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Polymerization Catalysts

Synthesis, Electronic Structure, and Ethylene Polymerization Activity of Bis(imino)pyridine Cobalt Alkyl Cations**

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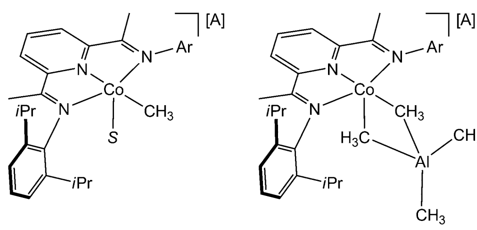
The independent discovery of ethylene polymerization by MAO-activated (MAO = methylaluminoxane) aryl-substituted bis(imino)pyridine iron and cobalt dihalide complexes ($(^{Ar}PDI)MCl_2$ by Brookhart,[1] Gibson,[2] and their respective co-workers has attracted both academic and industrial attention and renewed interest in base-metal catalysis.[3] Despite the numerous studies on catalyst optimization by ligand substituent modification,[4] much remains to be learned about the active species formed upon treatment with MAO, and the propagating species responsible for monomer enchainment. The possibility of different oxidation and spin states of both iron and cobalt, coupled with the ability of the bis(imino)pyridine ligand to directly participate in the electronic structure[5] and undergo chemical modification such as alkylation,[6] presents challenges in understanding the mechanism of polymerization and the identity of the propagating species.

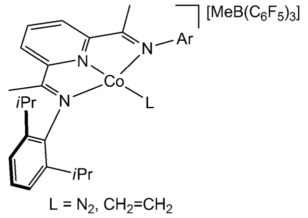
Considerable effort has been devoted to elucidating the active species of bis(imino)pyridine iron and cobalt ethylene polymerization catalysts. Our research group recently reported the synthesis of bis(imino)pyridine iron alkyl cations $[(^{iPr}PDI)FeR]^+$ ($^{iPr}PDI = 2,6\text{-}(2,6\text{-}iPr_2\text{-}C_6H_3N{=}CMe)_2C_5H_3N$; $R = CH_2SiMe_3, CH_2CMe_3, CH_3$), and demonstrated the utility of these species as single-component ethylene polymerization catalysts without the need for an activator.[7,8] Oxidation of the corresponding neutral bis(imino)pyridine iron alkyl complexes $[(^{iPr}PDI)FeR]$ proved to be the most reliable and versatile synthetic route to the desired cationic derivatives.[8] The combination of metrical parameters from X-ray diffraction, magnetochemistry, ^{57}Fe Mössbauer spectroscopy, and DFT calculations established the electronic structure of these overall $S = 2$ complexes as high-spin Fe^{II} derivatives with a neutral bis(imino)pyridine chelate. Thus, oxidation of the neutral iron alkyl species $[(^{iPr}PDI^{1-})Fe^{II}R]$ to the corresponding cation is ligand-based. These results, together with Talsi and co-workers' observation of $[(^{iPr}PDI)Fe(\mu_2\text{-}Me_2AlMe_2)]$-[MeMAO] by NMR spectroscopy following treatment of $[(^{iPr}PDI)FeCl_2]$ with excess MAO, suggest that high-spin Fe^{II} complexes are the active propagating species in ethylene polymerization catalyzed by bis(imino)pyridine iron.[9]

For the corresponding cobalt catalysts, the nature of the active species remains a subject of controversy.[9] Seminal, independent studies from Gal,[10] Gibson,[11,12] and their respective co-workers, have reported that treatment of $[(^{iPr}PDI)CoCl_2]$ with two equivalents of LiR ($R = Me$, CH_2Ph, CH_2SiMe_3) resulted in reduction to the $[(^{iPr}PDI)CoR]$ derivatives, thus raising the possibility that complexes that contain formally Co^I centers are candidates for the propagating species. However, these cobalt alkyl complexes were inactive for ethylene polymerization. To activate these complexes, $[(^{iPr}PDI)CoCH_3]$ was treated with $B(C_6F_5)_3$ in the presence of N_2 or $CH_2{=}CH_2$ and furnished the cationic cobalt complexes with neutral ligands, $[(^{iPr}PDI)CoL][MeB(C_6F_5)_3]$ ($L = N_2$, $CH_2{=}CH_2$), which were reported to slowly polymerize ethylene (Scheme 1).[12] Erker and co-workers have since prepared bis(imino)pyridine cobalt cations with various neutral ligands with the $[B(C_6F_5)_4]^-$ anion and also observed slow ethylene polymerization. The absence of transferable alkyl groups led to the suggestion of a metal "alkyl-less" polymerization as a mechanistic possibility in bis(imino)pyridine cobalt catalyzed ethylene polymerization.[13,14]



S = Solvent or vacancy A = [MeMAO]⁻, $[B(C_6F_5)_4]^-$

Traditional Alkyl Pathway



$L = N_2, CH_2{=}CH_2$

"Alkyl-less" Catalysts

Scheme 1. Bis(imino)pyridine cobalt complexes proposed as active species in ethylene polymerization.

A more traditional pathway is that activation of $[(^{Ar}PDI)CoCl_2]$ with excess MAO generates cationic bis-

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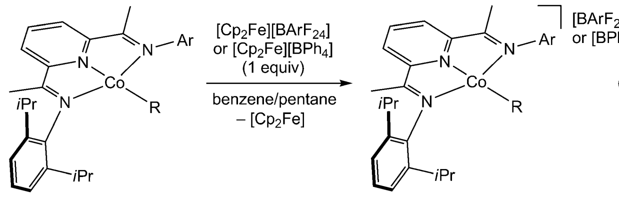
(imino)pyridine cobalt alkyl species that are similar to the iron derivatives. Experimental support for this activation pathway has been provided by Talsi and co-workers[15] by using ^{1}H and ^{2}H NMR spectroscopy to monitor the addition of MAO to [(^{Ar}PDI)CoCl$_2$] complexes. In a more recent report, the spectroscopic data were correlated with kinetic studies and support formation of the ion pairs [(^{Ar}PDI)Co^{II}(μ_2-Me$_2$AlMe$_2$)][A], [(^{Ar}PDI)Co^{II}(Me)S][A], and [(^{Ar}PDI)Co^{I}S][A] (A = [MeMAO]$^-$ or [B(C$_6$F$_5$)$_4$]$^-$, S = solvent or vacancy, Scheme 1).[16] Notably, addition of ethylene resulted in rapid reduction of the metal from formally Co^{II} to Co^{I}. However, none of these complexes were isolated and fully characterized, and the redox activity of the bis(imino)pyridine chelate was not established.

Inspired by these reports and our recent observations on iron complexes,[7,8] we targeted the preparation, isolation, and full characterization of well-defined, single-component [(^{iPr}PDI)CoR]$^+$ complexes. Such species could provide insight into the oxidation and spin state of the active cobalt complex, establish the participation, if any, of the bis(imino)pyridine, and possibly aid future catalyst design. Moreover, these studies will allow direct comparison of the activity to the previously isolated "alkyl-less" bis(imino)pyridine cobalt cations [(^{Ar}PDI)Co–L][A].

Given its success and versatility in the synthesis of the corresponding iron complexes,[8] oxidation of the neutral bis(imino)pyridine cobalt alkyl complexes [(^{iPr}PDI)CoR] (R = Me, Et) was initially explored as a route to the desired cations. Budzelaar and co-workers have previously established that these planar, formally Co^{I} complexes are in fact Co^{II} species that are antiferromagnetically coupled to a bis(imino)pyridine radical anion.[17] This result raises the possibility that electron loss could either be metal- or ligand-based. Treatment of a solution of (^{iPr}PDI)CoR (R = CH$_3$, Et) in benzene with either [Cp$_2$Fe][BPh$_4$] or [Cp$_2$Fe][BArF$_{24}$] resulted in oxidation and formation of the corresponding bis(imino)pyridine cobalt alkyl cations [(^{iPr}PDI)CoR][A] (A = BPh$_4$, BArF$_{24}$) in high yields [Eq. (1); Cp = cyclopentadienyl, BArF$_{24}$ = B(3,5-(CF$_3$)$_2$C$_6$H$_3$)$_4$)]. Other examples, namely [(^{iPr}PDI)CoR][BArF$_{24}$] (R = CH$_2$CMe$_3$, CH$_2$SiMe$_3$) and [(^{Mes}PDI)CoR][BArF$_{24}$] (R = CH$_3$, CH$_2$CMe$_3$), were also prepared using this method.



(1)

Each of the isolated [(^{iPr}PDI)CoR][A] complexes is paramagnetic. Characterization and elucidation of the electronic structure of [(^{iPr}PDI)CoCH$_3$][BArF$_{24}$] will be presented as a representative example (complete characterization of every cationic bis(imino)pyridine cobalt alkyl cation prepared in this work is given in the Supporting Information). The spin state of [(^{iPr}PDI)CoCH$_3$][BArF$_{24}$] was determined by SQUID magnetometry and EPR spectroscopy (a plot of $\mu_{\rm eff}$ versus temperature is presented in Figure S1 in the Supporting Information). At temperatures above 10 K, the effective magnetic moment $\mu_{\rm eff}$ is constant at 2.08 μ_B. Below this temperature, the $\mu_{\rm eff}$ value decreases because of field saturation and weak intermolecular interactions. This magnetic behavior is consistent with an $S = 1/2$ ground state, even though the $\mu_{\rm eff}$ value is higher than the expected spin-only value of 1.73 μ_B. To account for this deviation, the data were simulated[18] using a g value of 2.55, which is obtained from the simulation of the EPR data (see below). In addition, the best fit required 11.5 % diamagnetic impurity and a small Weiss temperature θ_W of -0.19 K to account for intermolecular interactions.

The EPR spectrum recorded in toluene glass at 77 K shows a rhombic signal consistent with an $S = 1/2$ ground state with large g anisotropy (Figure 1). Simulation of the data resulted in $g_1 = 3.42$, $g_2 = 2.26$, and $g_3 = 2.04$, and $A_1 = 360 \times 10^{-4}$ cm^{-1}, $A_2 = 100 \times 10^{-4}$ cm^{-1}, and $A_3 = 225 \times 10^{-4}$ cm^{-1} (I ^{59}Co = 7/2). The highly anisotropic g values and large hyperfine coupling constants are consistent with a cobalt-centered spin. The high g values indicate significant orbital contributions that result from mixing of low-lying excited states by spin–orbit coupling. In a square-planar ligand field, the difference in energies of the occupied d orbitals is small, thus allowing efficient mixing of states.

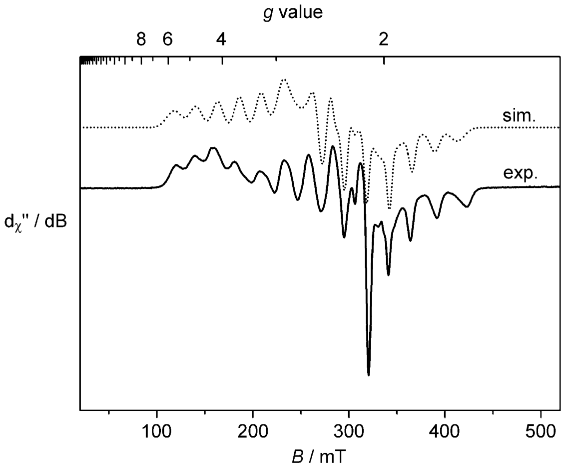


Figure 1. EPR spectrum of [(^{iPr}PDI)CoCH$_3$][BArF$_{24}$] recorded in toluene glass at 77 K (microwave frequency 9.43 GHz, power 1.00 mW, modulation frequency 2.5 mT).

The solid-state structure of [(^{iPr}PDI)CoCH$_3$][BArF$_{24}$] was determined by X-ray diffraction (Figure 2). The molecular geometry of the cobalt center is idealized-planar with the sum of the angles around the cobalt totaling 360.06(22)°; the aryl substituents are oriented nearly perpendicular to the metal–chelate plane. There are no obvious close contacts between the cation and the anion (see the Supporting Information). As is now well-established in bis(imino)pyridine chemistry, distortions to the ligand bond lengths are diagnostic of redox activity and are useful for assigning the oxidation state

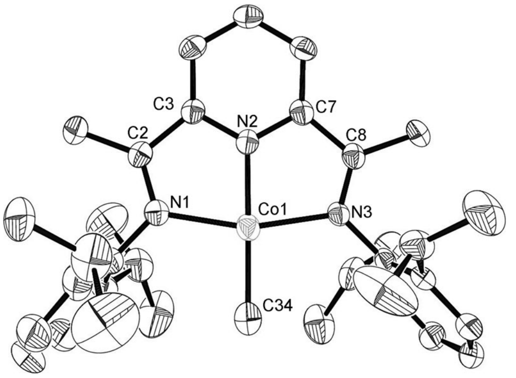


Figure 2. Solid-state molecular structure of the cationic portion of [(^{iPr}PDI)CoCH$_3$][BArF$_{24}$]. Thermal ellipsoids set at 30% probability, hydrogen atoms in the cation are omitted for clarity.

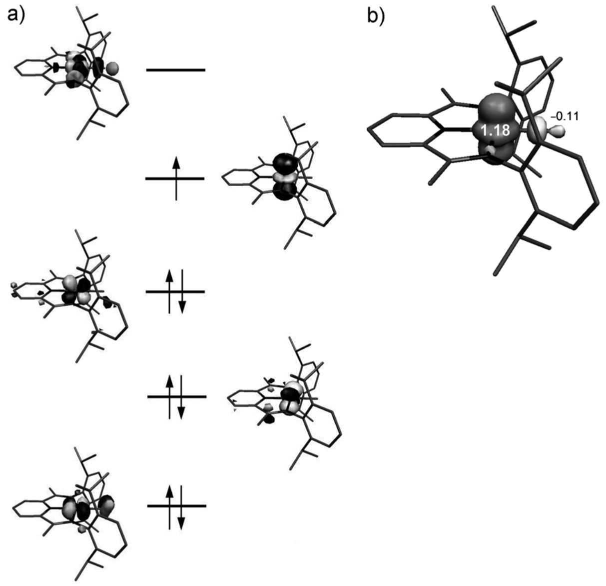


Figure 3. a) Qualitative molecular orbital diagram for [(^{iPr}PDI)CoCH$_3$]$^+$ from a geometry-optimized B3LYP DFT calculation. b) Spin density plot obtained from Mulliken population analysis (dark, positive spin density; light, negative spin density).

of both the metal and the supporting chelate.[5,19] The C_{imine}–N_{imine} distances of 1.298(4) (C8–N1) and 1.305(4) Å (C2–N1) are in the range established for a neutral bis(imino)pyridine. Accordingly, the C_{imine}–C_{ipso} bond lengths of 1.472(4) (C7–C8 >) and 1.469(4) Å (C2–C3) are relatively long and also diagnostic of a neutral chelate. The Co–N_{pyr} distance of 1.851(2) Å and the Co–N_{imine} distances of 1.971(2) (Co1–N3) and 1.990(2) Å (Co1–N1)are contracted and consistent with the magnetic measurements and EPR data that establish an $S = 1/2$ complex.

The electronic structure of [(^{iPr}PDI)CoCH$_3$][BArF$_{24}$] was also studied by density functional theory using the B3LYP functional. Only the cationic portion of the molecule [(^{iPr}PDI)CoCH$_3$]$^+$ was computed without further truncation. The optimized structure, based on the observed $S = 1/2$ ground state, successfully reproduced the metrical parameters determined by X-ray diffraction (see Table S2). A qualitative molecular orbital diagram and spin-density plot derived from these results are presented in Figure 3. This solution clearly establishes a low-spin Co^{II} complex with a neutral bis(imino)pyridine chelate, and is consistent with the experimental diffraction, spectroscopic, and magnetochemical data. The qualitative molecular-orbital diagram is as expected for a square-planar complex with three doubly occupied cloverleaf d orbitals and d_{z^2} (the z axis being defined as perpendicular to the chelate plane) as the singly occupied molecular orbital (SOMO). An orbital principally of $d_{x^2-y^2}$ origin is found in the unoccupied set. A closer analysis of the orbital manifold reveals that the d_{xz} and d_{yz} orbitals are nearly degenerate. These two orbitals are likely involved in the strong mixing of states by spin–orbit coupling.

The combined experimental and computational studies clearly establish the electronic structure of the bis(imino)pyridine cobalt alkyl cations [(^{iPr}PDI)CoR]$^+$ as low-spin Co^{II} complexes with a neutral bis(imino)pyridine chelate. While the presence of a neutral supporting ligand is consistent with the related iron complexes [(^{iPr}PDI)FeR]$^+$, the cobalt derivatives have low-spin rather than high-spin electronic configurations at the metal center. The electronic structure of the cobalt alkyl cation also demonstrates that oxidation of the neutral precursor [(^{iPr}PDI^{1-})Co^{II}CH$_3$] is ligand- rather than metal-based.

With a family of cationic bis(imino)pyridine cobalt alkyl complexes in hand, their ethylene polymerization activity was evaluated. Each polymerization experiment was conducted in 10 mL of toluene with 1 bar of ethylene at 23 °C (Table 1). The results of a control experiment in which ethylene polymerization was conducted with [(^{iPr}PDI)CoCl$_2$] and 1000 equivalents of MAO are also shown. In each case examined, the polymer melting temperatures are consistent with linear polyethylene and the polydispersity indices

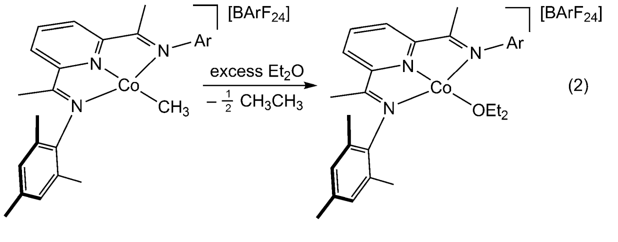
Table 1: Data for the polymerization of ethylene.[a]

Catalyst	Yield [g]	Reaction time [min]	Productivity[b]	M_w [g mol^{-1}][c]	PI[c]	m.p. [°C]
^{iPr}PDICoCl$_2$/1000 MAO	1.191	30	240	29600	1.98	131
[^{iPr}PDICoCH$_3$][BPh$_4$]	0.153	26	30	30300	1.83	131
[^{iPr}PDICoEt][BPh$_4$]	0.268	30	50	33600	1.94	132
[^{iPr}PDICoCH$_3$][BArF$_{24}$]	0.556	15	220	24800	1.92	132
[^{iPr}PDICoEt][BArF$_{24}$]	0.388	20	120	35800	2.11	132
[^{iPr}PDICoNp][BArF$_{24}$]	0.220	10	130	36000	1.94	133
[^{iPr}PDICoNs][BArF$_{24}$]	0.302	10	180	38100	2.13	133
[^{Mes}PDICoCH$_3$][BArF$_{24}$]	0.285	13	130	2100	1.70	124
[^{Mes}PDICoNp][BArF$_{24}$]	0.239	8	170	17500	4.15	131
[^{Mes}PDICoN$_2$][MeB(C$_6$F$_5$)$_3$]	0.005	15	2	–	–	–

[a] Polymerization was carried out using 0.010 mmol of catalyst in 10 mL toluene at 23 °C with 1 bar of ethylene. [b] Average values in mmol^{-1} h^{-1} bar^{-1}. [c] Polydispersity index determined by high-temperature GPC in 1,2,4-trichlorobenzene. [d] Np = CH$_2$CMe$_3$; Ns = CH$_2$SiMe$_3$.

indicate single-site catalysts. Both [($^{i\mathrm{Pr}}$PDI)CoCH$_3$][BPh$_4$] and [($^{i\mathrm{Pr}}$PDI)CoEt][BPh$_4$] are active for ethylene polymerization, albeit with relatively modest productivity. Use of the less coordinating anion, [BArF$_{24}$]$^-$, increased productivity with [($^{i\mathrm{Pr}}$PDI)CoCH$_3$]$^+$ yielding the most polymer per unit time. Importantly, each of the cationic bis(imino)pyridine cobalt alkyl cations [($^{\mathrm{Ar}}$PDI)CoR]$^+$ is significantly more active than the corresponding cationic cobalt dinitrogen complex [($^{\mathrm{Mes}}$PDI)CoN$_2$][MeB(C$_6$F$_5$)$_3$].[11] However, most of the single-component catalysts are less active than the MAO system; this behavior is likely a result of the high sensitivity of these catalysts. Anion effects are also likely to be important. As expected for a metal-based initiator, changing the identity of the cobalt alkyl complex did not result in significant differences in the productivity of the catalysts or the properties of the polymer produced. However, a substantial change in the weight-average molecular weight M_w of the polymer was observed when the aryl group on the chelate was changed from 2,6-diisopropylphenyl to a less sterically demanding mesityl group. This effect has also been observed by Brookhart and co-workers for Ni$^{\mathrm{II}}$ and Pd$^{\mathrm{II}}$ polymerization catalysts,[20] and is consistent with the calculations by Ziegler and co-workers,[21] whereby steric pressure promotes olefin insertion and disfavors β-hydrogen elimination.

The synthesis of well-defined, single-component cationic bis(imino)pyridine cobalt alkyl complexes also allows the opportunity to identify and to study catalyst deactivation pathways. Such information is essential for future catalyst design, and may help reconcile the controversy about the active species. Addition of a slight excess of diethyl ether to a solution of [($^{\mathrm{Mes}}$PDI)CoCH$_3$][BArF$_{24}$] in [D$_6$]benzene at 23 °C resulted in the formation of ethane (detected by ^{1}H NMR spectroscopy) over the course of 12 h and isolation of [($^{\mathrm{Mes}}$PDI)Co(OEt$_2$)][BArF$_{24}$] [Eq. (2)]. No methane was detected. A similar reaction was observed with [($^{i\mathrm{Pr}}$PDI)CoCH$_3$][BArF$_{24}$], although the reaction required 3 days rather than hours to reach completion at 23 °C and is suggestive of an associative process. For experimental convenience, all subsequent studies were carried out with [($^{\mathrm{Mes}}$PDI)CoCH$_3$][BArF$_{24}$] or its [D$_3$] isotopologue.



(2)

Diamagnetic [($^{\mathrm{Mes}}$PDI)Co(OEt$_2$)][BArF$_{24}$] was characterized by NMR spectroscopy, combustion analysis, and X-ray diffraction. A representation of the solid-state structure is shown in Figure 4. Unlike other structurally characterized bis(imino)pyridine cobalt cations with neutral ligands,[12,22] [($^{\mathrm{Mes}}$PDI)Co(OEt$_2$)]$^+$ is an idealized-planar complex with a monoanionic bis(imino)pyridine chelate that is antiferromagnetically coupled to a low-spin Co$^{\mathrm{II}}$ center. Notably, the addition of excess ethylene to this complex produced only trace amounts of polymer, similar to the results obtained with [($^{\mathrm{Mes}}$PDI)Co(N$_2$)]$^+$, thus supporting the conclusion that cationic cobalt alkyl complexes are more active polymerization initiators than the corresponding neutral ligand analogues.

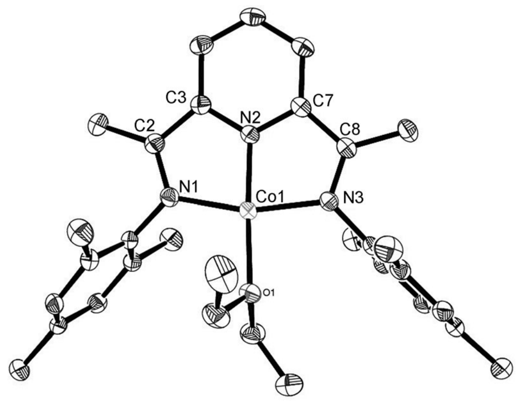


Figure 4. Solid-state molecular structure of the cationic portion of [($^{\mathrm{Mes}}$PDI)Co(OEt$_2$)][BArF$_{24}$]. Thermal ellipsoids set at 30% probability, hydrogen atoms in the cation are omitted for clarity.

A crossover experiment was conducted to gain additional insight into the mechanism of decomposition of [($^{\mathrm{Ar}}$PDI)CoCH$_3$]$^+$ complexes in the presence of diethyl ether to form [($^{\mathrm{Ar}}$PDI)Co(OEt$_2$)]$^+$. Addition of excess diethyl ether to a solution containing an equimolar mixture of [($^{\mathrm{Mes}}$PDI)CoCH$_3$]$^+$ and [($^{\mathrm{Mes}}$PDI)CoCD$_3$]$^+$ in [D$_6$]benzene resulted in formation of a mixture of CH$_3$CH$_3$, CH$_3$CD$_3$, and CD$_3$CD$_3$, as shown by a combination of ^{1}H and ^{2}H NMR spectroscopy. The observation of a near statistical mixture of ethane isotopologues is consistent with a bimolecular reductive coupling pathway. One possibility is homolysis of the cobalt–alkyl bond followed by attack of the alkyl radical on the residual starting material. However, the absence of methane formation raises questions about this pathway and demonstrates the need for additional experiments.

A similar experiment was conducted with the corresponding cationic cobalt ethyl complex [($^{\mathrm{Mes}}$PDI)CoEt][BArF$_{24}$]. Addition of excess diethyl ether to a solution of the complex in [D$_6$]benzene also produced [($^{\mathrm{Mes}}$PDI)Co(OEt$_2$)][BArF$_{24}$]. Analysis of the volatile products of the reaction by ^{1}H NMR spectroscopy established formation of a mixture of ethane, ethylene, and butane. The ethylene likely arises from β-hydrogen elimination from [($^{\mathrm{Mes}}$PDI)CoEt]$^+$ to form [($^{\mathrm{Mes}}$PDI)CoH]$^+$. This species can undergo bimolecular reductive coupling with the remaining [($^{\mathrm{Mes}}$PDI)CoEt]$^+$ to account for the experimentally observed ethane. Butane is formed by coupling two cobalt ethyl fragments. It should be noted that for both the cobalt methyl and ethyl complexes, decomposition was only observed when diethyl ether was added.

In summary, a family of [($^{\mathrm{Ar}}$PDI)CoR]$^+$ complexes have been synthesized and their electronic structures established as overall $S = 1/2$ with low-spin Co$^{\mathrm{II}}$ centers and neutral bis(imino)pyridine chelates. Each of the cationic alkyl complexes is active for ethylene polymerization, and is consistent with observations made by NMR spectroscopy for traditional

(^{Ar}PDI)CoCl$_2$/MAO catalyst mixtures. Conversion to cationic complexes likely by cobalt–alkyl bond homolysis was also identified as an important catalyst deactivation pathway to form inactive cationic bis(imino)pyridine cobalt complexes with a diethyl ether ligand.

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[1] a) B. L. Small, M. Brookhart, *J. Am. Chem. Soc.* **1998**, *120*, 7143; b) B. L. Small, M. Brookhart, A. M. A. Bennett, *J. Am. Chem. Soc.* **1998**, *120*, 4049; c) A. M. A. Bennett (Dupont), WO 98/27124, **1998**; [*Chem. Abstr.* **1998**, *129*, 122973x].

[2] a) G. J. P. Britovsek, V. C. Gibson, B. S. Kimberely, P. J. Maddox, S. J. McTavish, G. A. Solan, A. J. P. White, D. J. Williams, *Chem. Commun.* **1998**, 849; b) G. J. P. M. Bruce, V. C. Gibson, B. S. Kimberely, P. J. Maddox, S. Mastroianni, S. J. McTavish, C. Redhsaw, G. A. Solan, S. Stromberg, A. J. P. White, D. J. Williams, *J. Am. Chem. Soc.* **1999**, *121*, 8728.

[3] P. J. Chirik, K. Wieghardt, *Science* **2010**, *327*, 794.

[4] a) V. C. Gibson, C. Redshaw, G. A. Solan, *Chem. Rev.* **2007**, *107*, 1745; b) C. Bianchini, G. Giambastiani, I. G. Rios, G. Mantovani, A. Meli, A. M. Segarra, *Coord. Chem. Rev.* **2006**, *250*, 1391.

[5] a) Q. Knijnenburg, S. Gambarotta, P. H. M. Budzelaar, *Dalton Trans.* **2006**, 5442; b) S. C. Bart, K. Chlopek, E. Bill, M. W. Bouwkamp, E. Lobkovsky, F. Neese, K. Wieghardt, P. J. Chirik, *J. Am. Chem. Soc.* **2006**, *128*, 13901.

[6] J. Scott, S. Gambarotta, I. Korobkov, P. H. M. Budzelaar, *J. Am. Chem. Soc.* **2005**, *127*, 13019.

[7] M. W. Bouwkamp, E. Lobkovsky, P. J. Chirik, *J. Am. Chem. Soc.* **2005**, *127*, 9660.

[8] A. M. Tondreau, C. Milsmann, A. D. Patrick, H. M. Hoyt, E. Lobkovsky, K. Wieghardt, P. J. Chirik, *J. Am. Chem. Soc.* **2010**, *132*, 15046.

[9] I. E. Soshnikov, N. V. Semikolenova, A. N. Bushmelev, K. P. Bryliakov, O. Y. Lyakin, C. Redshaw, V. A. Zakharov, E. P. Talsi, *Organometallics* **2009**, *28*, 6003.

[10] T. M. Kooistra, Q. Knijnenburg, J. M. M. Smits, A. D. Horton, P. H. M. Budzelaar, A. W. Gal, *Angew. Chem.* **2001**, *113*, 4855; *Angew. Chem. Int. Ed.* **2001**, *40*, 4719.

[11] M. J. Humphries, K. P. Tellmann, V. C. Gibson, A. J. P. White, D. J. Williams, *Organometallics* **2005**, *24*, 2039.

[12] V. C. Gibson, M. J. Humphries, K. P. Tellmann, D. F. Wass, A. J. P. White, D. J. Williams, *Chem. Commun.* **2001**, 2252.

[13] W. Steffen, T. Blömker, N. Kleigrewe, G. Kehr, R. Fröhlich, G. Erker, *Chem. Commun.* **2004**, 1188.

[14] N. Kleigrewe, W. Steffen, T. Blömker, G. Kehr, R. Fröhlich, B. Wibbeling, G. Erker, J.-C. Wasilke, G. Wu, G. C. Bazan, *J. Am. Chem. Soc.* **2005**, *127*, 13955.

[15] N. V. Semikolenova, V. A. Zakharov, E. P. Talsi, D. E. Babushkin, A. P. Sobolev, L. G. Echevskaja, M. M. Khysniyarov, *J. Mol. Catal. A* **2002**, *182–183*, 283.

[16] I. E. Soshnikov, N. V. Semikolenova, A. N. Bushmelev, K. P. Bryliakov, O. Y. Lyakin, C. Redshaw, V. A. Zakharov, E. P. Talsi, *Organometallics* **2009**, *28*, 6003.

[17] Q. Knijnenburg, D. Hetterscheid, T. M. Kooistra, P. H. M. Budzelaar, *Eur. J. Inorg. Chem.* **2004**, 1204.

[18] E. Bill, http://www.mpibac.mpg.de/bac/index_en.php/logins/bill/jul-x_en.php.

[19] a) B. de Bruin, E. Bill, E. Bothe, T. Weyhermüller, K. Wieghardt, *Inorg. Chem.* **2000**, *39*, 2936; b) P. H. M. Budzelaar, B. de Bruin, A. W. Gal, K. Wieghardt, J. H. Lenthe, *Inorg. Chem.* **2001**, *40*, 4649.

[20] a) C. M. Killian, D. J. Tempel, L. K. Johnson, M. J. Brookhart, *J. Am. Chem. Soc.* **1996**, *118*, 11664; b) F. C. Rix, M. L. Brookhart, P. S. White, *J. Am. Chem. Soc.* **1996**, *118*, 4746.

[21] P. Margl, L. Deng, T. Zieger, *Organometallics* **1999**, *18*, 5701.

[22] A. C. Bowman, C. Milsmann, C. C. H. Atienza, E. Lobkovsky, K. Wieghardt, P. J. Chirik, *J. Am. Chem. Soc.* **2010**, *132*, 1676.

[23] CCDC 821611 ([(^{iPr}PDI)CoCH$_3$][BArF$_{24}$]) and 821612 [(^{Mes}PDI)Co(OEt$_2$)][BArF$_{24}$] contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.