Metallates

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Zwitterionic Stabilization of a Reactive Cobalt Tris-Isocyanide Monoanion by Cation Coordination**

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As a result of their metal-based nucleophilicity and ability to mediate a wide range of transformations involving main-group and carbon-based electrophiles, organometallic metallates have received considerable attention.[1] The homoleptic carbonyl metallates $[Fe(CO)_4]^{2-}$ and $[Co(CO)_4]^-$ serve as the prototypical examples of this molecular class and are stabilized in part by strong π-back-bonding interactions between the highly reduced metal centers and the CO ligands.[2] In addition, several metallates containing other π-acidic ligands, including olefins, arenes, isocyanides, and PF_3, have been reported.[1 h] However, in the vast majority of these cases the reduced metal centers possess coordinative and/or electronic saturation (i.e. 18 e^- configurations), which adds to their stability. Accordingly, the chemistry of metallates featuring coordinatively unsaturated metal centers is significantly underdeveloped,[3] despite the promise of coupling metal-based nucleophilic character with enhanced reactivity toward Lewis basic substrates.

In an effort to stabilize organometallic complexes featuring both highly reduced metal centers and coordinative unsaturation, we have surveyed the ligation properties of the encumbering and π-acidic *m*-terphenyl isocyanide ligands $CNAr^{Mes2}$ and $CNAr^{Dipp2}$ (Ar^{Mes2} = 2,6-(2,4,6-$Me_3C_6H_2$)C_6H_3); Ar^{Dipp2} = 2,6-(2,6-(*i*Pr)$_2C_6H_3$)C_6H_3).[4] Herein, we report the use of $CNAr^{Mes2}$ for the isolation of a zwitterionic complex that functions as a highly reactive source of the coordinatively unsaturated, tris-isocyanide cobalt monoanion $[Co(CNAr^{Mes2})_3]^-$ toward electrophilic reagents. In this respect, $[Co(CNAr^{Mes2})_3]^-$ serves as an isocyano mimic of the unstable tricarbonyl monoanion, $[Co(CO)_3]^-$, which has been observed exclusively in the gas phase.[5] Furthermore, we detail a unique method for the stabilization of the $[Co(CNAr^{Mes2})_3]^-$ anion that relies on η^2-arene coordination of the well-known and traditionally non-interacting bis-(triphenylphosphine)iminium cation, $[PhP_3{=}N{=}PPh_3]^+$ ($[PPN]^+$).[6]

Previously we reported the [PPN] salt, $[PPN][Co(CNAr^{Mes2})_4]$,[7] as a unique example of a discrete cobalt tetra-isocyanometallate unperturbed by anion–cation interactions.[8] Prolonged stirring (30 h) of this salt in *n*-hexane solution results in $CNAr^{Mes2}$ ligand dissociation and the precipitation of the black, zwitterionic tris-isocyanide complex [(η^2-PPN)Co($CNAr^{Mes2}$)$_3$, **1**; Figures 1 and 2]. Crystallographic characterization of (η^2-PPN)Co($CNAr^{Mes2}$)$_3$ (**1**) revealed a pyramidalized cobalt tris-isocyanide core accompanied by an η^2-arene interaction between the Co center and the *para* and *meta* carbon atoms of one PPN cation phenyl ring (Figure 1). Dearomatization of the bound phenyl ring in (η^2-PPN)Co($CNAr^{Mes2}$)$_3$ (**1**) is revealed from the crystallographic data, thus indicating that the $[Co(CNAr^{Mes2})_3]^-$ fragment functions as a strong π-base.[9] Notably, coordinatively induced dearomatization is well-known for mononuclear η^2-arene complexes of the 4d and 5d metals,[9,10] but is rare for complexes of the first transition series.[10,11] Despite significant π-back donation into the bound phenyl ring, the Co center in (η^2-PPN)Co($CNAr^{Mes2}$)$_3$ (**1**) remains considerably reduced in the solid state (KBr) as indicated by the low ν_{CN} bands of the $CNAr^{Mes2}$ ligands (1952, 1860, and 1824 cm^{-1}; free $CNAr^{Mes2}$ = 2118 cm^{-1}).

While the solid-state structure of (η^2-PPN)Co($CNAr^{Mes2}$)$_3$ (**1**) is suggestive of a strong η^2-arene interaction, ^{1}H NMR

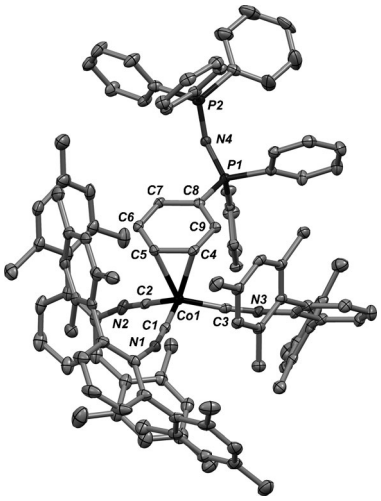

Figure 1. Molecular structure of (η^2-PPN)Co($CNAr^{Mes2}$)$_3$. Important bond lengths [Å]: Co1-C4 = 2.139(4), Co1-C5 = 2.166(4), C4-C5 = 1.434(6), C4-C9 = 1.419(6), C5-C6 = 1.411(6), C6-C7 = 1.359(6), C7-C8 = 1.437(6), and C8-C9 = 1.375(6).

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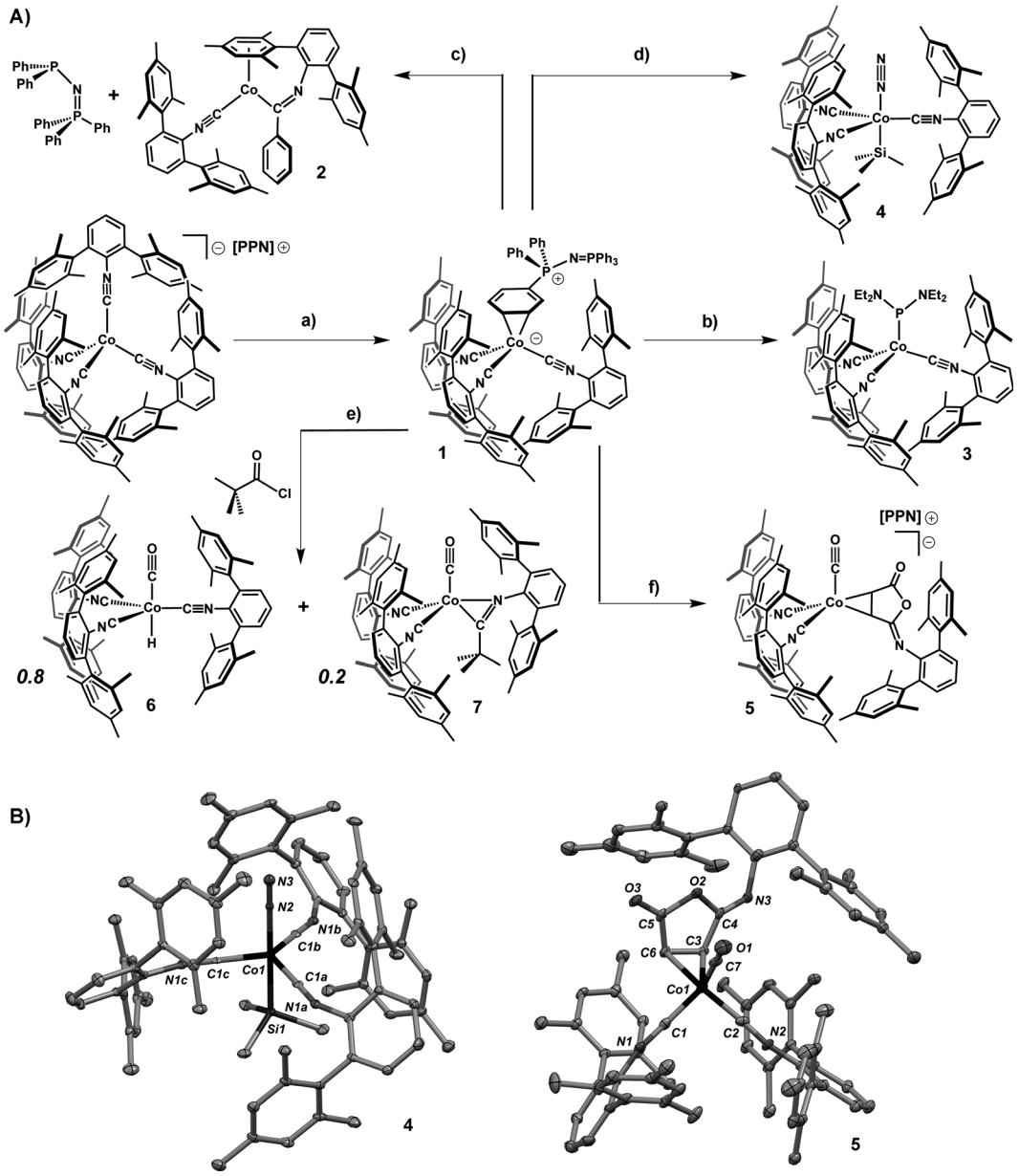

Figure 2. A) Synthesis and reaction pinwheel of $(\eta^2\text{-PPN})Co(CNAr^{Mes2})_3$ (**1**); a) *n*-C_6H_{14}, 30 h, $-CNAr^{Mes2}$; b) $ClP(NEt_2)_2$ (1.05 equivalents), Et_2O, −100 to 25 °C, −[PPN]Cl; c) Δ, RT, 24 h, C_6D_6, $-CNAr^{Mes2}$; d) $ClSiMe_3$ (1.05 equivalents), N_2, Et_2O, −100 to 25 °C, −[PPN]Cl, e) tetrahydrofuran (THF), −100 to 25 °C, −[PPN]Cl, and f) maleic anhydride (MA), −THF, −100 to 25 °C. B) Molecular structures of $(N_2)Co(SiMe_3)(CNAr^{Mes2})_3$ (**4**, left) and the anionic component of $[PPN][(\eta^2\text{-}C,C\text{-}(IMAr^{Mes2})Co(CO)(CNAr^{Mes2})_2]$ (**5**, right).

spectroscopy revealed that $[PPN]^+$ ligation to the $[Co(CNAr^{Mes2})_3]^-$ is both fluxional and labile in solution. At 20 °C in C_6D_6, the bound phenyl ring exhibits a C_s-symmetric 2:2:1 pattern of up-field ^1H NMR resonances for the *ortho*, *meta* and *para* protons, respectively. At this temperature, broadening is observed only for the *meta* position resonances, thus indicating rapid migration of the $[Co(CNAr^{Mes2})_3]^-$ fragment between equivalent C_{meta}/C_{para} sites of the bound phenyl ring. Variable-temperature ^1H NMR studies in $[D_8]$toluene were consistent with this notion and revealed that intraring migration remains fast on the NMR time scale down to −40 °C. In addition, ^1H EXSY NMR experiments at 20 °C in C_6D_6 solution revealed that the η^2-arene interaction within $(\eta^2\text{-PPN})Co(CNAr^{Mes2})_3$ (**1**) is indeed labile and that the $[Co(CNAr^{Mes2})_3]^-$ anion slowly migrates between all six phenyl rings of the $[PPN]^+$ cation.

Although opposite in charge, η^2-arene coordination of $[PPN]^+$ to $[Co(CNAr^{Mes2})_3]^-$ is reminiscent of η^2-*C*,*C*-coordination of tetraphenylborate ($[BPh_4]^-$) to highly Lewis acidic early transition-metal and lanthanide monocations that are active in α-olefin polymerization and small-molecule activation chemistry.[12,13] In these formally zwitterionic complexes, η^2-*C*,*C*-binding of the "weakly coordinating" $[BPh_4]^-$ anion serves to stabilize an otherwise highly reactive cationic d^0-metal fragment from both intra- and intermolecular decomposition pathways. Similarly, we believe that η^2-arene binding

of the traditionally non-coordinating $[PPN]^+$ cation is critical to the kinetic stabilization of the coordinatively unsaturated, electron-rich $[Co(CNAr^{Mes2})_3]^-$ anion. Accordingly, attempts to prepare alkali metal, alkaline-earth metal, tetra-alkylammonium or tetra-alkylphosphonium derivatives of $[Co(CNAr^{Mes2})_3]^-$ by chemical reduction, cation-exchange or cation-sequestration reactions have been unsuccessful to date, leading instead to intractable mixtures.[14] Furthermore, given the lability of the η^2-arene/Co interaction within (η^2-PPN)$Co(CNAr^{Mes2})_3$ (**1**), it is important to note that neutral arenes do not displace the $[\eta^2$-PPN$]^+$ cation from the coordination sphere of cobalt. Thus, dissolution of (η^2-PPN)$Co(CNAr^{Mes2})_3$ (**1**) in benzene, toluene, or fluorobenzene (C_6H_5F) does not result in intermolecular arene displacement (^{1}H NMR spectroscopy), irrespective of the electronic properties of the arene solvents. However, treatment of (η^2-PPN)$Co(CNAr^{Mes2})_3$ (**1**) with 2.0 equivalents of the soluble salt $[PPN][BAr^F_4]$ ($Ar^F = 3,5\text{-}(CF_3)_2C_6H_3$) in C_6D_6 solution does result in exchange of free and η^2-bound $[PPN]^+$ as assayed by ^{31}P EXSY NMR spectroscopy. We contend that this intermolecular cation-exchange reaction emphasizes the unique and favorable combination of electrostatic stabilization and coordinative protection afforded by the phenyl-containing $[PPN]^+$ cation to the coordinatively unsaturated $[Co(CNAr^{Mes2})_3]^-$ anion.

Despite its kinetic persistence at room temperature, zwitterionic (η^2-PPN)$Co(CNAr^{Mes2})_3$ (**1**) is observed to decompose slowly in C_6H_6 solution over 30 h to the η^6-arene, phenyl-substituted iminoacyl complex, (η^6-$MesAr^{Mes}N{=}C(Ph))Co(CNAr^{Mes2})$ (**2**, Figure 2). Decomposition of deuterium-labeled (η^2-[D_{30}]-PPN)$Co(CNAr^{Mes2})_3$ ([D_{30}]-**1**) under identical conditions results exclusively in (η^6-$MesAr^{Mes}N{=}C(C_6D_5))Co(CNAr^{Mes2})$ ([D_5]-**2**), thereby signifying that the iminoacyl Ph group originates from the $[PPN]^+$ cation. Analysis of the reaction mixture by mass spectrometry, ^{1}H NMR, ^{31}P{^{1}H} NMR and FTIR spectroscopy revealed that the byproducts of this decomposition are free $CNAr^{Mes2}$ and the known phosphinophosphazene, $Ph_2P\text{-}N{=}PPh_3$.[15] The formation of $Ph_2P\text{-}N{=}PPh_3$ is indicative of P–C bond cleavage of $[PPN]^+$ and formal transfer of a $[C_6H_5]^+$ cation unit to the Co-containing fragment. This process requires a two-unit, formal oxidation state increase at the Co center and is therefore distinct from the well-established and non-oxidative phenyl-anion transfer from $[BPh_4]^-$ to electrophilic transition-metal cations.[16] Most plausibly, the Co^I-phenyl tris-isocyanide complex, $[PhCo(CNAr^{Mes2})_3]$, is an intermediate in the decomposition of (η^2-PPN)$Co(CNAr^{Mes2})_3$ (**1**) and transforms further through α-phenyl migration, $CNAr^{Mes2}$ ejection and η^6-mesityl ring ligation to form (η^6-$MesAr^{Mes}N{=}C(Ph))Co(CNAr^{Mes2})$ (**2**). A similar α-aryl migration/CNAr-ejection sequence has been observed upon oxidative addition of aryl chlorides to the neutral Ni^0 tris-isocyanide complex $Ni(CNAr^{Dipp2})_3$.[17] Notably, $Ni(CNAr^{Dipp2})_3$ and $[Co(CNAr^{Mes2})_3]^-$ are isoelectronic with respect to their $[M(CNAr)_3]$ cores, which highlights the ability of electron-rich 3d-metal tris-isocyanides to activate strong carbon–element bonds.

Consistent with the presence of a labile $[\eta^2$-PPN$]^+$ cation, (η^2-PPN)$Co(CNAr^{Mes2})_3$ (**1**) functions readily as a source of three-coordinate $[Co(CNAr^{Mes2})_3]^-$ upon reaction with electrophilic substrates. For example, treatment of (η^2-PPN)$Co(CNAr^{Mes2})_3$ (**1**) with bis(diethylamino)chlorophosphine ($ClP(NEt_2)_2$) affords the pseudo-tetrahedral phosphide/phosphenium[18] complex $(Et_2N)_2PCo(CNAr^{Mes2})_3$ (**3**) concomitant with the release of [PPN]Cl (Figure 2). Complex **3** is an isocyanide variant of Lappert's tricarbonyl complex $(RR'P)Co(CO)_3$ ($R = N(iPr)_2$; $R' = N(SiMe_3)_2$),[19] and similarly possesses significant Co–P π-bonding as determined by X-ray diffraction (Co–P distance = 2.0198(10) Å), $^{31}P\{^1H\}$ NMR spectroscopy ($\delta = +277$ ppm) and DFT calculations. Zwitterionic (η^2-PPN)$Co(CNAr^{Mes2})_3$ also reacts smoothly with trimethylsilyl chloride ($ClSiMe_3$) in the presence of N_2 to form the trimethylsilyl-dinitrogen complex, $(N_2)Co(SiMe_3)(CNAr^{Mes2})_3$ (**4**, Figure 2). In this reaction, electrophilic silylation of the Co center presumably generates the coordinatively unsaturated complex $[Co(SiMe_3)(CNAr^{Mes2})_3]$, which then binds dinitrogen in an end-on fashion.[20] Importantly, the formation of complex **4** demonstrates that (η^2-PPN)$Co(CNAr^{Mes2})_3$ (**1**) can function as a nucleophilic metallate, but remain active for small-molecule binding after electrophilic functionalization of the Co center.

The ability to deliver a coordinatively unsaturated, metal-based nucleophile also enables (η^2-PPN)$Co(CNAr^{Mes2})_3$ (**1**) to induce multi-step transformations of electrophilic organic carbonyl compounds. As shown in Figure 3, treatment of (η^2-PPN)$Co(CNAr^{Mes2})_3$ (**1**) with maleic anhydride affords the isomaleimide-containing salt, $[PPN][(\eta^2\text{-}C,C\text{-}(IMAr^{Mes2})Co(CO)(CNAr^{Mes2})_2]$ (**5**; $IMAr^{Mes2} = 5\text{-}$

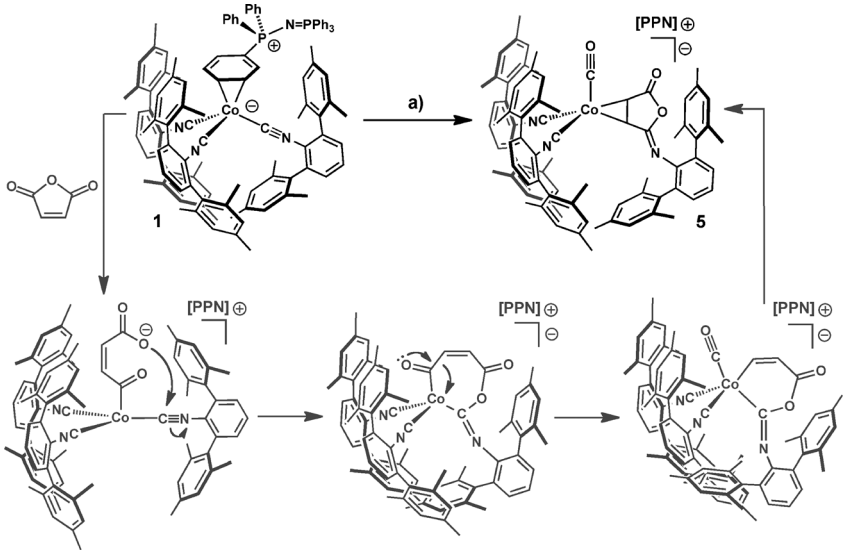

Figure 3. Proposed mechanism of formation for $[PPN][(\eta^2\text{-}C,C\text{-}(IMAr^{Mes2})Co(CO)(CNAr^{Mes2})_2]$ (**5**); a) MA, −THF, −100 to 25 °C.

(Ar^{Mes2}-imino)furanone), as determined by X-ray diffraction (Figure 2).[21]

Under current unoptimized conditions (Figure 3), complex **5** is isolated in low yield (about 20%), but is remarkable in that it represents a formally isovalent O for NAr^{Mes2} exchange within the maleic anhydride ring concomitant with the formation of a carbonyl ligand. Selective ^{13}C labeling of the $CNAr^{Mes2}$ isocyanide carbon atom, followed by treatment of (η^2-PPN)Co($^{13}CNAr^{Mes2}$)$_3$ ([C_1]-**1**) with maleic anhydride, revealed that the cobalt-bound carbonyl ligand in the labeled product (that is, [PPN][(η^2-*C*,*C*-(5-^{13}C-IMAr^{Mes2})Co(CO)($^{13}CNAr^{Mes2}$)$_2$]) is not isotopically enriched.[22] This result suggests that decarbonylation of a maleic anhydride C=O unit and full transfer of a $CNAr^{Mes2}$ group to the resultant isomaleimide ring is operative. Indeed, in a related reaction, treatment of (η^2-PPN)Co($CNAr^{Mes2}$)$_3$ (**1**) with pivaloyl chloride (*t*BuC(O)Cl, Figure 2) results readily in acyl-group decarbonylation en route to a 4:1 mixture of the monohydride HCo(CO)($CNAr^{Mes2}$)$_3$ (**6**) and the iminoacyl complex Co(CO)(η^2-*C*,*N*-(*t*BuC=NAr^{Mes2})($CNAr^{Mes2}$)$_2$ (**7**), through β-H elimination and *t*Bu α-migration, respectively. Notably, this decarbonylation behavior mirrors that of the reactive and unstable 16e$^-$ acyl cobalt tricarbonyl intermediates (i.e. R(O)CCo(CO)$_3$) proposed in Co-catalyzed hydroformylation cycles.[23] Accordingly, with respect to the formation of complex **5**, we currently favor the stepwise mechanism shown in Figure 3, which involves anhydride ring opening, metal–acyl decarbonylation and C–C bond reductive elimination to furnish the isomaleimide ring. However, additional studies detailing the mechanism and generality of the reactions between (η^2-PPN)Co($CNAr^{Mes2}$)$_3$ (**1**) and cyclic carbonyl compounds are underway.

As a point of contrast, it is noteworthy that the long-known tetra-carbonyl metallate salt, [PPN][Co(CO)$_4$],[24] does not undergo CO-ligand displacement by the [PPN]$^+$ cation.[2] Given the isolobal relationship between isocyanides and CO, we believe this behavioral difference further illustrates the unique aspects of *m*-terphenyl-isocyanide ligation in both the synthesis and stabilization of low-valent, low-coordinate transition-metal fragments. Further investigations into the nature of the [PPN]$^+$/Co interaction within (η^2-PPN)Co($CNAr^{Mes2}$)$_3$ (**1**), as well as its ability to serve as a reliable source of the anion [Co($CNAr^{Mes2}$)$_3$]$^-$ toward other electrophilic substrates, are continuing.

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