

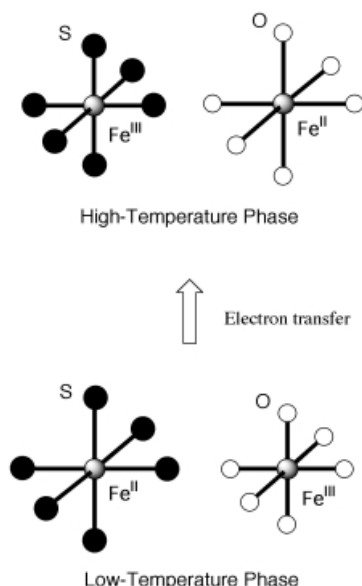


Figure 4. The relationship between the electron transfer and the metal–ligand bond lengths.

crossover phenomenon. However, the present calorimetric study clearly revealed that this novel phenomenon is quite different from usual (or classical) spin-crossover phenomenon.

Experimental Section

Synthesis of **1** is reported elsewhere.^[1, 4] Heat capacity measurements between 8 K and 300 K were made with a home-built adiabatic microcalorimeter.^[11, 12] The mass of the sample for calorimetry was 0.95853 g (1.4556 mmol). A small amount of He gas was sealed in the calorimeter cell to aid the heat transfer.

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Olefin Polymerization with $[\{\text{bis}(\text{imino})\text{pyridyl}\}\text{Co}^{\text{II}}\text{Cl}_2]$: Generation of the Active Species Involves $\text{Co}^{\text{I}*}$

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The independent discovery by the groups of Brookhart and Gibson that bis(imino)pyridyl (N_3) complexes of iron and cobalt (Figure 1) are precursors for active polymerization and oligomerization catalysts^[1] has put a new perspective on late transition metals as polymerization catalysts. However, there have been very few reports of successful extension of the system (other than trivial changes of substituents), which indicates that our understanding of this catalytic system is still incomplete.

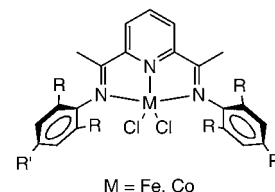


Figure 1. Previously reported bis(imino)pyridyl precatalysts $[\text{N}_3^{\text{R}}\text{FeCl}_2]$ and $[\text{N}_3^{\text{R}}\text{CoCl}_2]$.^[1]

The mechanism by which polymerization is believed to proceed is essentially the same as for early transition metals, that is, the active species is a cationic metal(II) alkyl complex. One recent publication contradicts this belief for the iron-based catalyst system.^[2] Mechanistic studies are difficult for several reasons. In addition to problems of high activity (and hence low concentration) and the large excess of MAO (MAO = methylaluminoxane) used, the Fe and Co systems are also paramagnetic, which complicates NMR spectroscopy studies. Gibson has mentioned some preliminary studies of iron–alkyl species which appear to support formation of $[\text{N}_3\text{FeR}]^+$ ^[3] moieties, but so far no reports on the corresponding Co systems have appeared. The groups of Gambarotta^[4a]

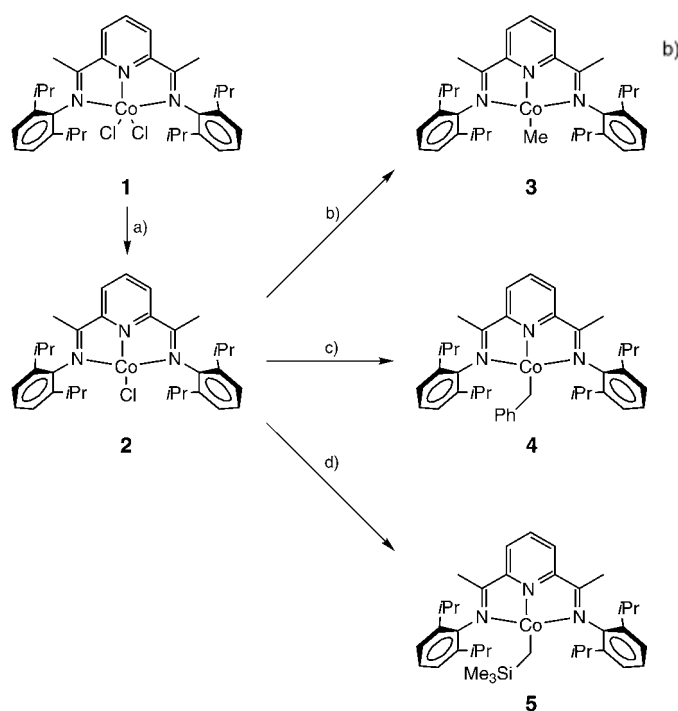
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and Brookhart^[4b] have used other metals (V, Rh/Ru) in the same ligand environment to model possible active species. The Fe and Co systems have also been studied theoretically.^[5] For Fe, Ziegler and co-workers obtained results in excellent agreement with the experimental data.^[5a] For the Co system, however, the predominant termination pathway could not be unambiguously assigned and the calculated olefin-complexation barrier was found to be rather high.^[5b] Thus, it is not immediately obvious that the active species in the Co system must be strictly analogous to that in the Fe system. We decided to study the Co system in more detail in the hope of establishing the nature of the active species and to understand the differences with the Fe system. Herein we describe our first results in this area.

Alkylating, $[\text{N}_3^{\text{iPr}}\text{Co}^{\text{II}}\text{Cl}_2]$ (**1**; $\text{N}_3^{\text{iPr}} = 2,6\text{-bis-[1-(2,6-diisopropylphenylimino)ethyl]pyridine}$; Scheme 1) with better defined alkylating agents than MAO (MeLi, Et₂Zn) we found that the Co^{II} chloride was not immediately alkylated, but instead was first reduced to a (presumably square planar) diamagnetic Co^I chloride.^[6] According to ¹H NMR spectroscopy, side products were formed in this reaction, but crystallization from toluene yielded the main product **2** as deep purple crystals.^[7]



Scheme 1. Synthesis of $[\text{N}_3^{\text{iPr}}\text{Co}^{\text{I}}]$ complexes. Reagents and conditions: a) 1.2 equiv MeLi, toluene, 5 h or 2 equiv MAO, toluene, instant; b) 1.1 equiv MeLi, diethyl ether, 3 days or 2 equiv MAO, toluene, instant; c) 2.0 equiv Bn_2Mg , toluene, 2 h; d) 1.2 equiv $\text{LiCH}_2\text{SiMe}_3$, toluene, 10 min.

Complex **2** could be selectively alkylated. Treatment of **2** with a slight excess of MeLi, Bn_2Mg , or $\text{LiCH}_2\text{SiMe}_3$ resulted in the corresponding neutral (also diamagnetic) Co^I alkyl complexes in three days, two hours, and ten minutes, respectively (Scheme 1). The upfield shift of the phenyl signals of the benzyl group in **4**, which results from shielding

by the aryl rings of the ligand, indicates that the alkyl moieties are located between the two aryl rings of the ligand. The ¹H NMR spectra of all the Co^I species showed unusual downfield shifts for the *para* pyridine (Py) hydrogen atom (9.5–10.3 ppm) and upfield shifts for the ketimine methyl hydrogen atoms (−1.2–0.1 ppm) that are as yet unexplained.

Crystals of **5** obtained from hexane were suitable for X-ray diffraction. In agreement with NMR spectroscopy data, **5** is a square-planar Co^I complex (Figure 2),^[8] and is the first structurally characterized Co^I–alkyl species with nitrogen

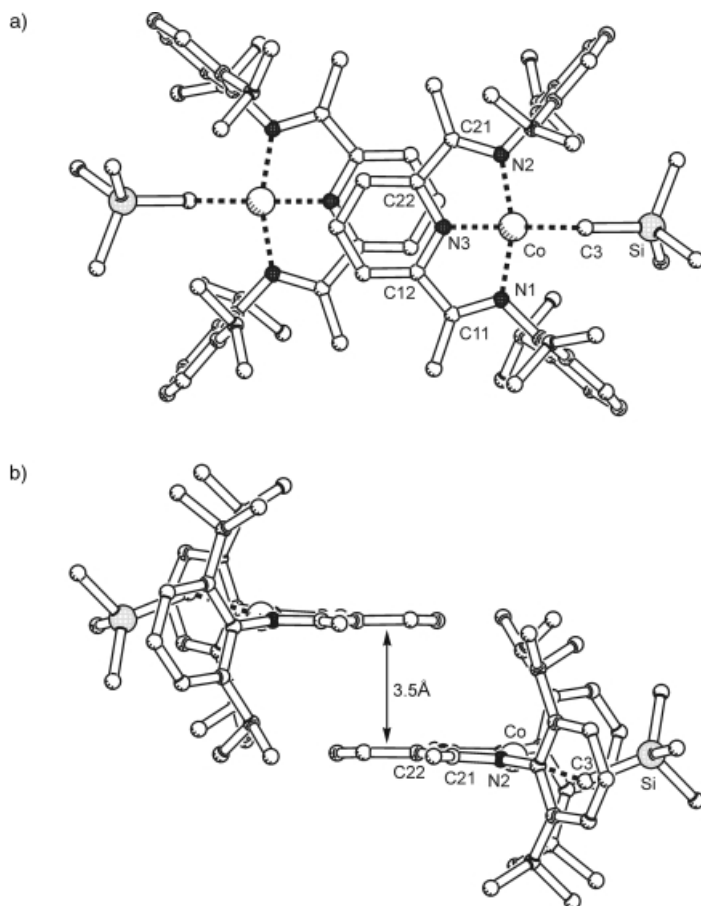


Figure 2. PLUTON^[9] drawing of the pairwise arrangement of **5** in the crystal lattice; a) top view, b) side view. Selected bond lengths [Å] and angles [°]: Co–N1 1.9291(17), Co–N2 1.9202(17), Co–N3 1.8369 (16), Co–C3 1.984(2), N1–C11 1.327(3), N2–C21 1.330(3), C11–C12 1.436(3), C21–C22 1.434(3); N1–Co–N2 161.00(7), N3–Co–C3 165.91(9).

donors. All the reported crystal structures of Co^I–alkyl complexes combine trimethylphosphane ligands with a π -acceptor ligand.^[10] The most notable difference between **5** and the corresponding Co^{II} dichloride^[14] is the shortening of the Co–N bonds by 0.2–0.3 Å, caused by the contraction of the cobalt radius because of the transition from high spin to low spin upon reduction from Co^{II} to Co^I. Since the bis(imino)-pyridyl ligands are very good π acceptors,^[11] the better π -backdonating properties of Co^I compared with Co^{II} centers might also play a role. The increased π backdonation is apparent from the long imine double bonds and the short $\text{C}_{\text{py}}\text{--C}_{\text{imine}}$ bonds.^[12] In the crystal lattice the molecules occur in pairs related by a center of inversion. The two molecules of

each pair have parallel pyridine rings in close contact with each other (the distance between ring planes is about 3.5 Å), suggestive of π stacking (Figure 2b). This appears to be a unique feature of complex **5**, since it is not observed in any of the reported crystal structures of iron(II) and cobalt(II) compounds with this type of ligand.

The reaction of **1** with either MeLi or Et₂Zn, to form **2** as described above, was accompanied by a color change from pale brown to deep purple, which is the same color change as initially observed on activation of **1** with 1000 equivalents of MAO. Therefore we investigated whether the Co^I complexes exhibit polymerization activity. Neither to Co^I chloride **2** nor the alkyls **3–5** are themselves active in polymerization. On activation with an excess of MAO, however, all of them polymerized ethene at approximately the same rate as the originally reported [N₃^{ipr}Co^{II}Cl₂] (**1**) when tested under identical conditions (Table 1).

The unbranched polyethenes (PE) obtained in all five experiments were very similar (as concluded from NMR spectroscopy and differential scanning calorimetry (DSC) analysis). In particular, the gel permeation chromatography (GPC) traces of the major polymer fraction were superimposable (Figure 3) with virtually identical peak molecular weights^[13] for the five precatalysts (Table 1). These results are consistent with polymerization involving the same catalyst active species in all cases.

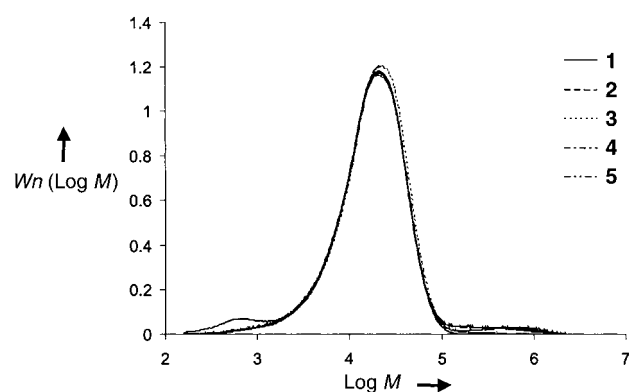


Figure 3. Molecular-weight distribution from GPC analysis of the polymers obtained with complexes **1–5** as precatalysts.

Thus, Co^I chlorides and alkyls might be intermediates in the activation mechanism with MAO. Indeed, when two equivalents of MAO were added to **1**, a ¹H NMR spectrum of **2** was obtained.^[14] Subsequent treatment with another two equiv-

alents of MAO resulted in the spectrum of **3**. Clearly, MAO converts **1** selectively and completely into a Co^IMe complex prior to the actual activation. This result makes the assumption of a Co^{II} active species (e.g.^[1d], ^[5b]) less logical;^[18] possibilities involving Co^I or even Co^{III} active species also deserve serious consideration.^[19] The unexpected generation of the active species via a Co^I species will have implications for the design of new cobalt polymerization catalysts.

Experimental Section

All reactions were carried out under N₂ using standard Schlenk techniques or in a dry box. NMR spectroscopic measurements were performed on Varian gemini 300 and Inova 400 spectrometers. Compound **1** was synthesized according to literature procedures.^[1d]

[N₃^{ipr}CoCl] (**2**): **1** (1.24 g, 1.83 mmol) and MeLi (46.4 mg, 2.12 mmol, 1.16 equiv) were suspended in toluene (10 mL). After stirring for 5 h at room temperature, the color had changed from pale brown to deep purple and the mixture was filtered over celite. Purple crystals were obtained from the filtrate at –35 °C. Washing with hexane and drying yielded **2** (323 mg, 0.561 mmol; 31 %). ¹H NMR (300 MHz, C₆D₆, 298 K): δ = 9.53 (t, 1H, ³J(H,H) = 7.7 Hz, Py–H_p), 7.41 (t, 2H, ³J(H,H) = 7.7 Hz, Ar–H_p), 7.26 (d, 4H, ³J(H,H) = 7.8 Hz, Ar–H_m), 6.91 (d, 2H, ³J(H,H) = 7.8 Hz, Py–H_m), 3.33 (sept, 4H, ³J(H,H) = 6.9 Hz, CHMe₂), 1.17 (d, 12H, ³J(H,H) = 6.9 Hz, CHMeMe), 1.05 (d, 12H, ³J(H,H) = 6.9 Hz, CHMeMe), 0.05 (s, 6H, N=CMe); ¹³C NMR (100 MHz, C₆D₆, 298 K): δ = 167.34 (N=C), 152.79 (Py–C_o), 150.87 (Ar–C_{ip}), 140.75 (Ar–C_o), 127.05 (Ar–C_p), 125.52 (Py–C_m), 123.75 (Ar–C_m), 114.89 (Py–C_p), 29.06 (CHMe₂), 24.01 (CHMeMe), 23.77 (CHMeMe), 21.22 (N=CMe); elemental analysis calcd (%) for C₃₃H₄₃N₃ClCo: C 68.80, H 7.52, N 7.29, Cl 6.15, Co 10.23; found: C 68.92, H 7.55, N 7.22, Cl 6.05, Co 10.06.

[N₃^{ipr}CoMe] (**3**): **2** (96 mg, 0.17 mmol) and MeLi (4.0 mg, 0.18 mmol, 1.1 equiv) were dissolved in diethyl ether (10 mL). After stirring for 3 days at room temperature, the mixture was filtered over celite. The purple filtrate was evaporated to dryness in vacuo. The residue contained **3** and **2** in a ratio of 5:1, according to ¹H NMR spectroscopy. ¹H NMR (300 MHz, C₆D₆, 298 K): δ = 10.19 (t, 1H, ³J(H,H) = 7.7 Hz, Py–H_p), 7.86 (d, 2H, ³J(H,H) = 7.8 Hz, Py–H_m), 7.49 (t, 2H, ³J(H,H) = 7.7 Hz, Ar–H_p), 7.37 (d, 4H, ³J(H,H) = 7.8 Hz, Ar–H_m), 3.13 (sept, 4H, ³J(H,H) = 6.9 Hz, CHMe₂), 1.18 (d, 12H, ³J(H,H) = 6.9 Hz, CHMeMe), 0.62 (d, 12H, ³J(H,H) = 6.9 Hz, CHMeMe), 0.58 (s, 3H, CoMe), –1.15 (s, 6H, N=CMe).

[N₃^{ipr}CoCH₂C₆H₅] (**4**): **2** (85 mg, 0.15 mmol) and Bn₂Mg·0.5 dioxane (38 mg, 0.15 mmol, 2.04 equiv) were dissolved in toluene (5 mL). After stirring for 2 h at room temperature, the color had changed from purple to blue. The mixture was filtered over celite and the blue filtrate was evaporated to dryness in vacuo. ¹H NMR of the residue showed that the conversion was quantitative. ¹H NMR (300 MHz, C₆D₆, 298 K): δ = 10.27 (t, 1H, ³J(H,H) = 7.8 Hz, Py–H_p), 7.68 (d, 2H, ³J(H,H) = 7.8 Hz, Py–H_m), 7.61 (t, 2H, ³J(H,H) = 7.8 Hz, Ar–H_p), 7.45 (d, 4H, ³J(H,H) = 7.8 Hz, Ar–H_m), 6.79 (t, 1H, ³J(H,H) = 7.5 Hz, Bn–H_p), 6.56 (t, 2H, ³J(H,H) = 7.5 Hz, Bn–H_m), 5.60 (d, 2H, ³J(H,H) = 7.2 Hz, Bn–H_o), 3.20 (sept, 4H, ³J(H,H) = 6.6 Hz, CHMe₂), 2.50 (s, 2H, Bn–CH₂), 1.15 (d, 12H, ³J(H,H) = 6.9 Hz, CHMeMe), 0.63 (d, 12H, ³J(H,H) = 6.9 Hz, CHMeMe), –1.16 (s, 6H, N=CMe); ¹³C NMR (100 MHz, C₆D₆, 298 K): δ = 165.99 (N=C), 157.48

Table 1. Polymerization results^[a]

Catalyst precursor	Yield of PE [g]	Rate [kg mmole ^{–1} bar ^{–1} h ^{–1}]	Rate relative to 1 [%]	Unsaturated examples ^[c]	Saturated examples ^[c]	M _p ^[d] [× 10 ^{–3}]	T _{m2} ^[e] [°C]	ΔH _f ^[f] [J g ^{–1}]
1	0.884	1.01	(100)	1.3	2.1	20.8	135.4	243.5
2	1.133	1.29	128	[g]	2.4	21.1	133.1	235.7
3 (84 % pure) ^[b]	0.744	0.85	84	0.9	1.2	22.3	[g]	[g]
4	1.002	1.15	114	0.8	1.6	21.1	[g]	[g]
5	0.818	0.93	92	0.7	1.2	21.7	133.1	232.1

[a] Catalyst (0.5 μmole), MAO (0.5 mmole, 1000 equiv), toluene (40 mL), ethene (7 bar), 15 min. [b] Remainder mostly **2**. [c] End groups per 1000 carbon atoms determined from ¹H NMR (unsaturated) and ¹³C NMR (saturated) spectroscopy. [d] Peak molecular weight determined by GPC methods. [e] Melting temperature determined by DSC (second heating run). [f] Enthalpy of melting determined by DSC (second heating run). [g] Not determined.

(Bn-C_{ip}), 155.61 (Py-C_o), 154.87 (Ar-C_{ip}), 141.39 (Ar-C_o), 127.55 (Bn-C_m, Bn-C_o), 126.93 (Ar-C_p), 124.82 (Ar-C_m), 123.98 (Py-C_m), 119.85 (Bn-C_p), 116.43 (Py-C_p), 28.62 (CHMe₂), 25.75 (N=CMe), 24.38 (CHMeMe), 23.35 (CHMeMe), 1.15 (Bn-CH₂).

[N₃^{ipr}CoCH₂SiMe₃] (**5**): **2** (71 mg, 0.12 mmol) and LiCH₂SiMe₃ (14 mg, 0.15 mmol, 1.2 equiv) of were dissolved in toluene (5 mL). After stirring for 10 min at room temperature, the mixture was filtered over celite. The purple filtrate was evaporated to dryness in vacuo. ¹H NMR spectroscopy of the residue showed that the conversion was quantitative. Purple crystals were obtained from a hexane solution at -35 °C. ¹H NMR (300 MHz, C₆D₆, 298 K): δ = 9.89 (t, 1H, ³J(H,H) = 7.8 Hz, Py-H_p), 7.62 (d, 2H, ³J(H,H) = 7.5 Hz, Py-H_m), 7.51 (t, 2H, ³J(H,H) = 7.5 Hz, Ar-H_p), 7.39 (d, 4H, ³J(H,H) = 7.5 Hz, Ar-H_m), 3.30 (sept, 4H, ³J(H,H) = 6.9 Hz, CHMe₂), 1.11 (d, 12H, ³J(H,H) = 6.9 Hz, CHMeMe), 1.04 (d, 12H, ³J(H,H) = 6.9 Hz, CHMeMe), 0.53 (s, 2H, CH₂SiMe₃), -0.54 (s, 9H, CH₂SiMe₃), -0.85 (s, 6H, N=CMe); ¹³C NMR (100 MHz, C₆D₆, 298 K): δ = 165.70 (N=C), 155.25 (Ar-C_{ip}), 154.20 (Py-C_o), 140.91 (Ar-C_o), 126.98 (Ar-C_p), 124.70 (Ar-C_m), 123.87 (Py-C_m), 115.90 (Py-C_p), 28.67 (CHMe₂), 25.19 (N=CMe), 24.69 (CHMeMe), 24.17 (CHMeMe), 3.12 (SiMe₃), CH₂SiMe₃ not visible; elemental analysis calcd (%) for C₃₇H₅₄N₃CoSi: C 70.78, H 8.67, N 6.69; found: C 70.66, H 8.73, N 6.85.

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- [6] This reduction is not restricted to N₃^{ipr}. Preliminary experiments indicate that also complexes of the 2,6-Me₂C₆H₃ and 2,4,6-Me₃C₆H₂ substituted ligands were reduced to the corresponding Co^I chloride when treated with MeLi in toluene.
- [7] Unfortunately, these crystals proved not to be suitable for X-ray diffraction.
- [8] Crystal size: 0.50 × 0.50 × 0.42 mm. Crystal data: monoclinic, space group *P*2₁/*n*, *a* = 13.5506(3), *b* = 14.8113(4), *c* = 17.8299(4) Å, β = 95.3671(17)°, *V* = 3562.81(15) Å³, ρ_{calcd} = 1.171 mg m⁻³, 2θ_{max} = 55.06°, *R* = 0.0421 (*I* > 2σ(*I*)), *wR*₂ (all data) = 0.1035. 14766 reflections were measured (8114 independent) and included in the refinement against |*F*²|, using the SHELXL program^[17] (392 parameters). Lorentz and polarization corrections were applied, no absorption correction was performed. Max. residual electron density: 0.607 e Å⁻³. The hydrogen atoms were placed at calculated positions, and refined isotropically in riding mode. The X-ray diffraction data were collected at 148(2) K on a Nonius Kappa CCD diffractometer with rotating anode using graphite monochromatized MoK_α radiation (λ = 0.71073 Å), φ en ω scan. The structure was solved by the PATTY option^[15] of the DIRDIF program system.^[16] Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-167159. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).
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- [13] The presence of trace amounts of low (**1**) or high molecular weight polymers (**2**–**5**) results in a slight broadening of the *M_w/M_n* values: **1**: 3.4; **2**: 3.7; **3**: 2.5; **4**: 3.2; **5**: 3.1.
- [14] The spectrum was partly obscured by the signals of MAO, toluene, and residual THF from the synthesis of **1**.
- [15] P. T. Beurskens, G. Beurskens, M. Strumpel, C. E. Nordman in *Patterson and Pattersons* (Eds.: J. P. Glusker, B. K. Patterson, M. Rossi) Clarendon Press, Oxford, **1987**, p. 356.
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- [18] There are, however, still possibilities for re-oxidation of Co^I to Co^{II} on activation. For example, alkyl abstraction from [N₃CoR] could produce [N₃Co]⁺ species, which could oxidize a second molecule of [N₃CoR] to the Co^{II} species [N₃CoR]⁺. Alternatively, [N₃Co(C₂H₄)]⁺, from ethene capture by [N₃Co]⁺, could be attacked by a Lewis acid A, to give a zwitterionic Co^{III} species [N₃Co(C₂H₄A)]⁺ which could comproportionate with [N₃CoR] to give the two Co^{II} complexes [N₃CoR]⁺ and [N₃Co(C₂H₄A)].
- [19] One possibility for a Co^I active species would be an [N₂CoMe] complex formed by MAO abstraction of an imine group from the metal center; this would be electronically similar to Ni^{II}/Pd^{II} diimine catalysts. A Co^{III} active species could be formed by Lewis acid attack on [N₃Co(C₂H₄)]⁺, as described above.^[18]