mol^{-1}). In this regard, while examples of both insertion of CO_2 into M–H bonds and the reverse decarboxylation of metal formates are known,[60,61,62] we are not aware of any examples of metal dithioformate compounds that eliminate CS_2 to form a metal hydride derivative. For example, $[2,6\text{-}(R_2PO)_2C_6H_3]Ni(\kappa^1\text{–}O_2CH)$ reacts with a large excess of CS_2 to afford $[2,6\text{-}(R_2PO)_2C_6H_3]Ni(\kappa^1\text{–}S_2CH)$, whereas the reverse reaction could not be observed.[19c] However, since the insertion of CS_2 into the Mg–H bond of $[Tism^{Pr^iBenz}]MgH$ is calculated to be less thermodynamically favorable than that for CO_2, we considered the possibility that the reaction between $[Tism^{Pr^iBenz}]Mg(\kappa^2\text{–}S_2CH)$ and CO_2 could afford $[Tism^{Pr^iBenz}]Mg(\kappa^2\text{–}O_2CH)$, and thereby provide potential evidence for elimination of CS_2. Significantly, $[Tism^{Pr^iBenz}]Mg(\kappa^2\text{–}S_2CH)$ does indeed convert to $[Tism^{Pr^iBenz}]Mg(\kappa^2\text{–}O_2CH)$ in the presence of CO_2 at 80°C (Scheme 2), although under these conditions the formate complex also undergoes slow conversion to an unidentified species. In accord with the formation of $[Tism^{Pr^iBenz}]Mg(\kappa^2\text{–}O_2CH)$ from $[Tism^{Pr^iBenz}]Mg(\kappa^2\text{–}S_2CH)$ and CO_2, the formate complex does not convert to $[Tism^{Pr^iBenz}]Mg(\kappa^2\text{–}S_2CH)$ in the presence of CS_2 under comparable conditions. While consistent with a mechanism that involves elimination of CS_2, it must be emphasized that other pathways could also be operative for the conversion of $[Tism^{Pr^iBenz}]Mg(\kappa^2\text{–}S_2CH)$ to $Tism^{Pr^iBenz}]Mg(\kappa^2\text{–}S_2CH)$ in the presence of CO_2.



Scheme 2.

Although the reaction between [Tism$^{Pr^iBenz}$]Mg(κ^2–S_2CH) and CO_2 requires elevated temperatures, the dithioformate complex reacts rapidly with Me_3SiX (X = Cl, Br) and Me_3SnX (X = F, Cl, Br) at room temperature to afford the corresponding halide derivative, [Tism$^{Pr^iBenz}$]MgX (Scheme 2).[25,63] Of these reactions, the formation of the fluoride derivative, [Tism$^{Pr^iBenz}$]MgF, is most notable because synthetic methods for terminal fluoride compounds are not common.[64] In addition to replacing the dithioformate ligand by the use of the silicon and tin reagents, Me_3SiX and Me_3SnX, MeI also reacts with [Tism$^{Pr^iBenz}$]Mg(κ^2–S_2CH) at room temperature to form [Tism$^{Pr^iBenz}$]MgI.[65] The formate complex [Tism$^{Pr^iBenz}$]Mg(κ^2–O_2CH) exhibits similar reactivity towards Me_3SiCl to afford [Tism$^{Pr^iBenz}$]MgCl, but does not react with MeI to afford [Tism$^{Pr^iBenz}$]MgI. Thus, while both the dithioformate and formate ligands of

[Tism$^{\mathrm{Pr^iBenz}}$]Mg(κ^2–S_2CH) and [Tism$^{\mathrm{Pr^iBenz}}$]Mg(κ^2–O_2CH) may be substituted by other ligands, it is evident that the former is more susceptible towards replacement.

SUMMARY

In summary, the magnesium hydride compound, [Tism$^{\mathrm{Pr^iBenz}}$]MgH, undergoes insertion of CS_2 into the Mg–H bond to give [Tism$^{\mathrm{Pr^iBenz}}$]Mg(κ^2–S_2CH), which is a rare example of a main group metal dithioformate complex. X-ray diffraction demonstrates that the dithioformate ligand coordinates in a bidentate manner, which is of note because other main group metal dithioformate compounds exhibit unidentate coordination. [Tism$^{\mathrm{Pr^iBenz}}$]Mg(κ^2–S_2CH) reacts with CO_2 at elevated temperatures to afford, *inter alia*, [Tism$^{\mathrm{Pr^iBenz}}$]Mg(κ^2–O_2CH). Other reactivity exhibited by [Tism$^{\mathrm{Pr^iBenz}}$]Mg(κ^2–S_2CH) includes the formation of [Tism$^{\mathrm{Pr^iBenz}}$]MgX derivatives by reactions with Me_3SiX (X = Cl, Br), Me_3SnX (X = F, Cl, Br) and MeI, of which an interesting aspect is that the transformations are more facile than corresponding reactions of the formate counterpart, [Tism$^{\mathrm{Pr^iBenz}}$]Mg(κ^2–O_2CH).

EXPERIMENTAL SECTION

General considerations

All manipulations were performed by using a combination of glovebox, high vacuum, and Schlenk techniques under an argon atmosphere.[66] Solvents were purified and degassed by standard procedures. NMR spectra were recorded on Bruker AVIII 300 and Bruker AVIII 500 spectrometers. ^{1}H NMR chemical shifts are reported in ppm relative to $SiMe_4$ ($\delta = 0$), and were referenced with respect to the protio solvent impurity ($\delta = 7.16$ for C_6D_5H).[67] ^{13}C NMR spectra are reported in ppm relative to $SiMe_4$ ($\delta = 0$) and were referenced internally with respect to the solvent ($\delta = 128.06$ for C_6D_5H). ^{29}Si NMR chemical shifts are reported in ppm relative to $SiMe_4$ ($\delta = 0.0$) and were obtained by using the $\Xi/100\%$ value of 19.867187.[68] Coupling constants are given in hertz. Infrared spectra were recorded on a Perkin Elmer Spectrum Two spectrometer in attenuated total reflectance (ATR) mode and are reported in reciprocal centimeters. [Tism$^{\text{PriBenz}}$]MgMe,[24] [Tism$^{\text{PriBenz}}$]MgH[25] and Me_3SnF[69] were obtained by literature methods, and CO_2, CS_2, $PhSiH_3$, MeI, Me_3SiX (X = Cl, Br), and Me_3SnX (X = Cl, Br) were obtained commercially and used as received.

X-ray Structure Determinations

X-ray diffraction data were collected on a Bruker Apex II diffractometer. The structure was 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).[70] Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre (CCDC 1842582).

Computational Details

Calculations were carried out using DFT as implemented in the Jaguar 8.9 (release 15) suite of *ab initio* quantum chemistry programs.[71] Geometry optimizations and frequency calculations were performed with the B3LYP density functional using the

LACVP** basis sets and Cartesian coordinates are provided in the Supporting Information.

Synthesis of [Tism$^{\mathrm{Pr^{i}Benz}}$]Mg(κ^2-S_2CH)

(i) [Tism$^{\mathrm{Pr^{i}Benz}}$]MgH was generated *in situ* by treatment of a solution of [Tism$^{\mathrm{Pr^{i}Benz}}$]MgMe (30 mg, 0.043 mmol) in C_6D_6 (*ca* 0.7 mL) with $PhSiH_3$ (10 mg, 0.092 mmol). The mixture was allowed to stand at room temperature for 16 hours, filtered, and then treated with CS_2 (4 mg, 0.052 mmol). The solution immediately turned bright yellow and was lyophilized to obtain [Tism$^{\mathrm{Pr^{i}Benz}}$]Mg(κ^2-S_2CH) as a yellow powder (18 mg, 55% yield). Gold crystals suitable for X-ray diffraction were obtained *via* vapor diffusion of pentane into a concentrated solution in benzene. Anal. calcd. for [Tism$^{\mathrm{Pr^{i}Benz}}$]Mg(κ^2-S_2CH): C, 59.6%; H, 6.9%; N, 11.0%. Found: C, 59.8%; H, 6.4%; N, 8.8%. ^{1}H NMR (C_6D_6): 0.55 [s, 18H, $(C_6H_4N_2CH(CH_3)_2CSi(C\underline{H}_3)_2)_3CMgSC(S)H$], 1.18 [d, J = 7 Hz, 18H, $(C_6H_4N_2CH(C\underline{H}_3)_2CSi(CH_3)_2)_3CMgSC(S)H$], 4.66 [sep, J = 7 Hz, 3H, $(C_6H_4N_2C\underline{H}(CH_3)_2CSi(CH_3)_2)_3CMgSC(S)H$], 6.96 [t, J = 8 Hz, 3H, $(C_6\underline{H}_4N_2CH(CH_3)_2CSi(CH_3)_2)_3CMgSC(S)H$], 7.09 [t, J = 8 Hz, 3H, $(C_6\underline{H}_4N_2CH(CH_3)_2CSi(CH_3)_2)_3CMgSC(S)H$], 7.14 [d, J = 8 Hz, 3H, $(C_6\underline{H}_4N_2CH(CH_3)_2CSi(CH_3)_2)_3CMgSC(S)H$], 8.90 [d, J = 8 Hz, 3H, $(C_6\underline{H}_4N_2CH(CH_3)_2CSi(CH_3)_2)_3CMgSC(S)H$], 11.80 [s, 1H, $(C_6H_4N_2CH(CH_3)_2CSi(CH_3)_2)_3CMgSC(S)\underline{H}$]. $^{13}C\{^1H\}$ NMR (C_6D_6): 5.53 [s, 6C, $(C_6H_4N_2CH(CH_3)_2CSi(\underline{C}H_3)_2)_3CMgSC(S)H$], 21.02 [s, 6C, $(C_6H_4N_2CH(\underline{C}H_3)_2CSi(CH_3)_2)_3CMgSC(S)H$], 50.12 [s, 3C, $(C_6H_4N_2\underline{C}H(CH_3)_2CSi(CH_3)_2)_3CMgSC(S)H$], 112.43 [s, 3C, $(\underline{C}_6H_4N_2CH(CH_3)_2CSi(CH_3)_2)_3CMgSC(S)H$], 122.12 [s, 3C, $(\underline{C}_6H_4N_2CH(CH_3)_2CSi(CH_3)_2)_3CMgSC(S)H$], 122.59 [s, 3C, $(\underline{C}_6H_4N_2CH(CH_3)_2CSi(CH_3)_2)_3CMgSC(S)H$], 122.77 [s, 3C, $(\underline{C}_6H_4N_2CH(CH_3)_2CSi(CH_3)_2)_3CMgSC(S)H$], 134.26 [s, 3C, $(\underline{C}_6H_4N_2CH(CH_3)_2CSi(CH_3)_2)_3CMgSC(S)H$], 143.91 [s, 3C,

($\underline{C}_6H_4N_2CH(CH_3)_2CSi(CH_3)_2)_3CMgSC(S)H$], 166.84 [s, 3C, ($\underline{C}_6H_4N_2CH(CH_3)_2CSi(CH_3)_2)_3CMgSC(S)H$], 240.82 [s, 1C, ($C_6H_4N_2CH(CH_3)_2CSi(CH_3)_2)_3CMgS\underline{C}(S)H$], not observed [($C_6H_4N_2CH(CH_3)_2CSi(CH_3)_2)_3\underline{C}MgSC(S)H$]. ^{13}C NMR (C_6D_6), selected data: 240.82 [d, $^1J_{C\text{-}H}$ = 174, 1C, ($C_6H_4N_2CH(CH_3)_2CSi(CH_3)_2)_3CMgS\underline{C}(S)H$]. ^{29}Si NMR (C_6D_6): -11.36 [s, 3Si, ($C_6H_4N_2CH(CH_3)_2C\underline{Si}(CH_3)_2)_3CMgSC(S)H$]. IR Data (ATR, cm^{-1}): 1462 (w), 1355 (w), 1354 (w), 1064 (w), 993 (s), 943 (s), 912 (s), 827 (w), 814 (m), 792 (m), 764 (w), 741 (s), 696 (w), 679 (w).

(ii) A solution of CS_2 (0.5 mg, 0.007 mmol) in C_6D_6 (*ca* 0.7 mL) was added to a sample of [Tism$^{Pr^iBenz}$]MgH (3 mg, 0.004 mmol) in an NMR tube equipped with a J. Young valve. The solution was monitored by ^1H NMR spectroscopy, thereby demonstrating the formation of [Tism$^{Pr^iBenz}$]Mg(κ^2-S_2CH) after a period of 10 minutes at room temperature.

Reactivity of [Tism$^{Pr^iBenz}$]Mg(κ^2-S_2CH) towards Me_3SiCl

A solution of [Tism$^{Pr^iBenz}$]Mg(κ^2-S_2CH) (2 mg, 0.003 mmol) in C_6D_6 (*ca* 0.7 mL) in an NMR tube equipped with a J. Young valve was treated with Me_3SiCl (*ca* 4 equivalents). The solution immediately turned colorless and was monitored by ^1H NMR spectroscopy, thereby demonstrating the formation of [Tism$^{Pr^iBenz}$]MgCl[72] after a period of 30 minutes.

Reactivity of [Tism$^{Pr^iBenz}$]Mg(κ^2-S_2CH) towards Me_3SiBr

A solution of [Tism$^{Pr^iBenz}$]Mg(κ^2-S_2CH) (2 mg, 0.003 mmol) in C_6D_6 (*ca* 0.7 mL) in an NMR tube equipped with a J. Young valve was treated with Me_3SiBr (*ca* 4 equivalents). The solution immediately turned colorless and was monitored by ^1H NMR spectroscopy, thereby demonstrating the formation of [Tism$^{Pr^iBenz}$]MgBr[72] after a period of 30 minutes.

Reactivity of [Tism$^{Pr^iBenz}$]Mg(κ^2-S_2CH) towards Me_3SnF

A solution of [Tism$^{Pr^iBenz}$]Mg(κ^2-S_2CH) (2 mg, 0.003 mmol) in C_6D_6 (*ca* 0.7 mL) in an NMR tube equipped with a J. Young valve was treated with Me_3SnF (*ca* 2 equivalents). The solution immediately turned colorless and was monitored by ^{1}H NMR spectroscopy, thereby demonstrating the formation of [Tism$^{\text{Pr}^{\text{i}}\text{Benz}}$]MgF[72] after a period of 30 minutes.

Reactivity of [Tism$^{\text{Pr}^{\text{i}}\text{Benz}}$]Mg($\kappa^2$-$S_2CH$) towards Me_3SnCl

A solution of [Tism$^{\text{Pr}^{\text{i}}\text{Benz}}$]Mg($\kappa^2$-$S_2CH$) (2 mg, 0.003 mmol) in C_6D_6 (*ca* 0.7 mL) in an NMR tube equipped with a J. Young valve was treated with Me_3SnCl (*ca* 4 equivalents). The solution immediately turned colorless and was monitored by ^{1}H NMR spectroscopy, thereby demonstrating the formation of [Tism$^{\text{Pr}^{\text{i}}\text{Benz}}$]MgCl[72] after a period of 30 minutes.

Reactivity of [Tism$^{\text{Pr}^{\text{i}}\text{Benz}}$]Mg($\kappa^2$-$S_2CH$) towards Me_3SnBr

A solution of [Tism$^{\text{Pr}^{\text{i}}\text{Benz}}$]Mg($\kappa^2$-$S_2CH$) (2 mg, 0.003 mmol) in C_6D_6 (*ca* 0.7 mL) in an NMR tube equipped with a J. Young valve was treated with Me_3SnBr (*ca* 4 equivalents). The solution immediately turned colorless and was monitored by ^{1}H NMR spectroscopy, thereby demonstrating the formation of [Tism$^{\text{Pr}^{\text{i}}\text{Benz}}$]MgBr[72] after a period of 30 minutes.

Reactivity of [Tism$^{\text{Pr}^{\text{i}}\text{Benz}}$]Mg($\kappa^2$-$S_2CH$) towards MeI

A solution of [Tism$^{\text{Pr}^{\text{i}}\text{Benz}}$]Mg($\kappa^2$-$S_2CH$) (2 mg, 0.003 mmol) in C_6D_6 (*ca* 0.7 mL) in an NMR tube equipped with a J. Young valve was treated with MeI (*ca.* 4 equivalents). The solution turned colorless over a period of five hours, and was monitored by ^{1}H NMR spectroscopy, thereby demonstrating the formation of [Tism$^{\text{Pr}^{\text{i}}\text{Benz}}$]MgI.[72]

Reactivity of [Tism$^{\text{Pr}^{\text{i}}\text{Benz}}$]Mg($\kappa^2$-$O_2CH$) towards Me_3SiCl

A suspension of [Tism$^{\text{Pr}^{\text{i}}\text{Benz}}$]Mg($\kappa^2$-$O_2CH$) (2 mg, 0.003 mmol) in C_6D_6 (*ca* 0.7 mL) was treated with Me_3SiCl (*ca* 4 equivalents) resulting in dissolution. The solution was monitored by ^{1}H NMR spectroscopy, thereby demonstrating the formation of [Tism$^{\text{Pr}^{\text{i}}\text{Benz}}$]MgCl[72] after 15 minutes.

Reactivity of $[\mathrm{Tism}^{\mathrm{Pr^iBenz}}]\mathrm{Mg}(\kappa^2\text{-}\mathrm{O_2CH})$ towards MeI

A suspension of $[\mathrm{Tism}^{\mathrm{Pr^iBenz}}]\mathrm{Mg}(\kappa^2\text{-}\mathrm{O_2CH})$ (2 mg, 0.003 mmol) in C_6D_6 (*ca* 0.7 mL) in an NMR tube equipped with a J. Young valve was treated with MeI (*ca* 4 equivalents). The suspension was monitored by ^{1}H NMR spectroscopy, thereby demonstrating no reactivity over a period of 18 hours at room temperature. Furthermore, no change was observed upon heating at 80° C for 3 days.

Reactivity of $[\mathrm{Tism}^{\mathrm{Pr^iBenz}}]\mathrm{Mg}(\kappa^2\text{-}\mathrm{S_2CH})$ towards CO_2

A solution of $[\mathrm{Tism}^{\mathrm{Pr^iBenz}}]\mathrm{Mg}(\kappa^2\text{-}\mathrm{S_2CH})$ (2 mg, 0.003 mmol) in C_6D_6 (*ca* 0.7 mL) in an NMR tube equipped with a J. Young valve was treated with CO_2 (1 atm). The solution was heated at 80°C and was monitored by ^{1}H NMR spectroscopy, thereby demonstrating formation of $[\mathrm{Tism}^{\mathrm{Pr^iBenz}}]\mathrm{Mg}(\kappa^2\text{-}\mathrm{O_2CH})$[73] over a period of 14 days, together with an unidentified product.

Reactivity of $[\mathrm{Tism}^{\mathrm{Pr^iBenz}}]\mathrm{Mg}(\kappa^2\text{-}\mathrm{O_2CH})$ towards CS_2

A suspension of $[\mathrm{Tism}^{\mathrm{Pr^iBenz}}]\mathrm{Mg}(\kappa^2\text{-}\mathrm{O_2CH})$ (2 mg, 0.003 mmol) in C_6D_6 (*ca* 0.7 mL) in an NMR tube equipped with a J. Young valve was treated with CS_2 (*ca* 10 equivalents). The sample was heated at 80°C and was monitored by ^{1}H NMR spectroscopy, demonstrating no conversion to $[\mathrm{Tism}^{\mathrm{Pr^iBenz}}]\mathrm{Mg}(\kappa^2\text{-}\mathrm{S_2CH})$ over a period of 14 days.

Electronic Supplementary Information (ESI) available:

Crystallographic data (CIFs), spectroscopic data and computational data for geometry optimized structures. CCDC reference number 1842582. See http://dx.doi.org/10.1039/b000000x/.

Conflicts of interest

There are no conflicts of interest to declare.

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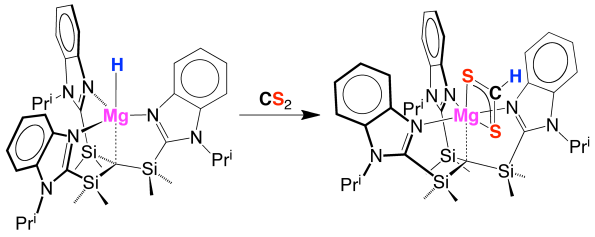
(72) Spectroscopic data for [Tism$^{\mathrm{Pr^iBenz}}$]MgX (X = F, Cl, Br, I) are reported in reference 25.

(73) Spectroscopic data for [Tism$^{\mathrm{Pr^iBenz}}$]Mg(κ^2-O_2CH) are reported in reference 26.

Graphical Abstract



Insertion of CS_2 into the Mg–H bond of [Tism$^{\mathrm{Pr^iBenz}}$]MgH affords [Tism$^{\mathrm{Pr^iBenz}}$]Mg(κ^2–S_2CH), the first structurally characterized magnesium dithioformate compound.