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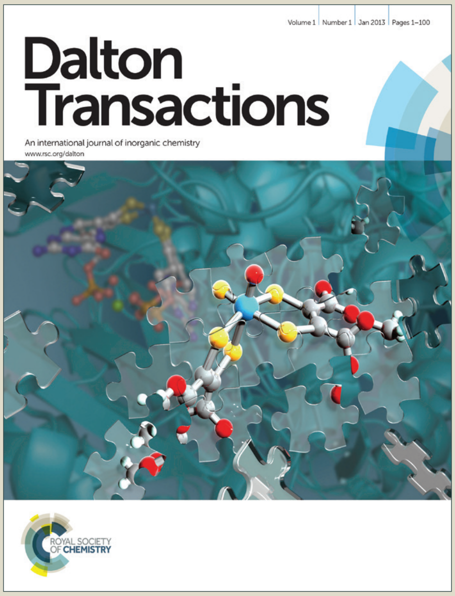

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Synthesis and characterization of β-tri-ketimine cobalt complexes and their behaviour in the polymerization of 1,3-butadiene

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Abstract

Three β-triketimine ligands, (L^1: $[CH\{CMeN(2,4,6\text{-}Me_3\text{-}C_6H_2)\}_2C(CMe_3N(2\text{-}MeO\text{-}C_6H_4)]$, L^2: $[CH\{CMeN(2,4\text{-}Me_2\text{-}C_6H_3)\}_2C(CMe_3N(2\text{-}MeO\text{-}C_6H_4)]$ and L^3: $[CH\{CMeN(2\text{-}Me\text{-}C_6H_4)\}_2C(CMe_3N(2\text{-}MeO\text{-}C_6H_4)])$, were synthesized and then characterized by ^1H and $^{13}C\{^1H\}$ NMR spectroscopy, elemental analysis and electrospray (ES) MS. β-triketimine cobalt(II) complexes were then prepared by the interaction of cobalt(II) bromide with L^{1-3} in the presence of NaBArF (BArF = $[\{3,5\text{-}(CF_3)_2\text{-}C_6H_3\}_4B]^-$). Five-coordinate dimeric bromide-bridged species $[(LCo\mu\text{-}Br)_2][BArF]_2$ were obtained. The geometry of the complexes was found by single-crystal X-ray diffraction to be slightly distorted square-pyramidal. The polymerization of 1,3-butadiene catalysed by these complexes upon activation with methylaluminoxane (MAO) in chlorobenzene yielded high *cis*-1,4-polybutadiene (>97% *cis*). The effect of steric and electronic properties of the ligands on the performance of the catalytic system was investigated: it was found that ligands with fewer methyl substituents gave more active catalytic systems. It was also found that increasing MAO: Co ratio resulted in higher activity. Stereoselectivity of all catalysts slightly decreased at higher temperature, whereas activities were maximised at 20 °C, where very high values of activity were recorded.

Introduction

Controlling chemo- and stereo-selectivities in diene polymerization is of interest to many academic and industrial research groups because of the myriad of their applications. The stereo- and chemo-selectivity of polymerization of dienes depend on the catalyst system used, where both the metal chosen and the nature of the ligands play important roles.[1, 2 3 4] Ziegler-Natta catalysts, in the widest terms, are considered the most efficient in the stereoselective polymerization of dienes; they are composed of complexes of metals such as Ti,[5] V,[6,7] Cr,[8] Fe,[9] Co,[10] Ni[11] and Nd[12] with a cocatalyst such as aluminium alkyl or aluminium alkyl chloride. Of late, those catalysts based on Nd are the most preferred industrially where a very high-*cis* 1,4 enchained polymer is desired.[13] However, when formulated industrially as salts of long-chain-branched carboxylate ligands, detailed understanding in the shape of structure-activity relationships has been hard to find. Some recent work has reported fully characterized, molecular examples of lanthanide catalysts of diene polymerization.[14] But cognisance must increasingly be paid to the finite global supply of readily minable concentrations of many elements.[15] While the absolute global abundance of neodymium is not problematic, it is very thinly distributed except in a few rare deposits, and difficult to separate from other lanthanides. Furthermore, the demand for its magnetic properties in energy generation is increasing even faster than the demand for synthetic rubbers. Consequently, there is a strong ecological as well as an economic and scientific case for seeking to impart the impressive activities and selectivities achievable with neodymium upon more available metals without competing uses. One such element is cobalt, readily available as a byproduct of the production of copper and nickel.[16] Much work has been published, encompassing oxygen, phosphorus and nitrogen-ligated Co(II), which has been reviewed.[1, 10] The ligands were found to have a strong effect on the form (*syn* or *anti*) of the intermediate allyl and the activity of the active centre during the polymerization.[3] These effects can be modified by changing the steric and electronic properties of the ligands.[17, 18] The most recent focus has been upon nitrogen-ligated cobalt complexes in diene polymerization, especially on those with tridentate ligands.[19, 20, 21] In this work we present the synthesis and characterisation of a new generation of cobalt catalysts using β-triketimine ligands recently employed to present a neutral N,N,N-ligand set in Cr, Mo, W,[22] Ni[23] and Tl complexes.[24] Our extension here to cobalt marks a departure from the recent work of others who employed exclusively planar, meridional N,N,N-ligands on cobalt,[19, 20, 21] since β-triketimines present a facial donor set. Chart 1 shows classes of N,N,N-Co(II) catalysts previously studied, **I**, **II** and **III**, alongside images of monomeric forms of the three precatalysts reported herein, **1-3**.

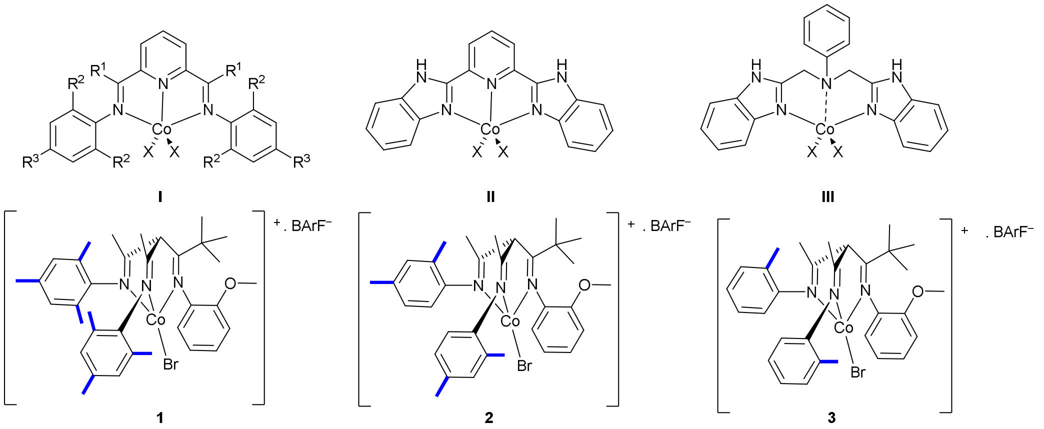


Chart 1. Monomeric forms of *fac* **1-3**, in comparison with previously reported *mer* precatalysts **I - III**.

We were interested to discover what effect this change from *mer* to *fac* donor set may have on activity and selectivity in polymerization of 1,3-butadiene. Furthermore, we probed the effect of subtle steric and electronic changes in the ligands L^{1-3} upon activity and selectivity in such polymerizations.

Results and discussion

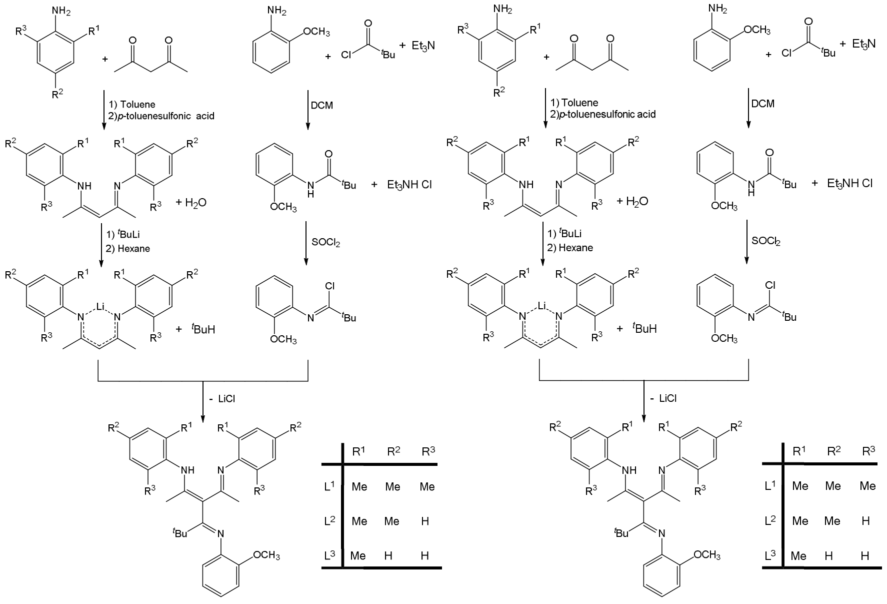
Synthesis and characterization of β-*tri*-ketimine cobalt complexes

β-triketimine ligands were synthesised through several reactions as shown in Scheme 2, according to the literature,[22] and they were fully characterized by NMR, IR, elemental analyses and electrospray mass spectrometry. These ligands were reacted with cobalt bromide in the presence of NaBArF reagent (Scheme 3). Brown crystals were formed which were suitable for single crystal X-ray diffraction.

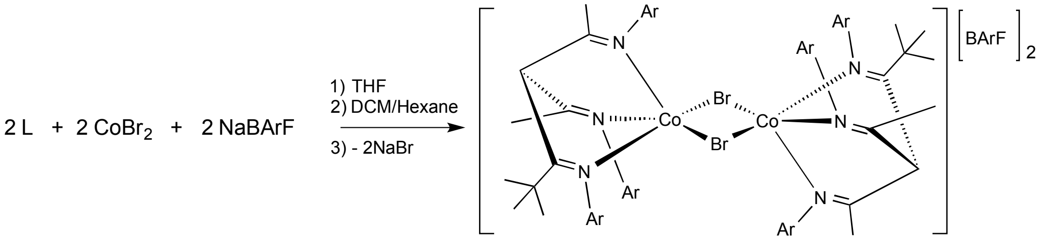
These complexes were found to be five-coordinate centrosymmetric dimeric bromide-bridged species $[(LCo\text{-}\mu\text{-}Br)_2][BArF]_2$ in the solid state, crystallizing isostructurally and isotypically, each with a single dichloromethane solvent molecule disordered over two sites. This structure possesses several rare features: There is only a single case known of a similar 5-co-ordinate doubly bromide-bridged complex with a tripodal ligand, $[\{PhB(CH_2PPh_2)_3CoBr\}_2]$.[25] However, in that case the ligand carried a negative charge on the fulcrum boron atom. In **1-3** this charge is carried on the non-co-ordinating BArF anions, making the dimers dications. Furthermore, the tris-phosphine anionic ligand is a much more powerful donor set than the triketimine in **1-**

3.[25] The closest precedent here, a dicationic Co_2Br_2 dimer with nitrogen-ligation, is $[\{N(CH_2CH_2N_2C_3H_3)_3CoBr\}_2].2BPh_4$. However, the tris-pyrazolyl-amine ligand in this dimer is tetradentate, leading to a pseudo-octahedral dimeric structure.[26] Compounds **1-3** are the first bromide-bridged cobalt dimers with a N_3Br_2 co-ordination sphere to be structurally characterized. However, there are some monomers with this co-ordination sphere, many of which have structures akin to **I**, and are hence trigonal bipyramidal. All 9 examples found showed meridional ligand geometry.[27-32] It is known that five- coordination can be square-pyramidal or trigonal-bipyramidal, but for many complexes the geometry adopted lies between these two extreme structures. In this case, the structural index parameter τ[33] was used in order to determine the position on the structural spectrum. A τ value of 0 signifies an idealized square pyramidal structure, whilst for an idealized trigonal bipyramidal structure the τ value is 1. In this case, β-triketimine cobalt complexes **1-3** were found to be square-pyramidal. Given that all prior examples of CoN_3Br_2 co-ordination spheres are trigonal bipyramidal,([27-32]) it is clear that the geometry was encouraged by the pre-organized *fac*-tridentate ligand. For instance, **1** had τ value equal to 0.05, which indicated a geometry only very partially distorted from the ideal square pyramidal. It was noticed that N2 occupied the axial site, whilst N1, N3, Br and Br$^{'}$ occupied equatorial sites. For the bonds lengths, it was found that Co-N2 (2.068(4) Å) was shorter than Co-N1 and Co-N3 at 2.107(4) and 2.176(4) Å respectively while Co-Br and Co-Br$^{'}$ were 2.4372(8) and 2.5082(8) Å respectively, indicating that the dimer was partially asymmetric. These Co-Br bond lengths are longer than those in the other square-based pyramidal bromide bridged dimer known, $[\{PhB(CH_2PPh_2)_3CoBr\}_2]$, which was also slightly asymmetric, with distances of 2.413(1) and 2.424(1) Å.[25] The slight lengthening might be ascribed to a different electronic structure, since the borate-triphosphine ligand imposes a rare low-spin configuration upon the cobalt(II) ion in the square-based pyramidal dimers, and even in the pseudo-tetrahedral monomers produced by their dissolution in toluene. While we suspect that the rather weak-field combination of imines and bromide ligands in **1-3** would give the more routinely expected high-spin weakly antiferromagnetically coupled configuration, which would make their combined electronic and geometric structure unique, we have not rigorously probed the electronic structure of the dimers **1-3**, since the focus of this work is on their function as polymerization catalysts, which almost certainly is preceded by break-up into monomers upon methylation by methylaluminoxane.

Returning to structural issues, the small variations in bond length shown in Table 1 are probably best explained via structural *trans* effects,[34] since the shorter Co-Br bond is *trans* to the longer Co-N bond, and the shortest Co-N bond is *trans* to a vacant site. In addition, the axial site was found to be bent toward N1 and N3 as judged from the facts that the angles of N2-Co-N1 and N2-Co-N3 were less than 90° while N2-Co-Br and N2-Co-Br were larger than 90° (close to 110°). However, the angles of N1-Co-Br and N3-Co-Br’ were 160° and 162° respectively (less than 180°) which indicates that the position of cobalt atoms was not in the equatorial plane but sitting proud of this plane, lying in the direction of N2 (figure 1).



Scheme 1 Synthetic pathway of β-*tri*-ketimine ligands



[(LCo-μ-Br)$_2$][BArF]$_2$

Ar = generalized substituted aryl ring

Scheme 2: Synthesis of [(LCo-μ-Br)$_2$][BArF]$_2$ complexes.

In the case of [(L^2)Co-μ-Br)$_2$][BArF]$_2$ (**2**) and [(L^{3}Co-μ-Br)$_2$][BArF]$_2$ (**3**), the values of τ were 0.07 and 0.11 respectively, which indicates that the geometry of these two complexes also tends to be square-pyramidal. As can be seen from Figures 2 and 3, N2 occupies the axial site, while N1, N3, Br and Br' occupy equatorial sites. Key angles and bonds length are listed in Table 1. It is clear from this data that the steric variations in **1**-**3** have a negligible effect on core structural aspects. However, an inspection of some non-bonded distances reveals the subtle structural effects of the varying substitution patterns: the mean of the distances separating the three nitrogen atoms in the tridentate ligands acts as convenient measure of the steric strain imposed by the ligand substituents. For **1**, this was 2.94(5) Å; for **2**, 2.88(1) Å, and for **3**, 2.87(2) Å hence barely any difference is observed between the 2-Me and the 2,6 dimethyl substituted complexes, and yet these mild perturbations in aryl methylation pattern generate significant variations in catalytic activity, *vide infra.* Furthermore, it should be noted that in all cases the methoxy substituent is remote from co-ordination to either metal in the dimers. It may have a function as a point of interaction with aluminoxane cocatalyst, however; the benefit of labile co-ordinating sites in butadiene polymerization has recently been discussed.[35]

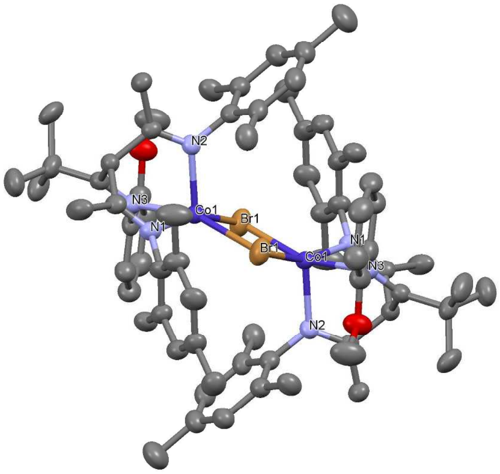


Figure 1 Structure of the dicationic unit in **1** with all hydrogen atoms and BArF ions omitted.

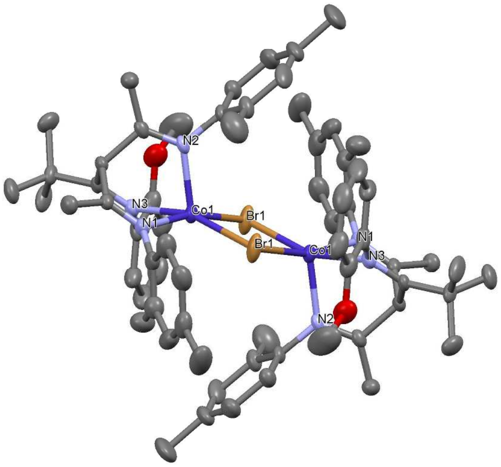


Figure 2 Structure of the dicationic unit in **2** with all hydrogen atoms and BArF ions omitted.

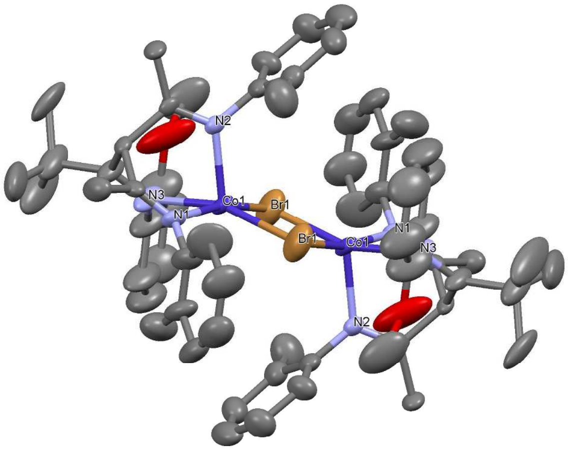


Figure 3 Structure of the dicationic unit in **3** with all hydrogen atoms and BArF ions omitted.

Table 1 Selected bond angles [°] and lengths [Å] of $[(LCo\text{-}\mu\text{-}Br)_2][BArF]_2$

	1	**2**	**3**
Co-N1	2.107(4)	2.116(5)	2.122(5)
Co-N2	2.068(4)	2.043(5)	2.065(5)
Co-N3	2.176(4)	2.149(5)	2.130(6)
Co-Br	2.4372(8)	2.4684(10)	2.4756(13)
Co-Br'	2.5082(8)	2.5032(11)	2.5125(14)
N2-Co-N1	89.46(15)	87.7(2)	87.42(19)
N2-Co-N3	87.79(15)	86.72(19)	86.6(2)
N2-Co-Br	110.07(11)	106.62(14)	104.17(14)
N2-Co-Br'	109.02(11)	110.96(14)	110.24(15)
N1-Co-Br	159.98(11)	165.51(15)	167.16(15)
N3-Co-Br'	162.01(11)	161.55(15)	160.58(19)

Butadiene polymerization

1,3-Butadiene was polymerized by β-triketimine cobalt(II) complexes in combination with MAO in chlorobenzene as solvent. This solvent was found to be preferable to toluene, since it more completely dissolved the BArF salts. Its higher dielectric constant (in comparison to toluene) may also have a role in promoting ion-separation during the polymerization process. The dimers **1**-**3** are assumed to break down into monomers when the bridging bromides are replaced by methyl groups, donating a single pair of electrons, from MAO. The ESMS information on the cations had isotope distributions which indicated that monomeric monocations were present in the gas phase. There is a rapid colour change upon addition of MAO. The β-triketimine ligands $L^{1\text{-}3}$ do not possess the reducibility of di-iminopyridine ligands such as those in **I** that have been associated with organoaluminium-mediated reduction,[36] so it is assumed that the d^7, Co(II) oxidation state is maintained. Current theories of diene polymerization are based upon the facts that metal-bound dienes are most stable when in the *s-cis* configuration,[37] which leads to the kinetically-controlled production of *anti*-allyl chain end upon attack by a nucleophile at an outer carbon of the bound butadiene, as shown in Scheme 3.[1,10] If this allyl acts as a nucleophile upon another *s-cis* bound monomer before it has an opportunity to re-arrange itself to the more thermodynamically stable *syn*-allyl, then *cis*-1,4 polybutadiene is produced. This theory requires an η^4 diene and a η^3-allyl anion to be concurrently bound to the d^7 Co(II), which, if it is assumed that the ligands L^{1-3} (and those in I-III, for that matter) remain κ^3-bound, gives an implausibly high valence electron count at cobalt of 21. It seems likely in all these cases that the denticity/hapticity of the three ligands at hand must vary from its maximum as the catalytic cycle is traversed. However, if the allyl was to become η^1, then isomerization would occur, which would result in *trans*-polybutadiene. The polymers produced by **1-3** were characterized by NMR in order to determine their microstructures, according with the literature.[38, 39, 40] The results are summarized in Table 2. In all these polymers, *trans* levels are very low, and so η^3-η^1-allyl isomerization (Figure 4) must be a rare event. If the diene was to become η^2, then 1,2 vinyl enchainment is likely, and this also is a rare event. Consequently, catalysts **1-3** give very high levels of *cis*-1,4 selectivity (>97%), meaning that the electron count at metal must be controlled by variations in denticity of ligands L^{1-3}, as has been postulated also for catalyst II (see Scheme 3).[3] In fact, as has previously been remarked upon,[21] there is a very small variation in regio-and stereo-selectivity amongst all of the catalysts prepared from *mer* **I-III** and *fac* **1-3**; even ligandless $CoCl_2$ or $CoBr_2$ can give similar selectivity levels,[39] which prompts the suspicion that the ligands may dissociate fully in all cases.[41] However, as found by others, there are stark variations in activity, molecular weight, and molecular weight distribution achieved by the various catalysts, difficult to reconcile with a hypothesis of full ligand dissociation. It must be the case that the lifetime of the η^3-allyl-η^4-butadiene intermediate which controls *cis/trans* levels in 1,4 enchained polybutadiene is similarly short for all catalysts, leading to the high *cis*-1,4 selectivity.[41]

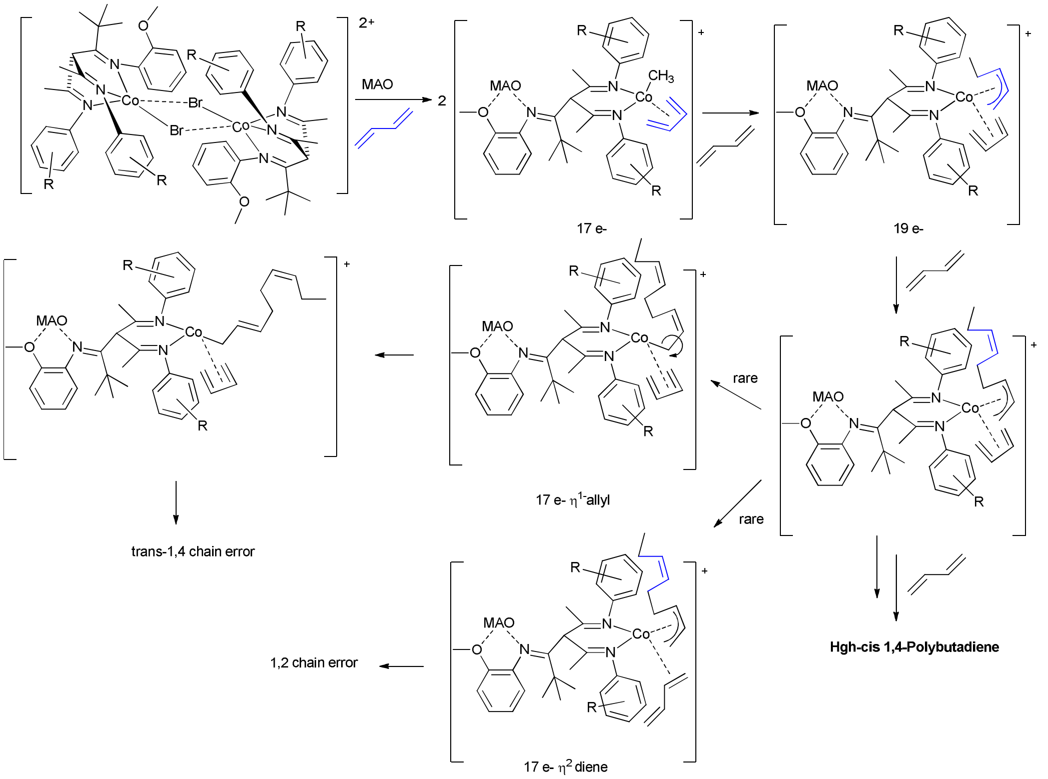
The lowest activity was found in the case of **1** (15,295 mol butadiene mol^{-1} Co h^{-1}). Removal of one *ortho*-methyl group from the mesityl complex **1** gave **2**, which increased the activity substantially to 25,185 mol butadiene mol^{-1} Co h^{-1}. Further reduction in bulk was in the *para*-position, which would have a greater electronic than steric effect, to give **3**. The resulting increase in activity was more modest, to reach 26,666 mol butadiene mol^{-1} Co h^{-1}. However, this value is higher than any yet recorded for cobalt complexes which yield high *cis*-1,4 polybutadiene. Phosphine complexes have given higher values, but these give mainly 1,2-enchained polymer.[8] In summary, the incoming monomer appears to find difficulty in coordinating to the cobalt centre in the bulkiest catalyst **1**, and progressive removal of aryl substituents enhances activity by reducing the steric strain. In addition, electronic factors may also play a role, in that as the number of electron donating methyl groups on the imino-aryl rings increases, this leads to an increase in the density of electrons on the active centre. As a result, the interaction between the cobalt centre and incoming monomers will decrease, and hence decrease the activity. This behaviour was also observed with 2,6-bis(imino)pyridyl Co(II) complexes of type **I**[17] in which ligands with fewer donor substituents, and more electron-withdrawing imine substituents, resulted in more active complexes. However, entirely unsubstituted aryls appear to make poorer catalysts, since **I** where R^2 and R^3 = H and R^1 = Me gave an activity corresponding to only 250 mol butadiene mol^{-1} Co h^{-1},[2] whereas an activity of 8,704 mol butadiene mol^{-1} Co h^{-1} was reported for **I** where R^2 and R^3 = Me and R^1 = Cl.[42]

Though our recorded activities are among the highest yet reported for high-*cis* 1,4-polybutadiene production, it should be noted that our control runs using unligated $CoCl_2$ and $CoBr_2$ (11,852 and 6,148 mol butadiene mol^{-1} Co h^{-1} respectively) are also higher than those reported by other workers.[39, 42] Hence, direct comparison of activities between different groups with different polymerization reactors and processes must be treated with caution. All that may be said with certainty is the catalysts **1-3** are more active than simple salts $CoCl_2$ or $CoBr_2$, with ligated examples giving more than double the activities of unligated $CoBr_2$ under similar conditions; this is perhaps due to an increase in the nucleophilicity of the terminal allyl of the polymeryl chain (Scheme 3) resulting from its weakened hold on an imine-ligated cobalt relative to an unligated one. Activities are, making allowance for differing polymerization conditions, broadly comparable with those reported for the best of examples of classes **I-III**; though our headline activity figures are in most cases higher than previous reports, this may be due to the fact that most prior work used a depleting stock from an initial charge of monomer, whereas we continuously supplied monomer. However, it could additionally be that the cationic nature of **1-3** helped activities, in that it obviated the requirement of MAO to act as a Lewis Acid. Furthermore, the high activities might be due to the ability of β-triketimines to more readily reduce denticity, thus controlling electron count at cobalt, than some of the more rigid ligand sets in **I-III**.

The molecular weights of polymers produced by **1-3** are also in general higher than most reported previously for Co complexes. This may be an effect of the constant high concentration of monomer favouring further monomer enchainment over chain transfer processes. Turning to comparisons within **1-3**, the relevant data are in Table 2, entries 1-3, which list set conditions of temperature and aluminium ratio. Though **1** had the lowest activity of **1-3**, it produced polymer of the highest M_n (540,000 g mol^{-1}) and the narrowest molar mass distribution, PDI = 2.44 (Table 2, entry 1). This is presumably because the higher bulk of **1** relative to **2** and **3** inhibited chain transfer. Evidence that a thermally activated chain transfer process is occurring comes from examination of entries 1, 4, 5 and 6, where it is seen that for **1** at constant Co:Al ratio, molar mass distribution increases linearly with temperature as M_n decreases. Evidence that the most important such process is chain transfer to aluminium comes from entries 1, 7, 8 and 9, which show that M_n decreases linearly with increasing Al:Co ratio (r^2 = 0.997). We can conclude that the enhanced bulkiness of **1** leads to the highest molar mass and narrowest molar mass distribution by most effectively inhibiting the approach of organoaluminium species, thus inhibiting formation of the Co-CH_3-Al-bridged species necessary to facilitate chain transfer. Furthermore, no explanation of these data is available if full ligand dissociation is assumed. Clearly, however, the fact that the PDI values are never lower than 2 suggests that these processes are never inhibited completely.

In contrast to some prior reports,[7, 43] there was no significant influence of Al:Co ratio on the microstructure of polybutadiene which was found to be predominantly *cis*-1,4 (around 97%) in all cases. On the other hand, the activity increased with MAO ratio, presumably by increasing the number of active centres.

Finally, the effect of polymerization temperature was studied; it was found that, in line with expectation and several prior reports, [19, 20, 42, 44] increasing temperature reduced stereo- and regio-selectivity of the polymerization. At higher temperature, a greater proportion of active centres may attain sufficient energy to isomerize from *anti* isomer (resulting in 1,4-*cis* content) to the more stable *syn* isomer (resulting in 1,4-*trans* content) as shown in Scheme 3. This process could be facilitated by a re-co-ordination of any of the β-triketimine ligand arms which may have dissociated to control the electron count at cobalt, which could also encourage η^2 butadiene co-ordination, thus explaining the slight increase in vinyl 1,2 addition at higher temperatures (Scheme 3).



Consequently, the highest *cis*-1,4 content (98%) was attained at 10 °C. This dropped to 96% at 40 °C. However, the dependence of polymerization activity on temperature was not linear: it was initially observed to display normal Arrhenius rate behaviour in increasing from 10 to 20 °C , but then dipped, reaching its lowest value at 40 °C. This may be ascribed to the lower concentration of butadiene dissolved in the chlorobenzene solvent at higher temperatures. Consequently, 20 °C was the optimum temperature found to maximise production of polymer.

Table 2 Butadiene polymerization with β-triketimine cobalt(II) catalysts

Entry	Catalyst	Al:Co	T	M_w[b] ×10^{-5} g/mol	M_n[b] ×10^{-5} g/mol	PDI[b]	Activity g.mmol^{-1} h^{-1}	Microstructure %[c]		
								cis	*trans*	1.2
1	**1**	1000	20	15.6	5.4	2.89	824	97.5	1.0	1.5
2	**2**	1000	20	10.4	3.4	3.06	1360	97.8	1.0	1.2
3	**3**	1000	20	10.5	3.4	3.09	1440	97.5	1.0	1.5
4	**1**	1000	10	14.3	5.7	2.51	400	98.0	1.0	1.0

5	**1**	1000	30	15.8	4.8	3.29	400	97.0	1.5	1.5
6	**1**	1000	40	12.7	3.4	3.74	200	96.0	2.5	1.5
7	**1**	500	20	15.4	6.3	2.44	750	97.0	1.0	2.0
8	**1**	1500	20	13.7	4.3	3.19	1100	96.5	2.0	1.5
9	**1**	2000	20	12.3	3.5	3.51	1200	97.5	1.5	1.0
10	$CoBr_2$	1000	20	12.7	5.6	2.27	332	97.0	1.5	1.0
11	$CoCl_2$	1000	20	14.4	6.4	2.25	640	98.0	1.0	10

[a] **Conditions**: catalyst: 10 µmol; co-catalyst: MAO; solvent: 40 mL chlorobenzene; 15 minutes. [b] Determined by GPC. [c] Determined by $^{13}C\{^1H\}$ NMR.

Conclusion

A series of β-triketimine cobalt(II) complexes were prepared and then characterised by X-ray crystallography. These complexes were examined in the polymerization of 1,3-butadiene and were found to produce predominantly 1,4-*cis* content (>97%). The complex with the fewest methyl substituents on imoino-aryl rings **(3)** was the most active (1440 g $mmol^{-1}$ h^{-1}). While comparisons with activity figures from other workers is fraught with difficulty due to the strong dependence on the conditions of the polymerization, these figures are among the highest yet reported for cobalt. The polymers produced had high molecular weight, limited only by chain transfer to aluminium. The ratio of co-catalyst to catalyst did not influence the microstructure of the polymer but the activity was increased markedly as the Al:Co ratio increased. In contrast, there was slight influence of polymerization temperature on the microstructure: 1,4-*cis* content was reduced with increasing temperature.

Experimental section

General considerations

All procedures were carried out under an atmosphere of nitrogen. The ligands, $CoBr_2$ and NaBArF were stored in a glovebox before they were transferred into Schlenk tubes. Nitrogen gas was dried by passage through a column of phosphorus pentoxide supported on vermiculite. The solvents toluene, hexane, diethyl ether and tetrahydrofuran (THF) were distilled from sodium/benzophenone, while *o*-anisidine, 2,4,6-trimethyl aniline, 2,4,-dimethyl aniline, 2-methyl aniline, dichloromethane (DCM), chlorobenzene and triethyl amine were distilled from calcium hydride. Butadiene was provided by ICI

Wilton and it was passed through a column of P_2O_5 supported on vermiculite, followed by another column filled with molecular sieves 4A. ^{t}Butyl acetyl chloride, acetylacetone, $SOCl_2$, ^{n}BuLi, $CoBr_2$ triethylamine, 2-methylaniline and methylaluminoxane were purchased from Sigma-Aldrich. 2,4,6-Trimethylaniline, 2,4-dimethylaniline and p-toluenesulfonic acid were purchased from Acros-Organic. NaBArF,[22, 45] ^{t}BuCONH-2-$OCH_3C_6H_4$[46] and ^{t}BuCClN-2-$OCH_3C_6H_4$[22] were synthesised according to literature procedures. A Bruker 400 MHz spectrometer was used in order to record the NMR spectra, using $CDCl_3$ as solvent. Infrared spectra were recorded on a Bruker Alpha-p spectrometer, using OPUS 6.5 software. The mass spectra were recorded using the electrospray (ES) and MALDI techniques, with acetonitrile as solvent. Gel permeation chromatography (GPC) was used to measure M_n, M_w and PDI. GPC was carried out at 35 °C using a PL 2MB500A column in THF at a flow rate of 1 cm^3 min^{-1};100 µl was injected using a Viscotek GPC max VE2001 and Viscotek VE2001 GPC was used as a detector. X-ray diffraction (XRD) was carried out to measure the structure of single crystals. The data for **1** and **2** were collected on an Oxford SMART CCD diffractometer with Mo K-α X-ray source (λ = 0.71073 Å) at 150 K, while the data of **(3)** was collected on Bruker-Prospector diffractometer with Cu K-α X-ray source (λ = 1.54184 Å) at 150 K. The collected data were solved using the SUPERFLIP[47] program and refined by the SHELX-97[48] and OLEX2[49] programs.

Synthesis and characterization of β-iminoenamines (HBDK

HBDK$^{2,4,6\text{-}Me3}$: In a modification of a literature procedure,[50] a solution of 2,4,6-trimethylaniline (30 cm^3, 0.213 mol) and acetylacetone (10 cm^3, 0.0973) in toluene (100 cm^3) was heated and refluxed for five hours in the presence of a small catalytic amount of *p*-toluenesulfonic acid. At the beginning of the reaction the solution was light green but after 15 minutes it changed to orange. After five hours, the water produced was removed using a Dean-Stark apparatus, then the solvent (toluene) and (Z)-4-(mesitylamino)pent-3-en-2-one were then removed by distillation with the aid of the Dean-Stark arm. A dark orange oil was formed and was treated with a small amount of cooled methanol, then scratched. The yellow crystals which formed were then filtered and washed with cold methanol (18.9 g, 58%), mp: 59-61 °C. ^{1}H NMR (400 MHz, CDCl$_3$): δ 1.62 (6H, s, CH$_3$C=N), 2.05 (12H, s, *o*-CH$_3$), 2.19 (6H, s, *p*-CH$_3$), 4.78 (1H, s, alkenyl C-H), 6.78 (4H, s, aromatic C-H), 12.08 (1H, s, N-H). IR(cm^{-1}): 2971-2837 (C-H), 1698 (C=N). Data were in accord with those published for this compound.[50]

HBDK$^{\mathbf{2,4\text{-}Me2}}$: The same procedure as for **HBDK$^{\mathbf{2,4,6\text{-}Me3}}$** was used; 2,4-dimethylaniline (24.1 cm^3, 0.195 mol), acetylacetone (10 cm^3, 0.0973 mol), a small catalytic amount of *p*-toluenesulfonic acid and toluene (100 cm^3) were used. A yellow oil (22.4 g, 75%) was formed. ^{1}H NMR (400MHz, CDCl$_3$): δ 1.80 (6H, s, CH$_3$C=N), 2.07 (6H, s, *o*-CH$_3$), 2.21 (6H, s, *p*-CH$_3$), 4.78 (1H, s, alkenyl C-H), 6.72 (2H, d, $^3J_{HH}$ = 8 Hz, *o*-CH), 6.86 (2H, dd, $^3J_{HH}$ = 8 Hz, $^4J_{HH}$ = 1.6 Hz, *m*-CH), 6.91 (2H, s, *m*-CH), 12.41 (1H, s, NH). This intermediate was not characterized further.

HBDK$^{\mathbf{2\text{-}Me}}$: In a modification of a literature procedure,[51] a solution of 2-methylaniline (18 cm^3, 0.167 mol), acetylacetone (8 cm^3, 0.08 mol) and *p*-toluenesulfonic acid (14 g, 0.081 mol) in toluene (100 cm^3) was heated and refluxed for five hours. White solid was formed which then was filtered and left stirring for half hour in a mixture of diethylether (250 mL), water (150 mL) and Na$_2$CO$_3$.10H$_2$O (23 g). The organic phase was then extracted and dried with MgSO$_4$, then the solvent was removed. A dark orange oil was formed which was treated with a small amount of cooled methanol, then scratched. Yellow crystals were formed, which were then filtered and washed with cold methanol (14.3 g, 64 %), mp: 35-36 °C. ^{1}H NMR (400 MHz, CDCl$_3$): δ 1.83 (6H, s, CH$_3$C=N), 2.12 (6H, s, *o*-CH$_3$), 4.82 (1H, s, alkenyl C-H), 6.84 (2H, dd, $^3J_{HH}$ = 8 Hz, $^4J_{HH}$ = 1.2 Hz, *o*-CH), 6.92 (2H, td, $^3J_{HH}$ = 7.6 Hz, $^4J_{HH}$ = 1.2 Hz, *m*-CH), 7.06 (2H, td, $^3J_{HH}$ = 8 Hz, $^4J_{HH}$ = 1.6 Hz, *p*-CH), 7.6 (2H, dq, $^3J_{HH}$ = 8 Hz, $^4J_{HH}$ = 0.8 Hz, *m*-CH), 12.45 (1H, s, NH). Data were in accord with those published.[51]

Synthesis and characterization of β-triketimines (L).

L$^{\mathbf{1}}$: HBDK$^{\mathbf{2,4,6\text{-}Me3}}$(1.86 g, 5.6 mmol) was dissolved in hexane (100 cm^3) and the solution was stirred in a Schlenk tube. ^{n}BuLi (4 cm^3 of a 1.6 M solution in hexane, 6.4 mmol) was added slowly to the solution through a syringe. This reaction was exothermic, so the mixture was cooled using an external ice-bath. The reaction was left stirring at 0 °C for 30 minutes. The mixture was heated using a gun heater to ensure that the reaction was complete. ^{t}BuCClN-2-MeOC$_6$H$_4$ (1.4 cm^3, 6.2 mmol) was then added, forming a heavy yellow precipitate. The mixture was left stirring overnight at room temperature and was then poured into water (200 cm^3), forming two phases. The organic phase was collected, while the aqueous phase was treated twice with diethyl ether (200 cm^3) and the organic phase collected each time. The combined organic layers were dried using magnesium sulphate and filtered, then the solvent (diethyl ether) was removed under vacuum. The orange oil so formed was treated with a small amount of cold methanol, then scratched. Yellow crystals were formed which were filtered and washed with cold methanol (2.35 g, 80%), mp: 158-160 °C. ^{1}H NMR (400MHz, CDCl$_3$): δ 1.34 (9H, s, C(CH$_3$)$_3$), 1.54 (6H, s, N=C-CH$_3$), 1.65 (6H, s, *p*-CH$_3$), 2.01 (6H, s, *o*-CH$_3$), 2.16 (6H, s, *o*-CH$_3$), 3.64 (3H, s, OCH$_3$), 6.47-6.93 (8H, aromatic, two different aromatic rings, extensive overlap, deconvolution unsuccessful), 13.45 (1H, s, NH). ^{13}C{^{1}H} NMR (400MHz, CDCl$_3$): δ peaks due to CH$_3$: 16.59 (2 N=C-CH$_3$), 17.04 (2 *p*-CH$_3$), 19.01 (2 *o*-CH$_3$), 19.78 (2 *o*-CH$_3$), 29.57 (C(CH$_3$)$_3$), 54.15 (1 OCH$_3$); peaks due to aromatic CH: 110.87, 119.86, 120.11, 123.97, 128.44, 128.50; peaks due to aromatic C: 130.32, 130.42, 132.57, 139.47, 140.09, 149.38; peaks due to aliphatic C: 41.08, 101.46, 158.17, 181.84. Elemental analysis, calculated for C$_{35}$H$_{45}$N$_3$O (%): C, 80.26; H, 8.65; N, 8.02. Found: C,79.9; H, 8.40; N, 7.99. Mass spectrometry (ESI$^+$) *m/z*: 524 [MH]$^+$. IR (cm^{-1}): 3005-2818 (C-H), 1589 (N=C), 1010 (C-O).

L^2 was prepared in a procedure similar to that used for L^1: **HBDK$^{2,4\text{-}Me2}$** (2.7 g, 8.8 mmol), ^{n}BuLi (6 cm^3, 9.6 mmol), ^{t}BuCClN-2-MeOC$_6$H$_4$ (2.1 cm^3, 9.3 mmol) and hexane (80 cm^3) were used. Yellow crystals were formed (3.7 g, 85%), mp: 108-110 °C. ^{1}H NMR (400MHz, CDCl$_3$): δ 1.34 (9H, s, C(CH$_3$)$_3$), 1.66 (6H,s, =C-CH$_3$), 1.78 (6H, s, *o*-CH$_3$), 2.19 (6H, s, *p*-CH$_3$), 3.65 (3H, s, OCH$_3$), 6.46-6.92 (10H, aromatic CH), 13.40 (1H, s, NH). ^{13}C{^{1}H} NMR (400 MHz, CDCl$_3$): peaks due to CH$_3$: δ 17.75 (2 *o*-CH$_3$), 20.50 (2 N=C-CH$_3$), 20.80 (2 *p*-CH$_3$), 30.58 (C(CH$_3$)$_3$), 55.20 (OCH$_3$); peaks due to CH: 110.93, 119.55, 120.17, 123.80, 123.98, 126.79, 130.99 (aromatic CH); peaks due to aliphatic C: 42.27 ($C(CH_3)_3$), 131.06 (C=C), 158.74 (NH-C-CH_3), 182.46 (NH-C=C) ,peaks due to aromatic C: 120.69, 122.36, 122.85, 133.57, 141.05. Elemental analysis, calculated for $C_{33}H_{41}N_3O_1$ (%): C, 79.96; H, 8.34; N, 8.48. Found: C, 79.49; H, 8.04; N, 8.50. Mass spectrometry (ESI$^+$) *m/z*: 496 $[MH]^+$.

L^3: As for L^1: **$HBDK^{2\text{-}Me}$** (2.01 g, 7.22 mmol), ^{n}BuLi (5 cm^3, 8.0 mmol), ^{t}BuCClN-2-MeOC_6H_4 (1.75 cm^3, 7.75 mmol) and hexane (100 cm^3) were used. Yellow crystals were formed (3.0 g, 89%), mp: 121-123 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.35 (9H, s, $C(CH_3)_3$), 1.68 (6H,s, =C-CH_3), 1.83 (6H, s, *o*-CH_3), 3.66 (3H, s, OCH_3), 6.47-7.06 (12H, aromatic CH), 13.50 (1H, s, NH). $^{13}C\{^1H\}$ NMR (400 MHz, $CDCl_3$): peaks due to CH_3: δ 17.84 (2 *o*-CH_3), 20.59 (2 N=C-CH_3), 30.61 ($C(CH_3)_3$), 55.26 (OCH_3); peaks due to CH: 111.03, 119.52, 120.22, 123.89, 124.06, 124.16, 126.23, 130.31 (aromatic CH); peaks due to aliphatic C: 42.26 ($C(CH_3)_3$), 104.34 (C=C), 158.55 (NH-C-CH_3), 182.33 (NH-C=C) ,peaks due to aromatic C: 131.28, 140.86, 144.23, 150.37. Elemental analysis, calculated for $C_{31}H_{37}N_3O_1$ (%): C, 79.62; H, 7.97; N, 8.99. Found: C, 79.51; H, 8.36; N, 8.90. Mass spectrometry (ESI$^+$) *m/z*: 468 $[MH]^+$.

Synthesis and characterization of β-triketimine cobalt complexes.

(1): A mixture of L^1 (1.04 g, 1.99 mmol), $CoBr_2$ (0.466 g, 2.13 mmol) and NaBArF (1.763 g, 1.99 mmol) was added to a Schlenk tube in the glovebox. THF (30 cm^3) was added to the mixture, forming a green solution which was left stirring overnight at room temperature under nitrogen. The THF was then removed, DCM (30 cm^3) was added and the solution was filtered through celite under nitrogen. The celite pad was washed with DCM (2×10 cm^3) and the combined filtrate was left stirring overnight. The solution was reduced in volume by 80% under vacuum, then layered with hexane (40 cm^3) and left for 7 days. Green-brown crystals of **(1)** were formed (0.85 g, 28%); mp: 199-201 °C. Elemental analysis, calculated for $C_{134}H_{114}N_6O_2F_{48}B_2Co_2Br_2$ (%): C, 52.74; H, 3.77; N, 2.75; Co, 3.86; Br, 5.24. Found: C, 52.43; H, 3.50; N, 2.70; Co, 3.68; Br, 5.36. MS (MALDI) *m/z*: 662-664 $[(L^1)CoBr]^+$.

(**2**): **L^2** (1 g, 2.02 mmol), $CoBr_2$ (0.5 g, 2.29 mmol), $NaBArF_4$ (1.7 g, 2.00 mmol); brown crystals (1.84 g, 61%); mp: 215-217 °C. Elemental analysis, calculated for $C_{130}H_{114}N_6O_2F_{48}B_2Co_2Br_2$ (%): C, 52.12; H, 3.57; N, 2.81; Co, 3.93; Br, 5.33. Found: C, 51.77; H, 3.52; N, 2.71; Co, 2.69; Br, 5.24. MS (MALDI) *m/z*: 634-638 $[(L^2)CoBr]^+$.

(**3**): **L^3** (1 g, 2.14 mmol), $CoBr_2$ (0.5 g, 2.29 mmol), $NaBArF_4$ (1.7 g, 2.00 mmol); brown crystals (1.72 g, 56%); mp: 217-219 °C. Elemental analysis, calculated for $C_{126}H_{98}N_6O_2F_{48}B_2Co_2Br_2$ (%): C, 51.49; H, 3.36; N, 2.86; Co, 4.01; Br, 5.44. Found: C, 51.60; H, 3.30; N, 2.79; Co, 4.05; Br, 5.36. MS (MALDI) *m/z*: 606-610 $[(L^3)CoBr]^+$.

Polymerization of 1,3-butadiene

In the glovebox, a known quantity of catalyst **1-3** (10 μmol) was transferred into a Schlenk tube, to which chlorobenzene (30 cm^3) was added after removal from the glovebox. The Schlenk tube was attached to a N_2/vacuum double manifold, and the solution was left stirring for ten minutes. To the solution, MAO (6.6 cm^3 of a 10% solution in toluene) was added in order to activate the catalyst. The solution was left stirring for five minutes. 1,3-Butadiene gas was then passed through the solution in the Schlenk tube. The polymerization was allowed to proceed for 15 minutes, before being terminated by stopping the 1,3-butadiene supply. The viscous solution so formed was immediately poured into acidified methanol (20 mL conc. HCl in 200 mL methanol) containing 2,6-di-tert-butyl-4-methylphenol (1.0 wt%) as antioxidant, causing the polymer to precipitate. The mixture was left stirring overnight. The polymer was filtered, washed with methanol and then dried under vacuum for 12 hours.

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M. N. Alnajrani and F. S. Mair, "Synthesis and characterization of β-triketimine cobalt complexes and their behaviour in the polymerization of 1,3-butadiene"

Graphical Contents Entry

Cobalt II ions ligated by *fac*-κ^3-β-triketimine ligands form bromide-bridged square-based pyramidal dimers which upon activation with MAO and fed with a constant supply of butadiene produce high-*cis*-1,4-polybutadiene with activities and molecular weights surpassing all previously seen for this metal.