Metal–Metal Interactions

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Amidinato– and Guanidinato–Cobalt(I) Complexes: Characterization of Exceptionally Short Co–Co Interactions**

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Low-coordinate, carbonyl-free first row transition metal(I) complexes are relatively rare but are finding increasing use in the activation of small molecules, as enzyme mimics, and so forth.[1] These complexes are generally very reactive species that are stabilized by a variety of sterically bulky, mono-, di-, tri-, and higher dentate ligands.[2] Perhaps the most versatile of these are the β-diketiminates (e.g., $[\{ArNC(Me)\}_2CH]^-$ (nacnac⁻; Ar = 2,6-diisopropylphenyl)), which have been utilized in the preparation of a range of Group 5–12 first row transition metal(I) complexes that have shown fascinating chemistry.[3] In recent years, we have employed the bulky amidinate and guanidinate ligands ($[(ArN)_2CR]^-$ (R = *t*Bu; piso⁻), $N(C_6H_{11})_2$ (giso⁻), or $NiPr_2$ (priso⁻))[4] for the stabilization of a variety of Group 2,[5] 13,[6] 14,[7] and 15[8] metal(I) complexes, and planar four-coordinate lanthanide(II) complexes.[9] These studies have highlighted close analogies (but also differences) between the stabilizing and ligating properties of the bulky amidinates and guanidinates, and the properties of β-diketiminates. With these characteristics in mind, we extended the coordination chemistry of the bulky ligand piso⁻ to the preparation of the first amidinato–iron(I) complex, $[(\kappa^2\text{-}N,N'\text{-piso})Fe(\eta^6\text{-toluene})]$ (cf. $[(\kappa^2\text{-}N,N'\text{-nacnac})Fe(\eta^6\text{-benzene})]$[3d]), which was shown to weakly activate dinitrogen to give $[\{(\kappa^1\text{-}N\text{-},\eta^6\text{-Ar-piso})Fe(\mu\text{-}N)\}_2]$ (cf. $[\{(\kappa^2\text{-}N,N'\text{-nacnac})Fe(\mu\text{-}N)\}_2]$[3d]), with an accompanying change in the coordination mode of the piso⁻ ligand.[10] Subsequent reports from another research group detailed unprecedented amidinato–chromium(I) complexes, which included the diamagnetic, amidinate bridged species, $[\{Cr[\mu\text{-}N(Ar')C(R)N(Ar')]\}_2]$ (R = H or Me, Ar′ = Ar or 2,6-$Et_2C_6H_3$), that contain very short Cr–Cr quintuple bonds (ca. 1.74 Å).[11]

These results motivated us to extend the coordination chemistry of bulky amidinate and guanidinate ligands toward other first row transition metal(I) centers.[12] We were particularly interested in preparing analogues of the β-diketiminate-stabilized cobalt(I) system $[(\kappa^2\text{-}N,N'\text{-nacnac})Co(\eta^6\text{-toluene})]$ (**1**),[2b] which, like other cobalt(I) complexes,[2] has been shown to activate an assortment of small molecules. In addition, we believed that the previously demonstrated coordinative flexibility of our ligands relative to that of β-diketiminates[10,13] could yield varying complex types, depending on the reaction conditions employed. Herein, we report the first amidinato– and guanidinato–cobalt(I) complexes, two dimeric examples of which exhibit the shortest Co–Co interactions reported to date. Preliminary further reactivity studies of these complexes are also reported.

The paramagnetic cobalt(II) precursor complexes **2a–c** (Scheme 1), were readily prepared in good yields by salt-methathesis reactions between $Co^{II}X_2$ (X = Br or I) and the potassium salt of the appropriate ligand.[14] The structural characterization of one complex, $[\{(priso)CoI\}_2]$, is the first to be reported for an amidinato– or guanidinato–cobalt(II) halide complex, and shows the complex to be dimeric with distorted tetrahedral cobalt centers. Upon reduction of **2a–c** with potassium (or magnesium) in toluene, the amidinato– and guanidinato–cobalt(I) complexes **3a–c** were obtained as crystalline solids in high yields. It is noteworthy that no nitrogen-coordinated complexes were obtained when the reductions were carried out under a dinitrogen atmosphere, as was the case with the reduction in toluene that gave **1**. Reduction of **2a** or **2b** with potassium in cyclohexane under a dinitrogen atmosphere afforded the dimeric cobalt(I) complexes **4a** and **4b** as extremely air-sensitive solids in good yields. We have seen no evidence so far for the conversion of

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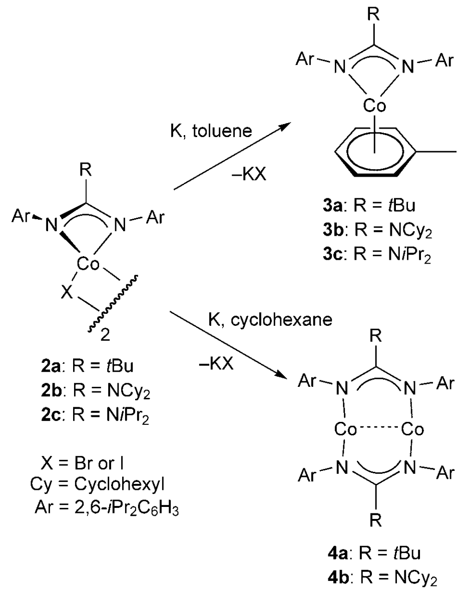
Supporting information for this article (synthetic, spectroscopic and crystallographic details for all compounds; ORTEP diagrams for **2c** (X = I), **3a**, **3c**, **4b**, **7**, **8**, and $[\{(priso)Co(\mu\text{-}N_3)\}_2]$; and full descriptions (including references) of the theoretical and magnetic studies) is available on the WWW under http://dx.doi.org/10.1002/anie.200900780.



Scheme 1. Preparation of compounds **3a–c**, **4a**, and **4b** (the dashed line represents a bond of indeterminate order).

4a or **4b** to **3a** or **3b** upon dissolution of the complexes in toluene.

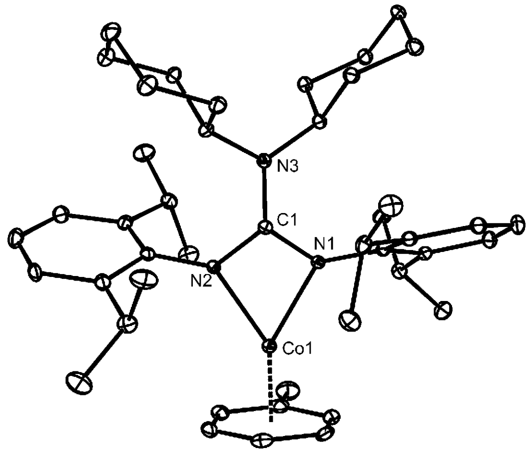


Figure 1. Molecular structure of compound **3b** (thermal ellipsoids at 25% probability; hydrogen atoms omitted). Relevant bond lengths [Å] and angles [°]: Co1–N1 2.046(3), Co1–N2 2.087(3), C1–N1 1.347(5), C1–N2 1.348(5), C1–N3 1.390(5); N1-Co1-N2 63.96(12), N1-C1-N2 108.6(3).

Compounds **3a–c** were crystallographically characterized and were shown to have similar monomeric structures (for **3b**, see Figure 1).[14] In each complex, the metal is η^6-coordinated by a toluene ligand and *N,N'*-chelated by the amidinate or guanidinate moiety. These structures are closely related to that of **1**, although the Co–centroid distance in **1** (1.747 Å) is significantly greater than in **3a–c** (**3a** 1.659 Å, **3b** 1.662 Å, **3c** 1.668 Å). This difference possibly arises because the amidinate and guanidinate ligands are less sterically imposing than nacnac, therefore the toluene ligand is closer to the metal centers of **3a–c** than that of **1**. The N centers of **3a–c** are, however, slightly further from the Co center than those of the nacnac complex (mean N–Co = 2.012 Å).[2b] The room-temperature solution ([D$_{12}$]cyclohexane) magnetic moments of **3a–c** (3.09–3.17 μ_B; cf. 2.7 μ_B for **1**) suggest that they are high-spin d^8 cobalt(I) complexes. The results of variable-temperature solid-state magnetic studies of **3c** are consistent with this view and revealed the compound to have an essentially constant μ_{eff} value of approximately 3.4 μ_B over the range 300–65 K. The plot of χ_M^{-1} against temperature shows that **3c** almost obeys Curie behavior over the range 300–65 K, but Curie–Weiss-like behavior over the full span of temperatures studied (300–2 K, $\theta = -11.80$ K, $C = 1.50$ cm^{3}mol^{-1}K[14]). These results indicate that **3a–c** are paramagnetic with $S = 1$ ground states. A degree of second-order spin–orbit coupling is also suggested, as the room-temperature μ_{eff} values for **3a–c** are higher than expected for the spin-only model.[15]

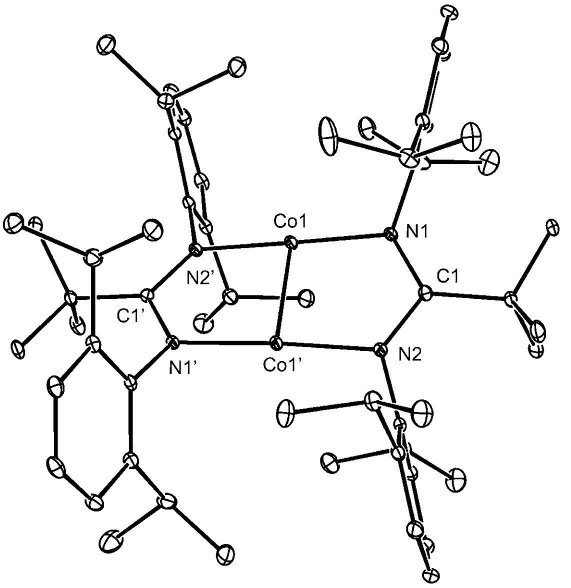


Figure 2. Molecular structure of compound **4a** (thermal ellipsoids at 25% probability; hydrogen atoms omitted). Relevant bond lengths [Å] and angles [°]: Co1–N2' 1.9185(14), Co1–N1 1.9276(14), Co1–Co1' 2.1404(10), N1–C1 1.347(2), C1–N2 1.347(2); N2'-Co1-N1 176.58(6), N2'-Co1-Co1' 88.82(5), N1-Co1-Co1' 93.53(4), N1-C1-N2 113.63(15). Symmetry operation: $'-x+1,y,-z+1/2$.

The solid-state structures of compounds **4a** (Figure 2) and **4b** are similar and show the complexes to be essentially planar amidinate- or guanidinate-bridged dimers.[14] No analogous β-diketiminate cobalt(I) compounds have been reported to date, but the structures of **4a** and **4b** are comparable to the aforementioned Cr–Cr quintuply bonded systems, [{Cr[μ-N(Ar')C(R)N(Ar')]}$_2$].[11] The Co–Co interactions in **4** (**4a** 2.1404(10) Å; **4b** 2.1345(7) Å) are significantly shorter than any of the more than 5600 other examples (range: 2.185–3.129 Å) in the Cambridge Crystallographic Database.[16] At first glance, this result seemed to imply that the compounds possess strong Co=Co bonds, as the normal Co–Co single-bond length is considered to be 2.46 Å.[17] If this hypothesis were valid, the Co centers of compounds **4a** and **4b** are best described as having T-shaped coordination geometries. In both compounds, the "open" cobalt coordination sites have a number of close contacts with isopropyl hydrogen atoms (closest C−H⋅⋅⋅Co distances are ca. 2.62 Å (**4a**); 2.30 Å (**4b**)). The intraligand bond lengths of the complexes are consistent with significant delocalization over their NCN fragments and their Co–N separations are considerably shorter than those in **3a** and **3b**. The presence of terminal or bridging hydride ligands in both complexes was contemplated, although no crystallographic or other evidence was found to support this hypothesis.[14]

The room-temperature solution ([D$_{12}$]cyclohexane) magnetic moments were found to be 5.35 μ_B (**4a**) and 5.10 μ_B (**4b**), which indicated four unpaired electrons per dimer. Variable-temperature solid-state magnetic studies on **4a** (Figure 3) gave a μ_{eff} value of 5.25 μ_B at 300 K, which decreased to 5.15 μ_B at 50 K. The rapid decrease below 50 K is indicative of zero-field splitting of the spin ground state, while the plot of χ_M^{-1} versus temperature almost obeys Curie behavior ($\theta = -3.07$ K, $C = 3.49$ cm^{3}mol^{-1}K). These data appear consistent with **4a** (and, by implication, **4b**) having isolated $S = 2$ ground states. However, the possibility that the compounds possess two high-spin d^8 metal centers (each $S = 1$) that have little magnetic communication cannot be totally ruled out.[14]

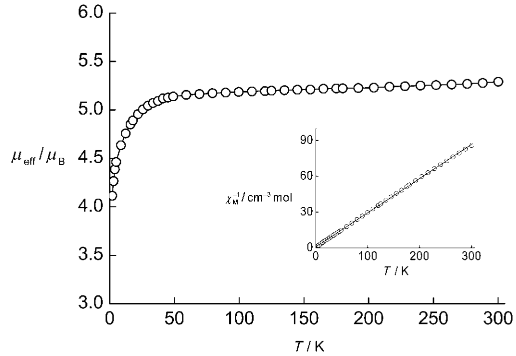
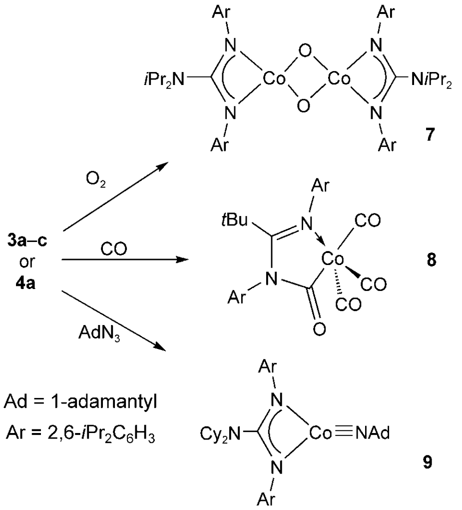


Figure 3. Plot of the effective magnetic moment and inverse molar magnetic susceptibility (inset) versus temperature for **4a**. The open circles show the experimental results and the solid lines are guides.

From a qualitative point of view, the nature of the metal–metal bonding in compounds **4a** and **4b** can be proposed when comparisons are drawn with the related diamagnetic chromium(I) dimers, [{Cr[μ-N(Ar′)C(R)N(Ar′)]}$_2$] (R = H or Me, Ar′ = Ar or 2,6-Et$_2$C$_6$H$_3$).[11] DFT calculations on a model complex suggested that the quintuple bonds of the dimers arise from filling five molecular orbitals that have predominantly metal–metal bonding character (1 σ, 2 π, and 2 δ). The unoccupied frontier molecular orbitals of the model system are largely metal–metal antibonding in character. If a similar ordering of molecular orbitals occurs for compounds **4a** and **4b**, then the extra six electrons that originate from the two cobalt centers (cf. chromium) could doubly occupy one molecular orbital, and singly occupy four molecular orbitals that have metal–metal antibonding character. This ordering would give rise to compounds that have quintet ground states and relatively strong Co–Co interactions (bond orders of ca. 2).

In order to ascertain if this ordering is indeed the case for **4a** and **4b**, theoretical calculations were carried out on the model complexes [{Co[μ-N(Ph)C(R)N(Ph)]}$_2$] (R = Me (**5**) or NMe$_2$ (**6**)). Attempts to optimize the geometries of these models were not successful and, as a result, non-optimized geometries constructed from cut-down coordinates taken from the crystal structures of **4a** and **4b** were utilized.[14] Initially, DFT (B3LYP/6-31G(d)) calculations were employed, but problems with the convergences of these calculations led to them being abandoned. Given the well known deficiencies of DFT in describing open-shell systems,[18] CASPT2 calculations (using appropriate basis sets) were also carried out on **5** and **6**, the geometries of which were slightly modified to fulfill C_i and C_2 symmetries, respectively. Consistent with the magnetic moments experimentally determined for **4a** and **4b**, these calculations showed that the ground states for both model complexes are quintets (**5** ^{5}A$_u$, **6** ^{5}B), with the first triplet states 9.06 and 11.67 kcal mol^{-1} higher in energy, respectively, than the ground states. Inspection of the natural orbital occupation numbers indicated highly multiconfigurational characters for the wavefunctions of the model compounds. For example, in the case of **5**, the ground state is characterized by two dominating electronic configurations, $(\sigma_u^*)^1(\pi_g^*)^1(\delta_u^*)^1(\delta_u^*)^1$ and $(\sigma_u^*)^1(\pi_g^*)^1(\delta_g)^1(\delta_g)^1$, with relative weights of 0.45 and 0.29, respectively. Given the difficulties in optimizing the geometries of the models, and the highly multiconfigurational nature of their metal–metal bonding, it is impractical to accurately estimate the absolute Co–Co bond orders of **5** and **6** from the calculations. These bond orders should, therefore, be considered indeterminate at this stage.[14,19,20]

In light of their high reactivity, preliminary studies were carried out to assess the ability of **3a–c** and **4a**, **4b** to activate small molecules (Scheme 2). Neither compound series reacted with dihydrogen or dinitrogen, but **3** (R = N*i*Pr$_2$) was oxidized with dioxygen to give the square-planar cobalt(III) oxide complex **7** in low yields (cf. the formation of



Scheme 2. Preparation of compounds **7**–**9**.

square-planar [{(nacnac)Co(μ-O)}$_2$] from **1** and O$_2$[2b]). When **3a** or **4a** were treated with CO, the unusual diamagnetic iminocarbamoyl complex **8** was formed in high yields. It is likely that these reactions occur by initial carbonylations of **3a** (with concomitant loss of toluene) or **4a**, followed by migratory insertions of a molecule of CO into the Co–N bonds of the complexes. A similar insertion has been observed upon carbonylation of a terphenyl cobalt(I) complex.[15] Reaction of **3b** with 1-adamantyl azide (AdN$_3$) gave a good yield of diamagnetic **9** (cf. the formation of [(nacnac)Co≡NAd] from **1** and AdN$_3$[2b]). There are only a handful of almost-linear terminal cobalt imides known that can be compared with **9**,[2b–c] but the Co≡N distance in **9** (1.621(3) Å, see Figure 4) is identical to that in [(nacnac)Co≡NAd],[2b] and both distances are shorter than in other examples of four-coordinate complexes.[16,21]

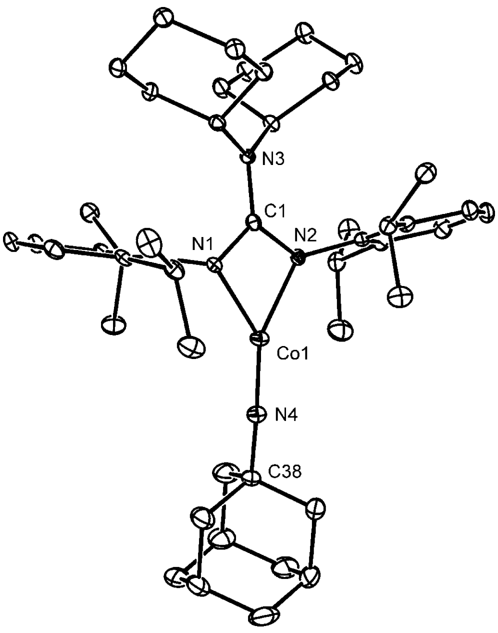


Figure 4. Molecular structure of compound **9** (thermal ellipsoids at 25% probability; hydrogen atoms omitted). Relevant bond lengths [Å] and angles [°]: Co1–N1 1.942(3), Co1–N2 1.947(3), Co1–N4 1.621(3); N1-Co1-N2 68.52(12), Co1-N4-C38 172.1(3).

In conclusion, monomeric and dimeric examples of the first amidinato– and guanidinato–cobalt(I) complexes have been prepared. The structures and reactivity of the monomeric complexes are closely related to those of an analogous β-diketiminate complex. The paramagnetic, ligand-bridged dimeric complexes display the shortest known Co–Co interactions, which, according to theoretical calculations, have highly multiconfigurational characters. We continue to explore the chemistry of bulky guanidinato and amidinato complexes of the 3d metals, and the application of these complexes to small-molecule activation.

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