Polyhedron 52 (2013) 78–90

Contents lists available at SciVerse ScienceDirect

Polyhedron

journal homepage: www.elsevier.com/locate/poly

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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ARTICLE INFO

Article history:
Available online 29 November 2012

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.

Keywords:
Cobalt complexes
Trisamidoamine ligands
Electrochemistry
Controlled radical polymerization
Catalysis
Atom-transfer reactions

ABSTRACT

The present work reports a new family of tripodal Co^{II} complexes bearing trianionic triphenylamido-amine ligands with a variety of pendant arms (aryl, acyl, alkyl). These complexes have been synthesized by the reaction of anhydrous $CoCl_2$ 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**), $[K(THF)_6][(L^5)Co^{II}]·1.5THF$ (**2**) and $[K(NCMe)_3(L^{13})Co^{II}–NCMe]$ (**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 $\{[K_2(DMA)_3(L^{10})_2Co^{II}_2]·0.5Et_2O\}_n$ (**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 yields 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.

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 [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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http://dx.doi.org/10.1016/j.poly.2012.11.020

(Co^{II}/Co^{III}) (Chart 1) [4,5]. The resulting $R^{\cdot}$ 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 ($P_n^{\cdot}$), 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 $CoCl_2$, $Cu(OAc)_2$ or tris(2-(dimethyl amino) ethyl)amine (Me_6TREN), improves the rate of the reaction, but the control over the polymerization is reduced ($M_w/M_n = 1.49$–1.74) [9]. The $CoCl_2/Me_6TREN$ system has been reported as catalyst for the ATRP of MMA, exerting modest control over the polymerization and molecular weight distribution of PMMA ($M_w/M_n = 1.63$–1.80) [12], which can be improved by addition of a small amount of hybrid deactivators ($FeBr_3/Me_6TREN$ or $CuBr_2/Me_6TREN$; $M_w/M_n = 1.15$–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 ($CuCl_2/Me_6TREN$) [14]. Among Co^{I} systems, $[CoX(PPh_3)_3]$ (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.

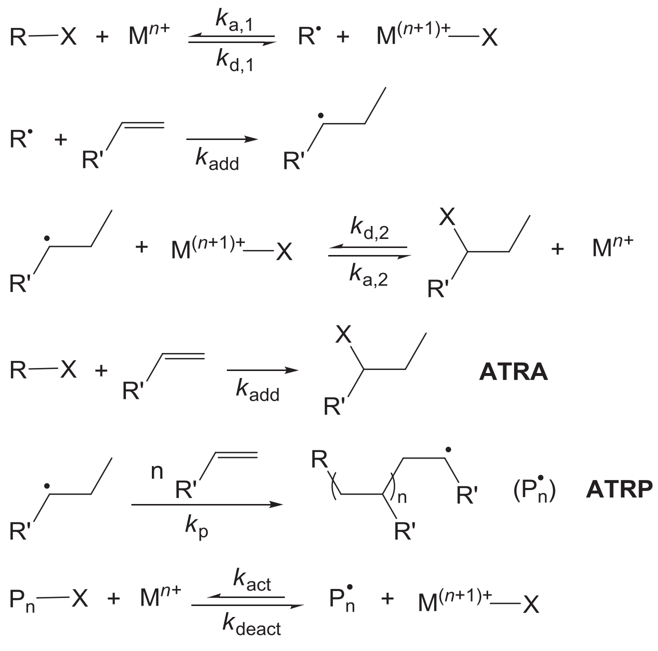

Chart 1.

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 ^{13}C 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, NJ, and on an in-house Perkin-Elmer 2400 CHN analyzer. HRMS data were collected on a Thermo Fisher Scientific LTQ-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