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Extremely Bulky Amido First Row Transition Metal(II) Halide Complexes: Potential Precursors to Low Coordinate Metal–Metal Bonded Systems

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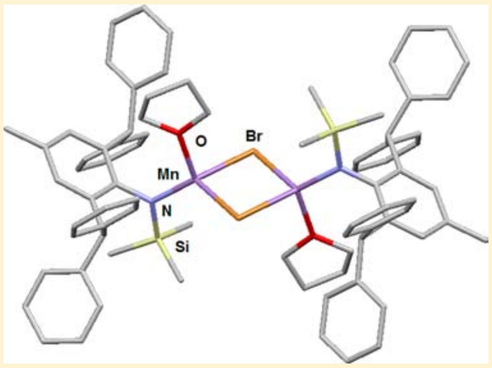
Supporting Information

ABSTRACT: Reactions of the extremely bulky potassium amide complexes, [KL′(η^6-toluene)] or [KL″] (L′/L″ = N(Ar*)(SiR$_3$), Ar* = $C_6H_2\{C(H)Ph_2\}_2Me$-2,6,4; R = Me (L′) or Ph (L″)), with a series of first row transition metal(II) halides have yielded 10 rare examples of monodentate amido first row transition metal(II) halide complexes, all of which were crystallographically characterized. They encompass the dimeric, square-planar chromium complexes, [{CrL′(THF)(μ-Cl)}$_2$] and [{CrL″(μ-Cl)}$_2$], the latter of which displays intramolecular η^2-Ph···Cr interactions; the dimeric tetrahedral complexes, [{ML′(THF)(μ-Br)}$_2$] (M = Mn or Fe), [{ML″(THF)(μ-X)}$_2$] (M = Mn, Fe or Co; X = Cl or Br) and [{CoL″(μ-Cl)}$_2$] (which displays intramolecular η^2-Ph···Co interactions); and the monomeric zinc amides, [L′ZnBr(THF)] (three-coordinate) and [L″ZnBr] (two-coordinate). Solution state magnetic moment determinations on all but one of the paramagnetic compounds show them to be high-spin systems. Throughout, comparisons are made with related bulky terphenyl transition metal(II) halide complexes, and the potential for the use of the prepared complexes as precursors to low-valent transition metal systems is discussed.



INTRODUCTION

The chemistry of metal–metal bonded complexes has rapidly expanded in recent decades.[1] Many advances have been made in this field, with the preparation of stable dimeric complexes containing s-[2] or p-block[3] metal(I)–metal(I) bonds being landmark examples. More than just being of fundamental interest, these highly reactive, two- or three-coordinate species have found a variety of applications in synthesis, small molecule activation, and so forth.[4] Related low coordinate systems containing carbonyl free, first row d-block metal(I)–metal(I) bonds are less developed, though a number of breakthroughs have been made since 2000. These include the bulky terphenyl coordinated complexes, [Ar′MMAr′] (M = Cr, Fe, Co, or Zn; Ar′ = $C_6H_3Dip_2$-2,6, Dip = $C_6H_3Pr^i_2$-2,6);[5−8] amidinate or guanidinate bridged systems, [$M_2(\mu\text{-}L^\#)_2$] (L$^\#$ = bulky amidinate or guanidinate, M = Cr, Fe, Co, Ni),[9−12] which contain extremely short M–M multiple bonds; unsupported Mn–Mn bonded systems, [L$^\#$MnMnL$^\#$] (L$^\#$ = β-diketiminate or amidinate);[10,13] and a considerable number of two- or higher-coordinate zinc(I) dimers, for example, [Cp*ZnZnCp*].[14] The further chemistry of all of these compound types has been explored to varying extents, and it has become clear that they hold significant potential for use in catalysis, synthesis, and so forth.

The stability of the previously reported transition metal(I) dimers mentioned above is derived from their metal centers being coordinated by very bulky ligands. This provides the compounds with kinetic protection from disproportionation and other decomposition processes. To the best of our knowledge, the only monodentate ligands that has been successfully applied to the preparation of such metal(I) dimers are the bulky terphenyls (e.g., Ar′) developed by Power and co-workers.[5] This is partly because terphenyl transition metal(II) halide precursors to these complexes, for example, [{Ar′M(THF)$_n$X}$_2$] (X = halide, n = 0 or 1), are readily available, are stable to redistribution reactions, and can be cleanly reduced to metal(I) dimers.[5] It is perhaps surprising that very bulky monodentate amide ligands (-NR$_2$), which have been utilized for decades to stabilize low coordinate transition metal complexes,[15] for example, two-coordinate [M(NR$_2$)$_2$],[16] have not been successfully employed in the preparation of related metal(I)–metal(I) dimers, for example, [LMML] (L = monodentate amide). This may result from the fact that reports of the most logical precursors to such compounds, that is, the amido metal(II) halides, [LMX], are sparse, despite the many hundreds of structurally characterized amido-transition metal complexes that populate the literature.[15] That said, monodentate amido metal(II) halides are not unknown, though they typically require bulky amide ligands to be isolated, for example, as in [{Cr(NC$_4$H$_2$Bu$^t_2$-2,5)(THF)(μ-Cl)}$_2$],[17] [FeCl{N(R)(Ar^F)}(tmeda)] (R = C(CD$_3$)$_2$CH$_3$, Ar^F = C_6H_3FMe-2,5)[18] and [MCl{N(SiMe$_3$)(Xyl)}(tmeda)] (M = Fe or Co, Xyl = 2,6-xylyl).[19] What is certain is that further examples of complexes of the type [LMX], with even bulkier amide ligands, will need to be

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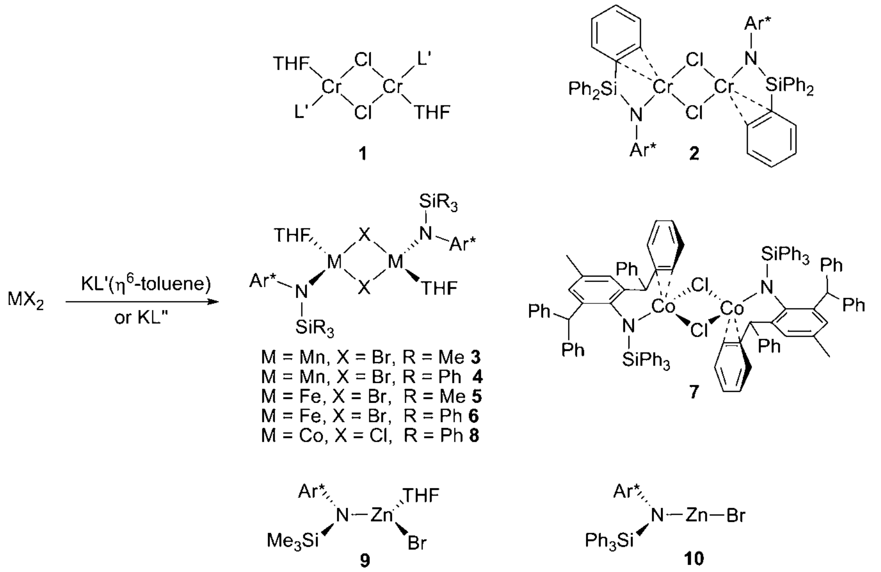
Scheme 1. Preparation of Compounds 1−10 (L′ = N(Ar*)($SiMe_3$), L″ = N(Ar*)($SiPh_3$); Ar* = $C_6H_2\{C(H)Ph_2\}_2Me$-2,6,4)[a]



[a]All reactions were carried out in THF (by-products omitted).

accessed if monodentate amido metal(I) dimer chemistry is to develop at any pace.

Toward this goal, we have developed an extremely bulky class of amido ligands, for example, -N(Ar*)(SiR_3) (Ar*= C_6H_2Me-$\{C(H)Ph_2\}_2$-4,2,6; R = Me (L′) or Ph (L″)),[20] which we have shown to have similar steric profiles and stabilizing properties to Power's widely used substituted terphenyls. This is reflected in the fact that these ligands have allowed us entry to a variety of unprecedented low coordinate main group metal amide complexes, which include monomeric chloro-tetrelenes, for example, [L′ECl] (E = Ge or Sn),[20] a singly bonded amido-digermyne [L′Ge-GeL′],[21] low coordinate metal(II) cations $[L'E:]^+$ (E = Ge or Sn),[22] an acyclic boryl-germylene [L′Ge{B(DAB)}] (DAB = $\{DipNCH\}_2$),[23] and one-coordinate group 13 metal(I) amides, [L′M:] (M = Ga, In or Tl).[24] Here, we now report the use of these bulky amides in the facile preparation of 10 amido first row transition metal(II) halide complexes. We believe these complexes hold considerable potential for synthetic chemists, not only as precursors to metal(I)−metal(I) bonded complexes, but also to other low-coordinate/low-oxidation state synthetic targets that might require considerable steric protection to be isolable under normal conditions.

■ RESULTS AND DISCUSSION

At the outset of this study, salt elimination reactions between alkali metal amides and transition metal dihalides were chosen to prepare the target complexes. Initially, reactions were carried out between the lithium amides, [LiL′] or [LiL″],[20] and a variety of first row transition metal dihalides. However, these reactions typically led to complex mixtures of unidentifiable products. It is of note that one reaction between [LiL′] and $MnBr_2$ in a diethyl ether/THF solvent mixture afforded a very low yield (<5%) of the crystalline "-ate" complex, [L′Mn(THF)(μ-Br)$_2$Li(OEt$_2$)$_2$]. No spectroscopic data were obtained for this compound, though details of its X-ray crystal structure can be found in the Supporting Information.

To circumvent the formation of "-ate" complexes, the reactions were repeated using the corresponding potassium amide complexes, [KL′(η^6-toluene)][24] and [KL″]. Tetrahydrofuran (THF) solutions of these amides were added to 1 equiv of $CrCl_2$, $MnBr_2$, $FeBr_2$, $CoCl_2$, or $ZnBr_2$, as suspensions or solutions in THF. Workup and subsequent recrystallization of the crude reaction mixtures from either THF or toluene afforded the amido metal halide complexes, **1−10** (Scheme 1), in yields ranging from 43% to 91%. It is of note that the no identifiable product could be isolated from the reaction of [KL′(η^6-toluene)] with $CoCl_2$, while treatment of both potassium amides with $CoBr_2$ in THF resulted in recovery of the potassium amides and the reproducible generation of the new cobalt bromide contact ion-pair complex, [(THF)$_4$Co(μ-Br)$_2$CoBr$_2$] (see Supporting Information for crystallographic details). It seems that dissolution of $CoBr_2$ in THF yields this complex, which has a low reactivity toward the potassium amide starting materials. Furthermore, all attempts to obtain amido nickel(II) or copper(I or II) complexes via reaction of the potassium amides with either $NiBr_2$ or copper halides in THF were not successful. No metal deposition was observed in any of these reactions.

Other features of the synthetic studies worth noting are that while all of the reactions were carried out in THF, and all of the products incorporating the L′ ligand have metal coordinated THF molecules, two of the products containing the bulkier L″ ligand (viz. **2** and **7**), instead have their coordination spheres completed by intramolecular η^2-interactions from one phenyl group of their $SiPh_3$ or Ar* fragments (see structural discussions below for further details). This suggests that the η^2-phenyl interactions in **2** and **7** successfully compete with THF coordination in these compounds. It seems that, at least in the case of **7**, this is a relatively finely balanced competition, as both it and the THF coordinated analogue of the complex, namely, **8**, can be obtained when the vacuum-dried crude reaction product is recrystallized from a toluene/hexane solution. If that solution is kept at room temperature for several days before crystallization occurs, only **7** is obtained. Moreover, solid samples of **8** appear to slowly lose their coordinated THF at ambient temperature, while dissolution of **7** in THF leads to the immediate and quantitative regeneration of compound **8**.

All of the compounds **1−10** were crystallographically characterized. This revealed them to possess varying coordina-

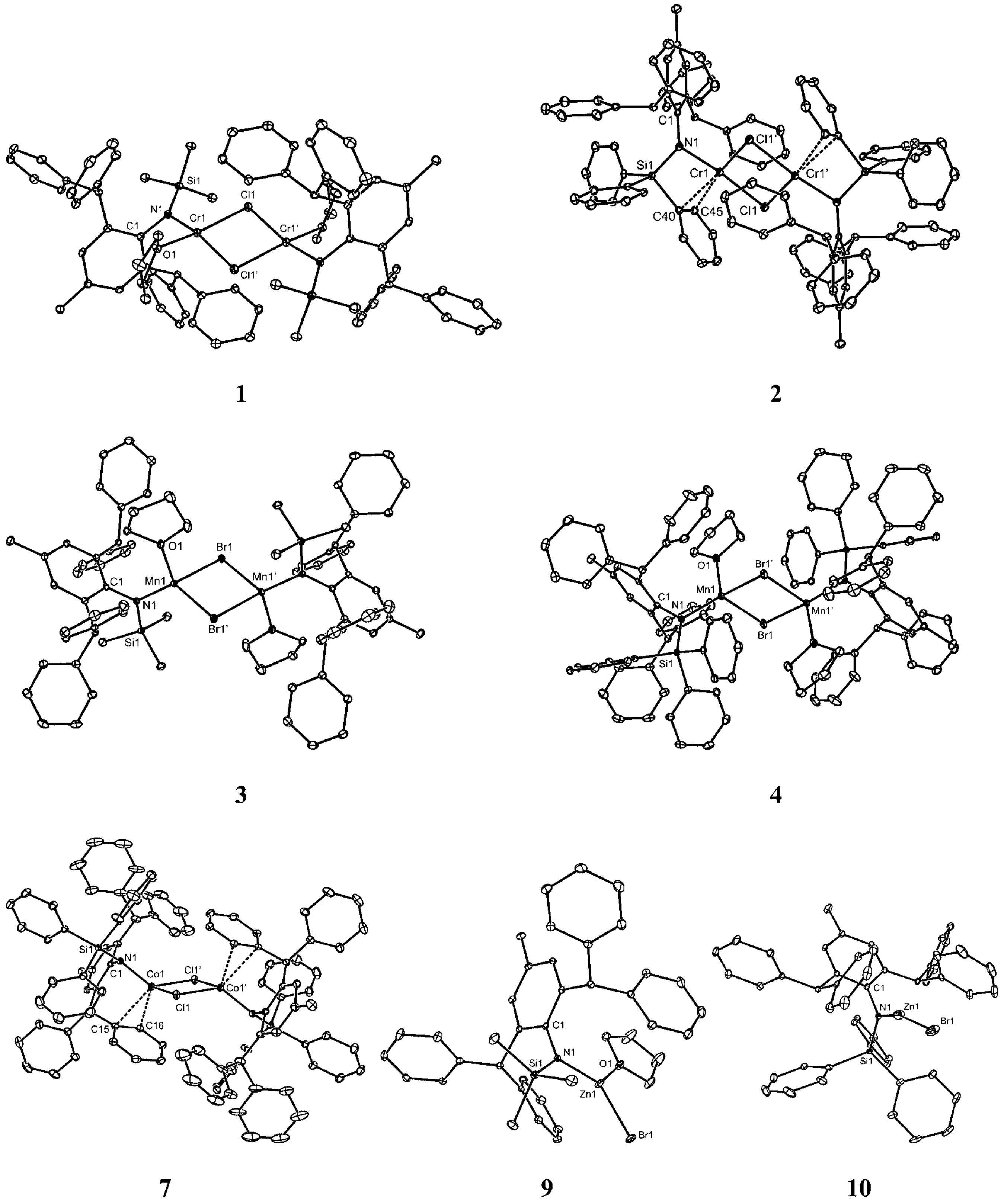


Figure 1. Thermal ellipsoid plots (25% probability surface) of the molecular structures of **1**−**4**, **7**, **9**, and **10**. Hydrogen atoms are omitted. Selected metrical parameters are given in Table 1.

tion geometries, which depend on the metal and amide ligand involved. Examples of the molecular structures of the compounds exhibiting unique ligand/structural motif combinations can be found in Figure 1 (see Table 1 for selected metrical parameters of all complexes), while ORTEP diagrams of **5**, **6**, and **8**, which are isostructural to either **3** or **4**, can be found in the Supporting Information. The amido chromium compounds, **1** and **2**, differ from the other complexes in the series in that they

Table 1. Selected Interatomic Distances (Å) and Angles (deg) for 1−10

	1	2	3	4	5	6	7	8	9	10
M−N	2.016(2)	2.014(2)	1.9849(13)	2.024(2)	1.924(2)	1.9363(15)	1.909(3)	1.936(2)	1.8765(16)	1.833(3)
M−X	2.3654(8)	2.3945(9)	2.5790(3)	2.6196(5)	2.5514(6)	2.5552(3)	2.3508(10)	2.3500(9)	2.2993(3)	2.2180(6)
M−X′	2.4248(8)	2.3567(8)	2.5968(3)	2.5912(5)	2.5671(5)	2.5455(3)	2.3209(9)	2.3487(8)		
M−O or M−$CC_{midpoint}$	2.0766(19)	2.423(2)	2.1034(12)	2.127(2)	2.041(2)	2.0507(13)	2.365(2)	2.027(2)	1.9936(16)	
M···M′	3.523(1)	3.503(1)	3.574(1)	3.724(1)	3.620(1)	3.685(1)	3.310(1)	3.342(1)		
X−M−X′	85.32(3)	84.99(3)	92.65(1)	88.76(2)	89.98(2)	87.48(1)	89.77(3)	89.34(3)		
M−X−M′	94.68(3)	95.01(3)	87.35(1)	91.24(2)	90.02(2)	92.52(1)	90.23(3)	90.66(3)		
N−M−O or N−M−$CC_{mid\ point}$	97.41(8)	81.48(7)	113.28(5)	114.96(8)	118.17(9)	118.71(6)	97.14(8)	108.60(10)	119.76(7)	
N−Zn−Br									131.30(5)	160.79(15)

both have distorted square planar metal geometries, the coordination sites of which are occupied by the amide, two approximately symmetrically bridging chlorides, and either a molecule of THF (**1**) or an intramolecular η^2-phenyl interaction (**2**). These structures are very similar to those of the distorted square planar terphenyl coordinated complexes, $[\{Ar'Cr(\mu\text{-}Cl)\}_2]$[25] and $[\{Ar^{CF3}Cr(THF)(\mu\text{-}F)\}_2]$ (Ar^{CF3} = $C_6H_2Dip_2(CF_3)$-2,6,4),[26] the former of which exhibits a close contact (2.435(3) Å) between each Cr center and one Dip *ipso*-C center of its Ar′ ligand. This contact constitutes the fourth coordination site at each Cr center (cf. **2**). The Cr−N distances in **1** and **2** are in the normal range for Cr^{II} amides,[27] but are slightly less than the sum of the covalent radii for Cr and N (2.10 Å).[28] Although the Cr···η^2-C-$C_{midpoint}$ distances in **2** (2.423(2) Å) are longer than normal Cr−C covalent bonds, for example, 2.041(3) Å in $[\{Ar'Cr(\mu\text{-}Cl)\}_2]$,[25] they clearly signify relatively strong Cr···phenyl interactions.

Compounds **3**−**6** and **8** are essentially isostructural, in that their metal centers all possess distorted tetrahedral geometries involving coordination by terminal amido and THF ligands, and by two close to symmetrically bridging halides. There are no equivalent structural types for terphenyl manganese or iron halide complexes, though for both metals, preliminary reports of the crystal structures of $[\{Ar^{\dagger}Mn(\mu\text{-}I)\}_2]$ and $[\{Ar^{\dagger}Fe(\mu\text{-}I)\}_2]$ ($Ar^{\dagger}$ = $C_6HPr^i_2Trip_2$-3,5,2,6; Trip = $C_6H_2Pr^i_3$-2,4,6), which incorporate extremely bulky terphenyl ligands, reveal planar three-coordinate metal geometries.[5] Comparisons can, however, be made between the cobalt complex, **8**, and the terphenyl cobalt bromide species, $[\{Ar^{Mes}Co(THF)(\mu\text{-}Br)\}_2]$ (Ar^{Mes} = $C_6H_3Mes_2$-2,6; Mes = mesityl),[29] both of which have similar distorted tetrahedral cobalt geometries. It is of note that within the series, **3**−**6** and **8**, there is a general decrease in the M-N and/or M-O distances with increasing molecular weight of the metal. This is consistent with the decreasing high spin covalent radii reported for the metal sequence Mn (1.61 Å) > Fe (1.52 Å) > Co (1.50 Å).[28] Although the N-centers in all of **3**−**6** and **8** have planar geometries, none of their M-N distances are especially short, and therefore they do not indicate significant degrees of N→M π-bonding in the complexes. Moreover, their M···M separations are not indicative of any substantial metal−metal bonding.

The crystal structure of **7** resembles those of **3**−**6** and **8** in that it has a distorted tetrahedral cobalt geometry, though the metal center is not coordinated by THF and the fourth coordination site is instead taken up by an η^2-phenyl interaction. At first glance, this appears similar to the situation in **2**. However, in that compound the interaction derives from a phenyl group of the $SiPh_3$ fragment, whereas in **7** it comes from a phenyl substituent of the Ar* ligand. This difference presumably results from the contrasting metal geometries in the complexes.

The solid state structures of the amido zinc bromide complexes, **9** and **10**, differ from the others in that the two compounds are monomeric. Compound **9** has a three-coordinate zinc center, including coordination by a molecule of THF. Although two Ar* phenyl substituents lie above and below the zinc coordination plane, the closest Zn···C_{phenyl} distance (3.048 Å) is too long to imply any significant interaction. The Zn−N distance in the compound is at the short end of the known range (1.844−2.344 Å),[27] and the SiCZnBrO fragment of the compound is close to planar. In contrast to **9**, there is no coordinated THF molecule in **10**, despite the fact that it was prepared in that solvent. This most likely arises from the larger steric bulk of its amide ligand, relative to that in **9**. As a result, the compound possesses a two-coordinate zinc center, with an N−Zn−Br angle of 160.41(9)°, and one of the shortest known Zn−N distances (1.833(3) Å). The bending in the NZnBr fragment might be due to an interaction between the Zn center and an Ar* phenyl group, but as the closest Zn···C_{phenyl} distance is long at 2.824 Å, this interaction must be considered weak at best. Compound **10** represents the first structurally characterized example of a two-coordinate zinc halide complex, and it differs from corresponding solvent free terphenyl zinc halide complexes, for example, $[\{Ar'Zn(\mu\text{-}I)_2\}_2]$, which are three-coordinate, halide bridged dimers.[30]

All of the compounds prepared in this study (except **8**) are very thermally stable solids, and are indefinitely stable in solution at ambient temperature. Little information could be gained from the NMR spectroscopic data of all but the zinc amides, **9** and **10**, because of the paramagnetic nature of the compounds. This gave rise to broad signals in their ^1H NMR spectra that typically were observed over wide chemical shift ranges. The ^1H NMR spectra of **9** and **10**, on the other hand, exhibit sharp resonances, and are consistent with the compounds retaining their solid state structures in solution.

Although it was not the intention of this study to carry out in-depth solid state magnetochemical studies of **1**−**8**, the room temperature solution state effective magnetic moments of all but **2** were determined using the Evans method.[31] The very low solubility of **2** in noncoordinating deuterated solvents prevented its magnetic moment determination. While the magnetic moment obtained for **1** (μ_{eff} = 5.81 μ_B per dimer) is less than the spin-only value for two noninteracting, high-spin Cr^{2+} centers (6.93 μ_B), it lies in the range previously reported for related square-planar halide bridged Cr^{II} dimers, for example, $[\{Ar^{CF3}Cr(THF)(\mu\text{-}F)\}_2]$ (μ_{eff} = 6.94 μ_B per dimer)[26] and $[\{Cr[\{N(Dip)\}_2CNMe_2](\mu\text{-}Cl)\}_2]$ (μ_{eff} = 3.82 μ_B per dimer).[9b] This suggests the compound is high-spin and exhibits a degree of antiferromagnetic coupling over the Cr_2Cl_2 core. Similarly, the magnetic moments obtained for all the tetrahedral dimers, **3**−**8**, indicate that they are high-spin complexes, the metal centers of which are antiferromagnetically coupled to varying extents. Specifically, the effective magnetic moments for the manganese complexes, **3** (5.90 μ_B per dimer) and **4** (6.85 μ_B per dimer), are markedly less than the spin-only value (8.36 μ_B). It is difficult to draw comparisons here as we are not aware of any structurally authenticated tetrahedral, halide bridged Mn^{II} dimers that have been the subjects of magnetochemical studies. The only exceptions are several dimeric, tetrahedral manganese dihalide adducts, for example, $[\{Mn(NEt_3)I(\mu\text{-}I)\}_2]$ (μ_{eff} = 6.8 μ_B), for which significant antiferromagnetic coupling between the Mn centers was proposed.[32] The magnetic moments obtained for the Fe^{II} and Co^{II} dimers, **5** (5.38 μ_B per dimer), **6** (6.61 μ_B per dimer), **7** (4.86 μ_B per dimer), and **8** (5.20 μ_B per dimer), are also somewhat less than the spin-only values (Fe: 6.93 μ_B, Co: 5.40 μ_B,). The observed magnetic moments are, however, comparable to those for related four-coordinate complexes, for example, $[\{(^{Dip}Nacnac)Fe(\mu\text{-}F)\}_2]$ (6.2 μ_B per dimer)[33] and $[\{Ar^{Mes}Co(THF)(\mu\text{-}Br)\}_2]$ (4.7 μ_B per dimer).[29]

CONCLUSIONS

In summary, two extremely bulky amide ligands have been utilized in the preparation of rare examples of monodentate amido first row transition metal(II) halide complexes. All prepared complexes have been spectroscopically characterized and their X-ray crystal structures determined. The Cr, Mn, Fe, and Co complexes are all high-spin, halide bridged dimers which possess square-planar (Cr) or tetrahedral (Mn, Fe, and Co) metal coordination geometries. The two amido zinc halides are monomeric and display either planar three-coordinate, or distorted linear metal geometries, depending on the steric bulk of the amido ligand involved. Where possible, comparisons have been made with bulky terphenyl metal(II) halide complexes, which have proved of great synthetic value in the preparation of low oxidation state/low coordination number transition metal complexes in recent years. We believe that the novel complexes reported in this study will similarly prove ideal precursors for the preparation of related low-valent amido transition metal complexes. We are currently exploring this possibility with encouraging results, which we will report on in due course.

EXPERIMENTAL SECTION

General Methods. All manipulations were carried out using standard Schlenk and glovebox techniques under an atmosphere of high purity dinitrogen. THF, hexane, and toluene were distilled over molten potassium. ^1H, $^{13}C\{^1H\}$, and $^{29}Si\{^1H\}$ NMR spectra were recorded on either Bruker AvanceIII 400 or Varian Inova 500 spectrometers and were referenced to the resonances of the solvent used, or external $SiMe_4$. Mass spectra were obtained from the EPSRC National Mass Spectrometric Service at Swansea University. IR spectra were recorded using a Perkin-Elmer RX1 FT-IR spectrometer as Nujol mulls between NaCl plates. Microanalyses were carried out by the Science Centre, London Metropolitan University. A reproducible microanalysis for **4** could not be obtained because of its highly air sensitive nature, and because total removal of the hexane and THF of crystallization proved difficult by vacuum drying the compound at elevated temperature. A reproducible microanalysis for **8** could not be obtained as it slowly loses its THF of coordination in the solid state, yielding **7**. Melting points were determined in sealed glass capillaries under dinitrogen and are uncorrected. Solution state effective magnetic moments were determined by the Evans method.[31] The compound $[KL'(\eta^6\text{-toluene})]$ was prepared by the literature method.[24] $[KL'']$ was prepared by reacting $L''H$ with $[KN(SiMe_3)_2]$ in toluene at 20 °C for 2 h. Volatiles were removed in vacuo and the solid residue washed with hexane to give $[KL'']$, which was used without further purification. All other reagents were used as received.

Preparation of $[\{CrL'(THF)(\mu\text{-}Cl)\}_2]$ *(**1**).* To a suspension of $CrCl_2$ (0.096 g, 0.779 mmol) in THF (30 mL) at −80 °C was added a solution of $[KL'(\eta^6\text{-toluene})]$ (0.50 g, 0.779 mmol) in THF (10 mL) over 5 min. The reaction mixture was warmed to room temperature and stirred for 2 h, whereupon volatiles were removed in vacuo. The residue was extracted with warm toluene (40 mL), the extract filtered and volatiles removed in vacuo to give **1** as a turquoise solid (0.38 g, 73%). X-ray quality blue-green crystals of **1** were obtained by recrystallizing this solid from warm THF. M.p.: 248−250 °C (decomp.); ^1H NMR (499 MHz, C_6D_6, 298 K): δ = −11.71 (br.), −4.42 (br), 10.15 (br), 10.94 (br), 16.61(br), 36.09 (br); IR υ/cm^{-1} (Nujol): 1597(m), 1015(m), 917(s), 857(s), 829(s), 748(m), 716(m), 702(s), 603(m), 559(m); MS/EI *m*/*z* (%): 511.3 ($L'H^+$, 87), 439.2 ($Ar^*NH_2^+$, 79), 167.0 (Ph_2CH^+, 33), 73.0 (Me_3Si^+, 20); μ_{eff} (Evans, C_6D_6, 298 K): 5.81 μ_B; Anal. Calc. for $C_{80}H_{88}Cl_2Cr_2N_2O_2Si_2$: C 71.67%, H 6.62%, N 2.09%, found: C 71.82%, H 6.51%, N 2.13%.

Preparation of $[\{CrL''(\mu\text{-}Cl)\}_2]$ *(**2**).* To a solution of $CrCl_2$ (0.092 g, 0.747 mmol) in THF (30 mL) at −80 °C was added a solution of $[KL'']$ (0.50 g, 0.679 mmol) in THF (10 mL) over 5 min. The reaction mixture was warmed to room temperature and stirred for 2 h, whereupon volatiles were removed in vacuo. The residue was extracted with toluene (40 mL), the extract filtered, and volatiles removed in vacuo to give **2** as a green solid (0.41 g, 81%). X-ray quality green crystals of **2** were obtained by recrystallizing this solid from toluene. M.p.: 156−159 °C; ^1H NMR (499 MHz, D_8-toluene, 298 K): δ = −12.88 (br.), 1.83 (br.), 3.02 (br), 7.51 (br.), 10.05 (br), 14.97 (br); IR υ/cm^{-1} (Nujol): 1597(m), 1029(m), 944(m), 790(m), 720(s), 700(s), 604(m), 560(m), 539(m), 507(m); MS/EI *m*/*z* (%): 697.4 ($L''H^+$, 81), 439.2 ($Ar^*NH_2^+$, 83), 259.1 (Ph_3Si^+, 100), 167.0 (Ph_2CH^+, 17); Anal. Calc. for

$C_{102}H_{84}Cl_2Cr_2N_2Si_2$: C 78.09%, H 5.40%, N 1.79%, found: C 77.99%, H 5.49%, N 1.83%. N.B. A reliable magnetic moment determination for this compound using the Evans method could not be carried out, because of the low solubility of the compound in D_8-toluene.

Preparation of $[\{MnL'(THF)(\mu\text{-}Br)\}_2]$ ***(3)***. To a suspension of $MnBr_2$ (0.184 g, 0.857 mmol) in THF (30 mL) at −80 °C was added a solution of $[KL'(\eta^6\text{-toluene})]$ (0.50 g, 0.779 mmol) in THF (10 mL) over 5 min. The reaction mixture was warmed to room temperature and stirred for 2 h, whereupon volatiles were removed in vacuo. The residue was extracted with warm toluene (40 mL), the extract filtered and slowly cooled to 5 °C overnight to give **3** as pink crystals (0.42 g, 75%). M.p.: 222−224 °C (decomp. on melting); ^1H NMR (499 MHz, C_6D_6, 298 K): δ = −32.21 (br.), 1.36 (br), 7.54 (br), 34.45 (br), 41.06 (br); IR ν/cm^{-1} (Nujol): 1598(m), 1013(m), 916(s), 906(s), 856(s), 832(s), 727(s), 700(s), 674(m), 622(m), 606(m), 554(m), 531(m); MS (EI) *m/z* (%): 511.2 ($L'H^+$, 100), 438.2 (Ar^*NH^+, 23), 167.0 (Ph_2CH^+, 25); μ_{eff} (Evans, C_6D_6, 298 K): 5.90 μ_B; Anal. Calc. for $C_{80}H_{88}Br_2Mn_2N_2O_2Si_2$: C 66.94%, H 6.18%, N 1.95%, found: C 66.84%, H 6.26%, N 1.98%.

Preparation of $[\{MnL''(THF)(\mu\text{-}Br)\}_2]$ ***(4)***. To a suspension of $MnBr_2$ (0.143 g, 0.747 mmol) in THF (30 mL) at −80 °C was added a solution of $[KL'']$ (0.50 g, 0.679 mmol) in THF (10 mL) over 5 min. The reaction mixture was warmed to room temperature and stirred for 2 h, whereupon volatiles were removed in vacuo. The residue was extracted with toluene (40 mL), the extract filtered, and volatiles removed in vacuo to give **4** as a pale pink solid (0.38 g, 62%). X-ray quality pale pink crystals of **4** were obtained by crystallizing this solid from a mixture of toluene and hexane with a trace of THF added. M.p.: 296−299 °C (decomp. on melting); ^1H NMR (499 MHz, C_6D_6, 298 K): δ = −34.71(br), 1.37 (br.), 13.20 (br.), 33.04 (br), 40.81 (br); IR υ/cm^{-1} (Nujol): 1597(m), 903(s), 798(m), 736(m), 729(s), 702(s), 605(m), 577(m), 556(m), 540(m), 504(m); MS/EI *m/z* (%): 697.3 ($L''H^+$, 54), 439.2 ($Ar^*NH_2^+$, 18), 259.0 (Ph_3Si^+, 100), 167.0 (Ph_2CH^+, 11); μ_{eff} (Evans, C_6D_6, 298 K): 6.85 μ_B.

Preparation of $[\{FeL'(THF)(\mu\text{-}Br)\}_2]$ ***(5)***. To a suspension of $FeBr_2$ (0.185 g, 0.857 mmol) in THF (30 mL) at −80 °C was added a solution of $[KL'(\eta^6\text{-toluene})]$ (0.50 g, 0.779 mmol) in THF (10 mL) over 5 min. The reaction mixture was warmed to room temperature and stirred for 2 h, whereupon volatiles were removed in vacuo. The residue was extracted with toluene (40 mL), the extract filtered and volatiles removed in vacuo to give **5** as a yellow solid (0.32 g, 57%). X-ray quality yellow crystals of **5** were obtained by crystallizing this solid from a mixture of THF and hexane. M.p.: 88−92 °C (decomp.); ^1H NMR (400 MHz, C_6D_6, 298 K): δ = −21.01 (br), −4.07 (br), 3.99 (br), 13.36 (br), 15.19 (br), 21.35 (br), 28.35 (br), 71.19 (br); IR υ/cm^{-1} (Nujol): 1598(m), 917(m), 902(s), 860(s), 836(s), 766(m), 749(m), 730(s), 703(s), 605(m), 555(m), 535(m); MS/-veCI (CH_4) *m/z* (%): 647.0 ($L'FeBr^-$, 100), 435.1 ($Ar^*NH_2^-$, 17); μ_{eff} (Evans, C_6D_6, 298 K): 5.38 μ_B; Anal. Calc. for $C_{80}H_{88}Br_2Fe_2N_2O_2Si_2$: C 66.85%, H 6.17%, N 1.95%, found: C 66.92%, H 6.25%, N 2.06%.

Preparation of $[\{FeL''(THF)(\mu\text{-}Br)\}_2]$ ***(6)***. To a suspension of $FeBr_2$ (0.161 g, 0.747 mmol) in THF (30 mL) at −80 °C was added a solution of $[KL'']$ (0.50 g, 0.679 mmol) in THF (10 mL) over 5 min. The reaction mixture was warmed to room temperature and stirred for 2 h, whereupon volatiles were removed in vacuo. The residue was extracted with toluene (40 mL), the extract filtered and volatiles removed in vacuo to give **6** as a yellow solid (0.43 g, 70%). X-ray quality yellow crystals of **6** were obtained by recrystallizing this solid from a mixture of toluene and hexane. M.p.: 276−279 °C; ^1H NMR (400 MHz, C_6D_6, 298 K): δ = −41.70 (br), 3.50 (br), 5.57 (br), 12.64 (br), 64.17 (br), 73.59 (br); IR υ/cm^{-1} (Nujol): 1596(m), 918(m), 903(s), 884(m), 852(m), 791(m), 743(m), 725(s), 696(s), 604(m), 579(m), 558(m), 548(m), 506(m); MS/EI *m/z* (%): 833.3 ($L''FeBr^+$, <1), 697.3 ($L''H^+$, 82), 439.2 ($Ar^*NH_2^+$, 20), 259.0 (Ph_3Si^+, 100), 167.0 (Ph_2CH^+, 10); μ_{eff} (Evans, C_6D_6, 298 K): 6.61 μ_B; Anal. Calc. for $C_{110}H_{100}Br_2Fe_2N_2O_2Si_2$: C 73.01%, H 5.57%, N 1.55%, found: C 72.96%, H 5.41%, N 1.57%.

Preparation of $[\{L''Co(\mu\text{-}Cl)\}_2]$ ***(7)***. To a suspension of $CoCl_2$ (0.088 g, 0.679 mmol) in THF (30 mL) at −80 °C was added a solution of $[KL'']$ (0.50 g, 0.679 mmol) in THF (10 mL) over 5 min. The reaction mixture was warmed to room temperature and stirred for 12 h, whereupon volatiles were removed in vacuo. The residue was extracted with toluene (40 mL), the extract filtered, and volatiles were removed in vacuo. The residue was washed with hexane (20 mL) to give **7** as an orange solid (0.23 g, 43%). X-ray quality orange crystals of **7** were obtained by recrystallizing this solid from a minimum volume of toluene/hexane mixture. M.p.: 241−244 °C; ^1H NMR (499 MHz, C_6D_6, 298 K): δ = −52.82 (br.), −49.44 (br.), −40.48 (br.), 7.58 (br.), 12.11 (br.), 14.29 (br.), 16.29 (br.), 25.62 (br.), 59.17 (br.), 75.70 (br.), 123.04 (br); IR υ/cm^{-1} (Nujol): 1598(m), 895(s), 797(m), 722(s), 708(s), 697(s), 624(m), 574(m), 557(m), 540(m), 502(m); MS/EI *m/z* (%): 755.3 ($L''Co^+$, 4), 697.3 ($L''H^+$, 80), 438.2 (Ar^*NH^+, 10), 259.1 (Ph_3Si^+, 100), 167.0 (Ph_2CH^+, 10); μ_{eff} (Evans, C_6D_6, 298 K): 4.86 μ_B; Anal. Calc. for $C_{102}H_{84}Cl_2Co_2N_2Si_2$: C 77.40%, H 5.35%, N 1.77%, found: C 77.31%, H 5.37%, N 1.80%.

Preparation of $[\{L''Co(THF)(\mu\text{-}Cl)\}_2]$ ***(8)***. Compound **7** (0.100 g, 0.063 mmol) was dissolved in THF (5 mL), and the mixture stirred for 5 min at room temperature to give a blue/green solution. Volatiles were removed in vacuo to yield **8** as a green solid (0.109 g, 100%). N.B. X-ray quality green crystals were obtained by recrystallizing this solid from a mixture of toluene, hexane, and THF. M.p.: 118−121 °C turns orange/brown, 239−243 °C melts; ^1H NMR (499 MHz, C_6D_6/D_8-THF, 298 K): δ = −22.13 (br.), −14.11 (br.), −0.99 (br.), 10.22 (br.), 11.88 (br.), 18.07 (br.), 49.56 (br.), 54.56 (br.); IR υ/cm^{-1} (Nujol): 1597(m), 896(m), 880(m), 799(s), 738(m), 697(s), 604(m), 542(m), 504(m); μ_{eff} (Evans, C_6D_6/D_8-THF, 298 K): 5.20 μ_B.

Preparation of $[L'ZnBr(THF)]$ ***(9)***. To a suspension of $ZnBr_2$ (0.192 g, 0.857 mmol) in THF (30 mL) at −80 °C was added a solution of $[KL'(\eta^6\text{-toluene})]$ (0.50 g, 0.779 mmol) in THF (10 mL) over 5 min. The reaction mixture was warmed to room temperature and stirred for 2 h, whereupon volatiles were removed in vacuo. The residue was extracted with toluene (40 mL), the extract filtered, and volatiles were removed in vacuo to give **9** as an off white solid (0.43 g, 76%). X-ray quality colorless crystals of **9** were obtained by recrystallizing this solid from a mixture of THF and hexane. M.p.: 176−180 °C; ^1H NMR (400 MHz, C_6D_6, 298 K): δ = 0.52 (s, 9H, $Si(CH_3)_3$), 0.83 (m, 4H, CH_2), 1.98 (s, 3H, $ArCH_3$), 2.66 (m, 4H, CH_2O), 6.54 (s, 2H, Ph_2CH), 6.91−7.50 (m, 22H, ArH); $^{13}C\{^1H\}$ NMR (101 MHz, C_6D_6): δ = 4.0 ($Si(CH_3)_3$), 21.3 ($ArCH_3$), 24.6 (CH_2), 52.0 (Ph_2CH), 70.1 (CH_2O), 126.4, 126.8, 128.5, 129.4, 129.7, 129.8, 130.2, 130.4, 141.7, 144.7, 145.4, 150.2 (Ar-C); $^{29}Si\{^1H\}$ NMR (80 MHz, C_6D_6): δ = 1.0 (s); IR υ/cm^{-1} (Nujol): 1597(m), 931(s), 860(s), 849(s), 829(s), 767(m), 733(s), 709(s), 697(s), 604(m), 554(m); MS/+veCI *m/z* (%): 656.1 (M^+-THF, 2), 512.3 ($L'H_2^+$, 100), 440.2 ($Ar^*NH_3^+$, 35), 167.0 (Ph_2CH^+, 19); Anal. Calc. for $C_{40}H_{44}BrNOSiZn$: C 65.98%, H 6.09%, N 1.92%, found: C 66.07%, H 6.13%, N 2.06%.

Preparation of $[L''ZnBr]$ ***(10)***. To a suspension of $ZnBr_2$ (0.168 g, 0.747 mmol) in THF (30 mL) at −80 °C was added a solution of $[KL'']$ (0.50 g, 0.679 mmol) in THF (10 mL) over 5 min. The reaction mixture was warmed to room temperature and stirred for 2 h, whereupon volatiles were removed in vacuo. The residue was extracted with toluene (40 mL), the extract filtered, and volatiles were removed in vacuo to give **10** as an off white solid (0.45 g, 79%). X-ray quality colorless crystals of **10** were obtained by recrystallizing this solid from a mixture of toluene and hexane. M.p.: 248−250 °C; ^1H NMR (400 MHz, C_6D_6, 298 K): δ = 1.89 (s, 3H, $ArCH_3$), 6.14 (s, 2H, Ph_2CH), 6.45−7.66 (m, 37H, ArH); $^{13}C\{^1H\}$ NMR (101 MHz, C_6D_6): δ = 21.3 ($ArCH_3$), 53.0 (Ph_2CH), 126.5, 128.4, 128.5, 128.6, 129.1, 129.8, 130.2, 130.4, 130.5, 131.3, 132.5, 136.8, 137.2, 142.3, 144.6, 144.7 (Ar-C); $^{29}Si\{^1H\}$ NMR (80 MHz, C_6D_6): δ = −18.9 (s); IR υ/cm^{-1} (Nujol): 1597(m), 924(s), 909(s), 879(m), 849(s), 763(m), 756(m), 737(s), 700(s), 602(s), 575(m), 555(s), 506(s); MS/EI *m/z* (%): 841.2 (M^+, 7), 697.4 ($L''H^+$, 100), 439.2 ($Ar^*NH_2^+$, 81), 259.1 (Ph_3Si^+, 71), 167.0 (Ph_2CH^+, 16); Anal. Calc. for $C_{51}H_{42}BrNSiZn$: C 72.73%, H 5.03%, N 1.66%, found: C 72.84%, H 5.13%, N 1.56%.

X-ray Crystallography. Crystals of **1**−**10**, $[L'Mn(THF)(\mu\text{-}Br)_2Li(OEt_2)_2]$, and $[(THF)_4Co(\mu\text{-}Br)_2CoBr_2]$ suitable for X-ray structural determination were mounted in silicone oil. Crystallographic measurements were carried out at 123 K with an Oxford Gemini Ultra diffractometer using a graphite monochromator with Mo Kα radiation (λ = 0.71073 Å). The structures were solved by direct methods and refined on F^2 by full matrix least-squares (SHELX97)[34] using all unique

Table 2. Summary of Crystallographic Data for 1−10

	1·(THF)$_4$	**2**·(toluene)$_4$	**3**·(toluene)$_4$	**4**·(hexane)$_2$(THF)$_2$	**5**
empirical formula	$C_{96}H_{120}Cl_2Cr_2N_2O_6Si_2$	$C_{130}H_{116}Cl_2Cr_2N_2Si_2$	$C_{108}H_{120}Br_2Mn_2N_2O_2Si_2$	$C_{130}H_{144}Br_2Mn_2N_2O_4Si_2$	$C_{80}H_{88}Br_2Fe_2N_2O_2Si_2$
formula weight	1629.02	1937.33	1803.94	2124.35	1437.22
crystal system	triclinic	monoclinic	triclinic	triclinic	monoclinic
color, habit	blue-green, block	green, block	pink, block	pink, block	yellow, block
space group	$P\bar{1}$	$P2_1/c$	$P\bar{1}$	$P\bar{1}$	$P2_1/n$
a (Å)	11.8071(5)	15.1465(12)	11.7659(4)	14.1515(6)	16.4622(14)
b (Å)	13.1447(6)	20.9444(12)	12.7628(3)	14.3059(6)	12.6193(7)
c (Å)	15.4536)8)	17.2104(15)	17.1373(6)	14.5230(6)	18.6176(14)
α (deg.)	70.737(4)	90	106.413(3)	103.914(4)	90
β (deg)	71.481(4)	111.995(10)	103.649(3)	95.548(4)	114.497(10)
γ (deg.)	81.584(4)	90	97.608(2)	103.950(4)	90
vol (Å^3)	2144.58(17)	5062.4(7)	2343.51(13)	2732.2(2)	3519.5(4)
Z	1	2	1	1	2
ρ (calcd) (g cm^{-3})	1.261	1.271	1.278	1.291	1.356
μ (mm^{-1})	0.399	0.345	1.198	1.040	1.630
F(000)	868	2040	946	1118	1496
reflections collected	12924	18451	34600	17958	13984
unique reflections	7659	9051	10204	10654	6877
R_{int}	0.0375	0.0613	0.0279	0.0316	0.0617
R1 indices [$I > 2\sigma(I)$]	0.0497	0.0530	0.0299	0.0452	0.0451
wR2 indices (all data)	0.1262	0.1262	0.0766	0.1280	0.1187
CCDC No.	914036	914038	914039	914040	914041

	6·(toluene)$_{1.8}$(hexane)$_{1.2}$	**7**·(toluene)$_{1.5}$	**8**·(toluene)$_2$	**9**	**10**
empirical formula	$C_{129.8}H_{131.2}Br_2Fe_2N_2O_2Si_2$	$C_{112.5}H_{96}Cl_2Co_2N_2Si_2$	$C_{124}H_{116}Cl_2Co_2N_2O_2Si_2$	$C_{40}H_{44}BrNOSiZn$	$C_{51}H_{42}BrNSiZn$
formula weight	2078.87	1720.85	1911.13	728.13	842.23
crystal system	triclinic	monoclinic	triclinic	monoclinic	triclinic
color, habit	yellow, block	orange, block	green, block	colorless, block	colorless, block
space group	$P\bar{1}$	$P2_1/c$	$P\bar{1}$	$C2/c$	$P\bar{1}$
a (Å)	14.0504(4)	13.3383(7)	11.8902(4)	15.6064(5)	10.6299(4)
b (Å)	14.5583(5)	18.1137(8)	14.0389(4)	15.0567(4)	10.7824(5)
c (Å)	15.2887(5)	19.0342(11)	15.2789(5)	30.4145(8)	19.9387(9)
α (deg.)	64.520(3)	90	81.973(2)	90	84.799(4)
β (deg)	70.367(3)	99.164(5)	79.402(3)	97.485(3)	89.581(3)
γ (deg.)	78.910(3)	90	89.569(2)	90	63.163(4)
vol (Å^3)	2654.80(15)	4540.1(4)	2481.94(14)	7085.9(3)	2029.30(15)
Z	1	2	1	8	2
ρ (calcd) (g cm^{-3})	1.300	1.259	1.279	1.365	1.378
μ (mm^{-1})	1.103	0.502	0.467	1.887	1.656
F(000)	1090	1802	1006	3024	868
reflections collected	39120	30822	16246	23865	27739
unique reflections	10417	8912	9697	7732	7958
R_{int}	0.0269	0.0329	0.0297	0.0275	0.0266
R1 indices [$I > 2\sigma(I)$]	0.0318	0.0605	0.0537	0.0347	0.0523
wR2 indices (all data)	0.0820	0.1802	0.1439	0.0848	0.1642
CCDC No.	914042	914043	914044	914045	914037

data. All non-hydrogen atoms are anisotropic with hydrogen atoms included in calculated positions (riding model). Two crystallographically independent molecules of [(THF)$_4$Co(μ-Br)$_2$CoBr$_2$] were refined in the asymmetric unit of its crystal structure. There are no significant geometric differences between them. Crystal data, details of data collections and refinement are given in Table 2 and the Supporting Information.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Crystallographic data as CIF files for all crystal structures; ORTEP diagrams for **5**, **6**, and **8**; full crystallographic details for [L′Mn(THF)(μ-Br)$_2$Li(OEt$_2$)$_2$] and [(THF)$_4$Co(μ-Br)$_2$CoBr$_2$]. 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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