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Synthesis and characterization of a family of Co(II) triphenylamido-amine complexes and catalytic activity in controlled radical polymerization of olefins

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Dedicated to the memory of Alfred Werner, the founder of modern coordination chemistry, on the 100th Anniversary of his Nobel Prize in Chemistry in 1913.

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ABSTRACT

The present work reports a new family of tripodal Co^{II} complexes bearing trianionic triphenylamidoamine ligands with a variety of pendant arms (aryl, acyl, alkyl). These complexes have been synthesized by the reaction of anhydrous CoCl₂ with the deprotonated ligands and exhibit stoichiometric and structural variation. The solid-state structures of these compounds reveal that in all cases the four nitrogen-atom residues of the ligands are coordinated to the metal center in a distorted trigonal-pyramidal geometry. In two cases, the presence of acetonitrile adds a fifth moiety to the coordination sphere. Among the aryl-armed Co^{II} reagents, $[K(L^3)Co^{II}-NCMe]_n$ (1), $[K(THF)_6][(L^5)Co^{II}] \cdot 1.5THF$ (2) and $[K(NCMe)_3(L^{13}) \cdot 1.5THF$ (2) and $[K(NCMe)_3(L^{13}) \cdot 1.5THF]$ Co^{II}–NCMe] (6), the two five-coordinate structures (1, 6) exhibit distorted trigonal bipyramidal geometries, with that of **6** being the least distorted. The four-coordinate species **2** is the only compound with a distinct anionic $[(L^5)Co^{II}]^-$ component, since the K⁺ ion is solely coordinated by solvent molecules. The acyl-armed Co^{II} compounds $[K(THF)_2(L^8)Co^{II}]_n$ (**3**) and $\{[K_2(DMA)_3(L^{10})_2Co^{II}_2] \cdot 0.5Et_2O\}_n$ (**5**) are strictly four-coordinate species, with the carbonyl moieties oriented exo with respect to the cavity of the vacant coordination site. Finally, compound $[K_2(L^9)_2Co^{II}_2]_n$ (4) is the only example bearing an alkyl-armed ligand, and exhibits a geometry featuring a repeating $-[Co(1)-K(1)-Co(2)-K(2)]_n$ sequence. All compounds have been characterized by spectroscopic and electrochemical techniques. Compounds 1, 2, 4, and 6 show reversible or semi-reversible Co^{II}/Co^{III} redox couples, whereas the electron-deficient complexes 3 and 5 exhibit irreversible anodic waves. The catalytic reactivity of these complexes towards controlled radical polymerization (CRP) of styrene (St) and methyl methacrylate (MMA) has been studied and preliminary results are presented. Compounds 4 and 5 seem to be the most reactive with both monomers, giving high vields of polymers (60–86%), **3** efficiently induces styrene polymerization (90%), whereas **2** and **6** provide lower yields (12-16% for PS and 30-45% for PMMA). The steric factor seems to play an essential role, since Co^{II} compounds that feature a less hindered fifth coordination site show the highest reactivity and better control over polymerization. The polymers obtained are predominately syndiotactic, consistent with radical polymerization, with two exceptions (1, 2) that exhibit unusually high ratios of isotactic triads. Interestingly, in many cases, the polymers obtained feature bimodal distributions, while the molecular weight distributions are not very broad (1.40-2.00), and this strongly indicates that two parallel mechanisms may be in operation.

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1. Introduction

Radical polymerization reactions mediated by cobalt reagents [1] have played a historic role in the development of controlled radical polymerization (CRP) processes, owing to the early, seminal contributions of Wayland et al. [2] and Harwood and co-workers

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[3]. More recent work has shown that cobalt reagents can be intriguingly more complex in their mode of operation, and can induce CRP reactions not only via atom-transfer radical polymerization (ATRP) mechanisms, but also via organometallic-mediated radical polymerization (OMRP) pathways that rely on the well-known propensity of the Co–C bond towards cleavage and generation of carbon-centered radicals.

For the mechanistically related atom-transfer radical addition (ATRA) and polymerization (ATRP) reactions, the key step is a reversible halogen-atom transfer between an organohalide (RX) and the cobalt site, shuttling between two oxidation states



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 (Co^{II}/Co^{III}) (Chart 1) [4,5]. The resulting R radical could then add to an olefin to generate a new organic radical, which would either be halogenated to provide the monomeric product (ATRA) [6] or continue adding olefin to afford a living polymer (ATRP). Its success relies on the control exercised by the dynamic equilibrium $(K_{ATRP} = k_{act}/k_{deact})$ established between the halide-capped dormant species (P_n-X) and the propagating radical (P_n'), which is very sensitive to the catalyst, olefin monomer, and RX (initiator) used, and depend on the solvent and the reaction conditions [7].

On the other hand, the OMRP process (or CMRP, for cobalt-mediated radical polymerization) relies on an equilibrium (Chart 2(a), demonstrated by vinyl acetate) heavily favoring a cobalt-capped dormant form of the polymer radical (Co^{III}–P_n). An alternative, albeit related, process, known as catalytic chain transfer polymerization (CCTP), applies to substrates that are prone to β-H elimination (methacrylates, α-methylstyrene, methacrylonitrile), inasmuch as the Co^{III}–P_n species may induce β-H atom abstraction to generate a Co^{III}–H and a polymer chain with an unsaturated terminal group (Chart 2(b), demonstrated for methyl methacrylate (MMA)). The Co^{III}–H is a key ingredient of the catalytic cycle, because it can generate the primary radical species via insertion of the hydride into the monomer (for instance MMA).

The ATRP mechanism is apparently followed by cobaltocene, acting as a precatalyst in the polymerization of styrene (St) and MMA [8]. Other common Co^{II} species, such as cobalt carboxylates are also known to induce ATRP reactions of MMA and St (oligomerization) [9-11]. In particular, cobalt acetate polymerizes MMA in good yields (82%) and narrow polydispersity (M_w/M_n = 1.26). Addition of small amounts of CoCl₂, Cu(OAc)₂ or tris(2-(dimethyl amino) ethyl)amine (Me₆TREN), improves the rate of the reaction, but the control over the polymerization is reduced (M_w) $M_{\rm n}$ = 1.49–1.74) [9]. The CoCl₂/Me₆TREN system has been reported as catalyst for the ATRP of MMA, exerting modest control over the polymerization and molecular weight distribution of PMMA (M_w) $M_{\rm p}$ = 1.63–1.80) [12], which can be improved by addition of a small amount of hybrid deactivators (FeBr₃/Me₆TREN or CuBr₂/Me₆₋ TREN; $M_w/M_n = 1.15 - 1.46$). Heterogeneous versions have also been developed, such as a Co^{II}/Cu^{II} bimetallic catalyst immobilized on a cross-linked poly(acrylic acid) resin [13] or a "hybrid" catalyst,



consisting of Co^{II} immobilized on an ion exchange resin along with a small amount of soluble catalyst (CuCl₂/Me₆TREN) [14]. Among Co^I systems, [CoX(PPh₃)₃] (X = Cl, Br, I) are the first compounds reported to mediate ATRP reactions [15], with the iodide being the most reactive. On the other hand, the OMRP mechanism is reportedly obeyed by [Co(acac)₂] in the polymerization of vinyl acetate, and co-polymerization of vinyl acetate and vinyl chloroacetate [16–19], as well as by Co^{II} porphyrin complexes in the polymerization of acrylate monomers [2,20–22]. Finally, low-spin Co^{II} complexes, such as cobaloximes [23], Co^{II}-5,10,15,20-tetraphenyl-21*H*,23*H*-porphine [24], and Co^{II}-glyoximato species [25–28] operate via the CCTP mechanism in the (co)polymerization of (meth)acrylates, α -methylstyrene and styrenes, yielding low molecular weight macromolecules in organic and aqueous media.

Recently, we, and others, have been exploring the synthesis and reactivity of a series of tripodal transition metal compounds (M = Fe, Mn, Co) with rigid triphenylamido-amine cores and a variety of pendant arms (R = aryl, acyl, alkyl) (Chart 3) [29–38]. While we have been largely investigating catalytic C–O and C–N bond construction via oxo- and nitrene-transfer chemistry, we have more recently recognized that many members of this family of reagents are active in CRP catalysis, enabled by a reversible or semi-reversible $M^{n+}/M^{(n+1)+}$ couple at easily accessible, and frequently highly reducing potentials. In this manuscript we are reporting the synthesis and characterization of a series of tripodal Co^{II} triphenylamido-amine complexes bearing a selection of aryl, acyl and alkyl arms. We are also disclosing CRP related data, mediated by these reagents.

2. Experimental

2.1. Materials and physical measurements

All operations were performed under anaerobic conditions under a pure dinitrogen or argon atmosphere using Schlenk techniques on an inert gas/vacuum manifold or in a dry-box (O_2 , $H_2O < 1$ ppm). Anhydrous diethyl ether, acetonitrile, tetrahydrofuran, hexane, pentane, toluene, chloroform, dimethylformamide (DMF), and dimethylacetamide (DMA) were purchased from Sigma–Aldrich. Methanol was distilled over the corresponding magnesium alkoxide, and acetone was distilled over drierite. Solvents were degassed by three freeze–pump–thaw cycles. Unless otherwise noted, all other reagents were purchased at the highest purity available. Potassium hydride was provided as dispersion in mineral oil and was thoroughly washed prior to use with copious amounts of tetrahydrofuran followed by hexane. Compounds L^3H_3 , L^5H_3 , L^8H_3 and L^9H_3 have been prepared according to literature methods [31].

¹H NMR and ¹³C NMR spectra were recorded on a Varian XL-400, a Varian INOVA/UNITY 400 MHz and a Varian 300 Unity Plus NMR spectrometers. IR spectra were obtained on a Perkin-Elmer 883 IR spectrometer and FT-IR spectra on a Shimadzu IR-Affinity-1 spectrometer. UV-Vis spectra were obtained on a Hewlett-Packard 8452A diode array, a Varian Cary 50, and a Varian Cary 300 spectrophotometers. Microanalyses were done by Galbraith Laboratories, Knoxville, TN, Quantitative Technologies Inc., Whitehouse, NI, and on an in-house Perkin-Elmer 2400 CHN analyzer, HRMS data were collected on a Thermo Fisher Scientific LTO-Orbitrap XL hybrid mass spectrometer, using the Orbitrap analyzer for acquisition of high-resolution accurate mass data. Samples were infused using the integrated syringe pump at 3 µL/min and ionization was via the electrospray source with source settings at their defaults. In general, settings for the ion optics were determined automatically during the regular tuning and calibration of the instrument. For high-resolution data, the Orbitrap analyzer is set











to a resolution of 100000. SEC experiments were carried out at 40 °C using a modular instrument consisting of a Waters model 510 pump, U6K sample injector, 401 refractometer, 486 UV spectrophotometer, and a set of 5 l-Styragel columns with a continuous porosity range from 500 to 10^6 Å. The columns were housed in an oven thermostated at 40 °C. CHCl₃ was the carrier solvent at a flow rate of 1 mL/min. The system was calibrated with nine PS standards having molecular weights in the range of 970–600,000.

Cyclic voltammetry was carried out with an Eco Chemie Autolab PGSTAT100 electrochemical workstation fitted in a Dry Box and controlled with a General Purpose Electrochemical Software (GPES) or with a Bipotentiostat AFCBP1 from Pine Instrument Company fitted in a Dry Box and controlled with the PineChem 2.7.9 software. Experiments were performed using a gold disk working electrode (2 mm diameter) and a Ag/Ag^+ (0.01 M $AgNO_3$ and 0.5 M $[(n-Bu)_4N]PF_6$ in MeCN or DMF) non-aqueous reference electrode (Bioanalytical Systems, Inc.) with a prolonged bridge $(0.5 \text{ M} [(n-Bu)_4\text{N}]\text{PF}_6$ in MeCN or DMF). A thin Pt foil or gauge (8 cm², Sigma–Aldrich) was employed as counter electrode. The working electrode was polished using successively 6, 3, 1 µm diamond paste on a DP-Nap polishing cloth (Struers, Westlake, OH), washed with water, acetone and air-dried. The Pt foil and gauge electrodes were cleaned in a $H_2O_2/H_2SO_4(conc)$ solution (1:4 v:v) and oven-dried. The concentrations of the samples were between 1 and 3 mM and that of $[(n-Bu)_4N]PF_6$ (supporting electrolyte) was 0.5 M. The potential sweep rate varied between 10 and 1000 mV/s. All potentials are reported versus the ferrocenium/ferrocene (Fc^+/Fc) couple.

2.2. Synthesis

2.2.1. Synthesis of $[(tert-butyl-O-CO)-NH-(2-C_6H_4)]_3N (L^{10}H_3)$

In a 100 mL Schlenk flask was added $(2-NH_2-C_6H_4)_3N$ (1.16 g, 4.0 mmol) and NaH (0.43 g, 18.0 mmol) in THF (30 mL), and the mixture was refluxed for 2 h. The reaction mixture was allowed to cool at room temperature, di-tert-butyldicarbonate (3.45 mL, 15.0 mmol) was added, and then the mixture was refluxed for 12 h. Water (5.0 mL) was then added to the reaction mixture. followed by further refluxing for 6 h. The solvent was removed, and the crude residue was dissolved in dichloromethane. This solution was dried over Na₂SO₄. The product was purified by column chromatography (silica gel), and the fragment eluting with petroleum ether/ethyl acetate (8:1) was collected to give the ligand as a white crystalline solid (1.94 g, 82%). ¹H NMR (CDCl₃, 7.27 ppm): δ 7.58 (d, 3H, aryl), 7.08 (t, 3H, aryl), 7.03 (s, 3H, NH), 6.95 (t, 3H, aryl), 6.74 (d, 3H, aryl), 1.32 (s, 27H). 13 C NMR (CDCl₃, 77 ppm): δ 153.28, 138.18, 131.93, 124.88, 124.50, 124.18, 79.77, 28.09. IR (KBr, cm⁻¹): 3427, 3360, 3239, 3119, 2980, 2931, 1734, 1692, 1595, 1528, 1476, 1443, 1391, 1366, 1300, 1277, 1239, 1152, 1052, 1025, 942, 923, 857, 757, 619. HRMS calcd. for C₃₃H₄₂N₄O₆ (M⁺): 590.30955; found 590.31183. Elem. Anal. Calc. for C₃₃H₄₂N₄O₆: C, 67.10; H, 7.17; N, 9.48. Found: C, 67.14; H, 7.23; N, 9.53%.

2.2.2. Synthesis of $[(2,6-di-methyl-C_6H_3)-NH-(2-C_6H_4)]_3N(L^{13}H_3)$

In a 100 mL Schlenk flask, $[Pd_2(dba)_3]$ (tris(dibenzylideneacetone)dipalladium, 0.0912 g, 0.10 mmol) and BINAP (2,2'bis(diphenylphosphino)-1,1'-binaphthyl, 0.1866 g, 0.30 mmol) were stirred in anhydrous toluene (10 mL), and heated until BINAP dissolved. To the resulting cherry-red solution was added (2-NH₂-C₆H₄)₃N (0.58 g, 2.0 mmol), 2,6-dimethylbromobenzene (2.22 g, 12.0 mmol), and *tert*-Bu-ONa (1.96 g, 20.0 mmol). The slurry was refluxed for 48 h to give a brown solution, with precipitation of a solid. The mixture was allowed to cool to room temperature, the solution was filtered, and the filtrate was evaporated under vacuum to give a brown residue. The residue was purified by column chromatography (silica gel). The fragment eluting with petroleum ether/ethyl acetate (50:1 v/v) was collected, and the resulting pale yellow solid was recrystallized from THF/petroleum ether to afford the ligand as a crystalline solid suitable for X-ray diffraction analysis (0.77 g, 64%). ¹H NMR (CDCl₃, 7.27 ppm): δ 7.19 (d, 3H, aryl), 6.93 (m, 12H, aryl), 6.73 (t, 3H, aryl), 6.16 (d, 3H, aryl), 5.6 (s, 3H, NH), 2.22 (s, 9H), 1.8 (s, 9H), 1.52 (s, 9H). ¹³C NMR (CDCl₃, 77 ppm): δ 141.08, 137.88, 136.05, 135.81, 132.22, 128.61, 128.46, 126.21, 125.91, 118.55, 112.75, 17.99, 17.41. IR (KBr, cm⁻¹): 3378, 3342, 3064, 3032, 2948, 2916, 2851, 1925, 1586, 1499, 1473, 1454, 1307, 1263, 1225, 1153, 1099, 1036, 916, 770, 745, 692, 623. HRMS calcd. for C₄₂H₄₂N₄ (M⁺): 602.33983; found 602.34180. Elem. *Anal.* Calc. for C₄₂H₄₂N₄: C, 83.68; H, 7.02; N, 9.29. Found: C, 83.54; H, 7.11; N, 9.27%.

2.2.3. Synthesis of $[K(L^3)Co^{II}-NCMe]_n$ (1)

The ligand $L^{3}H_{3}$ (0.463 g. 0.5 mmol) was dissolved in degassed THF (15.0 mL), and KH (0.060 g, 1.5 mmol) was added to this solution. The mixture was allowed to stir overnight, followed by addition of anhydrous CoCl₂ (0.065 g, 0.5 mmol). This mixture was stirred for an additional 24 h to afford a dark brown solution. The solution was refrigerated (-30 °C) for about 6 h. The insoluble salts were filtered off on an anaerobic frit, the filtrate was evaporated to dryness, and the residue was dissolved in acetonitrile (3.0 mL). Diethyl ether (10.0 mL) was carefully layered over acetonitrile, and pentane (10.0 mL) was further carefully layered over the ether. The system is allowed to slowly mix at room temperature to afford brown crystalline material of the title compound, suitable for X-ray diffraction analysis (0.383 g, 72%). IR (KBr, cm⁻¹): 3435, 3043, 2974, 2873, 1610, 1587, 1482, 1466, 1388, 1276, 1171, 1127, 1047, 996, 965, 859, 747, 702, 682, 668, 614, 545, 486, 425. UV-Vis (MeCN, nm), (*ε*, M⁻¹ cm⁻¹): 338 (33100), 473 (sh), 575 (sh), 745 (110). Elem. Anal. Calc. for C44H24N5F18CoK: C, 49.71; H, 2.28; N, 6.59. Found: C, 49.61; H, 2.31; N, 6.64%.

2.2.4. Synthesis of $[K(THF)_6][(L^5)Co^{II}] \cdot 1.5THF$ (2)

The ligand $L^{5}H_{3}$ (0.363 g, 0.5 mmol) was dissolved in degassed THF (15.0 mL), and KH (0.060 g, 1.5 mmol) was added to this solution. The mixture was allowed to stir overnight, followed by addition of anhydrous CoCl₂ (0.065 g, 0.5 mmol). This mixture was stirred for an additional 24 h to afford a green-brown solution. The solution was refrigerated $(-30 \circ C)$ overnight and the insoluble salts were filtered off on an anaerobic frit. The filtrate was reduced to 3.0 mL by evaporation, and pentane (10.0 mL) was carefully layered over the THF solution. The system is allowed to slowly mix at room temperature to afford green crystalline material, suitable for X-ray diffraction analysis (0.386 g, 57%). FT-IR (KBr, cm^{-1}): 3448, 3097, 3057, 2974, 2872, 1560, 1540, 1534, 1478, 1438, 1330, 1283, 1220, 1157, 1103, 1048, 981, 963, 891, 857, 826, 788, 753, 747, 669, 620, 594, 583, 547, 489. UV–Vis (THF, nm), (*ε*, M⁻¹ cm⁻¹): 420 (sh), 457 (sh), 606 (160); (DMF, nm), (ϵ , M⁻¹ cm⁻¹): 528 (1900), 556 (2000). Elem. Anal. Calc. for C₆₆H₈₁N₄Cl₆O_{7.5}CoK: C, 58.27; H, 6.00; N, 4.12. Found: C, 58.37; H, 6.09; N, 4.23%.

2.2.5. Synthesis of $[K(THF)_2(L^8)Co^{II}]_n$ (**3**)

The ligand L^8H_3 (0.289 g, 0.5 mmol) was dissolved in degassed THF (15.0 mL), and KH (0.060 g, 1.5 mmol) was added to this solution. The mixture was allowed to stir overnight, followed by addition of anhydrous CoCl₂ (0.065 g, 0.5 mmol). This mixture was stirred for an additional 12 h to afford a dark purple solution. The solution was refrigerated (-30 °C) overnight and the insoluble salts were filtered off on an anaerobic frit. The filtrate was reduced to 3.0 mL by evaporation, and was allowed to stand at room temperature to afford dark purple crystalline material, suitable for X-ray diffraction analysis (0.368 g, 90%). FT-IR (KBr, cm⁻¹): 3434, 3067, 2974, 2873, 1679, 1646, 1592, 1481, 1453, 1420, 1254, 1207, 1161, 1142, 1055, 953, 946, 910, 826, 773, 760, 748, 727,

712, 665, 622, 562, 552, 498, 463. UV–Vis (THF, nm), (ε , M⁻¹ cm⁻¹): 277 (sh), 464 (sh), 578 (30); (DMF, nm), (ε , M⁻¹ cm⁻¹): 540 (200), 576 (243). Elem. *Anal.* Calc. for C₃₂H₂₈N₄F₉O₅CoK: C, 46.99; H, 3.45; N, 6.85. Found: C, 47.09; H, 3.49; N, 6.83%.

2.2.6. Synthesis of $[K_2(L^9)_2 \text{Co}^{ll}_2]_n$ (4)

The ligand L⁹H₃ (0.208 g, 0.5 mmol) was dissolved in degassed THF (15.0 mL), and KH (0.060 g, 1.5 mmol) was added to this solution. The mixture was allowed to stir overnight, followed by addition of anhydrous CoCl₂ (0.065 g, 0.5 mmol). This mixture was stirred for an additional 12 h to afford a dark purple solution. The solution was refrigerated ($-30 \,^{\circ}$ C) overnight and the insoluble salts were filtered off on an anaerobic frit. The filtrate was reduced to 3.0 mL by evaporation, and was allowed to stand at room temperature to afford dark purple crystalline material, suitable for X-ray diffraction analysis (0.218 g, 85%). FT-IR (KBr, cm⁻¹): 3399, 3046, 2963, 2866, 1654, 1599, 1587, 1560, 1541, 1508, 1478, 1383, 1326, 1303, 1262, 1235, 1173, 1150, 1117, 1045, 987, 894, 821, 741, 627, 536. UV–Vis (DMF, nm), (ε , M⁻¹ cm⁻¹): 598 (700), 619 (sh). Elem. *Anal.* Calc. for C₂₇H₃₃N₄CoK: C, 63.37; H, 6.50; N, 10.95. Found: C, 63.44; H, 6.41; N, 10.86%.

2.2.7. Synthesis of $\{[K_2(DMA)_3(L^{10})_2Co^{ll}_2] \cdot 0.5Et_2O\}_n$ (5)

The ligand $L^{10}H_3$ (0.295 g, 0.5 mmol) was dissolved in degassed DMA (5.0 mL), and KH (0.060 g, 1.5 mmol) was added to this solution. The mixture was allowed to stir overnight, followed by addition of anhydrous CoCl₂ (0.065 g, 0.5 mmol). This mixture was stirred for an additional 24 h to afford a blue-violet solution. The solution was refrigerated (-30 °C) overnight, and the insoluble salts were filtered off on an anaerobic frit. Diethyl ether (20 mL) was carefully layered over the DMA filtrate, and pentane (10 mL) was layered over the diethyl ether. The setup was allowed to stand at room temperature to afford pink-violet crystalline material, suitable for X-ray diffraction analysis (0.250 g, 59%). FT-IR (KBr, cm⁻¹): 3448, 3061, 2977, 2929, 1635, 1587, 1485, 1449, 1388, 1363, 1239, 1177, 1113, 1050, 1027, 939, 842, 780, 751, 621, 592, 493, 475, 453, 425, UV–Vis (DMA, nm), (ϵ , M⁻¹ cm⁻¹); no peaks; (MeCN, nm), (*ε*, M⁻¹ cm⁻¹): 270 (sh), 535 (54). Elem. Anal. Calc. for C41H57.5N5.5O8CoK: C, 57.23; H, 6.74; N, 8.95. Found: C, 57.59; H, 6.74; N, 9.11%.

2.2.8. Synthesis of $[K(NCMe)_3(L^{13})Co^{II}-NCMe]$ (6)

The ligand L¹³H₃ (0.301 g, 0.5 mmol) was dissolved in degassed THF (15.0 mL), and KH (0.060 g, 1.5 mmol) was added to this solution. The mixture was allowed to stir overnight, followed by addition of anhydrous $CoCl_2$ (0.065 g, 0.5 mmol). This mixture was stirred for an additional 24 h to afford a deep green-brown solution. The solution was refrigerated (-30 °C) overnight and the insoluble salts were filtered off on an anaerobic frit. The filtrate was evaporated to dryness, and the residue was dissolved in acetonitrile (10.0 mL). This solution was reduced to approximately 5 mL by evaporation, and layered first with diethyl ether (10 mL) and then with pentane (5 mL) to afford green-brown crystalline material, suitable for X-ray diffraction analysis (0.297 g, 69%). FT-IR (KBr, cm⁻¹): 3446, 3386, 3224, 3045, 2916, 2257, 2125, 1636, 1592, 1582, 1560, 1507, 1479, 1443, 1336, 1302, 1207, 1144, 1091, 965, 916, 854, 829, 766, 736, 625, 524, 354. UV-Vis (MeCN, nm), (*ε*, M⁻¹ cm⁻¹): 254 (36500), 370 (sh), 459 (1700), 542 (sh). Elem. Anal. Calc. for C₅₀H₅₁N₈CoK: C, 69.65; H, 5.97; N, 13.00. Found: C, 69.63; H, 5.90; N, 12.89%.

2.3. X-ray crystallography

Intensity data sets for compounds **1–6** were collected on a Bruker Smart Apex diffractometer using SMART software [39]. Suitable crystals were selected and mounted on a glass fiber using

Table
Table

Crystallographic Data for Co^{II} compounds **1–6**.

Crystallographic parameters	1	2	3	4	5	6
Formula	C44H24CoF18KN5	C66H81Cl6CoKN4O7.5	C32H28C0F9KN4O5	C54H66C02K2N8	C82H115C02K2N11O16	C50H51CoKN8
Mr	1062.71	1361.08	817.61	1023.21	1706.91	862.02
Color	light brown	green	purple	green	light blue	light brown
Crystal system	monoclinic	monoclinic	monoclinic	triclinic	triclinic	triclinic
Space group	$P2_1/n$	C2	P21	ΡĪ	ΡĪ	ΡĪ
a (Å)	14.2383(16)	23.804(3)	9.9316(10)	9.520(2)	10.4909(12)	12.3029(13)
b (Å)	13.5103(15)	13.7687(17)	17.0639(17)	13.186(3)	19.816(2)	12.4441(14)
c (Å)	21.573(2)	21.403(3)	10.3409(11)	20.212(4)	21.881(3)	14.9916(16)
α (°)	90	90	90	88.959(3)	83.0470(10)	86.1900(10)
β (°)	93.938(2)	105.120(2)	101.872(2)	80.804(3)	88.0360(10)	81.9630(10)
γ (°)	90	90	90	85.954(4)	81.2780(10)	86.5190(10)
V (Å ³)	4140.0(8)	6771.8(2)	1715.0(3)	2498.5(9)	4462.6(9)	2264.6(4)
Ζ	4	4	2	2	2	2
$D_{\text{calc}} (\text{mg m}^{-3})$	1.705	1.335	1.583	1.360	1.270	1.264
T (K)	140(2)	173.2(4)	130(2)	130(2)	136(2)	136(2)
λ (Å)	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073
μ (mm $^{-1}$)	0.638	0.606	0.717	0.876	0.532	0.514
$R_1^{a} (I > 2\sigma(I))$	0.0524	0.0582	0.0336	0.0861	0.0409	0.0370
$wR_2^{b}(I > 2\sigma(I))$	0.1157	0.1466	0.0759	0.2094	0.1083	0.1007

^a $R_1 = \Sigma ||F_0| - |F_c|| / \Sigma |F_0|$.

^b $wR_2 = [\Sigma w (F_o^2 - F_c^2)^2 / \Sigma w (F_o^2)^2]^{1/2}.$

epoxy-based glue. The data sets were collected at low temperatures employing a scan of 0.3° in ω with an exposure time of 20 s/frame. The cell refinement and data reduction were carried out with SAINT [40], the program SADABS was used for the absorption correction. The structure was solved by direct methods using SHELxs-97 [41] and difference Fourier syntheses. Full-matrix leastsquares refinement against $|F^2|$ was carried out using the SHELXTL-PLUS suit of programs. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed geometrically and held in the riding mode during the final refinement. In compound 5, there were disorders in the solvent molecules, for example two dimethyl acetamide molecules existed in two different orientations and two carbon atoms of the diethyl ether had large thermal parameters. The ratios of the two different orientations were obtained by freely refining the occupancies of the atoms, which revealed the ratio of 50:50 for one DMA and 70:30 for the other. The carbon atoms with large thermal parameters for the ether were also divided into two positions and their occupancies were refined freely. Soft restraints were used to keep bond lengths within reasonable values. Pertinent crystallographic data are collected in Tables 1 and S1. Selected bond distances and angles for compounds 1-6 are given in Tables 2 and 3, respectively.

2.4. Polymerization reactions

2.4.1. Typical experimental procedure

All operations were carried out under an inert atmosphere. The Co^{II} compound (0.01 mmol; e.g. $[K(L^3)Co^{II}-NCMe]_n$ (1): 10.6 mg) and the solvent (toluene, 1.0 mL) were added to a Schlenk flask, followed by the monomer (styrene (St), 1.0 g, 9.6 mmol or methyl methacrylate (MMA), 1.0 g, 10.0 mmol) and the initiator (ethyl-2bromo-isobutyrate, 7.5 μL , 5.1 \times 10^{-5} mol). The flask was immediately immersed in the oil bath at 110 °C and kept for a given time (Tables 5 and 6). After heating was stopped, the reaction vessel was cooled to room temperature and a large excess of MeOH was added to precipitate the polymer formed. The resulting solids were filtered, washed with methanol and redissolved in toluene, where Dowex ion exchange resin was added to remove any metal compound before analysis. The colorless solution was then decanted and concentrated to a small volume (~1 mL). MeOH was added again to precipitate the polymers, which were then dried in vacuo for several hours. Polymers were characterized by SEC in CHCl₃ and by ¹H NMR in CDCl₃ at room temperature.

2.4.2. Reinitiation experiment 1

Compound $[K_2(L^9)_2 \text{Co}^{II}_2]_n$ (4) (10.2 mg, 0.01 mmol) and the solvent (toluene, 2.0 mL) were added to a Schlenk flask, followed by St (1.0 g, 9.6 mmol) and the initiator (ethyl-2-bromo-isobutyrate, 7.5 µL, 5.1 × 10⁻⁵ mol). The flask was immediately immersed in the oil bath at 110 °C and kept for 20 h. After heating was stopped, the reaction vessel was cooled to room temperature and an aliquot (0.5 mL) was taken. To this aliquot a large excess of MeOH was added to precipitate the polymer formed, which was purified and characterized as described above.

To the rest of the reaction mixture, St (1.0 g, 9.6 mmol) was added and was left to react for another 20 h at 110 °C. After heating was stopped, the reaction vessel was cooled to room temperature and a large excess of MeOH was added to precipitate the polymer formed, which was purified and characterized as described above.

2.4.3. Reinitiation experiment 2

Compound $[K(THF)_6][(L^5)Co^{II}] \cdot 1.5THF$ (2) (13.6 mg, 0.01 mmol) and the solvent (toluene, 2.0 mL) were added to a Schlenk flask, followed by MMA (1.0 g, 10.0 mmol) and the initiator (ethyl-2-bromo-isobutyrate, 7.5 µL, 5.1 × 10⁻⁵ mol). The flask was immediately immersed in the oil bath at 110 °C and kept for 16 h. After heating was stopped, the reaction vessel was cooled to room temperature and a large excess of MeOH was added to precipitate the polymer formed, which was purified and characterized as described above.

The PMMA obtained was redissolved in toluene (2.0 mL), where the metal complex (13.6 mg, 0.01 mmol) and St (1.0 g, 9.6 mmol) were added and the mixture was left to react for another 20 h at 110 °C. After heating was stopped, the reaction vessel was cooled to room temperature and a large excess of MeOH was added to precipitate the polymer formed, which was purified and characterized as described above.

3. Results and discussion

3.1. Synthesis and characterization

The syntheses of ligands $L^{x}H_{3}$ (x = 3, 5, 8, 9) have been previously reported [31]. Ligands $L^{10}H_{3}$ and $L^{13}H_{3}$ (Fig. S1) have been prepared by analogous protocols to those employed for installation of acyl and aryl arms to the tripodal trisamino-amine (2-NH₂-C₆H₄)₃N (TRPHEN), respectively. The synthesis of the Co^{II} complexes (**1–6**; Scheme 1 (minimal structure of first coordination

Table 2 Selected interatomic distances (Å) for compounds 1-6.

	1	2	3	4	5	6
Co(1)-N(1)	2.171(2)	2.091(3)	2.1359(19)	2.096(6)	2.1833(18)	2.2270(13)
Co(1)-N(2)	1.980(2)	1.934(4)	1.9799(19)	1.994(6)	1.9644(18)	1.9930(13)
Co(1)-N(3)	2.035(2)	1.944(4)	1.9895(19)	1.965(6)	1.9569(18)	1.9884(14)
Co(1)-N(4)	2.018(2)	1.947(4)	1.9911(17)	1.941(5)	1.9555(18)	1.9669(13)
Co(1)-N(5)	2.070(2)					2.1092(14)
Co(2)-N(5)				2.103(6)	2.1584(16)	
Co(2)-N(6)				1.954(6)	1.9743(17)	
Co(2)-N(7)				1.964(6)	1.9646(17)	
Co(2)-N(8)				1.940(6)	1.9616(18)	
Co(1)–[N(2), N(3), N(4)] ^a	0.238	0.173	0.295	0.223	0.311	0.319
Co(2)–[N(6), N(7), N(8)] ^a				0.190	0.277	

^a Distance of Co from mean plane.

Table 3

Selected angles (°) for compounds 1-6.

	1	2	3	4	5	6
N(2)-Co(1)-N(4)	123.54(9)	118.66(16)	112.64(8)	114.4(2)	115.74(8)	119.08(5)
N(2)-Co(1)-N(3)	110.35(9)	118.98(17)	114.04(8)	118.4(2)	119.67(8)	113.81(5)
N(4)-Co(1)-N(3)	117.74(9)	119.97(16)	126.74(8)	123.4(2)	117.18(8)	119.47(5)
N(2)-Co(1)-N(1)	81.74(9)	84.98(14)	81.55(8)	82.2(2)	80.99(7)	80.47(5)
N(4)-Co(1)-N(1)	79.77(8)	85.31(15)	80.63(8)	84.5(2)	81.21(7)	80.36(5)
N(3)-Co(1)-N(1)	79.45(8)	84.26(18)	82.22(8)	83.7(2)	80.43(7)	81.39(5)
N(5)-Co(1)-N(1)	175.64(9)					178.05(5)
N(2)-Co(1)-N(5)	102.61(9)					101.21(5)
N(4)-Co(1)-N(5)	97.91(9)					99.58(5)
N(3)-Co(1)-N(5)	98.53(9)					96.98(5)
N(8)-Co(2)-N(6)				123.3(2)	116.02(7)	
N(8)-Co(2)-N(7)				115.5(2)	120.46(7)	
N(6)-Co(2)-N(7)				118.4(3)	117.67(7)	
N(8)-Co(2)-N(5)				85.5(2)	81.66(7)	
N(6)-Co(2)-N(5)				84.2(2)	82.16(7)	
N(7)-Co(2)-N(5)				83.5(2)	81.93(7)	

Table 4

Electrochemical data for compounds 1-6.

Compound	Solvent	$E_{1/2}$ (or $E_{p,a}$) (V vs. Fc^+/Fc)	$\Delta E (mV)$
$[K(L^3)Co^{II}-NCMe]_n$ (1)	MeCN	-0.090	72
$[K(THF)_6][(L^5)Co^{II}] \cdot 1.5THF (2)$	DMF	-0.258	102
$[K(THF)_2(L^8)Co^{II}]_n$ (3)	DMF	0.719	
$[K_2(L^9)_2Co^{II}_2]_n$ (4)	DMF	-0.654, -0.500	88, 75
$\{[K_2(DMA)_3(L^{10})_2Co^{II}_2] \cdot 0.5Et_2O\}_n$ (5)	DMA	0.559	
$[K(NCMe)_3(L^{13})Co^{II}-NCMe] (6)$	MeCN	-0.665	78

Table 5

Reactions of compounds **1–6** with styrene (St).^a

Entry	Compound	<i>t</i> (h)	Yield (%)	$M_{\rm n} ({ m th})^{ m b}$	$M_n (\exp)^c$	$M_{\rm w}/M_{\rm n}$
1	$[K(L^3)Co^{II}-NCMe]_n(1)$	16	15	3000	d	d
2	$[K(THF)_6][(L^5)Co^{II}] \cdot 1.5THF(2)$	20	14	2800	9600	2.78
3		20	12 ^e	1200	7100	2.39
4	$[K(THF)_2(L^8)Co^{II}]_n$ (3)	2	12	2400	81900	1.47
5		18	90 ^f	18000	110500	1.56
6	$[K_2(L^9)_2Co^{II}_2]_n$ (4)	22	86	17200	57400	1.57
7	$\{[K_2(DMA)_3(L^{10})_2Co^{II}_2] \cdot 0.5Et_2O\}_n$ (5)	2	51	10200	86100	1.82
8		16	86 ^f	17200	38900	2.00
9	$[K(NCMe)_3(L^{13})Co^{II}-NCMe]$ (6)	22	16	3200	5700	1.97
10	-	16	21	4200	326500	1.54

^a Conditions: catalyst (0.01 mmol), styrene (9.6 mmol), ethyl-2-bromo-isobutyrate (0.05 mmol), 1.0 mL toluene, reflux at 110 °C.

^a Conditions: catalyst (0.01 limitol), stylenc (3.0 lim)
 ^b M_n (th) = (g of monomer/mol initiator) × % yield.
 ^c By SEC in CHCl₃ at r.t.
 ^d Very broad molecular weight distribution.
 ^e Ethyl-2-bromo-isobutyrate (0.10 mmol).

^f 2.0 mL of toluene.

Table 6

Reactions of	compounds	1-6	with	methy	l methacry	ilate	(MMA) ^a
Reactions of	compounds	1-0	VVILII	IIIC UIV.	i incuiaci v	/latt	

Entry	Compound	<i>t</i> (h)	Yield (%)	$M_{\rm n} ({\rm th})^{\rm b}$	$M_{\rm n}({\rm exp})^{\rm c}$	$M_{\rm w}/M_{\rm n}$
1	$[K(L^3)Co^{II}-NCMe]_n$ (1)	20	5	1000	14,500	1.26
2		16	3 ^d	600	16700	1.16
3	$[K(THF)_6][(L^5)Co^{II}] \cdot 1.5THF(2)$	15	30	6000	37900	1.43
4		15	33°	3300	24 500	1.40
5		21	13 ^f	870	20700	1.26
6	$[K(THF)_2(L^8)Co^{II}]_n$ (3)	16	6	1200	439800	1.24
7		15	12 ^d	2400	300800	1.29
8	$[K_2(L^9)_2Co^{II}_2]_n$ (4)	17	70	14000	51 400	1.52
9	$\{[K_2(DMA)_3(L^{10})_2Co^{II}_2] \cdot 0.5Et_2O\}_n$ (5)	15	72	14400	67000	2.00
10		15	60 ^e	6000	57 300	1.91
11	$[K(NCMe)_3(L^{13})Co^{II}-NCMe]$ (6)	15	40	8000	55800	1.54
12		21	45 ^d	9000	54700	1.58
13	-	17	9	1800	356700	1.20

^a Conditions: catalyst (0.01 mmol), methyl methacrylate (10 mmol), ethyl-2-bromo-isobutyrate (0.05 mmol), 1.0 mL toluene, reflux at 110 °C.

^b M_n (th) = (g of monomer/mol initiator) × % yield.

^c By SEC in CHCl₃ at r.t.

^d 2.0 mL of toluene.

^e Ethyl-2-bromo-isobutyrate (0.10 mmol).

^f Ethyl-2-bromo-isobutyrate (0.15 mmol).



sphere is shown)) has been accomplished by (i) deprotonation of the tripodal ligands (L^xH_3) with 3 equiv. of KH, and (ii) addition of anhydrous CoCl₂ under inert atmosphere, followed by filtration to separate the insoluble KCl. The reactions are carried out in THF, except for the reaction with $L^{10}H_3$, in which case DMA is used, because of the low solubility of the ligand in THF. For the isolation of the crude Co^{II} complexes, the filtrate is concentrated and layered with pentane over THF, or diethylether over DMA. Crystals suitable for X-ray diffraction analysis are obtained at low temperature from concentrated THF solutions (**3**, **4**), and from layering of two (THF/ pentane, **2**) or three solvents (MeCN/Et₂O/pentane, **1**, **6**; DMA/ Et₂O/pentane, **5**).

The solid-state structures of these compounds reveal similarities in the coordination mode of the ligands, since in all cases the four nitrogen-atom residues of the ligands are coordinated to the metal center in a distorted trigonal-pyramidal geometry. However, there are also significant differences. Two of the compounds are five-coordinated (1 and 6), due to the presence of a good donor solvent (MeCN) as a ligand occupying the fifth site. In spite of the presence of THF or DMA, the remaining compounds are fourcoordinated (2–5). In sharp contrast, the corresponding $[K(THF)_2][(L^3)Fe^{II}-THF]$ and $[K(DMA)][(L^8)Fe^{II}-DMA)]$ species are five-coordinated [31], although the L⁹ coordinated Fe^{II} and Co^{II} (4) compounds are essentially isostructural, and do not include any solvent molecules (coordinated or solvated). Another interesting feature is the intricate role played by potassium ions in generating polymeric tertiary structures (compounds 1, 3–5) by establishing contacts with ligand residues (largely N_{amido} atoms, amidato carbonyl moieties and aromatic units). A more detailed analysis of the solid-state structures is provided below.

Among the aryl-armed Co^{II} reagents (**1**, **2**, **6**; Figs. 1–3), the two five-coordinate structures (**1**, **6**) exhibit distorted trigonal bipyramidal geometries, with that of **6** being the least distorted ($\tau = 0.97$ (**6**), 0.87 (**1**)). Compound **6** also possesses the most rigid



Fig. 1. ORTEP drawing of $[K(L^3)Co^{II}-NCMe]_n$ (1) with 50% probability displacement ellipsoids. Hydrogen atoms are omitted for clarity.



Fig. 2. ORTEP drawing of the anion of $[K(THF)_6][(1^5)Co^{II}] \cdot 1.5THF$ (2) with 50% probability displacement ellipsoids. Hydrogen atoms are omitted for clarity.

cavity among the three aryl-bearing reagents, due to the 2,6rather than 3,5-aryl substitution, which locks the aryl arms in a perpendicular position versus the corresponding phenylene groups of the TRPHEN framework. The four-coordinate species 2 is a benchmark case, because this is the only Co^{II} compound reported here, in which the K⁺ ion is solely coordinated by solvent molecules (THF), leaving the $[(L^5)Co^{II}]^-$ anion structure unperturbed by any potassium close contacts. As a result the average Co^{II}-N_{amido} bond distance in **2** is the shortest available (1.942(7) Å) and with the smallest deviation, not only with respect to the five-coordinate 1 and 6, but also among all four-coordinate species. Similarly, compound **2** has the shortest Co^{II} displacement (0.173 Å) from the mean plane generated by the three equatorial N_{amido} atoms. In contrast, compound 1 shows significant elongation of the Co-N(3) and Co-N(4) bonds due to the interference of the K⁺ ion, which establishes close contacts between these two N_{amido} moieties in adjacent molecules, thus giving rise to an one-dimensional polymeric structure. In addition, K⁺-arene interactions, involving phenylene moieties of the TRPHEN framework, are evident in **1** and **6**. In the latter case, these are the only contacts between the K⁺ ion and the ligand (phenylene rings between atoms N(1) and N(2) and, to a lesser extent, N(1) and N(3)), resulting in modest elongation of the



Fig. 3. ORTEP drawing of $[K(NCMe)_3(L^{13})Co^{II}-NCMe]$ (**6**) with 50% probability displacement ellipsoids. Hydrogen atoms are omitted for clarity.



Fig. 4. ORTEP drawing of $[K(THF)_2(L^8)Co^{II}]_n$ (3) with 50% probability displacement ellipsoids. Hydrogen atoms are omitted for clarity.

corresponding Co–N(2) and Co–N(3) bonds. Otherwise, **6** is a molecular entity because the coordination of K^+ is limited to K^+ -arene interactions with the same ligand and solvation by three MeCN molecules.

The acyl-armed Co^{II} reagents **3** and **5** (Figs. 4 and 5) are strictly four-coordinate species, in keeping with cobalt's late transitionmetal character, and are thus devoid of the complications observed in analogous Fe^{II} reagents, in which the acyl group contributes to metal coordination via amidato -N-C(R)=0...M or -N=C(R)-0-M modes. As a matter of fact, the carbonyl moieties are oriented exo with respect to the cavity of the vacant coordination site. The strong electron-withdrawing character of the CF₃CO– arm in **3** is evident in the longer average Co^{II}–N_{amido} bond distance (1.987(6) Å) with respect to that of **5** (1.963(7) Å). Both structures demonstrate complicated three-dimensional architectures, owing to solvated K⁺ ions connecting acyl derived carbonyl moieties. The tertiary structure of **3** is simpler and reminiscent of the corresponding Fe^{II}-containing structure, inasmuch as equivalent [K(THF)₂]⁺ ions are coordinated by all three carbonyl residues



Fig. 5. ORTEP drawing of {[K₂(DMA)₃(L¹⁰)₂Co^{II}₂]·0.5Et₂O}_n (5) with 50% probability displacement ellipsoids. Hydrogen atoms are omitted for clarity.



Fig. 6. ORTEP drawing of $[K_2(L^9)_2Co^{II}_2]_n$ (4) with 50% probability displacement ellipsoids. Hydrogen atoms are omitted for clarity.

(O(1), O(2), O(3)), each oxygen belonging to a different molecule. The corresponding structure of **5** distinguishes between two independent Co^{II} sites (Co(1) and Co(2)), differing slightly in metrical parameters, and two solvated K^+ ions ([K(DMA)]⁺ for K(1) and [K(DMA)₂]⁺ for K(2)), each interconnecting three Co^{II} sites. K(1) is associated with carbonyl residues (O(3), O(5)) of two separate Co(1) sites and a carbonyl residue (O(7)) of one Co(2) site, whereas K(2) is coordinated by carbonyl residues (O(9), O(11)) from two different Co(2) sites and a carbonyl residue (O(1)) belonging to a Co(1) site. Therefore, all carbonyl moieties associated with Co(1) and Co(2) sites are involved in close contacts with K⁺ ions.

Finally, compound **4**(Fig. 6) is the sole example of an alkyl-armed ligand, and, as in the case of the corresponding Fe^{II} species [31], exhibits a unique geometry, featuring a repeating $-[Co(1)-K(1)-Co(2)-K(2)]_n$ - sequence. The K(1) ion interconnects residues belonging to ligands attached to Co(1) and Co(2), namely atoms N(2) and N(6), and phenylene rings via K⁺-(η^x -arene) contacts (phenylenes between N(1)/N(4) (x = 6) and N(5)/N(7) (x = 3)). Ion K(2) is largely involved in K⁺-(η^6 -arene) interactions (phenylene groups between N(1)/N(2) and N(5)/N(8)) and long-range contacts with N(3) and N(7). As a result, all Co-N_{amido} bond distances are affected to various degrees, the most elongated one being that of Co(1)–N(2).

As has been the case with the corresponding Fe^{II} compounds, it is exceedingly difficult to determine whether the structural complexity observed in the solid state, largely due to intimate K⁺ contacts with ligand and solvent moieties, is retained intact in fluid matrices. Detailed EPR and magnetic data will be presented in due course, as part of a study that includes a wider family of ligands, to further advance our understanding of solution structure. In the meantime, the electrochemical data reported below in a variety of solvents, support the notion that, in many instances, well-defined mono-anionic structures are present in solution to support reversible one-electron transfer chemistry.

3.2. Cyclic voltammetry

The electrochemical properties of compounds 1-6 have been studied by cyclic voltammetry. Electrochemical data for the Co^{II}/ Co^{III} couple are listed in Table 4 and the corresponding waves are shown in Fig. 7. The complete voltammograms are shown in Figs. S2–S7. Compound $[K(NCMe)_3][(L^{13})Co^{II}-NCMe]$ (6), which bears the electron-donating aryl substituent 2,6-(CH₃)₂ is oxidized at the most negative potential. The presence of the electron-withdrawing aryl substituents $3,5-(CF_3)_2$ and $3,5-Cl_2$ in $[K(L^3)Co^{II}-$ NCMe]_n (1) and $[K(THF)_6][(L^5)Co^{II}] \cdot 1.5THF$ (2) respectively, shifts the oxidation redox potential to more positive values. Complex $[K_{2-}]$ $(L^9)_2 Co^{II}_2|_n$ (**4**) shows two overlapping redox waves, which may reflect the two distinct Co^{II} ions observed in the repeating dinuclear unit of the solid-state structure. The potential values are close to that of compound **6** and are in agreement with the electron-rich nature of the arylalkylamido-amine ligand. Finally, as expected, the electron-withdrawing COO^tBu and COCF₃ substituents of {[K₂₋ $(DMA)_3(L^{10})_2Co^{II}_2] \cdot 0.5Et_2O_n$ (5) and $[K(THF)_2(L^8)Co^{II}]_n$ (3) cause significant anodic shift. The assignment of these irreversible waves



Fig. 7. Cyclic voltammograms $(Co^{II}/Co^{III} \text{ redox couple})$ of compounds $[K(L^3)Co^{II}-NCMe]_n$ (1) and $[K(NCMe)_3(L^{13})Co^{II}-NCMe]$ (6) in $MeCN/[(n-Bu)_4N]PF_6$, $[K(THF)_6]-[(L^5)Co^{II}] \cdot 1.5THF$ (2), $[K(THF)_2(L^8)Co^{II}]_n$ (3) and $[K_2(L^9)_2Co^{II}_2]_n$ (4) in DMF/ $[(n-Bu)_4N]PF_6$, and $\{[K_2(DMA)_3(L^{10})_2Co^{II}_2] \cdot 0.5Et_2O]_n$ (5) in DMA/ $[(n-Bu)_4N]PF_6$, as indicated, with a Au disk electrode (1.6 mm in diameter); scan rate 0.1 V/s.

to the Co^{II}/Co^{III} couple is tentative. Contributions from ligand-centered events cannot be excluded at the present time, especially for compound **3**, for which a large $i_{p,a}$ value is observed. These results are consistent with the electronic character of the ligands and prior electrochemical data obtained for the analogous Fe^{II} complexes [31], although the potentials of the Co^{II} compounds have been shifted anodically, as expected, by a factor of 0.4–0.7 V.

3.3. Polymerization results

Compounds 1, 2, 4, and 6 have properties that make them promising reagents for use as ATRP catalysts. They provide reversible or semi-reversible Co^{II}/Co^{III} couples at easily accessible potentials, as shown by the electrochemical data. They have either a vacant coordination site, or a weakly bound ligand (solvent molecule), which makes it possible for a halide or (pseudohalide) ligand to enter the coordination sphere. Compounds 3 and 5, which feature an irreversible Co^{II}/Co^{III} couple, have also been studied, as the halidophilicity is in some cases a factor of equal or even higher importance. Indeed, it has been found that the activity of an ATRP catalyst mainly depends on the redox potential of the $M^{n+}/M^{(n+1)+}$ couple and the halidophilicity of the $M^{(n+1)+}$ complex. For Cu-based catalysts the key factor seems to be the redox potential, for Ru- and Os-complexes the halidophilicity, while for other metal catalysts the two factors have intermediate effects [42]. In addition, since ATRP is not the only possible pathway for Co-induced radical polymerizations, other parameters, such as the strength and reactivity of Co^{III}–C or Co^{III}–H bonds, can play a dominant role.

The catalytic activity of compounds **1–6** towards the polymerization of styrene (St) and methyl methacrylate (MMA) has been studied in toluene solutions at 110 °C using ethyl-2-bromo-isobutyrate as initiator. The results are summarized in Tables 5 and 6. Blank experiments are also included for comparison purposes. Compounds **1**, **5** and **6** are readily soluble in toluene, **2** is partially dissolved, whereas **3** and **4** are insoluble. However, the solutions become homogeneous after the addition of the monomer and the initiator, with the only exception of compound **3**, which gets partly dissolved during the reaction with St and remains insoluble during the reaction with MMA. The reaction mixtures were allowed to react for a given time. In some cases, high-viscosity mixtures had formed at that time. The catalyst/monomer/initiator ratio was 1/ 1000/5, unless otherwise stated. The polymers, polystyrene (PS) and poly(methyl methacrylate) (PMMA), were obtained after addition of MeOH and were purified by Dowex ion exchange resin in toluene solutions.

From the data shown in Table 5, higher yields of PS have been obtained with compounds 3-5. The reaction mixtures containing 3 and 5 had gelled after 2 h (entries 4 and 7). For this reason, they were repeated with 2.0 mL of toluene instead of 1.0 mL. It is notable however that the reaction with 5 gave high yields (51%) in a short period of time. When a larger amount of solvent (2.0 mL; entry 8) was used, the reaction proceeds in a more controlled fashion, giving a polymer with molecular weight closer to the theoretical value, although with a bimodal distribution (Fig. S8), which causes broadening of the molecular weight distribution $(M_w/M_p = 2.00)$. Among the three systems, **4** and **5** showed better control over the molecular weight of the PS obtained (entries 6 and 8), while compounds 3 and 4 gave PS with bimodal distribution and yet relatively narrow (1.56 and 1.57, respectively; entries 5 and 6; Figs. S9 and S10). The other three compounds show low reactivity (entries 1-3 and 9), yielding polymers with broad molecular weight distributions.

Similar reactivity has been observed in MMA polymerization in most cases, with compounds **4** and **5** being the most reactive in terms of polymer yields. The only notable exception is compound 3 (Table 6, entries 6 and 7), which is the most reactive compound for St polymerization, and one of the least reactive for MMA polymerization. In fact, the complex has no control over the reaction, as the molecular characteristics of the polymers formed do not differ from the blank experiment (entry 13). This result is not unexpected, since compound 3 is totally insoluble in the reaction mixture. The molecular weight of PMMA obtained with compound 4 shows the best agreement with the theoretical value, compared to the other samples, and the molecular weight distribution is not very broad (M_w/M_p = 1.52; entry 9; Fig. S11). Compound **5** gives high yields of PMMA, although with higher molecular weights and bimodal molecular weight distributions (entries 9 and 10: Fig. S12). With compounds 2 and 6 lower yields are obtained (entries 3, 11 and 12), but the metal complex seems to have a better control over the reaction, giving PMMA with relatively narrow molecular weight distribution, especially with compound 2 (1.40). Addition of 0.10 and 0.15 mmol of initiator (entries 4 and 5) does not significantly alter the controllability of the reaction, although the GPC plots have different characteristics (Fig. 8), which will be discussed below. In the latter case, the yield is reduced. Finally, 1 is the least reactive of the compounds studied (entries 1 and 2).

A common characteristic of all experiments is that the experimental molecular weights are higher than the theoretical ones, which shows that termination reactions take place during the polymerization. Another interesting point is that in many cases a bimodal distribution is observed (PS and PMMA obtained with compounds 2-5), resulting in the broadening of the molecular weight distribution. This is indicative of the presence of at least two reactive centers, and given that the molecular weight distributions are not very broad (1.40–2.00, except for the 2/St system), these results strongly indicate that two parallel mechanisms are in operation. The reactions of compound **2** with MMA further support this argument. Three experiments have been carried out, with different quantities of initiator (0.05, 0.10 and 0.15 mmol). In all cases, the GPC plots show bimodal distributions, but the ratio of the two peaks differ from one experiment to the other, as shown in Fig. 8. These results show that the reaction proceeds with two distinct mechanisms, and that the amount of initiator used can favor one over the other.



Fig. 8. SEC traces for PMMA obtained from the reaction of $[K(THF)_6][(L^5)Co^{II}]$ -1.5THF (**2**) (0.01 mmol) with MMA (10.0 mmol) and ethyl-2-bromo-isobutyrate (0.05 mmol, top; 0.10 mmol, middle; 0.15 mmol, bottom) in toluene (1.0 mL) under reflux at 110 °C.

In order to gain more evidence on the controlled nature of the polymerization and the operation of the ATRP mechanism, we examined the ability of the polymers formed to reinitiate the polymerization reaction.

In the first experiment, St has been polymerized with compound $[K_2(L^9)_2Co^{II}_2]_n$ (**4**) for 20 h. A small aliquot of the solution was taken and MeOH was added, yielding PS with M_n = 50200 and M_w/M_n = 1.80 (Fig. 9). To the rest of the reaction mixture, St was added and was left to react for another 20 h, providing PS with M_n = 67000 and M_w/M_n = 1.59 (Fig. 9). The fact that the molecular weight has increased and the molecular weight distribution has decreased is a strong indication that the polymerization does not proceed through free radicals but in a rather controlled way, where the Co^{II} complex plays a crucial role.

For the second experiment, MMA was polymerized with $[K(THF)_6][(L^5)Co^{II}]$ 1.5THF (2) and 0.05 mmol of the initiator, because under these conditions one mechanism seems to be dominant. After the end of the reaction (20 h), the PMMA formed was precipitated and characterized ($M_n = 23700$ and $M_w/M_n = 1.33$). Then, it was redissolved in toluene, where the metal complex and St were added, and kept under reflux for 20 h) yielding a PMMA-b-PS block copolymer with $M_{\rm n}$ = 72400 and $M_{\rm w}/M_{\rm n}$ = 1.60. From the comparison of the chromatographic traces (Fig. 10), it is obvious that the peak of PMMA at 36.9 min is absent in the GPC of the copolymer, which indicates that the end-Br groups of the PMMA chains were exclusively employed as initiation sites for the polymerization of St or in other words that PMMA served as macroinitiator for the synthesis of PMMA-b-PS block copolymers. The bimodality of the GPC trace of the final product can be attributed to possible termination reactions and/or the increase of viscosity of the reaction medium leading to polymerization under non-homogeneous conditions. The successful synthesis of the block copolymer was verified by ¹H NMR spectroscopy (Fig. S14; PMMA-b-PS 20-80% mol). This result confirms that the polymerization does not proceed through a coordination mechanism of the monomer to the metal center, since in this case the results would be a mixture of PMMA and PS homopolymers.

The tacticity of the PMMA macromolecules, formed in the present study, has been determined by ¹H NMR spectroscopy. The



Fig. 9. SEC traces for PS obtained from the reaction of $[K_2(L^9)_2Co^{II}_2]_n$ (**4**) (0.01 mmol) with St (9.6 mmol) and ethyl-2-bromo-isobutyrate (0.05 mmol) in toluene (2.0 mL) under reflux at 110 °C (top) and PS obtained after the second addition of St (9.6 mmol, bottom).



Fig. 10. SEC traces for PS obtained from the reaction of $[K(THF)_6][(L^5)Co^{II}] \cdot 1.5THF$ (**2**) (0.01 mmol) with MMA (10.0 mmol) and ethyl-2-bromo-isobutyrate (0.05 mmol) in toluene (2.0 mL) under reflux at 110 °C (top) and PMMA-b-PS obtained after the reaction of **2** (0.01 mmol) with St (9.6 mmol) and PMMA (0.05 mmol) in toluene (2.0 mL) under reflux at 110 °C (bottom).

results are summarized in Table 7 and a representative spectrum in shown in Fig. S13. The polymers obtained by conventional radical polymerization are mainly syndiotactic (rr:rm:mm = 64:32:4), due to the repulsion between the substituents of the chain end and less-controlled chain propagation [43]. The sequence distribution of the tacticity of PMMA is approximately Bernoullian. Similar microstructural results have been reported from ATRP of MMA using various catalytic species, such as those based on Rh [44], Fe [45,46], Ni [47,48], Cu [49] and Ru [50] complexes. The polymers obtained in this study were predominately syndiotactic, consistent with radical polymerization. Compounds 1 and 2 exhibit unusually high ratios of isotactic triads. It is known that several Co^{II} complexes act as efficient chain transfer agents during methacrylate polymerization. The Co^{II} radical may interact with the propagating radical and induce single-handed helical structures in the polymerization of bulky methacrylates [51]. The polymerization proceeds with a different mechanism from typical catalytic chain transfer although the detailed mechanism is not clear [52]. It is possible

Table 7	
Tacticity of poly(methyl methacrylate) (PMMA). ^{a,b}	

Entry	Compound	mm (%)	mr (%)	rr (%)
1	$[K(L^3)Co^{II}-NCMe]_n$ (1)	28	31	41
2		8	36	56
3	$[K(THF)_6][(L^5)Co^{II}] \cdot 1.5THF(2)$	16	33	51
4		10	37	53
5		8	39	53
6	$[K(THF)_2(L^8)Co^{II}]_n$ (3)	7	38	55
7		5	35	60
8	$[K_2(L^9)_2Co^{II}_2]_n$ (4)	10	38	52
9	$\{[K_2(DMA)_3(L^{10})_2Co^{II}_2]\cdot 0.5Et_2O\}_n$ (5)	6	40	54
10		10	39	51
11	$[K(NCMe)_3(L^{13})Co^{II}-NCMe]$ (6)	7	39	54
12		7	40	53
13	-	6	38	56

^a Calculated from ¹H NMR spectra.

^b The experiments are presented in the same order as in Table 6.

that a similar situation exists, at least to some extent, with compounds **1** and **2** leading to increased isotacticities. Further mechanistic studies are needed to clarify this finding.

Although a firm correlation between the reactivity and the structure or the redox potential of the complexes cannot be made at this time, our preliminary results indicate that the steric rather than the electronic factor is the most important in the polymerization reactions, since compounds **4** and **5** that show the highest reactivity feature a less hindered fifth coordination site. The experimental data, in most cases, suggest that more than one mechanism is operative. Between the three mechanisms that have been established for cobalt-catalyzed CRP reactions, namely, ATRP, OMRP and CCTP, the last one seems to be the least possible in our case, because the lack of extra coordination sites in the metal compounds under study would make the β -H elimination very challenging. Finally, in the unique case of compound **3**, an heterogeneous mechanism for St polymerization cannot be excluded.

The experimental findings strongly support the conclusion that the Co^{II} complexes prepared in this work, were efficiently involved in the controlled radical polymerization of MMA and St. However, more work is needed to identify the experimental polymerization conditions that will provide the best control over the structural and molecular characteristics.

4. Conclusions

The following are the main results and conclusions of the present research:

- (1) A series of Co^{II} reagents, coordinated by a family of tripodal [N₃N]³⁻ ligands bearing a triphenylamido-amine core and aryl, acyl and alkyl arms, have been synthesized and characterized by a variety of physico-chemical techniques.
- (2) X-ray structural analysis reveals that all Co^{II} complexes demonstrate a distorted trigonal pyramidal geometry generated by three ligand-derived N_{amido} residues and an apical N_{amine} atom. In the presence of a good donor solvent such as MeCN, five-coordinate trigonal bipyramidal geometries are obtained, otherwise four-coordinate species are preferred in contrast to the corresponding Fe^{II} reagents. Owing to K⁺ contacts with aromatic, N_{amido} and/or O_{acyl} residues belonging to adjacent molecules, polymeric structures are observed in four compounds.
- (3) Electrochemical data establish that all aryl- and alkyl-armed ligands give rise to reversible or semi-reversible Co^{II}/Co^{III} couples, with redox potentials ranging by as much as 575 mV. On the other hand, the electron-withdrawing acyl-armed ligands demonstrate irreversible features,

exhibiting anodic waves at high positive voltages, for which ligand participation cannot be excluded.

- (4) Our preliminary results show that compounds 2–6 can induce the controlled radical polymerization (CRP) of styrene and methyl methacrylate. Some compounds (3, 4 and 5) provide good yields (60–90%; 3 is active only in St polymerization), whereas others (2 and 6) have better control over the polymerization reactions, albeit with lower yields (12–16% for PS and 30–45% for PMMA). Although a firm correlation between the reactivity and the structure or the redox potential cannot be made at this point, the steric factor seems to play an essential role, since compounds that feature a less hindered fifth coordination site show the highest reactivity and better control over the polymerization reaction.
- (5) The polymers obtained are predominately syndiotactic, consistent with radical polymerization, with two exceptions that exhibit unusually high ratios of isotactic triads. In many cases bimodal distributions are observed, although the molecular weight distributions are not very broad (1.40–2.00), and this strongly indicates that two parallel mechanisms are in operation. Among the three predominant mechanisms (ATRP, OMRP and CCTP) that have been established for cobalt-mediated CRP reactions, the first two seem to be more likely for our systems. A detailed mechanistic study is under way.

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Appendix A. Supplementary data

CCDC 879541, 879542, 879543, 879544, 879545, 879546 and 879547 contain the supplementary crystallographic data for **1–6** and $L^{13}H_3$, respectively. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/ 10.1016/j.poly.2012.11.020.

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