

Generation of bis(iminoalkyl)pyridine cobalt(i) cations under metal alkyl free conditions that polymerize ethene†

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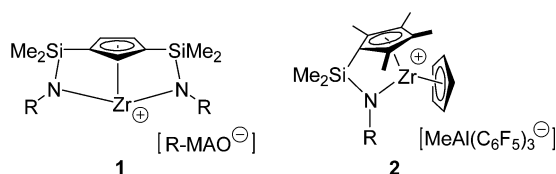
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Treatment of the bis(iminoethyl)- or bis(iminobenzyl)pyridine cobalt dichlorides **3a,b** with "butadiene-magnesium" (**a**, R = CH₃) or methyllithium (**b**, R = Ph) yields the corresponding bis(iminoalkyl)pyridine cobalt(i) chloride complexes **7a,b**. Chloride abstraction with Li[B(C₆F₅)₄] in toluene generates the corresponding cations (**9**) which are low activity catalysts for the polymerization of ethene. The pyridine-stabilized [bis(iminoethyl)pyridineCo(i)(NC₅H₅)⁺][B(C₆F₅)₄⁻] salt was characterized by X-ray diffraction.

It is commonly assumed that homogeneous Ziegler–Natta catalyst systems require the presence of a reactive transition metal bonded σ -alkyl ligand at the stage of the active catalyst species. However, Royo *et al.* have shown that the doubly silylamido-bridged cyclopentadienyl zirconium cation complex **1** (Scheme 1), derived from the corresponding [Zr]–benzyl precursor by treatment with B(C₆F₅)₃ or with methylalumoxane, actively polymerizes ethene.¹ This is remarkable since **1** does not contain a metal σ -alkyl ligand. Subsequently, Chen *et al.* described a related early metal system (**2**) that was obtained from the corresponding [Zr]–CH₃ complex and Al(C₆F₅)₃. He proposed that alkyl transfer from [RAl(C₆F₅)₃⁻] to the corresponding ethene complex of **2** probably represents the essential C–C bond forming step.²

Similar observations were made in the chemistry of homogeneous Ziegler–Natta catalyst systems derived from bis(iminoethyl)pyridine complexes of some late metals. Gibson *et al.* showed that treatment of the cobalt(ii) complex **3a** with methyllithium led to reduction and formation of the corresponding neutral σ -methyl cobalt(i) complex (**4a**: [Co]–CH₃) that subsequently gave the cationic dinitrogen complex (**5**: [Co]⁺–N₂) or the η^2 -olefin complex (**6**: [Co]⁺–CH₂=CH₂) when treated with B(C₆F₅)₃ in the presence of N₂ or ethene, respectively. Complex **6** (with [CH₃B(C₆F₅)₃⁻] anion) slowly polymerized ethene.³ Gal *et al.* isolated the cobalt(i) chloride complex (**7a**: [Co]–Cl) from the **3a**–MeLi reaction mixture and converted it to a variety of mono- σ -alkyl cobalt(i) compounds (**4**: [Co]–R, R = CH₃ (**a**), R = CH₂Ph (**b**), CH₂SiMe₃ (**c**)). The systems **4** are catalytically inactive, but polymerize ethene when treated with excess methylalumoxane.⁴ In principle, both the Gal⁴ and the Gibson³ systems contain anions that feature alkyl–[B] or alkyl–[Al] moieties, so that the mechanism proposed by Chen *et al.*² (see above) could in principle be operative here, although alternatives were discussed.^{3,5} We have now prepared closely related bis(iminoalkyl)pyridine cobalt(i) cation–[B(C₆F₅)₄⁻] systems, which feature no easily transferable simple alkyl groups, and found that such systems still show some ethene polymerization



Scheme 1

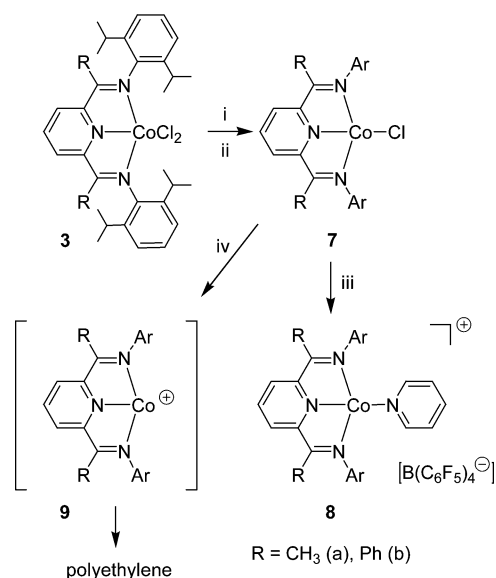
activities, although they are less active than some of the previously published systems.

The bis(*N*-aryliminoethyl)pyridineCoCl₂ complex **3a** was prepared as previously described by Gibson *et al.* (Scheme 2)⁶ The synthesis of the related substituted bis(*N*-aryliminobenzyl)pyridine ligand system was carried out according to a procedure described by Esteruelas *et al.*⁷ Subsequent treatment with CoCl₂ in *n*-butanol at 80 °C gave **3b** (72% isolated).

The cobalt(ii) dichloride complex **3a** was reacted with the "butadiene–magnesium" reagent [(C₄H₆Mg·2 THF)_n].⁸ In contrast to similar reactions of chelate bis(imine)NiCl₂ complexes,⁵ the formation of the corresponding (butadiene)cobalt complex was not observed, but **3a** was again cleanly reduced to the cobalt(i) chloride complex **7a**.⁹ Treatment of **3b** with methyllithium under conditions similar to the reactions described by Gal *et al.* gave **7b** (73%).

Treatment of the cobalt(i) chloride complex **7a** with lithium tetrakis(pentafluorophenyl)borate in toluene solution (–78 °C to room temperature) led to a clean abstraction of the chloride ligand with precipitation of LiCl. Subsequent addition of a slight excess of pyridine gave the corresponding pyridine adduct **8a**. Recrystallization from bromobenzene furnished single crystals of **8a** that were used for the X-ray crystal structure determination (Fig. 1).⁹

In the crystal, complex **8a** contains well separated metal complex cations and [B(C₆F₅)₄⁻] anions (and bromobenzene solvent molecules).[‡] The cobalt(i) center exhibits a distorted square-planar geometry with a N15–Co bond length of 1.799(3) Å and two longer adjacent N11–Co (1.946(3) Å) and N22–Co (1.918(3) Å) bonds. The Co–N1 bond length to the coordinated pyridine ligand amounts to 1.946(3) Å. The angles around the central cobalt atom were found at 81.6(1)° (N15–Co–N11), 81.5(1)° (N15–Co–N22), 99.4(1)° (N1–Co–N22), and 97.9(1)° (N1–Co–N11). The plane of



Scheme 2 i) R = CH₃, + (butadiene–Mg·2 THF)_n, toluene; ii) R = Ph, MeLi, toluene; iii) R = CH₃, Li[B(C₆F₅)₄], toluene, 1 h, then pyridine, crystals from bromobenzene; iv) R = CH₃ or Ph, Li[B(C₆F₅)₄], toluene, rt 1 h, then ethene (2 bar), –20 °C, 1 h.

† Dedicated to Professor Helmut Werner on the occasion of his 70th birthday.

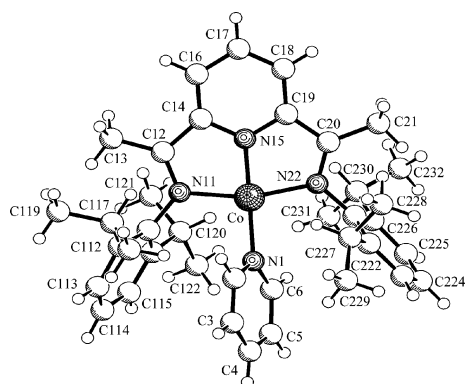


Fig. 1 Molecular geometry of **8a** (the cation is depicted).

the single pyridine ligand is rotated by 64.6° from the average coordination plane of the Co(II) center. The 2,6-diisopropylphenyl substituents at the imino-nitrogen atoms of the chelate ligand are both rotated almost perpendicular to the central ligand plane.

Complex **7a** (50 mg) was treated with a *ca.* 5 fold excess of $\text{Li}[\text{B}(\text{C}_6\text{F}_5)_4]$ at ambient temperature in toluene to generate **9**. The mixture was then cooled to -20°C and purged with ethene (2 bar). After 1 h the mixture was quenched with methanol. Workup gave 170 mg of linear polyethylene (mp 128°C), which corresponds to a catalyst activity of *ca.* $2\text{ g PE mmol}[\text{Co}]^{-1}\text{ bar (ethene)}^{-1}$. The analogous polymerization reaction was carried out with the **7b**– $\text{Li}[\text{B}(\text{C}_6\text{F}_5)_4]$ system (50 mg/300 mg employed) to yield 350 mg of polyethylene (*a* $\approx 5\text{ g PE mmol}[\text{Co}]^{-1}\text{ bar (ethene)}^{-1}$).

The activation of these catalysts was carried out in the absence of any initial transferable alkyl group. We have neither employed an alkyl-boron or -aluminium activator (nor their corresponding Lewis acid components) nor did the transition metal component contain an abstractable alkyl group as in the previous cases.^{1–5,10} Nevertheless, the **7**– $\text{Li}[\text{B}(\text{C}_6\text{F}_5)_4]$ systems were active in ethene polymerization, albeit with rather low catalyst activities. We must, therefore, conclude that there seem to be additional mechanistic pathways of transition metal catalyzed olefin polymerization that follow other than the established pathways of concurrent C–C and M–C bond formation. Whether metallacyclopentane formation is involved,^{3,11} or pathways utilizing more than one metal center or other mechanistic alternatives may be favoured is an open question at this time.

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Notes and references

‡ CCDC 230096. See <http://www.rsc.org/suppdata/cc/b4/b401122h/> for crystallographic data in .cif or other electronic format.

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- 7a**: The reaction of **3a** (4.88 g, 7.92 mmol) with 1.94 g (8.75 mmol) of "magnesium-butadiene" in toluene (12 h, -78°C to room temperature) gave 0.92 g (56%) of complex **7a** after recryst. from toluene at -30°C . Anal. calcd. for $\text{C}_{33}\text{H}_{43}\text{N}_3\text{ClCo}$ (576.1): C 68.80, H 7.52, N 7.29; found: C 68.50, H 7.53, N 7.19%. Complex **7a** was characterized by X-ray crystal structure analysis (details can be obtained from the authors). **7b**: Complex **3b** (0.70 g, 0.95 mmol) was treated with methyl lithium (1.05 mmol, 0.65 ml of a 1.6 M solution in ether) in toluene (150 ml) for 12 h to yield 0.49 g (73%) of complex **7b** after recryst. from toluene at -30°C . Anal. calcd. for $\text{C}_{43}\text{H}_{47}\text{N}_3\text{ClCo}$ (700.3): C 73.76, H 6.77, N 6.00; found: C 73.40, H 6.94, N 5.94%. $^1\text{H NMR}$ (d_6 -benzene, 600 MHz): δ 9.53 (t, 1H) and 7.23 (d, 2H, pyr), 7.82 (d, 4H), 7.04 (t, 4H), and 7.32 (t, 2H, *o*-, *m*-, *p*-Ph), 7.46 (t, 2H), 7.25 (d, 4H), 3.66 (sept, 4H), 1.16 (2d, each 12H, $\text{C}_5\text{H}_3(\text{CHMe}_2)_2$). $^{13}\text{C NMR}$ (d_6 -benzene, 150 MHz): δ 168.1 (C=N), 155.3, 123.8, 117.5 (pyr), 140.0, 123.6, 128.3, 128.0 (*ipso*-, *o*-, *m*-, *p*-Ph), 152.0, 140.9, 128.6, 127.1 (*ipso*-, *o*-, *m*-, *p*- $\text{C}_5\text{H}_3(\text{CHMe}_2)_2$), 29.3 (CHMe_2), 24.6 and 23.3 ($\text{CH}(\text{CH}_3)_2$). **8a**: Complex **7a** (100 mg, 396 μmol) was reacted with $\text{Li}[\text{B}(\text{C}_6\text{F}_5)_4]$ (308 mg, 450 μmol) in 15 ml of toluene at room temp. for 1 h. Then dry pyridine (0.03 ml) was added. Lithium chloride was removed by filtration. Toluene was removed *in vacuo* and the deep blue salt **8a** dissolved in bromobenzene. Diffusion of pentane vapor into this solution gave crystals of **8a**, which were dried *in vacuo* to remove some of the incorporated bromobenzene solvent. Anal. calcd. for $\text{C}_{62}\text{H}_{48}\text{N}_4\text{BF}_2\text{Co}$ (1298.8): C 57.34, H 3.73, N 4.31; found: C 56.75, H 3.77, N 3.74. X-Ray crystal structure analysis: Crystal data for $[\text{C}_{38}\text{H}_{48}\text{CoN}_4]^+[\text{B}(\text{C}_6\text{F}_5)_4]^- \cdot \text{C}_6\text{H}_5\text{Br}$, *M* = 1455.79, monoclinic, space group $P2_1/c$ (No. 14), *a* = 20.027(1), *b* = 12.241(1), *c* = 25.895(1) Å, β = $93.75(1)^\circ$, *V* = 6334.6(7) Å³, *D_c* = 1.526 g cm⁻³, μ = 10.07 cm⁻¹, *Z* = 4, λ = 0.71073 Å, *T* = 198 K, 20215 reflections collected ($\pm h, \pm k, \pm l$), $[(\sin\theta)/\lambda] = 0.59\text{ \AA}^{-1}$, 11147 independent (*R_{int}* = 0.063) and 6954 observed reflections [*I* $\geq 2\sigma(I)$], 866 refined parameters, *R* = 0.056, *wR*² = 0.114. Spectroscopic characterisation of **9** was attempted, but has remained inconclusive so far due to solubility problems.
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