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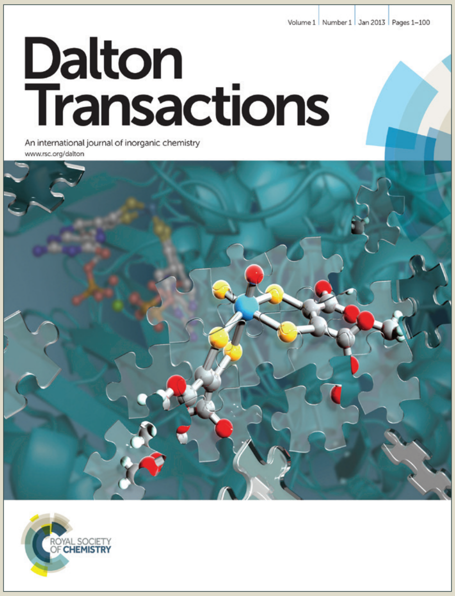

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Cobalt(II) Amido Complexes Derived from a Monodentate Arylamido Ligand Featuring a Highly Electron-withdrawing C_6F_5 Substituent

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ABSTRACT

A series of cobalt(II) complexes of a highly electron-withdrawing amido ligand, $[N(C_6F_5)(C_6H_3Pr^i{}_2–2,6)]^–$ (L), were synthesized and structurally characterized. Mononuclear [CoL(Cl)(TMEDA)] (**3**) and heterobimetallic $[CoL_2(\mu–Cl)Li(THF)_3]$ (**4**), were obtained by direct metathetical reactions of anhydrous $CoCl_2$ with one molar equivalent of [LiL(TMEDA)] (**1**) (TMEDA = $Me_2NCH_2CH_2NMe_2$) and $[LiL(THF)_3]$ (**2**), respectively. Complex **3** underwent facile ligand substitution reactions with LiMe and NaN_3, yielding the corresponding mixed-ligand complexes [CoL(X)(TMEDA)] (X = Me **5**, N_3 **6**). Treatment of **3** with NaOMe led to the heterobimetallic complex $[CoL_2(\mu–OMe)Na(TMEDA)]$ (**7**). The solid-state structures of complexes **1**–**7** were established by X-ray diffraction analysis.

INTRODUCTION

Amido ligands of the general formula [–NRR'] (R, R' = H, alkyl, aryl or silyl) are versatile ligands which form stable complexes with a wide range of metals.[1] The steric and electronic properties of this ligand system can be readily modified through choice of appropriate R and R' substituents attached to the nitrogen atom. Amido complexes of the 3d metals have attracted considerable interest in the past decades. They have found a variety of applications in synthesis, polymerization, small molecule activation, and material science.[2-13] One notable feature that distinguishes early and late 3d metal amides is the stability of the $M–NR_2$ bonds. It is believed that late transition metal amides are kinetically more labile as compared with their early transition metal counterparts due to (i) a "mis-match" of the *hard* amido nitrogen atom and the *soft* late transition metal ion, and (ii) a d←p π repulsion between the lone-pair electrons on the p orbital of the amido nitrogen atom and the d electrons on the late transition metal ion.[1,14] Nevertheless, the use of sterically bulky amido ligands has proved to be successful for stabilization of kinetically labile low-coordinate amido complexes of the late 3d metals.[1,10-13,15]

A diverse coordination chemistry of amido systems can also be achieved by varying the electronic properties of the R substituents. A number of amido systems containing highly electron-withdrawing polyfluorophenyl substituents have been reported in the literature, including the tripodal trianionic $[(ArNCH_2CH_2)_3N]^{3-}$ (Ar = $4–FC_6H_4$ or C_6F_5)[16] and $[HC\{SiMe_2N(2–FC_6H_4)\}_3]^{3-}$,[17] the tridentate monoanionic $[N(4–HC_6F_4)(CH_2CH_2NR_2)]^{-}$ (R Me, Et),[18] the bidentate dianionic $[(Ar'NCH_2CH_2)_2NMe]^{2-}$ (Ar' = $3–CF_3C_6H_4$ or $3,4,5–F_3C_6H_2$),[19] and the monodentate monoanionic $[N(R)(C_6F_5)]^{-}$ (R = H, $SiMe_3$ or and $[N(2–FC_6H_4)(C_6H_3Pr^i_2–2,6)]^–$.[23] In addition, a few main group and transition metal complexes supported by *N*–substituted 2-pyridyl amido system of the type $[N(Ar^F)(2–C_5H_4N)]^–$ (Ar^F = $2–FC_6H_4$, $2,6–F_2C_6H_3$, $2,4,6–F_3C_6H_2$ or C_6F_5) have also been reported.[24-26] It is well documented that organofluorine ligands can stabilize low-valent metal complexes as well as metal complexes with unusual molecular structures.[27,28] One interesting feature with these fluorinated ligand systems is the presence of M···F interactions, which can induce the activation of the strong C–F bonds on the ligands. Moreover, some these complexes can generate an active ligand periphery by virtue of weak M···F which may modify the reactivity at the metal centre.[17,23]

We are interested in the chemistry of metal amides, especially synthesis and chemistry of amido complexes of divalent 3d metals and lanthanide metals.[29-33] Earlier, we have reported on the chemistry of a few Fe(II) and Co(II) complexes supported by the monodentate *N*–silylated and *N*–alkylated arylamido system $[N(R)(C_6H_3R'_2–2,6)]^–$ (R = $SiMe_3$, CH_2Bu^t; R' = Me, Pr^i).[32] It was noted that minor modifications in the steric and electronic properties of the R and R' substituents in this system can change the metal-ligand stoichiometry of the corresponding metal amides.[32,34] Continuing our work on this system, we have prepared the $[N(C_6F_5)(C_6H_3Pr^i_2–2,6)]^–$ ligand and examined its properties with divalent 3d metals. The highly electron-withdrawing C_6F_5 substituent on ligand can reduce the charge density on the amido nitrogen atom and, hence, it may enhance the stability of the M–N bond. Moreover, the presence of M···F interactions may lead to a different coordination behaviour of the arylamido system and reactivity of the corresponding metal complexes. In this article, we report on the synthesis and reaction chemistry of cobalt(II) complexes containing the $[N(C_6F_5)(C_6H_3Pr^i{}_2\text{–}2,6)]^-$ ligand.

RESULTS AND DISCUSSION

Ligand Synthesis. Two lithium complexes of the $[N(C_6F_5)(C_6H_3Pr^i{}_2\text{–}2,6)]^-$ (L) ligand were prepared and used as ligand-transfer reagents in the present study. The ligand precursor compound $[HN(C_6F_5)(C_6H_3Pr^i{}_2\text{–}2,6)]$ (HL) was prepared according to a procedure described in the literature with minor modifications.[35] Treatment of HL with $LiBu^n$ in the presence of *N,N,N′,N′*–tetramethylethylenediamine (TMEDA) afforded mononuclear, three-coordinate lithium amide [LiL(TMEDA)] (**1**), whereas lithiation of HL in THF, in the absence of TMEDA, yielded the four-coordinate THF-adduct $[LiL(THF)_3]$ (**2**) (Scheme 1). Both complexes **1** and **2** were isolated as colourless crystalline solids in good (90% for **1**) or satisfactory (68% for **2**) yields. These two lithium amides are soluble in common aprotic solvents such as THF, diethyl ether and toluene, but only slightly soluble in hexane. The ^1H NMR spectra of complexes **1** and **2** showed one set of resonance signals which are assignable to the amido ligand L and the respective donor ligands, *i.e.* TMEDA for **1** and THF for **2**.[36] The $^{13}C\{^1H\}$ NMR spectra of both complexes displayed one set of signals due to the $2,6\text{–}Pr^i{}_2C_6H_3$ substituent of L and the TMEDA or THF ligands. ^{13}C NMR signals for the C_6F_5 substituent are broad and barely resolved at room temperature, but these ^{13}C NMR signals slightly sharpened upon warming the sample solutions to 40–50°C. The room temperature ^{19}F NMR spectra of **1** and **2** each shows five broad signals. These ^{13}C and ^{19}F NMR spectral data suggest a slow rotation of the C_6F_5 substituent due to intramolecular Li···F interactions at room temperature.

The solid-state structures of **1** and **2** were determined by single-crystal X-ray diffraction analysis (Figures 1 and 2). Selected bond distances and angles for these complexes are listed in the respective figure legends. Complex **1** consists of an almost three-coordinate lithium centre (sum of bond angles around Li(1) = 346.0°). The Li–N(amide) bond [Li(1)–N(1)] measures 1.967(7) Å, whereas the Li–N(TMEDA) bond distances are longer, namely 2.146(8) Å [Li(1)–N(2)] and 2.119(7) Å [Li(1)–N(3)]. A short Li···F interaction of 2.355(7) Å [Li(1)···F(5)] is observed in the solid-state structure. Complex **2** exhibits a distorted tetrahedral structure. The coordination sphere of the lithium ion consists of one monodentate amido ligand [Li(1)–N(1) = 2.030(4) Å] and three coordinated THF molecules [Li(1)–O(1) 2.067(5) Å, Li(1)–O(2) 1.998(6) Å and Li(1)–O(3) 2.008(5) Å]. A slightly longer Li···F contact, *viz.* Li(1)···F(1) 2.698(3) Å, is present in the solid-state structure of **2**.

Synthesis and Characterization of Cobalt(II) Complexes of L. Initial attempts to synthesize a cobalt(II) derivative of L by the reaction of anhydrous $CoCl_2$ with one molar equivalent of **1** in toluene under ambient conditions were unsuccessful. Only the starting materials were recovered after the reaction. Accordingly, the reaction was repeated at 40°C for 12 h. After work-up, deep blue, crystalline [CoL(Cl)(TMEDA)] (**3**) was obtained in 78% yield (Scheme 1). The formulation of **3** was confirmed by elemental analysis and single-crystal X-ray diffraction (*vide infra*). Complex **3** is paramagnetic with an effective magnetic moment of 3.98 μ_B (in toluene-d_8 at 298K),[37] which is consistent with a high-spin cobalt(II) centre with three unpaired electrons. The solid-state structure of the solvated **3**·$0.5C_7H_8$ was determined by X-ray diffraction (Figure 3). The cobalt(II) centre is four-coordinated by one monodentate amido ligand L, one chloride ligand and one chelating

TMEDA ligand. The amido nitrogen atom N(1) exhibits a trigonal planar geometry (sum of bond angles around N(1) ≈ 359.8°). The Co–N(amide) bond distance is 1.977(4) Å [Co(1)–N(1)], whereas the Co–Cl distance is 2.252(2) Å [Co(1)–Cl(1)]. These bond distances are similar to the corresponding bond lengths of 1.922(2) Å (Co–N) and 2.2714(7) Å (Co–Cl) in the closely related cobalt(II) mono(amido) complex $[Co\{N(SiMe_3)(C_6H_3Me_2\text{–}2,6)\}(Cl)(TMEDA)]$ reported earlier by our group.[32] The Co–N(amide) bond length in **3** is also similar to those of 1.979(3) and 1.989(3) Å reported for the mononuclear $[Co\{N(C_6F_5)\}_2(py)_2]$,[20b] but is slightly longer than those of 1.910(5) and 1.922(5) Å in $[Co\{N(SiMe_3)_2\}_2]_2$.[38] The closest Co···F distance in **3** is 2.560(4) Å [Co(1)···F(1)], which is marginally longer than the Co···F distance of 2.507(2) Å reported for $[Co\{N(C_6F_5)\}_2(py)_2]$.[20b] The ^1H NMR spectrum of **3** in C_6D_6 showed a set of broad and paramagnetically shifted signals which could not be unambiguously assigned. The ^{19}F NMR spectrum of this complex exhibits three resonance signals with an approximate integral ratio of 2:2:1, suggesting that the Co···F interaction is labile in the solution state.

Attempts to synthesize a cobalt(II) bis(amido) complex by treatment of $CoCl_2$ with two equivalents of **1** were unsuccessful. In our hands, only the mono(amido) complex [CoL(Cl)(TMEDA)] (**3**) was obtained in ~70% yield. Apparently, the ligand environment in **3** provides sufficient steric shielding such that this complex does not undergo further metathetical reaction with another molecule of **1**. Earlier, we have reported on the coordination properties of the related $[N(SiMe_3)(C_6H_3R_2\text{–}2,6)]^-$ (R = Me, Pr^i) ligands with iron(II) and cobalt(II) ions.[32] Only the corresponding mono(amido) complexes were isolated with the *N*-silylated amido system, irrespective of the metal-ligand stoichiometric ratios being employed.

In order to prepare a cobalt(II) bis(amido) complex, the reaction of $CoCl_2$ with the TMEDA-free $[LiL(THF)_3]$ (**2**) was examined. As shown in Scheme 1, treatment of $CoCl_2$ with two molar equivalents of **2** afforded blue, crystalline cobalt(II) bis(amido) complex $[CoL_2(\mu\text{–}Cl)Li(THF)_3]$ (**4**). The formulation of **4** was confirmed by elemental analysis. The complex is paramagnetic with an effective magnetic moment of 3.94 μ_B, which is consistent with a high-spin cobalt(II) centre with three unpaired electrons.[37] The solid-state structure of **4** was determined by single-crystal X-ray diffraction (Figure 4). The asymmetric unit of **4** consists of two independent molecules of similar structures. Selected bond distances and angles for only one of these molecules are listed in the legend of Figure 4. One remarkable feature of complex **4** is a trigonal planar cobalt(II) centre (sum of bond angles around Co(1) = 359.96° and Co(1') = 359.98°), which is bonded to the amido nitrogen atoms of a pair of L ligands and a bridging chloride ligand. The latter is also bonded to a lithium ion forming a heterobimetallic complex. The Co–N(amide) distances in **4** fall within the range of 1.916(6)–1.930(5) Å. They are slightly shorter than that of the four-coordinate complex **3** [1.976(4) Å]. Short Co···F contacts of 2.354(4)–2.465(3) Å [Co(1)···F(1), Co(1)···F(10), Co(1')···F(1') and Co(1')···F(6')] are observed in **4**. These Co···F interactions are relatively short as compared to those of 2.559(4) Å in **3**, 2.507(2) Å in $[Co\{N(C_6F_5)_2\}_2(py)_2]$[20b] and 2.65(2) Å in $[Co\{HB(3,5\text{−}Me_2Pz)_3\}(C_6F_5)]$.[39] Unfortunately, the ^{19}F NMR spectrum of **4** in C_6D_6 at room temperature is complicated, showing a greater-than-expected number of signals probably due to the paramagnetic cobalt(II) centre and/or speciation of the complex in solution. Therefore, a prediction of the solution-state structure of complex **4** is not straightforward.

The reaction of 1:1 $CoCl_2$/**2** was also examined in the present work. Instead of a mono(amido) complex of L, only the bis(amido) complex **4** was obtained as the only isolable product in our hands. Notably, TMEDA plays a crucial role which facilitates the preparation of the mono(amido) complex [CoL(Cl)(TMEDA)] (**3**). On the other hand, the absence of TMEDA allows for isolation of the bis(amido) complex $[CoL_2(\mu{-}Cl)Li(THF)_3]$ (**4**), despite the metal-ligand stoichiometries used. In a further investigation, we also examined the reaction of complex **4** with TMEDA in order to explore any possibility of converting the bis(amido) complex **4** to the mono(amido) derivative **3**. Additional experiments were carried out by treating a solution of **4** in THF with two equivalents of TMEDA at room temperature. Unfortunately, no crystalline products were isolated from the latter reactions, but only a dark green oily residue was obtained after removal of all the volatiles. This oily crude product mixture was characterized by NMR spectroscopy. Owing to the presence of paramagnetic cobalt species in the product mixture, its ^1H and ^{19}F NMR spectra showed a set of complicated, greater-than-expected number of signals, rendering their peak assignments difficult to carry out. Interestingly, its ^7Li NMR spectrum showed one single resonance signal at 1.35 ppm, which is very different from the ^7Li NMR signal of 44.7 ppm recorded for $[CoL_2(\mu{-}Cl)Li(THF)_3]$ (**4**), but close to that of 0.96 ppm for [LiL(TMEDA)] (**1**) and 0.44 ppm for $[LiL(THF)_3]$ (**2**) despite the fact that the presence of paramagnetic species in the crude product mixture may lead to anisotropic shift of the signals. Based on these spectroscopic data, it is possible that complex **4** might have reacted with TMEDA to form [CoL(Cl)(TMEDA)] (**3**) and either **1** or **2** through ligand rearrangement. Nevertheless, other reaction pathways cannot be excluded at this stage of our studies.

Reactivity Studies

The presence of a terminal chloride ligand in **3** renders this compound a potential synthon for other mixed-ligand cobalt(II) complexes via ligand substitution reactions. As we have mentioned above, the steric stability of **3** renders this complex relatively inert towards metathetical reactions with sterically bulky ligands. Therefore, we set off by employing several sterically less hindered ligands, namely methyl, azide and methoxide ligands. Treatment of **3** with LiMe in diethyl ether resulted in a dark green solution from which green, crystalline [CoL(Me)(TMEDA)] (**5**) was isolated in 26% yield (Scheme 2). Complex **5** is soluble in common aprotic organic solvents, and is extremely sensitive to air and moisture.[40] It is a mononuclear high-spin complex with solution magnetic moment of 3.92 μ_B.[37] The room temperature ^1H and ^{19}F NMR spectra of **5** showed a set of complicated, paramagnetically shifted signals which could not be unambiguously assigned. The solid-state structure of **5** was elucidated by X-ray crystallography. It is noteworthy that structurally authenticated cobalt(II) methyl-amide complexes are rare.[41-43] As shown in Figure 5, the cobalt(II) centre in **5** is coordinated to one monodentate amido ligand L, one methyl ligand and one chelating TMEDA molecule. This ligand set constitutes a distorted tetrahedral geometry around the cobalt(II) centre. The Co–N(amide) distance [Co(1)–N(1) 1.998(6) Å] in **5** is marginally longer the corresponding distance of 1.976(4) Å in the precursor complex **3** and 1.960(2) Å in [Co{N(SiMe$_3$)(C$_6$H$_3$Me$_2$–2,6)}(Me)(TMEDA)].[32]

The Co–Me distance in **5** [Co(1)–C(25) 2.04(1) Å] is almost identical to the corresponding distance [Co–Me 2.038(2) Å] in the latter complex,[32] and comparable to those of 2.12(1) Å in [Tp^{tBu}]CoMe[42] and 2.052(3) Å in [PhTt^{tBu}]CoMe.[43] The closest Co···F distance in **5** was found to be 2.607(7) Å [Co(1)···F(5)].

The reaction of **3** with NaN_3 in THF at 40°C resulted in isolation of the corresponding amide-azide complex [CoL(N_3)(TMEDA)] (**6**). An X-ray diffraction analysis showed that complex **6** is mononuclear with a similar molecular structure to those of **3** and **5** (Figure 6). The cobalt–amide bond Co(1)–N(1) measures 1.961(4) Å, whereas the cobalt–azide bond Co(1)–N(2) is 1.930(6) Å. The azide ligand is almost linear [N(2)–N(3)–N(4) 175.4(7)°] with identical nitrogen–nitrogen distances [N(2)–N(3) 1.169(7) Å and N(3)–N(4) 1.166(8) Å]. The closest Co···F distance in **5** is Co(1)···F(5) (2.563(3) Å). The ^{19}F NMR spectra of this complex showed three resonance signals, suggesting that the Co···F interaction is labile in the solution.

Our initial attempts to synthesize an analogous cobalt(II) amide-methoxide complex by the reaction of complex **3** with NaOMe in THF under ambient conditions were unsuccessful. Complex **3** was recovered almost quantitatively after work-up. When the reaction was carried out in THF at 40°C, a greenish blue crystalline product (**7**) was isolated.[40] The solid-state structure of **7** was determined by X-ray crystallography. Complex **7** crystallizes as a one-dimensional chain (Figure 7). Adjacent [CoL_2(μ–OMe)Na(TMEDA)] molecules in the polymeric chain are linked up through intermolecular Na···F interactions, *i.e.* Na(1)···F(2A) [2.450(5)Å] and Na(1)···F(3A) [2.980(5) Å]. It is interesting to note that both Co(1) and Na(1) in **7** adopt a three-coordinate geometry. Co(1) is bound by two amido nitrogen atoms [N(1) and N(2)] and one μ–methoxide ligand, which form a rare trigonal planar geometry around the cobalt(II) centre (sum of bond angles around Co(1) = 360°). The methoxide ligand bridges Co(1) and the sodium ion Na(1). Coordination of a bidentate TMEDA molecule to Na(1) completes a "flattened" trigonal pyramidal geometry around the sodium centre (sum of bond angle around Na(1) = 333.7°). In comparison with other three-coordinate cobalt(II) alkoxide complexes, the Co–OMe bond [Co(1)–O(1) 1.862(4) Å] in **7** is slightly shorter than the Co–O(bridging) distances in $[Li\{Co(N(SiMe_3)_2)(OCBu^t{}_3)_2\}]$ [1.925(6)–1.939(6) Å],[44] $[Co\{OC(C_6H_{11})_3\}_2]_2$ [1.944(4)–1.966(5) Å][45] and $[Co(OCPh_3)_2]_2$ [1.946(4)–1.982(4) Å].[45] It is also shorter than the Co–O(bridging) distances of 1.977(3)–1.993(3) Å in the binuclear $[Co(OSiPh_3)_2(THF)]_2$,[45] the latter complex has four-coordinate cobalt(II) centres. The Co–N(amide) bond lengths [Co(1)–N(1) 1.957(4) Å and Co(1)–N(2) 1.955(5) Å] in **7** are comparable to those of 1.916(6)–1.930(5) Å in the three-coordinate $[CoL_2(\mu\text{–}Cl)Li(THF)_3]$ (**4**) and 1.976(4) Å in the four-coordinate precursor complex **3**. Another noteworthy feature of **7** is the presence of a short intramolecular Co(1)···F(1) interaction of 2.365(3) Å. It is believed that this cobalt···fluoride interaction can enhance the stability of the three-coordinate, 12-electron cobalt(II) complex **7**. Besides, a weak intramolecular interaction [2.873(5) Å] between the three-coordinate Na(1) and F(6) is also observed.

In summary, utilization of the pentafluorophenyl-substituted amido ligand $[N(C_6F_5)(C_6H_3Pr^i{}_2\text{–}2,6)]^-$ (L) has led to isolation of a few coordinatively unsaturated cobalt(II) complexes, namely the mononuclear [CoL(X)(TMEDA)] (X = Cl **3**, Me **5**, N_3 **6**), and the heterobimetallic [CoL_2(μ–Cl)Li$(THF)_3$] (**4**) and [CoL_2(μ–OMe)Na(TMEDA)] (**7**). The cobalt(II) centres in **4** and **7** exhibit a rare trigonal planar geometry with a low electron count of 12. Results of this work and our previous studies[32,34] have shown that *N*–substituted arylamido ligands of the type $[N(R)(C_6H_3R'_2–2,6)]^-$ (R = $SiMe_3$, CH_2Bu^t, C_6F_5; R' = Me, Pr^i) are good candidates for stabilizing low-coordinate 3d metal complexes. It is also noted that TMEDA plays a crucial role in stabilizing the corresponding iron(II) and cobalt(II) mono(amido) complexes of the type [ML(Cl)(TMEDA)] (M = Fe, Co). Although C–F bond activation has been reported for a number of fluorinated ligand systems due to the presence of strong M···F interactions (see, for example, references 18 and 26), it has not been observed in the present cobalt(II) complexes of the $[N(C_6F_5)(C_6H_3Pr^i_2–2,6)]^-$ ligand. Studies on the chemistry of other late transition metal complexes of this arylamido system are currently in progress in our laboratory.

EXPERIMENTAL

General Procedures. All manipulations were carried out under a purified nitrogen atmosphere using modified Schlenk techniques or in a Braun MB 150-M drybox. Solvents were dried over sodium wire and distilled under nitrogen from sodium/potassium alloy (hexane and toluene) or sodium/benzophenone (diethyl ether and THF), and degassed by freeze-thaw cycles twice prior to use. Anhydrous $CoCl_2$ was purchased from Strem and used as received.

Physical Measurements. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AV-400 spectrometer operating at 400.13 MHz and 100.62 MHz, or a Bruker AV-500 spectrometer at 500.30 MHz and 125.80 MHz, respectively. ^{7}Li and ^{19}F NMR spectra were recorded on the Bruker AV-400 spectrometer operating at 376.55 MHz. All spectra were recorded in $CDCl_3$ or C_6D_6 with the chemical shifts referenced to residue solvent protons at 7.26 and 7.16 ppm (in ^{1}H NMR), and 77 and 128 ppm (in ^{13}C NMR), respectively. Chemical shifts of ^{7}Li and ^{19}F NMR spectra were referenced to that of LiCl (0 ppm) and trifluorotoluene (–63.72 ppm), respectively Solution magnetic moments were measured by the Evans NMR method in toluene at 298 K, using a JEOL 60 MHz NMR spectrometer. Mass spectra were obtained on a Finnigan MAT 95XL mass spectrometer (E.I. 70 eV). Melting points were recorded on an Electrothermal melting-point apparatus and were uncorrected. Elemental analysis (C, H, N) was performed by MEDAC Ltd., Brunel University, UK.

Synthesis of $[HN(C_6H_3Pr^i{}_2\text{–}2,6)(C_6F_5)]$ (HL). To a solution of 2,6-diisopropylaniline

(8.85 g, 50 mmol) in THF (50 mL) at 0°C was added a solution of $LiBu^n$ in hexane (37.5 mL, 1.6 M, 60 mmol). The resulting solution was stirred at room temperature for 2 h, after which the solution was slowly added to a stirring suspension of $LiNH_2$ (1.15 g, 50 mmol) and hexafluorobenzene (9.3 g, 50 mmol) in THF (50 mL) at 0°C. The reddish brown mixture was stirred at room temperature for another period of 8 h and then quenched with H_2O (50 mL). The organic fraction was separated and dried over magnesium sulphate. All the volatiles were removed *in vacuo*. The product was obtained as a yellow liquid by vacuum distillation at 85°C at 0.01 mmHg (12.9 g, 37.5 mmol, 75%). ^1H NMR (400.19 MHz, $CDCl_3$): δ 7.31 (t, J = 7.7 Hz, 1H, ArH), 7.17 (d, J = 7.7 Hz, 2H, ArH), 5.03 (br, 1H, NH), 3.22 (septet, J = 6.4 Hz, 2H, CHMe$_2$), 1.18 (d, J = 6.4 Hz, 12H, CHMe_2). $^{13}C\{^1H\}$ NMR (100.63 MHz, $CDCl_3$): δ 147.3, 138.7 (dt, $^1J_{C-F}$ = 247.5 Hz, $^2J_{C-F}$ = 13.9), 137.1 (d, $^1J_{C-F}$ = 240.8 Hz), 134.6, 133.2 (dt, $^1J_{C-F}$ = 247.5 Hz, $^2J_{C-F}$ = 13.9), 128.3, 123.9 (m), 123.7, 28.7, 23.7. ^{19}F NMR (376.55 MHz, $CDCl_3$): δ –161.39 (dm, $^3J_{F-F}$ = 22.6 Hz, 2F, *m*-F), –164.22 (dt, $^3J_{F-F}$ = 22.6 Hz $^4J_{F-F}$ = 3.8 Hz, 2F, *o*-F), –173.4 (tt, $^3J_{F-F}$ = 22.6 Hz, $^4J_{F-F}$ = 7.5 Hz, 1F, *p*-F). MS (EI, 70 eV): m/z (%) 343 (62) $[L]^+$, 328 (100) $[L–Me]^+$, 177 (9) $[L–C_6F_5]^+$, 162 (37) $[L–C_6F_5–Me]^+$, 43 (6) $[Pr^i]^+$.

Synthesis of $[Li\{N(C_6H_3Pr^i_2–2,6)(C_6F_5)\}(TMEDA)]$ (1). To a Schlenk flask containing a mixture of **HL** (4.80 g, 14 mmol) and TMEDA (2.1 mL, 14 mmol) in diethyl ether (30 mL) at 0°C was added a solution of $LiBu^n$ in hexane (1.6 M, 8.8 mL, 14 mmol). The resulting solution was stirred at room temperature for 2 h and then concentrated *in vacuo* to ca. 15 mL. Complex **1** was obtained as colourless crystals at room temperature (5.86 g, 12.6 mmol, 90%). M.p.: 121−123°C. ^{1}H NMR (500.30 MHz, C_6D_6): δ 7.19−7.21 (m, 3H, Ar*H*), 3.52 (septet, *J* = 7 Hz, 2H, C*H*Me$_2$), 1.62 (s, 12H, N*Me*$_2$), 1.49 (s, 4H, NC*H*$_2$), 1.30 (br, 12H, CH*Me*$_2$). ^{13}C{^{1}H} NMR (125.8 MHz, C_6D_6): δ 150.1, 142.5, 140.9 (br d, $^1J_{C–F}$ = 245 Hz) 138.8 (br d, $^1J_{C–F}$ = 268 Hz), 136.4, 126.2 (br d, $^1J_{C–F}$ = 227 Hz), 122.8, 122.0, 56.2, 44.7, 28.4, 24.5. ^{7}Li NMR (155.5 MHz, C_6D_6): δ 0.96 (s). ^{19}F NMR (376.6 MHz, C_6D_6): δ −165.2 (br s, 1F, C_6F_5), −167.1 (br s, 1F, C_6F_5), −170.5 (br s, 1F, C_6F_5), −176.0 (br s, 1F, C_6F_5), −192.9 (tt, $^3J_{F–F}$ = 23.6 Hz, $^4J_{F–F}$ = 15.1 Hz, 1F, C_6F_5). Anal. Found: C, 61.78; H, 7.20; N, 9.07%. Calc. for $C_{24}H_{33}F_5N_3Li$: C, 61.93; H, 7.15; N, 9.02%.

Synthesis of [Li{N($C_6H_3Pr^i{}_2$–2,6)(C_6F_5)}(THF)$_3$] (2). A solution of LiBu^n in hexane (7.5 mL, 1.6 M, 12 mmol) was slowly added via a syringe to **HL** (4.12 g, 12 mmol) in THF (30 mL) at 0°C. The resulting solution was stirred at room temperature for 2 h. It was concentrated *in vacuo* to ca. 10 mL yielding complex **2** as colourless crystals (4.61 g, 8.2 mmol, 68%). M.p.: 85−87°C (dec.). ^{1}H NMR (500.30 MHz, C_6D_6): δ 7.21 (d, *J* = 7.4 Hz, 2H, Ar*H*), 7.10 (m, 1H, Ar*H*), 3.57 (septet, *J* = 6.9 Hz, 2H, C*H*Me$_2$), 3.32 (m, 8H, THF),[33] 1.29 (m, 20H, CH*Me*$_2$ and THF). ^{13}C{^{1}H} NMR (125.8 MHz, C_6D_6): δ 150.3, 142.6, 141.4 (br d, $^1J_{C–F}$ = 231 Hz), 139.1 (br d, $^1J_{C–F}$ = 230 Hz), 136.2 (t, $^2J_{C–F}$ = 9 Hz), 126.2 (br d, $^1J_{C–F}$ = 228 Hz), 122.8, 121.8, 68.2, 28.3, 25.4, 24.5. ^{7}Li NMR (155.5 MHz, C_6D_6): δ 0.44 (s). ^{19}F NMR (376.6 MHz, C_6D_6): δ −166.4 (br s, 1F, C_6F_5), −168.4 (br s, 1F, C_6F_5), −171.0 (br s, 1F, C_6F_5), −175.4 (br s, 1F, C_6F_5), −194.0 (tt, $^3J_{F–F}$ = 22.6 Hz, $^4J_{F–F}$ = 15.4 Hz, 1F, C_6F_5).

Synthesis of [Co{N($C_6H_3Pr^i{}_2$–2,6)(C_6F_5)}Cl(TMEDA)] (3). A solution of **1** (1.28 g, 2.76

mmol) in toluene (20 mL) was slowly added to a slurry of $CoCl_2$ (0.36 g, 2.76 mmol) in toluene (10 mL) at room temperature. Stirring was continued at 40°C for 12 h, after which the solution was filtered and concentrated to ca. 5 mL. The *title complex* was obtained as deep blue crystals (1.29 g, 2.15 mmol, 78%). M.p.: 221−224°C (dec.). ^{19}F NMR (376.55 MHz, C_6D_6): δ −25.5 (br s), −65.6 (br s), −172.1 (br s). $\mu_{eff} = 3.98\ \mu_B$ (in C_7D_8 at 298K). Anal. Found: C, 54.91; H, 6.27; N, 7.21%. Calc. for $C_{24}H_{33}F_5N_3ClCo\cdot(0.5C_7H_8)$: C, 55.14; H, 6.23; N, 7.01%.

Synthesis of $[Co\{N(C_6H_3Pr^i_2–2,6)(C_6F_5)\}_2(\mu–Cl)Li(THF)_3]$ (4). To a slurry of $CoCl_2$ (0.32 g, 2.46 mmol) in THF (10 mL) was slowly added a solution of **2** (2.78 g, 4.92 mmol) in the same solvent (20 mL) at room temperature and stirring was continued for 12 h. All the volatiles were removed *in vacuo*, and the residue was extracted with diethyl ether (30 mL). Filtration followed by concentration of the solution to ca. 5 mL afforded complex **4** as blue crystals (1.04 g, 1.03 mmol, 42%). M.p. 101−104°C (dec.). $\mu_{eff} = 3.94\ \mu_B$ (in C_7D_8 at 298K). ^7Li NMR (155.5 MHz, C_6D_6): δ 44.7 (s). Anal. Found: C, 56.87; H, 6.40; N, 3.18%. Calc. for $C_{48}H_{58}F_{10}N_2O_3ClLiCo$: C, 57.52; H, 5.83; N, 2.79%.

Synthesis of $[Co\{N(C_6H_3Pr^i_2–2,6)(C_6F_5)\}(Me)(TMEDA)]$ (5). A solution of LiMe in diethyl ether (1.5 mL, 1.6 M, 2.4 mmol) was slowly added to a stirring solution of complex **3** (1.34 g, 2.24 mmol) in toluene (40 mL) at 0°C. The reaction mixture was brought to room temperature and stirred for 12 h. All the volatiles were removed *in vacuo* and the residue was extracted with hexane (50 mL). The solution was filtered and concentrated under reduced pressure to ca. 5 mL. Standing the solution at room temperature for one day yielded the complex **5** as green crystals (0.31 g, 0.58 mmol, 26%). M.p.: 128−132°C (dec.). $\mu_{eff} = 3.92\ \mu_B$ (in C_7D_8 at 298K). Anal. Found: C, 58.02; H, 7.04; N, 8.30%. Calc. for $C_{25}H_{36}F_5N_3Co$: C, 56.39; H, 6.81; N, 7.89%.

Synthesis of [Co{N($C_6H_3Pr^i_2$–2,6)(C_6F_5)}(N_3)(TMEDA)] (6). NaN_3 (0.18 g, 2.77 mmol) was added to a stirring solution of complex **3** (1.67 g, 2.79 mmol) in THF (40 mL) at 0°C. The reaction mixture was allowed to warm to 40°C and stirring was continued for 12 h. All the volatiles were removed *in vacuo* and the residue was extracted with toluene (50 mL). The solution was filtered through Celite and the filtrate was concentrated under reduced pressure to ca. 5 mL, yielding complex **6** as dark blue block-shaped crystals (0.72 g, 1.29 mmol, 46%). M.p.: 160−164°C (dec.). ^{19}F NMR (376.55 MHz, C_6D_6): δ −171.1 (br s), −213.7 (br s), −218.7 (br s). $\mu_{eff} = 3.83\ \mu_B$ (in C_7D_8 at 298K). Anal. Found: C, 51.18; H, 6.02; N, 15.28%. Calc. for $C_{24}H_{33}F_5N_6Co$: C, 51.52; H, 5.95; N, 15.02%.

Synthesis of [Co{N($C_6H_3Pr^i_2$–2,6)(C_6F_5)}$_2$(μ–OMe)Na(TMEDA)] (7). A solution of **3** (1.47 g, 2.45 mmol) in THF (30 mL) was added to a stirring suspension of NaOMe (0.16 g, 2.96 mmol) in the same solvent (10 mL) at room temperature. Stirring was continued at 40°C for 12 h, after which all the volatiles were removed *in vacuo*. The residue was extracted with toluene (40 mL). The solution was filtered and concentrated to ca. 5 mL, giving complex **7** as greenish blue crystals (0.90 g, 0.98 mmol, 40%). M.p.: 192−195°C (dec.). $\mu_{eff} = 3.82\ \mu_B$ (in C_7D_8 at 298K). Anal. Found: C, 55.01; H, 5.39; N, 6.07%.

Calc. for $C_{43}H_{53}F_{10}N_4ONaCo$: C, 56.52; H, 5.85; N, 6.13.[40]

Crystallographic Analysis. Single crystals of complexes **1**–**7** suitable for X-ray diffraction studies were mounted in glass capillaries and sealed under nitrogen. Data were collected on a Bruker SMART 1000 CCD diffractometer using graphite-monochromatized Mo–K_{α} radiation (λ = 0.71073 Å). The structures were solved by direct phase determination using the computer program SHELX-97 and refined by full-matrix least squares with anisotropic thermal parameters for non-hydrogen atoms.[46] Hydrogen atoms were introduced in their idealized positions and included in structure factor calculations with assigned isotropic temperature factors. Details of the data collection and crystallographic data are given in Table 1. CCDC 1050084–1050090 contain the supplementary crystallographic data for complexes **1**–**7**, respectively. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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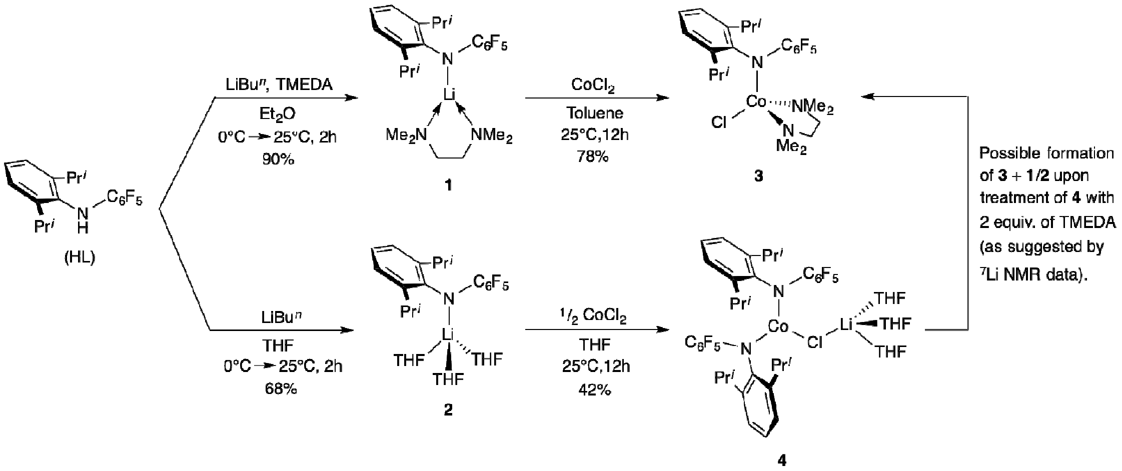
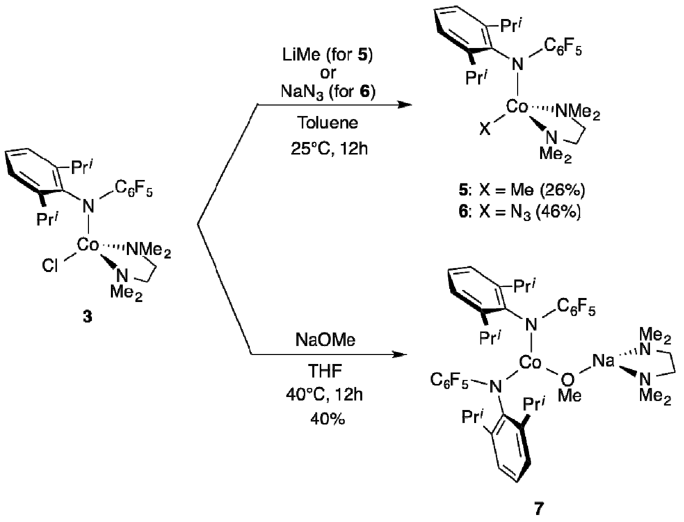


Scheme 1. Synthesis of lithium amides **1** and **2**, and cobalt(II) amido complexes **3** and **4**.



Scheme 2. Reactions of **3** with LiMe, NaN3 and NaOMe, respectively.

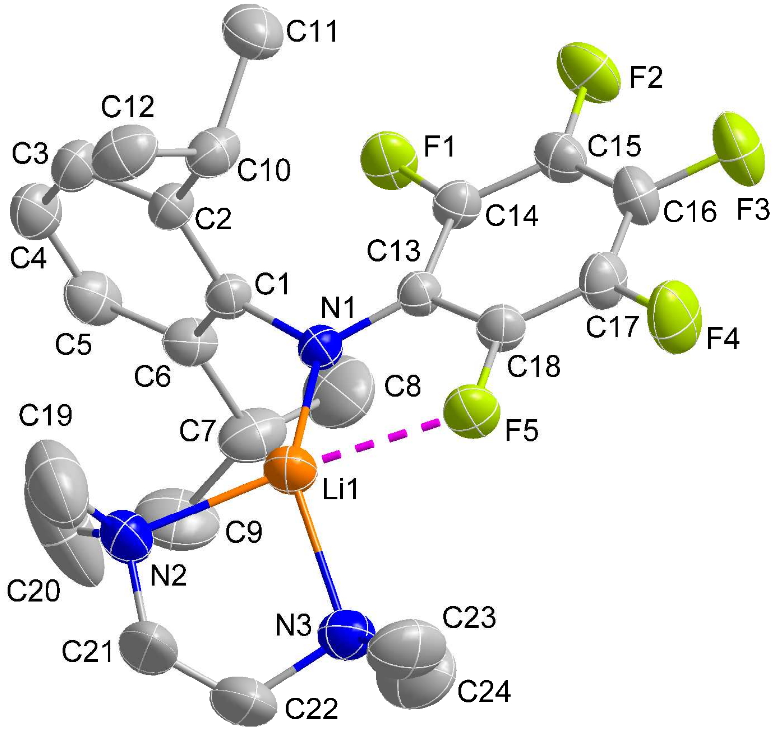


Figure 1. Molecular structure of [LiL(TMEDA)] (**1**) (30% thermal ellipsoid) with atom labelling. The ethylene group of the TMEDA ligand is 2-fold disordered and only one of the two possible orientations is shown for clarity. Selected bond lengths (Å) and angles (deg): Li(1)–N(1) 1.967(7), Li(1)–N(2) 2.146(8), Li(1)–N(3) 2.119(7), Li(1)···F(5) 2.355(7), N(1)–C(1) 1.434(4), N(1)–C(13) 1.355(4); N(1)–Li(1)–N(2) 121.6(4), N(1)–Li(1)–N(3) 138.6(4), N(2)–Li(1)–N(3) 85.8(3), Li(1)–N(1)–C(1) 118.9(3), Li(1)–N(1)–C(13) 120.8(3), C(1)–N(1)–C(13) 118.4(3).

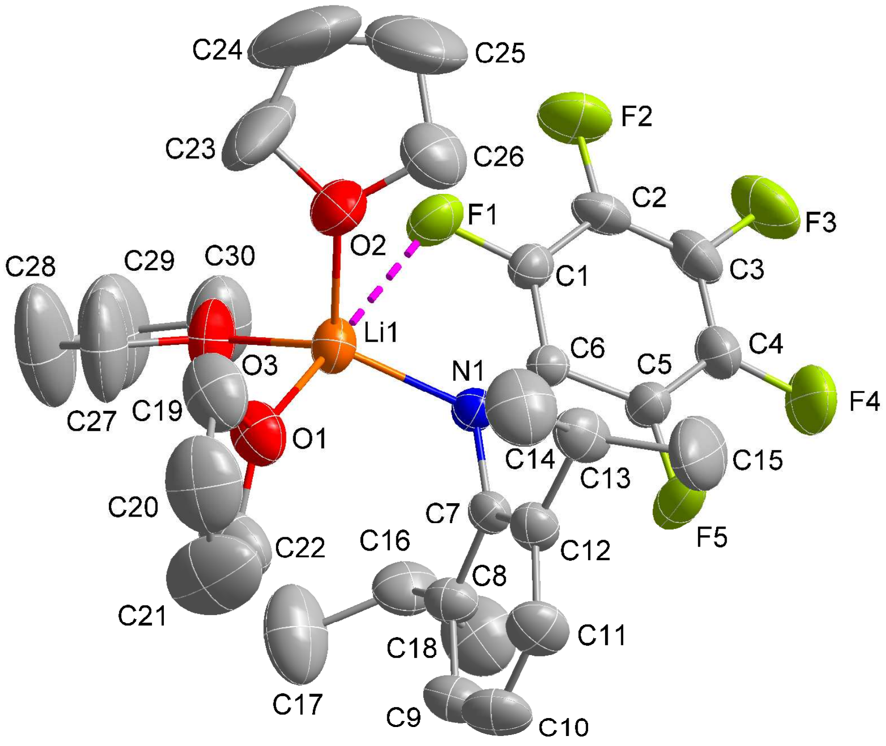


Figure 2. Molecular structure of [LiL(THF)$_3$] (**2**) (30% thermal ellipsoid) with atom labelling. Selected bond lengths (Å) and angles (deg): Li(1)–N(1) 2.030(4), Li(1)–O(1) 2.067(5), Li(1)–O(2) 1.998(6), Li(1)–O(3) 2.008(5), Li(1)···F(1) 2.698(3), N(1)–C(6) 1.345(3), N(1)–C(7) 1.416(3); N(1)–Li(1)–O(1) 112.9(9), N(1)–Li(1)–O(2) 117.3(3), N(1)–Li(1)–O(3) 120.6(5), Li(1)–N(1)–C(6) 127.6(2), Li(1)–N(1)–C(7) 112.6(3), C(6)–N(1)–C(7) 119.7(5).

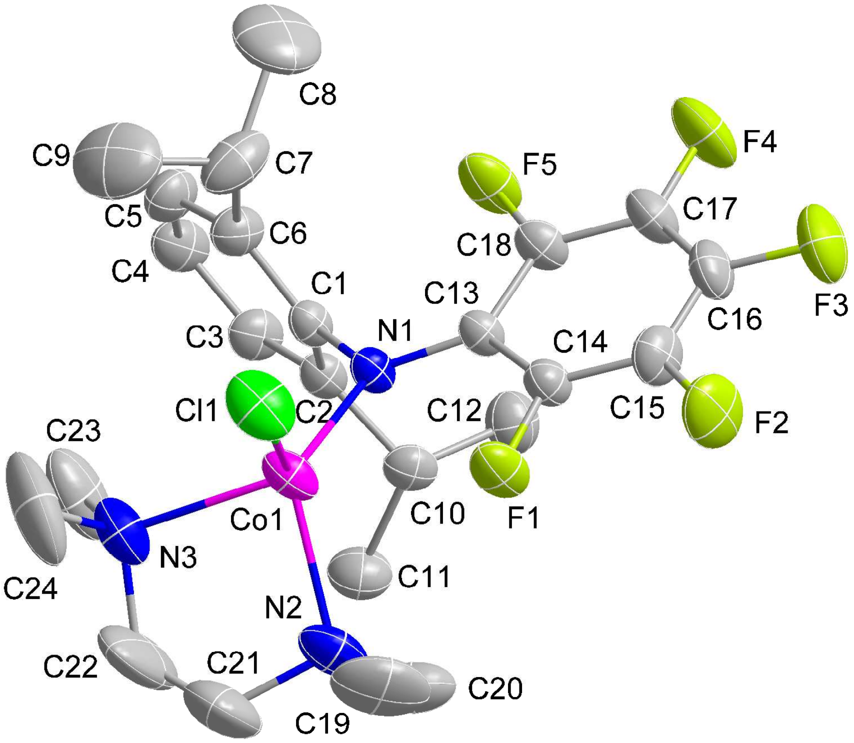


Figure 3. Molecular structure of [CoL(Cl)(TMEDA)]·0.5C_7H_8 (**3**·0.5C_7H_8) (30% thermal ellipsoid) with atom labelling. The toluene solvate molecule is omitted for clarity. Selected bond lengths (Å) and angles (deg): Co(1)–N(1) 1.977(4), Co(1)–N(2) 2.118(6), Co(1)–N(3) 2.168(6), Co(1)–Cl(1) 2.252(2), Co(1)···F(1) 2.560(4), N(1)–C(1) 1.453(7), N(1)–C(13) 1.362(7); N(1)–Co(1)–Cl(1) 114.8(1), N(1)–Co(1)–N(2) 120.2(2), N(1)–Co(1)–N(3) 116.9(2), N(2)–Co(1)–N(3) 85.9(3), N(2)–Co(1)–Cl(1) 111.0(1), N(3)–Co(1)–Cl(1) 103.7(1), Co(1)–N(1)–C(1) 117.8(3), Co(1)–N(1)–C(13) 123.1(3), C(1)–N(1)–C(13) 118.9(4).

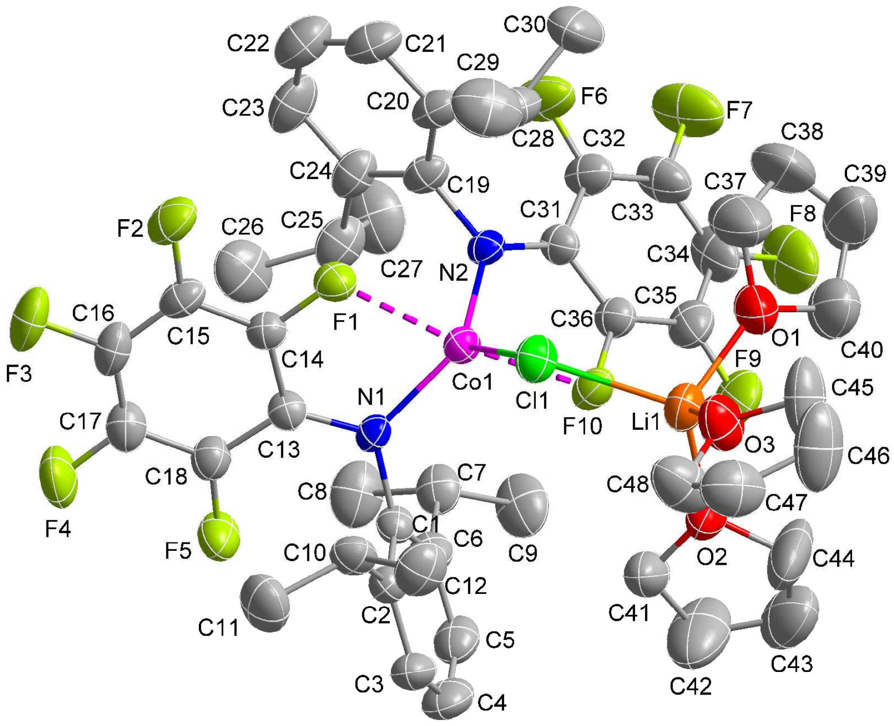


Figure 4. Molecular structure of $[CoL_2(\mu{-}Cl)Li(THF)_3]$ (**4**) (30% thermal ellipsoid) with atom labelling. Only one of the two independent molecules in the asymmetric unit is shown. Selected bond lengths (Å) and angles (deg): Co(1)–N(1) 1.927(5), Co(1')–N(1') 1.916(6), Co(1)–N(2) 1.917(4), Co(1')–N(2') 1.930(5), Co(1)–Cl(1) 2.265(2), Co(1')–Cl(1') 2.245(3), Co(1)···F(1) 2.354(4), Co(1')···F(1') 2.465(3), Co(1)···F(10) 2.439(4), Co(1')···F(6') 2.399(3), N(1)–C(1) 1.432(7), N(1')–C(1') 1.459(8), N(1)–C(13) 1.374(9), N(1')–C(13') 1.354(9), N(2)–C(19) 1.440(7), N(2')–C(19') 1.429(7), N(2)–C(31) 1.378(9), N(2')–C(36') 1.377(7), Li(1)–Cl(1) 2.38(1), Li(1')–Cl(1') 2.35(1), Li(1)–O(1) 1.93(1), Li(1')–O(1') 1.91(1), Li(1)–O(2) 1.88(1), Li(1')–O(2') 1.93(1), Li(1)–O(3) 1.96(1), Li(1')–O(3') 1.87(2); N(1)–Co(1)–N(2) 124.0(5), N(1')–Co(1')–N(2') 126.3(0), N(1)–Co(1)–Cl(1) 116.1(2), N(1')–Co(1')–Cl(1') 116.1(2), N(2)–Co(1)–Cl(1) 119.7(9), N(2')–Co(1')–Cl(1') 117.5(5), Co(1)–Cl(1)–Li(1) 116.5(4), Co(1')–Cl(1')–Li(1') 129.9(3).

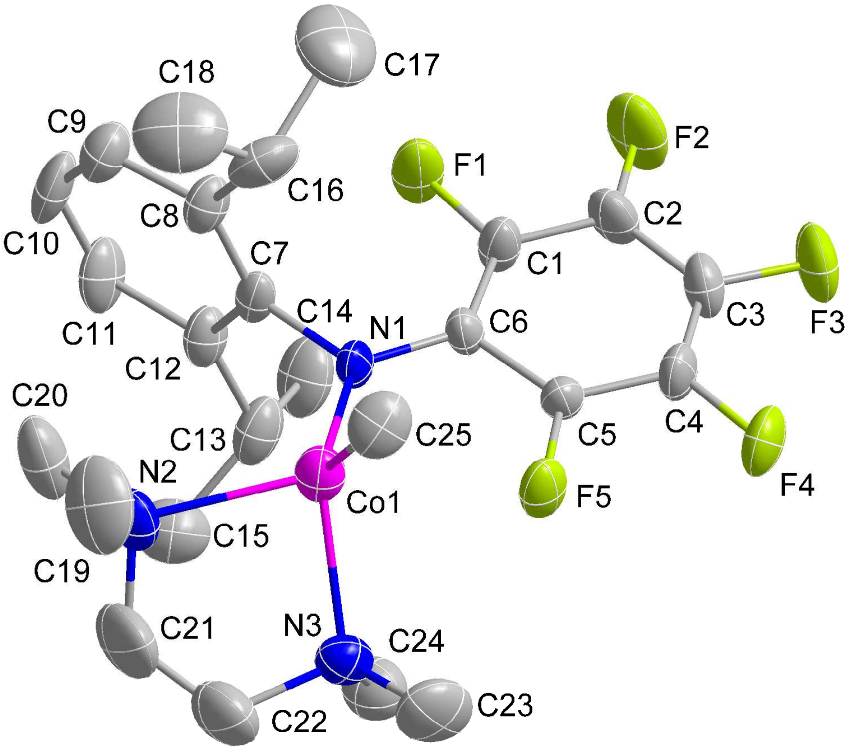


Figure 5. Molecular structure of [CoL(Me)(TMEDA)] (**5**) (30% thermal ellipsoid) with atom labelling. Selected bond lengths (Å) and angles (deg): Co(1)–N(1) 1.998(6), Co(1)–N(2) 2.19(1), Co(1)–N(3) 2.141(6), Co(1)–C(25) 2.04(1), Co(1)···F(5) 2.607(7), N(1)–C(7) 1.47(1), N(1)–C(6) 1.366(1); N(1)–Co(1)–C(25) 116.8(0), N(1)–Co(1)–N(2) 113.7(7), N(1)–Co(1)–N(3) 118.0(1), N(2)–Co(1)–N(3) 84.9(8), C(6)–N(1)–C(7) 116.0(8), C(7)–N(1)–Co(1) 117.6(9), C(6)–N(1)–Co(1) 125.2(8).

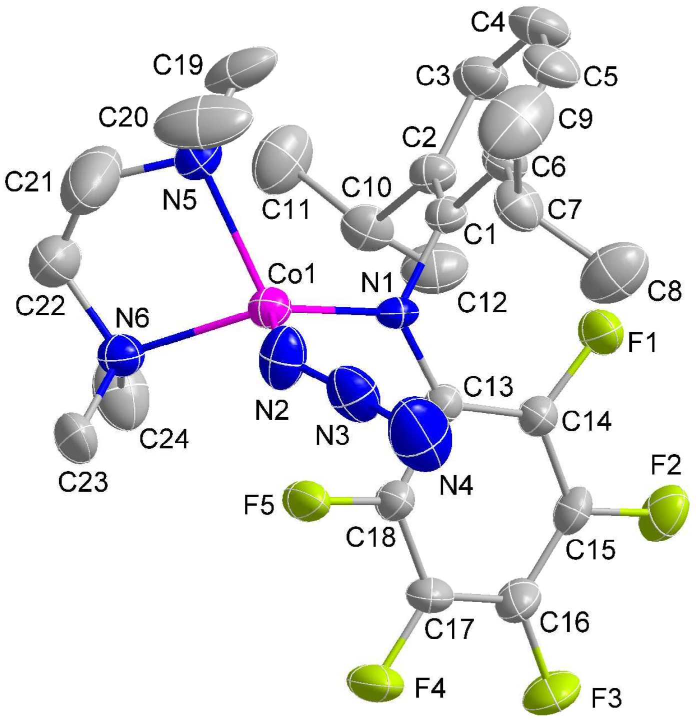


Figure 6. Molecular structure of [CoL(N_3)(TMEDA)] (**6**) (30% thermal ellipsoid) with atom labelling. Carbon atom C(21) of the TMEDA ligand is 2-fold disordered and only one of the two possible orientations is shown for clarity. Selected bond lengths (Å) and angles (deg): Co(1)–N(1) 1.961(4), Co(1)–N(2) 1.930(6), Co(1)–N(5) 2.147(5), Co(1)–N(6) 2.116(4), Co(1)···F(5) 2.563(3), N(1)–C(1) 1.441(6), N(1)–C(13) 1.381(5), N(2)–N(3) 1.169(7), N(3)–N(4) 1.166(8); N(1)–Co(1)–N(2) 116.7(2), N(1)–Co(1)–N(5) 116.8(1), N(1)–Co(1)–N(6) 122.7(1), N(5)–Co(1)–N(6) 85.1(1), N(2)–N(3)–N(4) 175.4(7), C(1)–N(1)–C(13) 117.3(4), C(1)–N(1)–Co(1) 118.3(3), C(13)–N(1)–Co(1) 124.4(3).

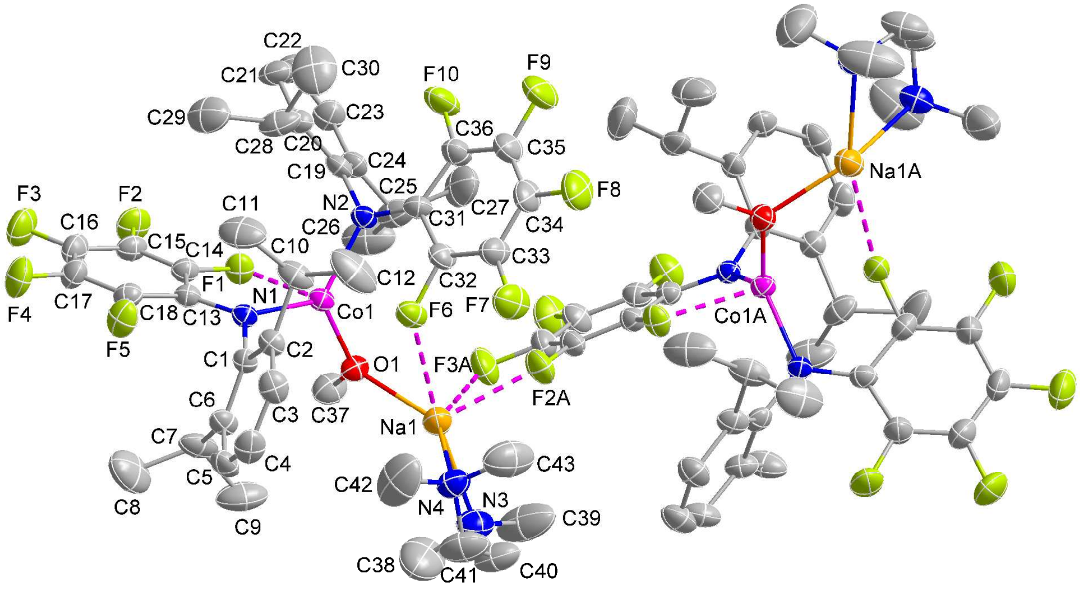


Figure 7. Polymeric structure of [CoL$_2$(μ–OMe)Na(TMEDA)]$_\infty$ (**7**) (30% thermal ellipsoid) showing intermolecular Na···F interactions Na(1)···F(2A) and Na(1)···F(3A). Selected bond lengths (Å) and angles (deg): Co(1)–O(1) 1.862(4), Co(1)–N(1) 1.957(4), Co(1)–N(2) 1.955(5), Co(1)···F(1) 2.365(3), Co(1)···Na(1) 3.543(3), Na(1)–O(1) 2.193(5), Na(1)–N(3) 2.443(7), Na(1)–N(4) 2.448(7), Na(1)···F(6) 2.873(5), Na(1)···F(2A) 2.450(5), Na(1)···F(3A) 2.980(5), O(1)–C(37) 1.407(7); N(1)–Co(1)–N(2) 122.3(2), N(1)–Co(1)–O(1) 116.9(1), N(2)–Co(1)–O(1) 120.8(8), Co(1)–O(1)–C(37) 122.8(5), Co(1)–O(1)–Na(1) 121.5(6), Na(1)–O(1)–C(37) 115.5(4), O(1)–Na(1)–N(3) 126.7(8), O(1)–Na(1)–N(4) 130.6(9), N(3)–Na(1)–N(4) 76.2(3), C(1)–N(1)–C(13) 119.1(2), C(1)–N(1)–Co(1) 120.3(4), C(13)–N(1)–Co(1) 118.6(5), C(31)–N(2)–C(19) 119.1(2), C(31)–N(2)–Co(1) 121.2(2), C(19)–N(2)–Co(1) 119.6(6).

Symmetry code: A: 1–x, 0.5+y, 0.5–z.

Table 1. Selected crystallographic data for complexes **1**–**7**.

	1	**2**	**3**·0.5C_7H_8
Molecular formula	$C_{24}H_{33}F_5LiN_3$	$C_{30}H_{41}F_5LiNO_3$	$C_{27.5}H_{37}ClCoF_5N_3$
Molecular weight	465.47	565.58	598.98
Crystal size, mm^3	0.50 × 0.40 × 0.30	0.40 × 0.30 × 0.20	0.40 × 0.30 × 0.20
Crystal system	Orthorhombic	Triclinic	Monoclinic
Space group	*Pbca*	$P\bar{1}$	$P2_1/c$
a, Å	16.136(6)	10.5988(4)	9.994(3)
b, Å	15.686(5)	11.3054(4)	14.749(4)
c, Å	20.361(7)	14.5494(5)	20.746(6)
α, deg	90	78.472(1)	90
β, deg	90	81.181(1)	93.793(6)
γ, deg	90	67.493(1)	90
Z	8	2	4
V, Å^3	5154(3)	1572.4(1)	3051(1)
Density, g cm^{-3}	1.200	1.195	1.304
Abs. coeff., mm^{-1}	0.095	0.095	0.700
Temperature, K	293(2)	296(2)	293(2)
Reflection collected	33329	22427	20371
Independent reflections	6202 (R_{int} = 0.0947)	7465 (R_{int} = 0.0418)	7409 (R_{int} = 0.1011)
Obs. data with $I \geq 2\sigma(I)$	2166	2734	2573
Final R indices $[I \geq 2\sigma(I)]^*$	$R1 = 0.0713$ $wR2 = 0.1824$	$R1 = 0.0628$ $wR2 = 0.1815$	$R1 = 0.0760$ $wR2 = 0.1887$
R indices (all data)	$R1 = 0.1918$ $wR2 = 0.2835$	$R1 = 0.1766$ $wR2 = 0.2376$	$R1 = 0.2203$ $wR2 = 0.2751$

$^*R1 = \sum| |F_o|-|F_c| | / \sum|F_o|$; $wR2 = \{\sum[w(F_o^2-F_c^2)^2] / \sum[w(F_o^2)^2]\}^{1/2}$

Table 1 (Cont'd). Selected crystallographic data for complexes **1**–**7**.

	4	**5**
Molecular formula	$C_{48}H_{58}ClCoF_{10}LiN_2O_3$	$C_{25}H_{36}CoF_5N_3$
Molecular weight	1002.28	532.50
Crystal size, mm^3	0.40 × 0.40 × 0.30	0.30 × 0.30 × 0.20
Crystal system	Triclinic	Monoclinic
Space group	$P\bar{1}$	$C2/c$
a, Å	12.420(1)	19.029(5)
b, Å	19.505(3)	19.750(5)
c, Å	23.260(3)	16.221(4)
α, deg	65.658(3)	90
β, deg	87.724(3)	117.007(6)
γ, deg	86.802(3)	90
Z	4	8
V, $Å^3$	5125(1)	5432(2)
Density, g cm^{-3}	1.299	1.302
Abs. coeff., mm^{-1}	0.463	0.683
Temperature, K	293(2)	293(2)
Reflection collected	35118	12749
Independent reflections	24220 (R_{int} = 0.0598)	4605 (R_{int} = 0.1403)
Obs. data with $I \geq 2\sigma(I)$	7304	1645
Final R indices $[I \geq 2\sigma(I)]$*	$R1 = 0.0806$ $wR2 = 0.1856$	$R1 = 0.0893$ $wR2 = 0.2305$
R indices (all data)	$R1 = 0.2428$ $wR2 = 0.2625$	$R1 = 0.1987$ $wR2 = 0.3341$

*$R1 = \sum| |F_o|-|F_c| | / \sum|F_o|$; $wR2 = \{\sum[w(F_o^2-F_c^2)^2] / \sum[w(F_o^2)^2]\}^{1/2}$

Table 1 (Cont'd). Selected crystallographic data for complexes **1**–**7**.

	6	**7**
Molecular formula	$C_{24}H_{33}CoF_5N_6$	$C_{43}H_{53}CoF_{10}N_4NaO$
Molecular weight	559.49	913.81
Crystal size, mm^3	0.40 × 0.40 × 0.30	0.30 × 0.30 × 0.20
Crystal system	Monoclinic	Orthorhombic
Space group	$P2_1/c$	$P2_12_12_1$
a, Å	17.693(3)	12.6998(7)
b, Å	10.155(1)	17.6511(9)
c, Å	15.929(3)	20.930(1)
α, deg	90	90
β, deg	108.922(3)	90
γ, deg	90	90
Z	4	4
V, Å^3	2707.4(8)	4691.9(4)
Density, g cm^{-3}	1.373	1.294
Abs. coeff., mm^{-1}	0.692	0.450
Temperature, K	293(2)	296(2)
Reflection collected	14467	24638
Independent reflections	4905 (R_{int} = 0.0946)	11102 (R_{int} = 0.0832)
Obs. data with $I \geq 2\sigma(I)$	2361	4830
Final R indices $[I \geq 2\sigma(I)]^*$	$R1 = 0.0584$ $wR2 = 0.1229$	$R1 = 0.0558$ $wR2 = 0.0892$
R indices (all data)	$R1 = 0.1288$ $wR2 = 0.1569$	$R1 = 0.1755$ $wR2 = 0.1205$

$^*R1 = \sum||F_o|-|F_c|| / \sum|F_o|$; $wR2 = \{\sum[w(F_o^2-F_c^2)^2] / \sum[w(F_o^2)^2]\}^{1/2}$

For Table of Contents Entry

A series of cobalt(II) complexes derived from the C_6F_5-substituted amido ligand $[N(C_6F_5)(C_6H_3Pr^i_2–2,6)]^-$ (L) have been prepared and structurally characterized.