Complexes of iron and cobalt with new tripodal amido-polyphosphine hybrid ligands†

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Divalent complexes of iron and cobalt with new, monoanionic tripodal amido-polyphosphine ligands have been thoroughly characterized, and XRD analysis reveals geometries that are distinct for this class of ligand.

Rational ligand design has figured prominently in the discovery of metal complexes with novel properties, and changes in ligand scaffolds can be utilized to tune reactivity both by the choice of donors and the geometry conferred about the metal center. Our group has been examining tris(phosphino)borate ligands that educe interesting reactivity patterns from iron and cobalt with various substrates, helping to stabilize a range of oxidation states. For example, complexes of iron and cobalt with tris(phosphino)borate ligands show a propensity to coordinate and stabilize multiply-bonded ligand moieties, and cobalt complexes supported by these ligands have revealed a number of unexpected electronic properties due to the strong field and distorted tetrahedral geometry conferred by the ligand. In this context, we were eager to consider analogues of the (phosphino)borates in which the negative charge would be carried by an X-type donor ligand rather than the borate backbone.

Particularly interesting to us were the mixed amide–phosphine hybrid ligands first developed by Fryzuk and coworkers. As Fryzuk has noted, these scaffolds combine “hard” amido and “soft” phosphine donors, allowing them to bind many transition metals, stabilize a variety of oxidation states, and induce interesting transformations. Several properties of these hybrid ligands were appealing to us. First, the amido donor bears the uninegative charge rather than a borate unit. We also anticipated that amido-polyphosphines would be electron-releasing, like their poly(phosphino)borates analogues, but with the distinction that the lone pair at the amido substituent would be available for π-donation. Such ligands should likewise support low- and mid-valent group transfer reactions, though it is likely that the potential for π-donation from the amido will alter the reactivity of other multiply-bonded ligands. While the chemistry of iron and cobalt amide-phosphine complexes is limited in scope, these general types of hybrid ligands have been productively used on second- and third-row late transition metals.

We report synthetic protocols for the preparation of the two new amido-polyphosphine ligands outlined in Scheme 1. Syntheses of the potentially tetradeinate [3NP3] ligand, an anionic relative to...
Associated with the reduction event at representation of [SiNP3]CoI. (a) Two essentially identical molecules were present in the asymmetric unit; one representative is depicted and hydrogen of low spin Complex of maroon 2b [TBA][PF6]/THF, scan rate 2b

**Complexes** of Li[SiNP2] and CoCl2 or CoI2, respectively.12 X-ray data for crystals of low spin 2a \( \mu_{\text{eff}} = 1.9 \mu_B \) in \( C_{4h}D_{4h} \), see ESI for X-ray data) and 2b were collected to confirm their similar structures. The structure of maroon 2b is shown in Fig. 1b, and that of 2a is in the ESI. Complex 2b features a trigonal bipyramidal Co(II) center in which the iodide ligand occupies an apical position. The metal–phosphine distances in 2b are shorter than those found in complex 1, consistent with its low spin configuration, and the axial Co–P bond is ca. 0.1 Å shorter than the equatorial Co–P2 and Co–P3 bonds. The amide, P2, and P3 ligands lie in a plane that contains the cobalt center, but the P1–Co–I axis is slightly bent (P1–Co–I = 172°) due to the iodide ligand being positioned away from the amide donor. A space-filling model of 2b (Fig. 1c) reveals an iodide ligand that is nestled within a binding pocket comprised of the phosphine phenyl substituents and a rotated disospropylphenyl group. Canting of the 2,6-diisopropylanilide donor minimizes steric interactions between the isopropyl groups and the phenylphosphine substituents and also tilts the lone pair of the amido ligand out of the equatorial plane. The cyclic voltammetry of 2a resembles that of 1, featuring a reversible Co^{III/II} couple at \(-0.43 \) V and an irreversible cathodic peak at \(-2.1 \) V. Once again, a new and irreversible anodic peak grows in at \(-1.0 \) V that appears to be associated with the reduction event at \(-2.1 \) V (see ESI for CV).

Unlike [SiNP3], the [SiNP2] ligand is geometrically predisposed to tridentate, facial coordination.13 This feature distinguishes it from other Fryzuk-type amide-polyphosphine ligands, for which meridional chelation dominates.17 Li[SiNP3] and FeCl3 reacted to generate [SiNP3]FeCl (3) cleanly in 83% isolated yield. Likewise, [SiNP3]CoCl (4a) and [SiNP3]CoI (4b) could be obtained using CoCl2 and CoI2, respectively. Complex 3 is high spin \( \mu_{\text{eff}} = 4.8 \mu_B \), consistent with the expected tetrahedral Fe(II) structure. XRD analysis of single crystals of 3 and 4b confirmed the tripodal binding mode of the [SiNP3] ligand (Fig. 3). Interestingly, the N–Fe–P and P–Fe–P angles in both 3 and 4b are much closer to 90° than we had anticipated, providing structures distinct from those of typical tetrahedra. In this regard, the [SiNP3] donors are better described as occupying three corners of an octahedron, in a manner analogous to tripodal borate ligands such as [Tp]14, [PhTtR]15 and [PhBP3]2. The propensity of the [SiNP3] ligand to enforce such a distorted tetrahedral geometry likely stems from the tight chelate that arises from having both phosphine arms branch from a common silyl linker. As expected, a space-filling model of 3 (Fig. 3c) reveals significantly less steric protection about the halide binding site in comparison to 2b. Additionally, it is interesting to note that for both 3 and 4b, the 2,6-diisopropylanilide donor lies perpendicular to the Co–I vector rather than canted as in 2b, likely because the environment is less sterically demanding. Giving this binding geometry and the additional presence of the arylamido donor ligand, we had expected that cobalt complexes 4a and 4b might adopt low spin configurations, akin to certain [PhBP3]CoO3-X systems we have previously described.2 However, both 4a and 4b are high spin. These assignments are consistent with their room temperature Evans method determinations \( \mu_{\text{eff}} = 3.7 \mu_B \) for 4a, 4.0 \( \mu_B \) for 4b and the elongated Co–P and Co–I bond distances revealed by the 100 K X-ray structure of 4b. In a comparative context, these data continue to underscore how unusual the electronic properties of the parent [PhBP3] ligand are compared with structurally related tripodal ligands.2

Complexes 3 and 4a were also examined by cyclic voltammetry (see ESI for voltammograms of each complex). The CV of 3 does not show any reversible redox events. An irreversible reduction peak beginning at \(-2.1 \) V is evident, as is an oxidative wave at
+0.24 V. A smaller reduction wave centered at −0.63 V grows in as a result of scanning through the oxidation process at + 0.24 V. The CV data for 4a show a quasi-reversible wave centered at −0.17 V, corresponding to a Co(II/III) oxidation event. Additionally, there is an irreversible reduction wave at −1.4 V and a smaller irreversible oxidative wave at −0.40 V. The putative Co(III) reduction event occurs at a potential ca. 0.7 V more positive for compound 4a compared with 2a.

In summary, we have introduced two new amido-polysulfone ligands and thoroughly characterized divalent iron and cobalt halide complexes of each system. The [SiNP2] and [SiNP3] ligands are related in that each is monoanionic and strongly electron-releasing. However, whereas the [SiNP2] ligand is predisposed to bind in a tridentate, tripodal fashion, the [SiNP3] ligand can adopt both tridentate and tetradentate binding modes depending on the electronic requirements of the metal center. The [SiNP3] ligand enforces a highly distorted geometry reminiscent of other triad ligands such as [Tp] and [PhBP]. We are currently exploring the affinity of these systems for binding N₂ and other π-acidic substrates under reducing conditions.

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Notes and references


12. Although [SiNP3]Co(III) was more readily crystallized than its chloride counterpart 2a, analytically pure bulk samples of 2a were more readily obtained.

