A Versatile Bulky Bidentate Ligand for Both Main Group and Transition Metals. Derivatives of Lithium, Potassium, Magnesium, Chromium, Manganese, and Cobalt Containing the $C(SiMe_3)_2(SiMe_2C_5H_4N\text{-}2)$ Group

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The compound $HC(SiMe_3)_2(SiMe_2C_5H_4N\text{-}2)$, **1**, reacts with methyllithium in THF to give a good yield of the lithium derivative $Li\{C(SiMe_3)_2(SiMe_2C_5H_4N\text{-}2)\}$, which has been isolated as a molecular THF adduct **2**. This reacts (a) with KO^tBu to give $K\{C(SiMe_3)_2(SiMe_2C_5H_4N\text{-}2)\}$, **3**, which crystallizes in a solvent-free ionic lattice, (b) with $MgBr_2$ to give the Grignard reagent $Mg(THF)Br\{C(SiMe_3)_2(SiMe_2C_5H_4N\text{-}2)\}$, **4**, and (c) with $CrCl_2$ to give $Cr\{C(SiMe_3)_2(SiMe_2C_5H_4N\text{-}2)\}_2$, **5**, along with the halide-bridged Grignard reagent analogue $[Cr(\mu\text{-}Cl)\{C(SiMe_3)_2(SiMe_2C_5H_4N\text{-}2)\}]_2\cdot THF$, **6**, which crystallizes in a lattice containing alternate THF-free molecules (**6a**) and molecules (**6b**) with coordinated THF. The reactions of **2** with $MnCl_2$ and $CoBr_2$ give the halide-bridged ate complexes $[Li(THF)_3(\mu\text{-}Cl)MnCl\{C(SiMe_3)_2(SiMe_2C_5H_4N\text{-}2)\}]$, **7**, and $[Li(THF)_2(\mu\text{-}Br)_2Co\{C(SiMe_3)_2(SiMe_2C_5H_4N\text{-}2)\}]$, **8**, respectively.

Introduction

During the last twenty years we and others have shown that organometallic compounds containing the bulky "trisyl" ligand $C(SiMe_3)_3$ adopt a range of unprecedented structures and are much more chemically and thermally stable than analogous derivatives with smaller alkyl groups.[1] Most of the compounds isolated so far have been of the s- and p-block elements; our attempts to make derivatives of the transition metals usually resulted in extensive reduction and formation of black intractable solids. Only two manganese(II) compounds, the ate complex $[Li(THF)_4][Mn_3\{C(SiMe_3)_3\}_3Cl_4(THF)]$ and the nine-electron dialkyl $Mn\{C(SiMe_3)_3\}_2$, and the platinum derivative $[PtCl\{PPh_2C(SiMe_3)_2SiMe_2CH_2\}\{PPh_2CH(SiMe_3)_2\}]$ were fully characterized (THF = tetrahydrofuran).[2]

Despite initial setbacks, we have continued to seek routes to tris(triorganosilyl)methyl derivatives of transition metals, because they should provide an opportunity to study metals with low electron counts in kinetically stabilized environments. We have recently found that the range of isolable main group organometallic compounds can be considerably extended by the use of ligands $C(SiMe_3)_2(SiMe_2X)$ or $C(SiMe_2X)_3$ (X = NMe_2 or OMe),[3] in which lone pairs from the groups X can occupy sites in the metal coordination sphere. Our success in isolating derivatives of Mn and Co[4] led us to think that the introduction of a softer donor group X might make compounds of other transition metals accessible also. Initial experiments were with compounds in which X = PPh_2,[5] but these were bedevilled by unwanted reactions at Si−P bonds. We turned therefore to the {dimethyl(2-pyridyl)silyl}bis(trimethylsilyl)methyl ligand, $C(SiMe_3)_2(SiMe_2C_5H_4N\text{-}2)$, which has bulk similar to that of the previously studied $C(SiMe_3)_3$ ligand but also has a donor site capable of binding to both hard and soft metal centers, and found that it could be used to obtain compounds of a wide range of metals. In this paper, we describe the syntheses of the ligand precursor $HC(SiMe_3)_2(SiMe_2C_5H_4N\text{-}2)$, **1**, and routes to potential

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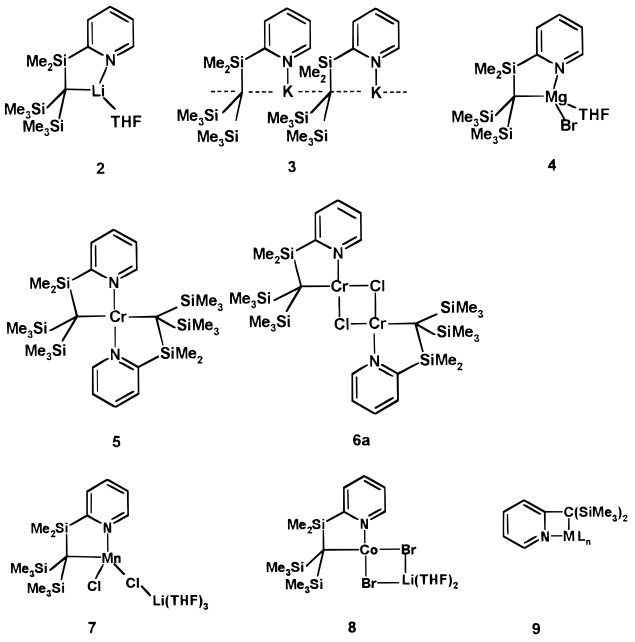
ligand transfer reagents, viz., the alkali metal compounds Li(THF)C(SiMe$_3$)$_2$(SiMe$_2$C$_5$H$_4$N-2), **2**, and KC(SiMe$_3$)$_2$(SiMe$_2$C$_5$H$_4$N-2), **3**, and the Grignard reagent Mg(THF)Br{C(SiMe$_3$)$_2$(SiMe$_2$C$_5$H$_4$N-2)}, **4**. We show that the lithium compound **2** can be used to make alkyl derivatives of the middle (d^4−d^7) first-row transition metals in oxidation state +2 and describe the structural characterization of the square-planar chromium derivatives Cr{C(SiMe$_3$)$_2$(SiMe$_2$C$_5$H$_4$N-2)}$_2$, **5**, and [Cr(μ-Cl){C(SiMe$_3$)$_2$(SiMe$_2$C$_5$H$_4$N-2)}]$_2$·THF, **6**, as well as the halide-bridged complexes [Li(THF)$_3$(μ-Cl)Mn{C(SiMe$_3$)$_2$(SiMe$_2$C$_5$H$_4$N-2)}Cl], **7**, and [Li(THF)$_2$(μ-Br)$_2$Co{C(SiMe$_3$)$_2$(SiMe$_2$C$_5$H$_4$N-2)}], **8**. Derivatives of Ni, Pd, Ge, Sn, and Pb are described elsewhere.[6] We draw some initial conclusions about the steric requirements of the new ligand and compare the transition metal derivatives with the previously described compounds ML$_n$C(SiMe$_3$)$_2$(C$_5$H$_4$N-2) **9**,[7] (M = Cr to Cu) in which the crowding at the metal is significantly lower and the chelate ring has a smaller bite angle.



Experimental Section

Standard Schlenk techniques, with flame-dried glassware and Ar as blanket gas, were used to exclude air and moisture. NMR spectra were recorded at 300.13 (^{1}H), 75.43 (^{13}C), and 99.36 Hz (^{29}Si) from samples in C$_6$D$_6$. Chemical shifts are relative to SiMe$_4$. Mass spectra were obtained at 70 eV; in assignments R = C(SiMe$_3$)$_2$(SiMe$_2$C$_5$H$_4$N-2) and *m*/*z* values are given for ions containing ^{24}Mg, ^{28}Si, ^{35}Cl, and ^{79}Br.

HC(SiMe$_3$)$_2$(SiMe$_2$Br). A solution of Br$_2$ (15.30 g, 95.7 mmol) in CCl$_4$ (50 mL) was added dropwise during 1 h to a solution of HC(SiMe$_3$)$_2$(SiMe$_2$H)[8] (20.9 g, 95.7 mmol) in CCl$_4$ (60 mL) at 0 °C, and the orange solution was stirred at room temperature for 18 h. The solvent was removed and the orange residue distilled (bp 54 °C/10^{-3} mmHg) to give a colorless oil that crystallized on standing, mp 42 °C. Yield: 24.3 g (85%). Anal. Calcd for C$_9$H$_{25}$BrSi$_3$: C, 36.4; H, 8.4. Found: C, 36.5; 8.3. ^{1}H NMR: δ −0.37 (1H, s, CH), 0.15 (18H, s, SiMe$_3$), 0.61 (6H, s, SiMe$_2$). ^{13}C NMR: δ 0.1 (Si$_3$C), 3.2 (SiMe$_3$), 7.8 (SiMe$_2$). ^{29}Si NMR: −0.4 (SiMe$_3$), 6.3 (SiMe$_2$Br). MS: *m*/*z* 281 (60, M − Me), 267(5), 237(30), 217 (15), 203 (20), 129 (100), 73 (75), 59 (30).

HC(SiMe$_3$)$_2$(SiMe$_2$C$_5$H$_4$N-2), 1. 2-Lithiopyridine was prepared by the addition of LiBu (63.5 mmol) in hexanes (25 mL) to a solution of 2-bromopyridine (10.0 g, 63.6 mmol) in Et$_2$O (25 mL) at −78 °C. The red solution was stirred for 20 min and then added to HC(SiMe$_3$)$_2$(SiMe$_2$Br) (18.9 g, 63.6 mmol) in Et$_2$O (200 mL) also at −78 °C. The mixture was allowed to warm to 20 °C and then stirred for 2 h. The solvent was removed to leave a brown oil that was extracted with hexanes (2 × 40 mL). The extract was filtered, solvent removed from the filtrate, and the residue distilled (bp 83−84 °C/10^{-3} mmHg) to give **1** as a viscous pale yellow oil. Yield: 11.4 g (61%). Anal. Calcd for C$_{14}$H$_{29}$NSi$_3$: C, 56.9; H, 9.9. Found: C, 56.9; H, 9.7. ^{1}H NMR: δ 0.09 (18H, s, SiMe$_3$), 0.18 (1H, s, CH), 0.46 (6H, s, SiMe$_2$), 6.64 (1H, t, 4-H), 7.02 (1H, t, 5-H), 7.21(1H, d, 3-H), 8.66 (1H, d, 6-H). ^{13}C NMR: 1.31 ($^1J_{CSi}$ = 39.2 Hz, SiMe$_2$), 1.34 (CH), 3.27 ($^1J_{CSi}$ = 51.3 Hz, SiMe$_3$), 122.4, 128.5, 133.6, 150.0, 170.2 (C$_5$H$_4$N). ^{29}Si NMR: δ −5.9 (SiMe$_2$), −0.1 ($^1J_{SiC}$ = 51.1 Hz, SiMe$_3$). MS: *m*/*z* 295 (80, M), 280 (100, M − Me), 264 (25 M − Me − CH$_4$), 250 (10), 217 (25, M − C$_5$H$_4$N), 201 (25), 192 (30), 136 (35), 73 (55).

Li(THF)C(SiMe$_3$)$_2$(SiMe$_2$C$_5$H$_4$N-2), 2. A solution of LiMe (3.8 mmol) in THF (15 mL) was added at room temperature to a stirred solution of **1** (1.12 g, 3.8 mmol) in THF (15 mL). Gas was evolved immediately. The red solution was stirred for 12 h and the solvent removed to leave a sticky pale brown solid, which was extracted into hexane (20 mL). The filtered extract was reduced to 5 mL and kept at −30 °C to give colorless blocks of **2**, mp 110 °C (decomp), suitable for an X-ray study. Yield: 0.95 g (67%). Anal. Calcd for C$_{18}$H$_{36}$LiNOSi$_3$: C, 57.8; H 9.6; N, 3.7. Found: C, 57.3; H, 9.3; N, 3.1. ^{1}H NMR: δ 0.38 (18H, s, SiMe$_3$), 0.63 (6H, s, SiMe$_2$), 1.23 (4H, m, THF), 3.41 (4H, m, THF), 6.65 (1H, m, 4-H), 7.05 (1H, s, 5-H), 7.46, (1H, d, 3-H), 7.98 (1H, d, 6-H). ^{13}C NMR: 0.7 (q, $^1J_{CLi}$ = 18.9 Hz, Si$_3$C), 5.6 ($^1J_{SiC}$ = 46.8 Hz, SiMe$_2$,), 7.5 ($^1J_{CSi}$ = 47.5 Hz, SiMe$_3$), 25.2 and 68.8 (THF), 121.7 (4-C), 129.1 (5-C), 135.3 (3-C), 147.7 (6-C), 182.6 (*ipso*-C). ^{7}Li NMR δ 2.94. ^{29}Si NMR: −10.7 (SiMe$_2$), −9.5 (SiMe$_3$). MS *m*/*z* 301 (25, RLi), 294 (65, R), 286 (90, RLi − Me), 280 (100, RH − Me), 264 (85, RH − Me − CH$_4$), 234 (20), 222 (30), 206 (25), 192 (50), 164 (25), 150 (50), 136 (60), 106 (35), 73 (80), 59 (50), 42 (80).

KC(SiMe$_3$)$_2$(SiMe$_2$C$_5$H$_4$N-2), 3. A solution of **2** (3.25 mmol) in THF (20 mL) was added to a stirred slurry of KO^{t}Bu (0.38 g, 3.39 mmol) in THF (15 mL) at −78 °C. The mixture was allowed to warm to room temperature and stirred for a further 56 h, and then the solvent was removed and the residue washed with pentane (2 × 30 mL). The residue was extracted into Et$_2$O (20 mL), the extract filtered, and hexane (20 mL) added to the filtrate. The volume was reduced to 10 mL and the solution kept at −30 °C for 1 week to give colorless blocks that were suitable for an X-ray study, mp 116 °C (decomp). Yield: 0.49 g (45%). A good C, H analysis could not be obtained, probably because of the extreme sensitivity of the compound toward air and moisture. ^{1}H NMR: δ 0.09 (18H, s, SiMe$_3$), 0.45

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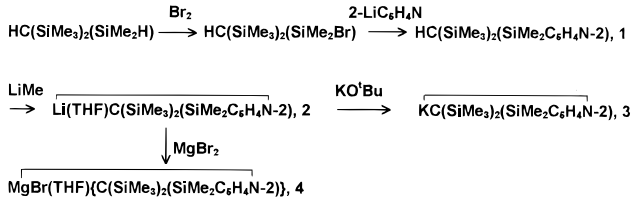
(6H, s, $SiMe_2$), 6.67 (1H, m), 7.10−7.23 (2H, m), and 8.66 (1H, m C_5H_4N). ^{13}C NMR: δ 1.3 ($SiMe_2$), 3.3 ($SiMe_3$), 122.2, 128.4, 133.5, 150.1 (C_5H_4N), 170.1 (*ipso*-C). The signal for CSi_3 was not detected. ^{29}Si NMR: −17.9 ($SiMe_3$), −11.5 ($SiMe_2$).

Mg(THF)Br{C(SiMe$_3$)$_2$(SiMe$_2$C$_5$H$_4$N-2)}, 4. A solution of **2** (0.54 g, 1.46 mmol) in THF (15 mL) was added to a slurry of $[MgBr_2(OEt_2)_2]$ (0.48 g, 1.46 mmol) in THF (20 mL) at −78 °C. The mixture was allowed to warm to room temperature during 14 h, and the solvent was then removed to leave an orange paste, which was washed with hexane (20 mL). When the filtered washings were kept at −30 °C, a few colorless needles (<0.1 g) separated and the ^1H NMR [δ 0.47 (18H, s, $SiMe_3$), 0.54 (6H, s, $SiMe_2$), 1.35 and 3.61 (8H, m, THF), 6.55-(t), 6.97(t), 7.20(d) and 8.63(d) (C_5H_4N)] and ^7Li NMR [δ −1.88] spectra were consistent with a composition $Li(THF)_2[MgBr_2$-{$C(SiMe_3)_2(SiMe_2C_5H_4N$-2)]. The residue, which was sparingly soluble in pentane, was then extracted with toluene (20 mL), and the extract was filtered, reduced to a volume of 10 mL, and kept at −30 °C for 1 week. Large colorless blocks of **4**, suitable for an X-ray study, were obtained, mp 285−290 °C (becoming opaque at 112 °C). Yield: 0.49 g, (60%). Anal. Calcd for $C_{18}H_{36}BrMgNOSi_3 \cdot C_7H_8$: C, 53.2; H, 7.8, N, 2.5. Found: C, 50.4, H, 7.9, N, 2.6. The poor C analysis may be associated with loss of toluene upon removal of the mother liquor. ^1H NMR: δ 0.03 and 0.31 (9H, s, $SiMe_3$), 0.37 and 0.39 (3H, s, $SiMe_2$), 1.13 and 3.49 (4H, m, THF), 2.02 (3H, s, toluene), 6.49 (1H, t, C_5H_4N), 6.87−7.16 (ca. 6H, m, C_5H_4N + toluene). 8.47 (1H, d, C_5H_4N). ^{13}C NMR: δ −0.9 ($^1J_{CSi}$ = 37.0 Hz, CSi_3), 1.3 and 4.6 ($SiMe_2$), 3.3 and 7.0 ($SiMe_3$), 21.4 (toluene), 25.0 and 69.5 (THF), 123.3, 129.3, 133.6, 150.0, and 170.2 (C_5H_4N), 125.6, 128.5, 137.3 (toluene). ^{29}Si NMR: δ −6.6 and −5.5 ($SiMe_3$), 4.0 ($SiMe_2$). MS: *m*/*z* 397 (5, RMgBr), 382 (60, RMgBr − Me), 295 (70, RH), 280 (100, RH − Me), 264 (90, RH − Me − CH_4), 192 (35), 164 (15), 136 (35), 106 (20), 73 (70).

[Cr{C(SiMe$_3$)$_2$(SiMe$_2$C$_5$H$_4$N-2)}$_2$], 5, and [Cr(μ-Cl){C(SiMe$_3$)$_2$(SiMe$_2$C$_5$H$_4$N-2)}]$_2$.THF, 6. A solution of **2** (1.66 mmol) in THF (15 mL) was added to a stirred slurry of $CrCl_2$ (0.20 g, 1.66 mmol) in THF (15 mL) at −78 °C, and the black mixture was allowed to warm to room temperature during 14 h. The solvent was removed to leave a sticky brown solid, which was extracted into hexane (2 × 20 mL). The extracts were combined and filtered, and the volume of the filtrate was reduced to 10 mL. The solution was then kept at −30 °C for one week, and the dark brown solid that separated was recrystallized from hexane (10 mL) to give extremely air-sensitive violet-pink crystals shown by an X-ray study to be **5** (0.2 g, 40% based on **1**) (no sharp mp, gives brown oil above 100 °C). Anal. Calcd for $C_{28}H_{56}CrN_2Si_6$: C, 52.4; H, 8.8; N, 4.4. Found: C, 51.9; H, 8.7; N, 4.5. μ_{eff} = 4.64 μ_B. MS: *m*/*z* 640 (40, M), 625 (10, M − Me), 346 (100, CrR), 330 (CrR − CH_4), 314 (65, CrR −2CH_4), 294 (45, R), 280 (30, RH − Me), 264 (70), 234 (10), 73 (25). The supernatant hexane solution was reduced in volume and again cooled to −30 °C to give more **5** and a very small amount of a green crystalline material. This was carefully extracted into cold pentane (5 mL, −10 °C), the solution filtered, and the filtrate cooled to −30 °C to give green crystals (softening at 105 °C and decomposing without melting up to 280 °C) shown to be **6** by an X-ray study.

[Li(THF)$_3$(μ-Cl)Mn{C(SiMe$_3$)$_2$(SiMe$_2$C$_5$H$_4$N-2)}Cl], 7. A solution of **2** (2.64 mmol) in THF (20 mL) was added to a slurry of $MnCl_2$ (0.33 g, 2.64 mmol) in THF (20 mL) at −78 °C. The mixture was allowed to warm to room temperature during 14 h to give a brown solution. The solvent was removed, and the residue was washed with hexane and then extracted into a mixture of toluene (15 mL) and THF (10 mL). The turbid solution was filtered through Celite and the volume of the filtrate reduced to 5 mL. The solution was kept at 5 °C for 2 weeks to give colorless crystals of **7** (yield: 0.70 g, 41%). Because of the extreme sensitivity of the crystals toward air, satisfactory C, H, and N analyses were not obtained, but the identity of the product was established by an X-ray study. μ_{eff} = 5.01 μ_B. MS *m*/*z* 369 (6, RMnCl − Me), 349 (95, RMn), 333 (10, RMn − CH_4), 295 (20, RH), 294 (15, R), 280 (55, RH − Me), 264 (100, R − 2Me). No peaks assignable to MnR_2 were observed in the MS of products from 2:1 mixtures of **2** and $MnCl_2$.

Scheme 1. Preparation of 2−4



Li(THF)$_2$(μ-Br)$_2$Co{C(SiMe$_3$)$_2$(SiMe$_2$C$_5$H$_4$N-2)}, 8. A solution of **2** (0.50 g, 1.33 mmol) in THF (15 mL) was added to a solution of $CoBr_2$ (0.29 g, 1.33 mmol) in THF (20 mL) at −78 °C. The deep blue solution became green as it was allowed to warm to room temperature during 12 h. The solvent was evaporated under vacuum and the sticky residue recrystallized from hexane (20 mL) at −30 °C to give dark green crystals of **8**, mp 169 °C (darkens 120 °C, softens 130 °C). Yield: 0.49 g (56%). The same product **8** was isolated from the reaction between $CoBr_2$ and 2 equiv of **2** under similar conditions. Anal. Calcd for $C_{22}H_{44}Br_2CoLiNO_2Si_3$: C, 39.7: H, 6.6. Found: C, 39.2: H, 6.2. MS: *m*/z 432 (5, RCoBr), 418 (85, RCoBr − Me), 360 (20), 294 (35, R), 280 (65, RH − Me), 264 (100, R − 2Me), 220 (65), 206 (30), 136 (35), 73 (55). μ_{eff} = 3.92 μ_B. g_{iso} = 1.98 (w, br).

Crystal Structure Determinations. Data were collected on an Enraf Nonius CAD4 (for **2** and **4**) or a Kappa CCD diffractometer (for **3**, **5**, **6**, and **8**), and structures were refined on F^2 using SHELXL-97, with non-H atoms anisotropic and H atoms in riding mode. Details are given in Table 1. For **2** about 10% of the molecules show an alternative orientation with a common Si2 site but different Si1 and Si3 sites. Only the Si sites could be located, and these were left isotropic in the refinement. For **8** the THF fragment containing O2B was modeled with C atoms isotropic but disordered equally over two sets of positions, except for C22B, for which a second dummy atom was included with identical parameters to allow calculation of H atom positions.

Results and Discussion

Syntheses. The organometallic reagents **2**−**4** have been obtained in good yield from readily available starting materials (Scheme 1).

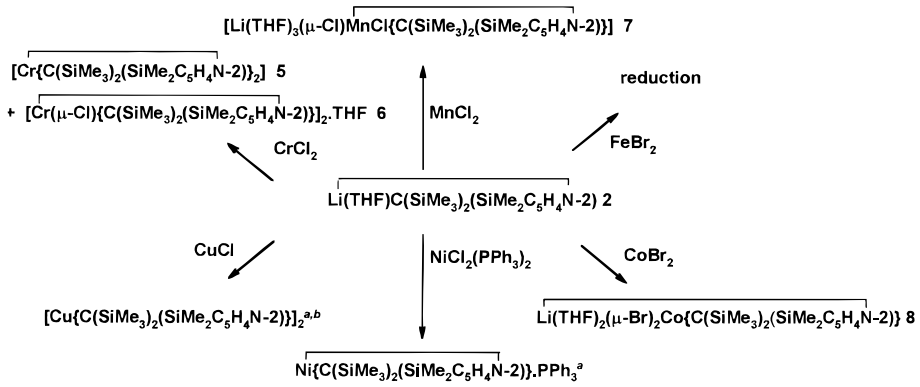
The potential of the lithium compound **2** as a ligand transfer reagent for the synthesis of new organometallic compounds is indicated in Scheme 2. Crystalline compounds containing metals with d^4, d^5, d^7, d^8, d^9 and d^{10} configurations have been isolated. We have not yet obtained products from reactions with Fe(II) halides, but preliminary experiments show that reduction to give black solids is slower than in the reactions of the Fe(II) halides with $LiC(SiMe_3)_3$. This suggests that it may be possible to obtain a variety of $C(SiMe_3)_2(SiMe_2C_5H_4N$-2) derivatives in the presence of stabilizing ligands. There is extensive reduction during the reaction of **2** with Ni(II) chloride, but an unusual Ni(I) species can be trapped in the presence of PPh_3.[6]

We have not yet had the opportunity to study the potential of **3** and **4** as ligand transfer reagents, but the Grignard reagent **4** will be investigated as an alternative to **2** in syntheses of organometallic compounds, e.g.,

Table 1. Summary of Crystallographic Data for 2, 3, 4, 5, 6, and 8

	2	3	4	5	6	8
chemical formula	$C_{18}H_{36}LiNOSi_3$	$C_{14}H_{28}KNSi_3$	$C_{25}H_{44}BrMgNOSi_3$	$C_{28}H_{56}CrN_2Si_6$	$C_{28}H_{56}Cl_2Cr_2N_2Si_6$·$C_{36}H_{72}Cl_2Cr_2N_2O_2Si_6$	$C_{22}H_{44}Br_2CoLiNO_2Si_3$
fw	373.7	333.74	563.10	641.29	1672.58	664.54
T/K	173(2)	173(2)	173(2)	173(2)	173(2)	173(2)
cryst syst	triclinic	triclinic	triclinic	monoclinic	triclinic	triclinic
space group	$P\bar{1}$ (No. 2)	$P\bar{1}$ (No. 2)	$P\bar{1}$ (No. 2)	*C*2/*c* (No. 15)	$P\bar{1}$ (No. 2)	$P\bar{1}$ (No. 2)
a/Å	10.195(4)	6.5726(3)	9.3693(12)	12.4621(7)	10.1148(3)	9.2957(4)
b/Å	10.246(7)	17.9327(9)	17.275(4)	14.0509(12)	12.8527(4)	18.6531(8)
c/Å	12.857(2)	18.1859(11)	19.660(4)	21.0341(12)	18.0204(5)	18.8990(10)
α/deg	68.81(4)	62.128(3)	104.187(18)	90	94.671(2)	85.156(2)
β/deg	72.28(3)	84.643(3)	90.026(14)	98.120(3)	96.179(2)	77.987(3)
γ/deg	71.47(5)	82.062(4)	97.739(16)	90	105.692(2)	82.326(2)
U/Å^3	1159.7(9)	1875.7(2)	3055.2(10)	3646.2(3)	2227.3	3171.3(3)
Z	2	4	4	4	1	4
μ/mm^{-1}	0.21	0.46	1.50	0.53	0.80	3.19
R1, wR2, $I > 2\sigma(I)$	0.062, 0.138	0.052, 0.110	0.068, 0.131	0.051, 0.114	0.044, 0.101	0.064, 0.112
all data	0.110, 0.164	0.093, 0.127	0.148, 0.163	0.065, 0.119	0.062, 0.111	0.132, 0.133
no. of measd/ indep rflns/ *R*(int)	4080/4080	19143/6517/ 0.0701	7455, 7455	9094/3187/ 0.0429	22117/10488/ 0.041	29531/11010/ 0.092
no. of rflns with $I > 2\sigma(I)$	2613	4311	4123	2654	8225	6451

Scheme 2. Reactions of 2 with Halides



[a] Reference 6. [b] Cyclic dimer.

those of iron,[6] that are sensitive toward reduction. The potassium compound **3**, which can be isolated pure and free from solvating ether, will be useful for the preparation of organometallic compounds that are known to cleave C−O bonds in ethers, e.g., derivatives of alkaline earth or lanthanide elements.[9a]

Alkali Metal Compounds 2 and 3. The lattice of the lithium compound **2**, like those of Li(OEt$_2$){C(SiMe$_3$)$_2$(SiMe$_2$Ph)} and Li(THF)C(SiMe$_2$Ph)$_3$,[9] contains discrete monomers with three-coordinate lithium. (Related internally solvated monomeric organolithium compounds have two coordinated THF molecules and four-coordinate lithium.[3]) The structure is shown in Figure 1, and bond lengths and angles are given in Table 2. The coordination at lithium is planar (sum of the angles 359.8°), with the C1−Li−O angle much larger and the ligand bite angle C1−Li−N much smaller than 120°. The Li−C, Li−N, and Li−O bond lengths are all at the short end of the usual range,[10] as expected from the low

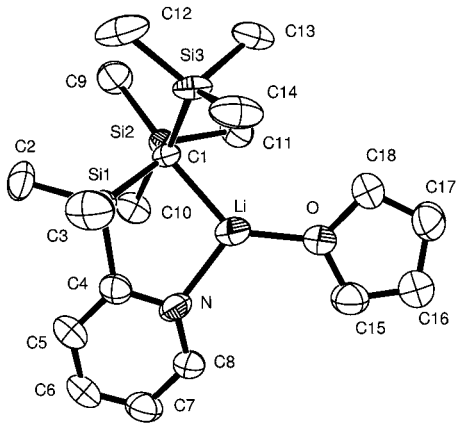


Figure 1. Molecular structure of **2**.

coordination number of the metal. The Si−C1 bonds (mean 1.819 Å) are much shorter than the Si−Me bonds (mean 1.888 Å), indicating that the carbanionic charge is delocalized into the CSi$_3$ system,[11a] and the longest Si−C bonds are to the atom C4 in the pyridine ring. The mean C1−Si−Me and Me-Si−Me angles are in the usual range, but individual values are significantly different from each other, suggesting that the ligand makes a number of adjustments from the most symmetrical structure to relieve internal strain. The signal

(9) (a) Eaborn, C.; Hawkes, S. A.; Hitchcock, P. B.; Smith, J. D. *Chem. Commun.* **1997**, 1961. Eaborn, C.; Hitchcock, P. B.; Izod, K.; Lu, Z.-R.; Smith, J. D. *Organometallics* **1996**, *15*, 4783. (b) Eaborn, C.; Clegg, W.; Hitchcock, P. B.; Hopman, M.; Izod, K.; O'Shaughnessy, P. N.; Smith, J. D. *Organometallics* **1997**, *16*, 4728. (c) Eaborn, C.; Hitchcock, P. B.; Smith, J. D.; Sullivan, A. C. *J. Chem. Soc., Chem. Commun.* **1983**, 1390.

(10) Setzer, W. N.; Schleyer, P. v. R. *Adv. Organomet. Chem.* **1985**, *24*, 353.

Table 2. Bond Lengths (Å) and Angles (deg) in Compounds 2, 3, 4, 5, 6, and 8 (M = Li, K, Mg, Cr, or Co)

	2[a]	**3**[b]	**4**[c]	**5**[d]	**6a**	**6b**	**8**[e]
M−C	2.144(8)	3.379(3)[f] 3.345(3)	2.189(9)[g]	2.303(3)	2.178(2)	2.220(2)	2.083(6)[g]
M−C′		3.207(3)[f] 3.228(3)					
M−N	2.036(8)	2.855(3)[f] 2.785(3)	2.097(9)[g]	2.114(3)	2.102(2)	2.130(2)	2.048(5)[g]
C1−Si	1.819(4)[g]	1.821(3)[g]	1.854(8)[g]	1.866(3)[g]	1.842(2) 1.868(2) 1.863(2)	1.836(2) 1.864(2) 1.869(2)	1.863(6)[g]
Si−Me	1.888(4)[g]	1.890(4)[g]	1.874(10)[g]	1.884(4)[g]	1.881(3)[g]	1.884(3)[g]	1.879(7)[g]
Si−py	1.912(4)	1.907(4)[g]	1.913(9)[g]	1.899(4)	1.893(3)	1.901(3)	1.906(7)[g]
M−N−C4	108.8(3)	117.0(2)[g]	114.6(6) 113.0(6)[f]	116.9(2)	116.49(17)	116.37(15)	112.1(4)[g]
N−C4−Si	117.0(3)	115.7(2)[g]	115.1(6) 116.7(6)[f]	113.9(3)	113.26(18)	115.52(17)	114.2(5)[g]
C4−Si−C1	109.50(17)	114.01(15)[g]	107.6(4)[g]	103.68(16)	104.57(11)	104.49(10)	104.8(3)[g]
Si1−C1−M	93.3(3)		98.2(4)[g]	96.60(14)	98.42(10)	100.68(10)	96.2(3)[g]
Si2−C1−M	100.6(3)			108.55(15)	113.19(11)	101.77(10)	106.9(3)[g]
Si3−C1−M	111.3(3)			119.78(16)	108.12(10)	118.92(11)	107.3(3)[g]
C1-M−N	102.1(4)		95.5(3)[g]	85.82(11)[i]	90.85(9)[j]	88.80(8)[j]	97.6(2)[f] 96.4(2)
Si1−C1−Si2	113.2(2)	114.88(17)[f] 115.81(18)	110.9(4)[f] 110.9(5)	110.11(17)	112.10(12)[g]	111.57(11)[g]	121.7(4)[f] 120.7(4)
Si1−C1−Si3	116.73(19)	120.96(18)[f] 126.72(19)	113.1(4)[f] 116.0(5)	108.28(17)			111.3(3) 112.1(3)
Si2−C1−Si3	117.52(19)	123.70(18)[f] 117.16(18)	113.2(4)[f] 113.4(4)	112.25(17)			111.4(3) 111.5(3)
C1−Si−Me	112.78(18)− 116.2(2)	112.52(17)− 117.48(17)[h]	107.4(4)− 118.0(4)[h]	113.02(17)− 119.91(18)	112.26(14)− 119.88(13)	112.39(12)− 119.15(12)	111.7(3)− 117.9(3)[h]
Me−Si−Me	103.1(2)− 107.2(2)	101.63(17)− 105.4(2)[h]	101.9(4)− 107.2(5)[h]	101.8(2)− 105.98(18)	104.64(15)− 106.28(16)	103.50(14)− 106.72(13)	102.2(3)− 106.8(2)[h]
fold angle[k]	15	56	29	30	40	37	39 40[f]

[a] Li−O 1.866(8), O−Li−C 136.6(4), O−Li−N 121.1(4). [b] K···Me contacts <3.5 Å: molecule A, K···C3 3.488, K···C13 3.130, K···C10 3.221, K···C1′ 3.207, K···C2′ 3.329; molecule B, K···Cl″ 3.228, K···C12″ 3.090, K···C10 3.331, K···C3 3.372. [c] Mg−O 2.005(7), 2.049(7); Mg−Br 2.487(3), 2.471(3); O−Mg−N 102.4(3), 99.8(3); Br−Mg−O 99.1(2), 100.1(2), Mean Br−Mg−Cl 130.3(2); Br−Mg−N 106.3(2), 107.5(2), C−Mg−N 95.8(3), 95.2(3). [d] For **5** N−Cr−N′ 174.37(16), N−Cr−C1′ 94.85(11), N−Cr−C1 85.82(11), C1−Cr−C1′ 166.26(17). [e] For **8** [values for second molecule in brackets] mean Co−Br 2.4532(11) [2.4534(11)]. Li−Br 2.528(13) [2.545(13)], Mean Li−O 1.903(13) [1.895(13)], Li···Co 3.193(12) [3.255(11)], O−Li−Br 103.6(6) to 119.5(7) [103.9(6) to 126.1(7)], mean Li−Br−Co 79.8(3) [81.2(3)], Br−Li−Br 98.1(4) [95.9(4)], Br−Co−Br 102.23(4) [100.73(4)]. [f] Data for independent molecules on separate lines. [g] Average for chemically equivalent bonds, in both independent molecules for **3**, **4**, and **8**, with esd's of individual measurements in parentheses. No individual values differ significantly from the mean. [h] Range includes both molecules. [i] C1′−Cr−N 94.85(11) in **5**. [j] For **6a** [values for **6b** in brackets] N−Cr−Cl 164.69(7) [172.94(6)]; C−Cr−Cl′ 99.10(6) [98.19(6)]; N−Cr−Cl 88.80(6) [91.30(6)]; C−Cr−Cl 163.43(7) [153.98(6)]; Cl−Cr−Cl′ 84.94(3) [82.01(2)]; Cr−Cl−Cr′ 95.06(3) [97.99(2)]. Cr−Cl 2.404(8) [2.4818(7)]; Cr−Cl′ 2.3803(9) [2.4088(7)]; Cr2−O1 2.4086(15); N−Cr2−O1 84.73(6); C−Cr2−O1 112.36(6). [k] At M···Si.

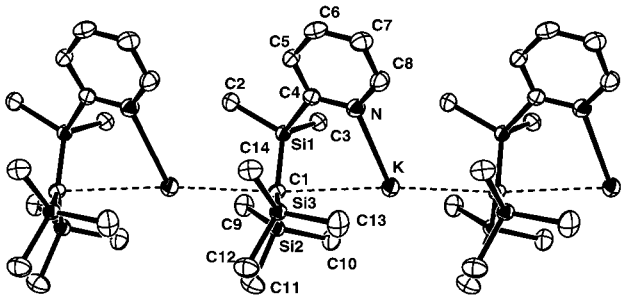
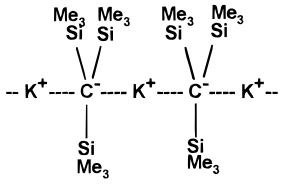


Figure 2. Structure of one of the chains in **3**.

from the central carbon appears as a quartet from coupling to ^{7}Li, showing that the Li−C bond is retained in benzene solution, and the presence of molecular species in the gas phase is shown by a strong signal in the mass spectrum.

In contrast to **2**, the potassium compound **3** crystallized from Et_2O/hexane in a solvent-free lattice. Each of the two independent molecules in the asymmetric unit is stacked in a chain parallel to the short *a* axis, and one such chain is shown in Figure 2. There are only minor differences in bond lengths and angles between the two molecules, but one stacks with an essentially linear $(KC)_n$ chain and the other with a slightly puckered chain (with C−K−C 172.6°). In both cases the coordination at the central carbanion is planar (sum of angles 359.6°), and, as in **2**, the C1−Si bonds are much shorter (mean over both molecules 1.820 Å) than the Si−Me (mean 1.890 Å) or Si−C4 bonds (mean 1.905 Å).



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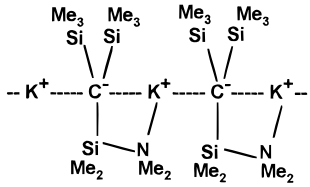

11

The structure as a whole is similar to those of $KC(SiMe_3)_3$, **10**,[11b] and $KC(SiMe_3)_2(SiMe_2NMe_2)$, **11**;[11c] in the symmetrical compound **10** the Si_3C plane is perpendicular to the $(KC)_n$ chain, but in **3** and **11** it is tilted because the Si bearing the nitrogen donor is pulled toward the potassium. The K−C1 distances [3.379(3) and 3.207(3) Å in one chain, 3.345(3) and 3.228(3) Å in the other] are longer than those (2.91−3.10 Å)[11d] in most organometallic compounds containing K−C *σ*-bonds, but similar to those in **10** [3.090(11), 3.104(11) Å][11b] or **11**

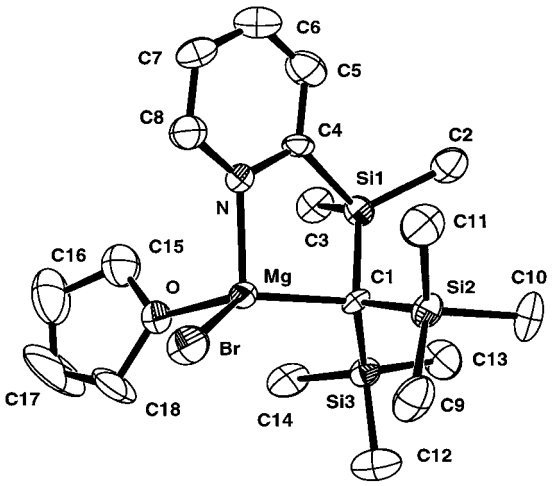

Figure 3. Structure of one of the independent molecules of **4**.

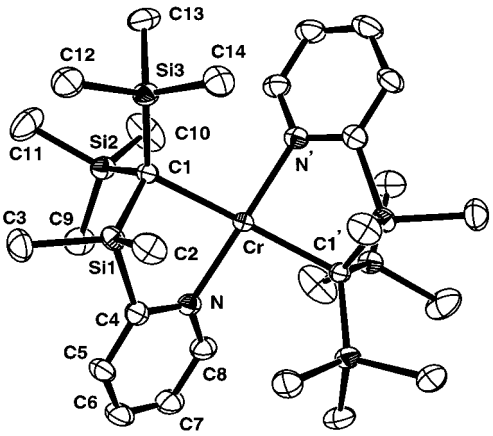

Figure 4. Molecular structure of **5**.

[3.1870(12), 3.2041(13) Å].[11c] The stronger K−C interaction in **11** is with the carbon from the anion bearing the coordinating nitrogen, but in **3** the stronger interaction is with the carbon of the adjacent anion. The K−N distances [2.855(3), 2.785(3) Å] in **3** are similar to that in **11** [2.8484(12) Å]; indeed in both compounds the K−N interaction is the only normal two-electron bond in the potassium coordination sphere. The K−C interactions are weaker and vary from compound to compound. Similar effects were noticed when a comparison was made between the structures of $MCPh_3$ and $MCPh_2C_5H_4N$ (M = Li, Na, K, or Cs).[12] As in **10** and **11**, there are in **3** several short K···Me contacts (See Table 2), but there is no X-ray evidence for methyl group distortion. The compound **3** is thus best described as ionic, with electrostatic attraction between K and C1 or N centers balanced by repulsion between K and Me groups surrounding the K−C1 axis. There is little difference between K−C1 and K−Me distances and only long-range electrostatic interaction between the chains. The planes of the pyridyl groups are almost parallel to the chain axis, but there is no evidence for interchain K−pyridyl interaction. The KNCSiC ring is folded at the K···Si axis.

Magnesium Compound 4. The Grignard reagent **4** also crystallizes in the triclinic system with two independent molecules in the asymmetric unit. These show no significant differences in bond lengths, but there are minor variations in bond angles. The structure of one of the molecules is shown in Figure 3. The chelate ligand in **2** appears to be sufficiently large to exclude a second THF molecule from the lithium coordination sphere. The magnesium atom in **4** is significantly larger (the Mg−C and Mg−N distances are about 0.5 Å greater than the corresponding Li−C and Li−N distances), and this, together with the presence of bromide as a less sterically demanding ligand than THF, allows the magnesium to be four- rather than three-coordinate. The difference between the inner and outer Si−C bond lengths is much less than that in the lithium compound **2**, which is as expected since the M−C bonds in the magnesium derivative are likely to be less ionic than those in the lithium compound.[11a] The conformation of the chelate MgCSiCN ring, with a fold of ca. 28° at the Mg···Si axis, is similar to that in **2**. The retention of the molecular chelated structure in solution is shown by the twin $SiMe_3$ and $SiMe_2$ resonances in the ^1H and ^{13}C NMR spectra. The appearance of the molecular ion (minus THF) in the mass spectrum is also noteworthy.

Chromium Compounds 5 and 6. The principal product from the reaction between $CrCl_2$ and 1 equiv of the lithium compound **2** was the dialkylchromium **5**, analogous to the compounds $Cr\{C(SiMe_3)_2C_5H_4N\text{-}2\}_2$, **12**,[7b] and $Cr(C_6H_4CH_2NMe_2\text{-}2)_2$, **13**,[13a] described previously. Compound **5** was isolated as extremely air- and moisture-sensitive crystals and was shown by an X-ray study to contain centrosymmetrical molecules (Figure 4) with a trans square-planar environment at chromium. The persistence of a monomeric high-spin d^4 structure in solution was shown by the magnetic moment of 4.64 μ_B (cf. 4.58 μ_B for **12** and 4.69 μ_B for **13**), and the presence of the molecular ion in the gas phase was shown by mass spectrometry. The Cr−C distance [2.303(3) Å] in **5** is significantly longer than those in **12** [mean 2.215(2) Å] and in the few other square-planar organochromium(II) complexes that have been structurally characterized, viz., CrR_2·dippe [R = CH_2CMe_3 or CH_2SiMe_3, dippe = 1,2-bis(diisopropylphosphino)ethane],[13b] $Mes_2Cr(THF)_2$·THF and $Mes_2Cr(bipy)$·THF (Mes = mesityl) [2.083(11)−2.149(4) Å],[13c] $Cr_2(C_6H_4NMe_2\text{-}2)_4$,[13a] and organochromate(II) complexes such as $[Li(TMEDA)_2]CrMe_4$ (TMEDA = tetramethylethylenediamine).[13d] The longer bond in **5** probably indicates that the interligand repulsion is greater than that in the other compounds investigated. The Cr−N distance in **5** is also longer than that in **12**, but similar to that in a number of other Cr−py derivatives. Table 2 shows that the intraligand dimensions in **5** are similar to those in **4**.

The mass spectra of the products of the reaction between $CrCl_2$ and **2** showed that there were other

(11) (a) Brain, P. T.; Mehta, M.; Rankin, D. W. H.; Robertson, H. E.; Eaborn, C.; Smith, J. D.; Webb, A. D. *J. Chem. Soc., Dalton Trans.* **1995**, 349. (b) Eaborn, C.; Hitchcock, P. B.; Izod, K.; Jagger, A. J., Smith, J. D. *Organometallics* **1994**, *13*, 753. (c) Al-Juaid, S. S.; Eaborn, C.; El-Hamruni, S.; Farook, A.; Hitchcock, P. B.; Hopman, M.; Smith, J. D.; Clegg, W.; Izod, K.; O'Shaughnessy, P. *J. Chem. Soc., Dalton Trans.* **1999**, 3267. (d) Smith, J. D. *Adv. Organomet. Chem.* **1999**, *43*, 267.

(12) Hoffmann, D.; Bauer, W.; Schleyer, P. v. R.; Pieper, U.; Stalke, D. *Organometallics* **1993**, *12*, 1193. Pieper, U.; Stalke, D. *Organometallics* **1993**, *12*, 1201.

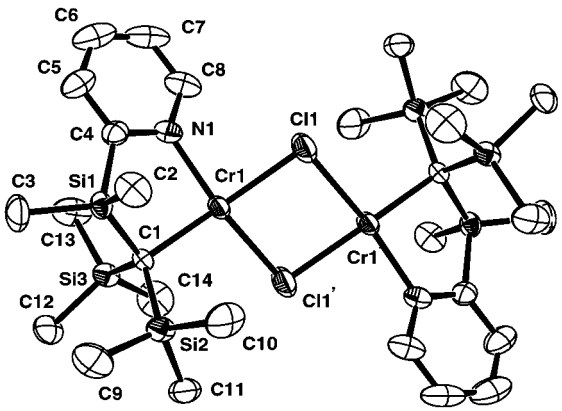

Figure 5. Structure of **6a**.

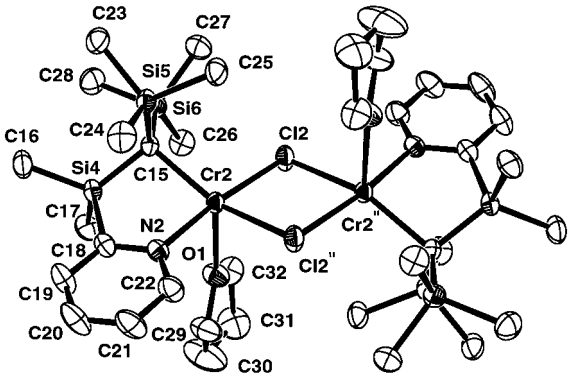

Figure 6. Structure of **6b**.

products besides the dialkylchromium **5**, and we succeeded in isolating a few (<10 mg) green crystals of one of these. We were unable to obtain sufficient compound for chemical analysis or magnetic measurements, but an X-ray determination showed that it was the Grignard reagent analogue $[\overline{CrCl\{C(SiMe_3)_2(SiMe_2C_5H_4N)\}}]_2$, **6**. The asymmetric unit comprises two independent centrosymmetrical chloride-bridged molecules: one, **6a** (Figure 5), contains square-planar four-coordinate chromium, and the other, **6b** (Figure 6), has an additional ligating THF and five-coordinate chromium. We are not aware of any other structurally characterized organochromium(II) halides of the general type RCrX, but phosphine-stabilized compounds $R\overline{Cr\{N(SiMe_2CH_2PPh_2)_2\}}$ have been reported.[13e] Since **6** contains only one bulky ligand per metal atom, there is less interligand repulsion than there is in **5**, and as a consequence, the Cr−C [2.178(2) Å] and Cr−N [2.102(2) Å] bond lengths are shorter and closer to those in related compounds.[7b,13] The corresponding bond lengths in **6b** are, as expected, intermediate between those in **6a** and **5**. The central Cr_2Cl_2 rings are unsymmetrical, with the bonds trans to C longer than those trans to N, in accord with the order of the trans influence better documented for d^8 complexes.

The Cr−O bond [2.4086(15) Å] is very long (for example, the bond length in $[Cr\{N(SiMe_3)_2\}_2(THF)_2]$ is 2.090(12) Å[13f]), indicating that the THF is only weakly coordinated. The formation of the extra Cr−O bond has an almost insignificant effect on the chromium coordination sphere since the square-planar array in **6b** is only slightly distorted from that in **6a**. The molecules **6a** and **6b** have different overall shapes, but they stack

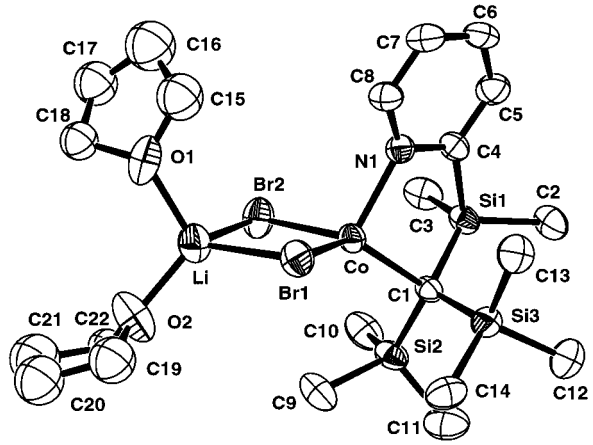

Figure 7. Structure of **8a**.

in an ordered 1:1 ratio with no disorder detectable from the X-ray data. The molecules show some resemblance to those of $Cr\overline{(C_6H_4CH_2NMe_2\text{-}2)_2}$, **13**, which contains four-coordinate square-planar chromium, and the adduct **13**·py, which has an extra pyridine molecule coordinated in the axial position by a very long Cr−N bond, but the molecules of **13** and **13**·py do not cocrystallize; **13** forms yellow, and **13**·py red, crystals.[13a]

Ate Complexes 7 and 8. The product from the reaction between $MnCl_2$ and 1 equiv of the lithium derivative **2** was a colorless solid that was difficult to crystallize. Eventually a crystalline sample was obtained, and an X-ray study indicated clearly that it consisted of the ate complex $Li(THF)_3(\mu\text{-}Cl)\overline{MnCl\{C(SiMe_3)_2(SiMe_2C_5H_4N\text{-}2)}$, **7**, with a single chloride bridge between the metal centers like that in the recently described $Li(THF)_3(\mu\text{-}Cl)\overline{MnCl\{C(SiMe_3)_2SiMe_2CH_2CH_2Me_2Si(Me_3Si)_2C}$.[14] We cannot report this structure in more detail because (a) the liquid nitrogen supply failed after only 95% of the data had been collected, (b) the extremely air-sensitive sample was lost when the crystal was mounted, and (c) samples made subsequently have not crystallized satisfactorily.

The reaction between $CoBr_2$ and 1 equiv of **2** gave the ate complex **8**, and the same product was obtained when an excess of **2** was used. The compound **8** has a magnetic moment of 3.92 μ_B, as expected for a d^7 tetrahedral configuration, and gives a broad ESR signal at $g = 1.98$. The structure was determined by an X-ray study. There were again two molecules in the asymmetric unit: one, **8a**, with a near planar $Li(\mu\text{-}Br)_2Co$ ring and shown in Figure 7, and the other, **8b**, with a fold angle of 15° at the Br···Br axis. Chemically equivalent bond lengths in the two molecules differ insignificantly, but there are a few minor differences in bond angles between the two

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configurations. For the most part average values are given in Table 2. Although the Co−C (or N) distances in **8** are very similar to the Li−C (or N) distances in **2**, the Co is four-coordinate, indicating that two bromine atoms are more easily accommodated than two THF molecules in the metal coordination sphere. The intraligand bond lengths and angles are similar to those in **4**−**6**, as expected from the similar electronegativities of Mg, Cr, and Co; the C1−Si bonds are significantly longer than those in **2** and **3**, suggesting that there is less delocalization of charge in the CSi_3 system of the carbanion.

Conclusions. The results described in this paper and elsewhere[6] show that the $C(SiMe_3)_2(SiMe_2C_5H_4N\text{-}2)$ ligand can be attached to a wide range of elements by simple ligand transfer from the lithium reagent **2**.

The molecular dimensions within the ligand vary only insignificantly from compound to compound so that the stoichiometry of the organometallic products frequently depends on the space available in the metal coordination sphere. The following points about the steric requirements of the bidentate ligand can be made from the data obtained so far.

(1) For **2**, **4**, and **6** the M−C bonds are 0.08−0.10 Å longer than the M−N bonds, suggesting that the balance between C- and N-coordination is similar for this series of compounds. In **8**, however, the Co−C bond is only 0.035 Å longer than the Co−N bond, indicating a weakening of M−N relative to M−C coordination like that observed in the compounds of the heavier group 14 elements. (In $PbCl\{C(SiMe_3)_2(SiMe_2C_5H_4N\text{-}2)\}$ the Pb−N is greater than the Pb−C distance.[6])

(2) The increase in metal radius from Co to Mg allows the Mg to accommodate the more bulky THF in place of Br to give a monomeric adduct, rather than a dimer with a bromide-bridged ring akin to that in **8**. The Cr(II) radius in **6** is similar to that of Mg in **4**, and there is room, even with a square-planar coordination sphere, for two Cl ligands as well as a loosely held THF molecule.

(3) We have so far been able to attach two $C(SiMe_3)_2(SiMe_2C_5H_4N\text{-}2)$ ligands only to chromium, the largest divalent element that we have studied, and the long Cr−C and Cr−N bonds show the crowding in the coordination sphere. All attempts so far to attach two ligands to manganese and cobalt have been unsuccessful, even though the smaller metals should be more easily accommodated in a tetrahedral than in a square-planar complex. In contrast, the compound $Co\{C(SiMe_3)_2C_5H_4N\}_2$, analogous to **12**, has been obtained.[7b] The smaller bite angles (67−70°) in the four-membered metallacycles (cf. 86° in **5**, 88° in **6b**, and 91° in **6a**) allow two chelating ligands to be accommodated without excessive steric repulsion between them.

The introduction of the $C(SiMe_3)_2(SiMe_2C_5H_4N\text{-}2)$ ligand has made it possible to isolate and characterize a much wider range of transition metal compounds than is possible with the simpler $C(SiMe_3)_3$ derivatives. Some of the problems of uncontrolled reduction by $LiC(SiMe_3)_3$ have been avoided and the pyridine-substituted derivatives are for the most part more easily handled than the unsubstituted analogues. The new ligand has considerable potential for further development to give fine control of the environment of both main group and transition metals in organometallic compounds and for providing restricted and selective access of substrates to electron-poor metal centers. For example, it should be possible to increase the steric demand of the ligand by placing substituents in the pyridine ring or by varying the organic groups attached to silicon in much the same way as we did in introducing the $C(SiMe_2Ph)_3$ or $C(SiMe_2{}^iPr)_3$ ligands,[1,15] and Uhl has done more recently with a range of triorganosilyl-substituted groups of various sizes.[16] The reactions of some of the compounds described in this paper are currently under investigation.

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