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N-Heterocyclic "Pincer" Dicarbene Complexes of Cobalt(I), Cobalt(II), and Cobalt(III)

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Summary: The complex Co(C−N−C)Br$_2$ (C−N−C = 2,6-bis(arylimidazol-2-ylidene)pyridine, aryl = 2,6-Pr$^i{}_2$C$_6$H$_3$), prepared by aminolysis of Co[N(SiMe$_3$)$_2$]$_2$ with the corresponding imidazolium salt (CH−N−CH)Br$_2$, was methylated to the square-planar Co(C−N−C)(CH$_3$) and oxidized with BrN(SiMe$_3$)$_2$ to give Co(C−N−C)Br$_3$. The Co(I), Co(II), and Co(III) complexes show no ethylene polymerization activity.

The use of N-heterocyclic carbenes (NHCs) in catalytic transition-metal systems has been an active area of research over the past decade.[1] Some of the most successful applications have been in alkene metathesis and C−C coupling reactions.[2] It is expected that, in the absence of other π-acidic coligands, the strongly σ-donating NHCs can give rise to highly reactive, electron-rich, low-oxidation-state complexes or stabilize high-oxidation-state metal centers.[3] These ideas have not been systematically investigated, especially in complexes with the early transition metals and metals from the first transition series. Analogous complexes with the electronically similar σ-donating trialkylphosphines (Me$_3$P, dmpe, etc.) have shown interesting reactivity, including C−H activation and formation of N$_2$ and molecular H$_2$ complexes.[4]

In the course of our ongoing studies involving the use of the versatile "pincer" ligand 2,6-bis(arylimidazol-2-ylidene)pyridine (C−N−C), for the stabilization of reactive organometallics, we have found that the aminolysis of [Fe(N(SiMe$_3$)$_2$]$_2$ by the bis(imidazolium) salts (CH−N−CH)Br$_2$ constitutes an excellent method for the high-yield synthesis of the desirable (C−N−C)FeBr$_2$, thereby allowing the study of its reactivity.[5a] In this communication we wish to describe (i) the application of the aminolysis methodology for the synthesis of the Co(II) complex (C−N−C)CoBr$_2$, (ii) the isolation of (C−N−C)-CoBr$_3$ by selective oxidation of the Co(II) precursor, and (iii) the characterization of the products obtained by attempted alkylations of (C−N−C)CoBr$_2$, i.e. Co(I) halide and methyl complexes. The complexes reported here constitute the first series of structurally characterized NHC cobalt complexes in oxidation states I−III, demonstrating the excellent spectator characteristics of the (C−N−C) ligand design. Furthermore, even though Co complexes with NHC ligands have been reported,[6] the compounds reported in this communication are the first examples of Co NHC complexes in low oxidation states which are not stabilized by back-bonding to π-acidic coligands (CO, NO, etc.). The tuning of the "pincer" ligand design by the incorporation of inert NHC wingtips is also a useful extension to the successful bis(imino)pyridines[7a,b] and bis(phosphine)pyridines[7c] and can assist in the understanding of the mode of action of these ligands in the catalytic polymerization of α-olefins.

The reaction of Co[N(SiMe$_3$)$_2$]$_2$[8] with 1 equiv of the bis(imidazolium) salt (CH−N−CH)Br$_2$[9] in THF (Scheme 1) gave quantitative yields of Co(C−N−C)Br$_2$ (**1**) as a red-purple, microcrystalline, moderately air-sensitive solid.

The reaction has been successfully scaled up (10−15 g of imidazolium salt). Complex **1** is paramagnetic (μ_{eff} = 2.00 μ_{B}) and was characterized by analytical methods. The synthesis of **1** currently is limited to carbenes substituted with the sterically demanding 2,6-Pr$^i{}_2$C$_6$H$_3$

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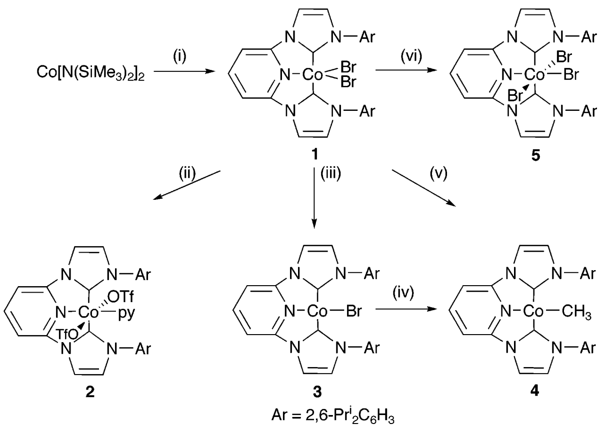
Scheme 1. Cobalt Complexes Described in This Paper[a]



[a] Reagents and conditions: (i) 1 equiv of (CH−N−CH)Br_2, THF; (ii) $TlOSO_2CF_3$, pyridine, THF; (iii) Na(Hg), toluene; (iv) 1.5 equiv of MeLi, toluene; (v) 4 equiv of MeLi, toluene, (vi) $BrN(SiMe_3)_2$, THF.

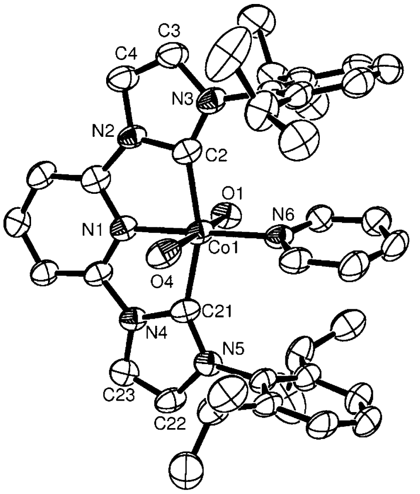


Figure 1. ORTEP representation of complex **2** showing 50% probability ellipsoids. H atoms and the CF_3SO_2 fragment of the triflates are omitted for clarity. Selected bond lengths (Å) and angles (deg) with estimated standard deviations: Co(1)−C(2) = 1.942(6); Co(1)−C(21) = 1.941(6); Co(1)−N(1) = 1.890(5); Co(1)−N(6) = 1.936(5); Co(1)−O(1) = 2.358(4); Co(1)−O(4) = 2.396(4); N(1)−Co(1)−C(2) = 80.4(2); C(2)−Co(1)−N(6) = 99.8(2).

group; less bulky aromatic or aliphatic groups gave products that have not been fully characterized to date.

Reaction of **1** with 2 equiv of $TlOSO_2CF_3$ in THF in the presence of pyridine gave yellow-green, air-stable, paramagnetic ($\mu_{eff} = 1.85\ \mu_B$) [*trans*-Co(C−N−C)(κ^1-$CF_3SO_3)_2$(py)] (**2**), which was characterized by analytical and single-crystal X-ray diffraction methods.[10] The molecule (Figure 1) adopts a distorted-octahedral geometry with the trifluoromethanesulfonate groups occupying trans sites.

The Co−C(carbene) bond lengths are very similar (ca. 1.941 Å), while the Co−N(pyridine) bond is shorter for the pyridine group of the "pincer". The Co−O(triflate) bonds are rather long (2.357−2.396 Å) but are in the range reported previously for Co(II) triflates.[11]

Complex **1** can be easily reduced in good yields by Na(Hg) in toluene to the green-brown square-planar diamagnetic Co(C−N−C)Br (**3**). Complex **3** is sensitive to oxygen and unstable in chlorinated and protic solvents. It was characterized by analytical, spectroscopic, and diffraction methods. The ^{1}H NMR spectrum shows an unusual downfield shift for the para pyridine hydrogens (9.55 ppm). This feature was more pronounced in the spectrum of **4** (see below). The presence of a square-planar Co(I) center in **3** was confirmed by X-ray crystallography (see the Supporting Information).[12] Complex **3** was also isolated as the only product from attempted alkylations of **1** with RLi or R_2Mg (R = CH_2SiMe_3, CH_2CMe_3, $CH_2C(Ph)Me_2$) under a variety of conditions. Similar observations were reported in attempted alkylations of [bis(imino)pyridyl]$CoCl_2$ complexes.[13] Complex **3** is oxidized instantaneously by air to the diamagnetic Co(C−N−C)(η^2-O_2)Br, while it reacts with $TlOSO_2CF_3$ in MeCN to give the salt [Co(C−N−C)(MeCN)](O_3SCF_3).[5b]

Attempted methylation of **1** by reaction with an excess of MeLi (4 equiv) in toluene gave the Co(I) methyl complex **4** as a red-brown air- and light-sensitive crystalline material, which was also obtained in better yields by the reaction of the bromide complex **3** with 1 equiv of MeLi in toluene. The ^{1}H NMR spectrum of **4** shows features similar to those of the bromide analogue **3**, in addition to the methyl resonance at −0.85 ppm. The structure of **4** (Figure 2) reveals a square-planar Co(I) center.[14] The pyridine and carbene rings coincide with the coordination plane, while the bulky aromatic rings are nearly perpendicular to it.

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[10] The compound **2**·2THF ($C_{42}H_{46}CoF_6N_6O_6S_2$·2THF) crystallized from THF/petrol in the monoclinic space group $P2_1/c$ with $a = 14.351(3)$ Å, $b = 17.219(4)$ Å, $c = 22.515(5)$ Å, $\beta = 98.507(3)°$, $V = 5503(2)$ Å^3, and $D_{calcd} = 1.342$ Mg m^{-3} for $Z = 4$. Data were collected at 120(2) K on a Bruker-Nonius KappaCCD diffractometer. Least-squares refinement of the model based on 8436 unique reflections (R_{int} = 14.54%) converged to a final R1 = 7.45% ($I > 2\sigma(I)$) and wR2 = 21.91%. The SHELX97 program was used for all X-ray data refinements (Sheldrick, G. M. SHELX97; University of Göttingen, Göttingen, Germany).

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[12] (a) Spectroscopic data for **3**: ^{1}H NMR (C_6D_6) δ 9.55 (1H, t, py H-*p*), 7.55 and 6.65 (2H each, d, imidazolylidene backbone), 7.32 (2H, t, Ar H-*p*), 7.20 (4H, d, Ar H-*m*), 5.78 (2H, d, py H-*m*), 4.37 (4H, septet, $CH(CH_3)_2$), 1.20 and 1.30 (12H each, two doublets, $CH(CH_3)_2$; $^{13}C\{^1H\}$ NMR (C_6D_6) δ 23.35 ($CH(CH_3)_2$), 24.75 ($CH(CH_3)_2$), 28.86 ($CH(CH_3)_2$), 106.64, 110.93, 111.21, 123.36, 129.20, 138.36, 144.93 (all aromatic carbons). The carbene carbon was not observed. (b) Compound **3** ($C_{35}H_{41}BrCoN_5$) crystallized from THF/petrol in the tetragonal space group $P\bar{4}2_1c$ with $a = 20.2600(7)$ Å, $c = 16.5838(7)$ Å, $V = 6807.1(4)$ Å^3 and $D_{calcd} = 1.309$ Mg m^{-3} for $Z = 8$. Data were collected at 120(2) K on a Bruker-Nonius KappaCCD diffractometer. Least-squares refinement of the model based on 7766 unique reflections (R_{int} = 10.74%) converged to a final R1 = 6.64% ($I > 2\sigma(I)$) and wR2 = 16.01%.

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[14] (a) Spectroscopic data for **4**: ^{1}H NMR (C_6D_6) δ 10.65 (1H, t, pyridine CH-*p*), 8.00 and 7.05 (2H each, d, imidazolylidene backbone), 7.32 (2H, t, aryl) 7.20 (4H, d, aryl), 6.02 (2H, d, pyridine CH), 3.65 (4H, septet, $CH(CH_3)_2$), 1.20 and 0.88 (12H each, two doublets, $CH(CH_3)_2$), −0.85 (3H, s, Co−CH_3); $^{13}C\{^1H\}$ NMR (C_6D_6) δ 23.78 ($CH(CH_3)_2$), 25.31 ($CH(CH_3)_2$), 29.34 ($CH(CH_3)_2$), 107.50, 107.69, 112.60, 124.03, 129.92, 140.38, 144.28, 145.79 (all aromatic carbons). The carbene carbon and Co−CH_3 were not observed. (b) Compound **4** ($C_{36}H_{44}CoN_5$) crystallized from THF/petrol in the triclinic space group $P\bar{1}$ with $a = 8.5799(6)$ Å, $b = 11.7006(10)$ Å, $c = 16.6014(15)$ Å, $\alpha = 87.348(3)°$, $\beta = 82.073(5)°$, $\gamma = 71.898(4)°$, $V = 1569.0(2)$ Å^3 and $D_{calcd} = 1.282$ Mg m^{-3} for $Z = 2$. Data were collected at 120(2) K on a Bruker-Nonius KappaCCD diffractometer. Least-squares refinement of the model based on 7096 unique reflections (R_{int} = 16.29%) converged to a final R1 = 8.30% ($I > 2\sigma(I)$) and wR2 = 19.00%.

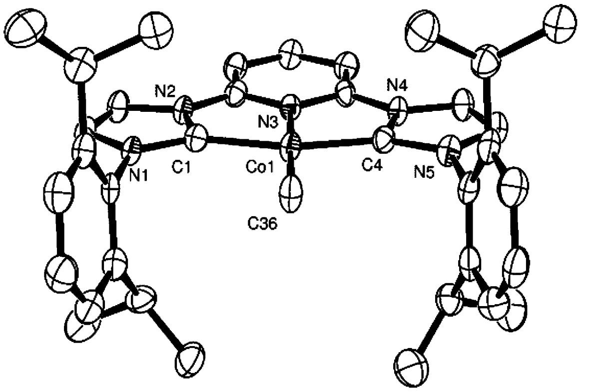

Figure 2. ORTEP representation of **4** showing 50% probability ellipsoids. H atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg) with estimated standard deviations: Co(1)−C(1) = 1.914(4); Co(1)−C(4) = 1.898(4); Co(1)−C(36) = 1.951(4); Co(1)−N(3) = 1.865(3); C(1)−Co(1)−N(3) = 80.41(16); C(4)−Co(1)−N(3) = 80.43(17).

The Co−C(carbene) and the Co−N(pyridine) bonds are shorter than in **1** (1.899−1.914 and 1.865 Å, respectively) but comparable to those of **3**. The Co−CH_3 bond (1.951 Å) is longer than the Co−C(carbene) bonds. Complex **4** is thermally stable in C_6D_6 up to 60 °C, but at higher temperatures, it decomposes to unidentified paramagnetic species. It is the first structurally characterized example of a Co(I)−alkyl species stabilized by NHC ligands and lacking any π-acceptor coligands. Preliminary reactivity data show that it reacts readily at room temperature with CH_3I, CH_3OTf, Brookhardt's acid, and H_2 to give products that are currently under further investigation but that it is unreactive toward aliphatic aldehydes, CO, and ethylene.

To establish the utility of the "pincer" NHC ligand as a spectator for the higher oxidation state Co(III) center, we oxidized **1** with $BrN(SiMe_3)_2$. The product obtained was the diamagnetic, air-stable Co(C-N−C)Br_3 (**5**). The ^1H NMR spectrum of **5** has broad features, supporting a C_s-symmetric structure. Crystals of this complex were obtained by layering a dilute THF solution with petroleum ether.[15] The metal center in **5** (Figure 3) is octahedral; the corresponding M−C, M−N, and M−Br bonds are longer than those observed in the Co(I) complexes, even though in both cases the bite angles of the "pincer" are identical.

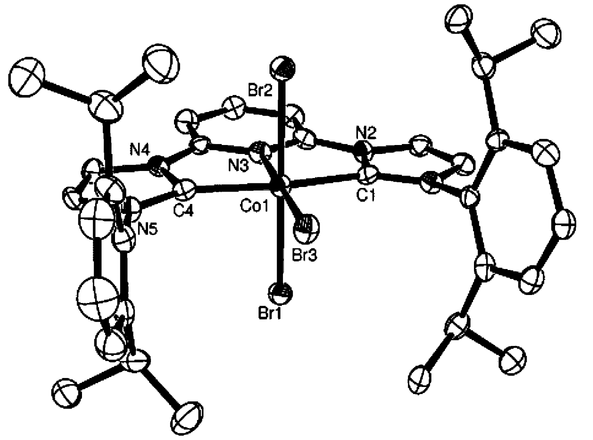

Figure 3. ORTEP representation of **5** showing 50% probability ellipsoids. H atoms and one THF solvent molecule are omitted for clarity. Selected bond lengths (Å) and angles (deg) with estimated standard deviations: Co(1)−C(1) = 1.962(7); Co(1)−C(4) = 1.962(7); Co(1)−Br(1) = 2.4262(12); Co(1)−Br(3) = 2.3894(11); Co(1)−N(3) = 1.894(5); C(1)−Co(1)−N(3) = 81.0(3); C(4)−Co(1)−N(3) = 81.0(3).

Complexes of the type [bis(imino)pyridine]MCl_2 (M = Fe(II), Co(II), bis(imino)pyridine = 2,6-ArN=C(Me)$_2C_5H_3N$, Ar = 2,6-$Pr^i{}_2C_6H_3$, mesityl), in the presence of MAO, were used as highly active polymerization catalysts of ethylene.[7a,b] Although the originally postulated mechanism involving cationic Co(II) alkyls as the active species has not yet found experimental verification, two preliminary papers[13] have described the isolation of Co(I) alkyls by the attempted alkylation of [bis(imino)pyridine]$CoCl_2$. In view of the analogies between **1** and **4** and the iminopyridine complexes, we undertook preliminary catalytic tests in order to assess the polymerization activity of the NHC complexes. In the presence of 500−1000 equiv of MAO, both **1** and **4** do not show any appreciable activity for the polymerization of ethylene. No activity was observed with **4** and $B(C_6F_5)_3$, even though reaction between the complex and the activator to unidentified Co-containing products was confirmed by NMR spectroscopy. It is interesting to speculate on possible reasons for the lack of activity of the NHC species. In the first instance, since the steric effects are not dissimilar between the NHC and imine systems, it is unlikely that they account for the observed behavior. Other differences include (i) the much stronger σ-basicity and weaker π-acidity of the NHC compared with the imine functionalities and (ii) the inert nature of the Co−carbene bond in comparison to the Co−imine bond. Moreover, it is possible that cationic [(C−N−C)-Co−R]$^+$ or [(C−N−C)Co(olefin)]$^+$ species could be stabilized by the NHC ligands, thus inhibiting further reaction. Alternatively, the inertness of the Co−carbene bond may inhibit the formation of plausible 14e$^-$ Co(I)−alkyl intermediates containing a (C−N−C) ligand coordinated in a *bidentate* mode, which would be active polymerization catalysts. At present, attempts to alkylate **2** and **4** by mild nonreducing alkyls have not been successful.

In conclusion, we have developed synthetic methods leading to "pincer" dicarbene complexes of cobalt in oxidation states I−III. The substitution of bromides by alkyls at the Co(II) center proceeds always with concomitant reduction to Co(I), as observed with similar bis[(imino)pyridine] "pincer" systems. The reason for the lack of polymerization activity of the NHC complexes with or without the presence of electrophilic activators is not clear but may be explained by a combination of factors, including the robust and inert coordination geometry imposed by the NHC ligand and the stabiliza-

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(15) (a) ^1H NMR (DMSO-d_6): δ 9.25−8.5 (3H, br m, pyridine CH), 7.55 (2H, t, aryl) 7.20 (4H, d, aryl), 7.65 and 7.45 (2H each, d, imidazolylidene backbone), 3.45 (4H, septet, CH(CH$_3$)$_2$), 1.20 and 1.30 (12H each, two doublets, CH(CH_3)$_2$). ^{13}C NMR data could not be obtained, due to the low solubility of **5** in thf and decomposition over long periods of time in DMSO. (b) The compound **5**·THF ($C_{35}H_{41}Br_3CoN_5$·THF) crystallized from THF/petrol in the monolinic space group $P2_1/c$ with $a = 10.8474(13)$ Å, $b = 18.896(2)$ Å, $c = 18.483(2)$ Å, $\beta = 95.138(2)°$, $V = 3773.2(7)$ Å^3 and $D_{calcd} = 1.589$ Mg m^{-3} for $Z = 4$. Data were collected at 120(2) K on a Bruker-Nonius KappaCCD diffractometer. Least-squares refinement of the model based on 8401 unique reflections ($R_{int} = 12.52\%$) converged to a final R1 = 7.98% ($I > 2\sigma(I)$) and wR2 = 14.88%.

tion of cationic Co(I) or Co(II) species. Work in progress is directed towards understanding the reactivity of these species and, hence, to the possibility of tailoring analogues with catalytic activity.

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Supporting Information Available: Text giving experimental methods for the preparation and characterization of complexes **1**−**5** and full details of the X-ray crystal structures, including complete tables of crystal data, atomic coordinates, bond lengths and angles, and positional and anisotropic thermal parameters; X-ray crystallographic data are also given as CIF files. This material is available free of charge via the Internet at http://pubs.acs.org.

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