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Protecting Groups

Thallium(I) as a Coordination Site Protection Agent: Preparation of an Isolable Zero-Valent Nickel Tris-Isocyanide**

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Low-coordinate, zero-valent metal isocyanide complexes [M(CNR)$_n$] are of interest as potentially isolable analogues to the unsaturated metal carbonyls studied by Burdett[1] and Turner[2] ([Cr(CO)$_3$], [Cr(CO)$_4$], [Fe(CO)$_4$], and [Ni(CO)$_3$]). Indeed, the electronic structure combination of coordinative unsaturation, coupled with strongly π-acidic ligands has, outside of gas-phase matrix isolation studies and the highly reduced carbonyl metalates championed by Ellis,[3] received limited attention. For neutral d^{10} [Ni(CO)$_3$], analogues possessing strongly σ-donating phosphines, such as [Ni(PR$_3$)$_3$], have been widely investigated,[4] whereas recent attention has been given to three-coordinate species featuring NHC ligands.[5,6] With respect to strongly π-acidic isocyanide ligands, studies by Otsuka[7] on [Ni(CN*t*Bu)$_4$] are noteworthy in that homoleptic [Ni(CN*t*Bu)$_3$] is proposed to be the reactive entity in solution. However, isolation or experimental verification of this species have not been achieved. Recently, we employed the sterically encumbering *m*-terphenyl isocyanide ligand CNAr$^{\text{Mes}_2}$ (Ar$^{\text{Mes}_2}$ = 2,6-(2,4,6-Me$_3$C$_6$H$_2$)$_2$C$_6$H$_3$) for the stabilization of coordinatively unsaturated Cu$^{\text{I}}$ complexes.[8] Herein we present the use of CNAr$^{\text{Mes}_2}$ in the isolation of the tris-isocyanide complex [Ni(CNAr$^{\text{Mes}_2}$)$_3$]. In addition, we detail a coordination site protection strategy for its preparation that exploits the ability of low-valent Ni to bind Tl$^{\text{I}}$ ions in a synthetically reversible fashion.

In an attempt to directly prepare [Ni(CNAr$^{\text{Mes}_2}$)$_3$], [Ni(cod)$_2$] (cod = 1,5-cyclooctadiene) was treated with three equivalents of CNAr$^{\text{Mes}_2}$ in THF solution. Instead of smoothly generating the desired tris-isocyanide, an equimolar mixture of the tetrakis-isocyanide complex [Ni(CNAr$^{\text{Mes}_2}$)$_4$] and the bis-isocyanide complex, [Ni(cod)(CNAr$^{\text{Mes}_2}$)$_2$] was obtained. Both [Ni(CNAr$^{\text{Mes}_2}$)$_4$] and [Ni(cod)(CNAr$^{\text{Mes}_2}$)$_2$] were independently synthesized (Scheme 1). Notably, the product distribution obtained from the treatment of [Ni(cod)$_2$] with [CNAr$^{\text{Mes}_2}$] was unchanged irrespective of the rate or order of addition, or upon heating of the mixture. Therefore, to obtain Ni(CNAr$^{\text{Mes}_2}$)$_3$ in pure form, we sought to protect the Ni center from binding a fourth isocyanide.

Inspired by Catalano's report[9] of unsupported Tl$^{\text{I}}$–Pt bonds in the platinum phosphine complexes [TlPt(PPh$_2$R)$_3$]X (R = py, Ph; X = NO$_3^-$, OC(O)Me$^-$), we postulated that addition of a Tl$^{\text{I}}$ capping group to a suitable low-valent Ni center may adequately protect a single coordination site from ligand substitution processes. Whereas the formation of Tl$^{\text{I}}$–M interactions has been well-studied,[10] considerably less attention has been paid to the behavior or persistence of these units in subsequent chemical reactions.[11] Furthermore, given the insolubility of Tl$^{\text{I}}$ halides in organic solvents with low dielectric constants, we reasoned that such a protecting group could be readily removed upon simple addition of external halide ions after the stepwise installation of three CNAr$^{\text{Mes}_2}$ ligands.

Treatment of an ethereal solution of the bis-isocyanide complex [Ni(cod)(CNAr$^{\text{Mes}_2}$)$_2$] with thallium triflate (TlOTf, OTf = [OSO$_2$CF$_3$]$^-$; 1.0 equivalents) led to the rapid precipitation of a single new diamagnetic species, as indicated by ^{1}H NMR spectroscopy (C$_6$D$_6$). X-ray structural characterization revealed the identity of this complex as [TlNi(cod)(CNAr$^{\text{Mes}_2}$)$_2$]OTf, in which a single Tl atom is incorporated into the Ni primary coordination sphere (Figure 1). Most notably, the direct interaction between Ni and Tl (Ni–Tl 3.0235(4) Å) elicited a conspicuous shift in the coordination geometry of Ni from tetrahedral in [Ni(cod)(CNAr$^{\text{Mes}_2}$)$_2$] to trigonal bipyramidal in [TlNi(cod)(CNAr$^{\text{Mes}_2}$)$_2$]OTf. The average Tl–C$_{\text{aryl}}$ distance in [TlNi(cod)(CNAr$^{\text{Mes}_2}$)$_2$]OTf is (3.73 ± 0.42) Å, with the shortest being 3.267(5) Å, thereby suggesting that interactions from the CNAr$^{\text{Mes}_2}$ ligand periphery are not responsible for holding the Tl atom in close proximity to the Ni center. However, it is notable that the Tl center makes a long but non-negligible contact with the triflate ion in the solid state (Tl–O1 2.696(2) Å). Indeed, a similar counterion–Tl contact was reported by Catalano in the case of [TlPt(PPh$_2$R)$_3$]OC(O)Me.[9]

Additional evidence for a significant Ni–Tl interaction was garnered from FTIR spectroscopy. In the solid state (KBr), [TlNi(cod)(CNAr$^{\text{Mes}_2}$)$_2$]OTf gave rise to isocyanide ν(CN) stretches of 2000 and 2070 cm^{-1}, which were shifted to markedly higher energy relative to those in [Ni(cod)(CNAr$^{\text{Mes}_2}$)$_2$] (1977 and 2045 cm^{-1}). Whereas this shift clearly indicates an electronic perturbation of Ni upon Tl coordination, the diminished electron density on the Ni center is reflective of the Tl ligand functioning as a Lewis acidic center. Remarkably, the Ni–Tl interaction within the [TlNi(cod)-

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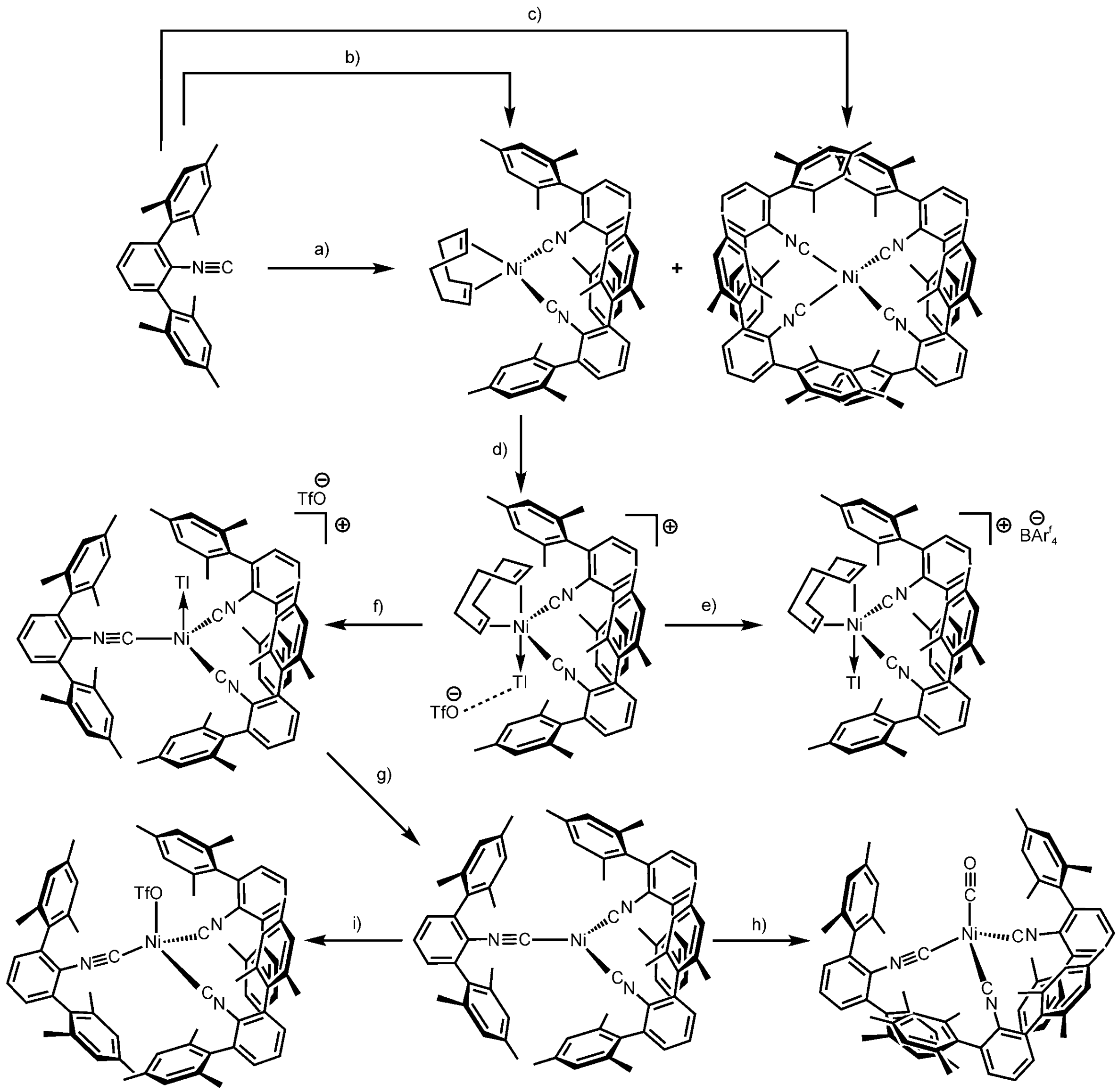

Scheme 1. Reactions of Ni complexes with $CNAr^{Mes_2}$ ligands: a) $[Ni(cod)_2]$ (0.33 equivalents), THF; b) $[Ni(cod)_2]$ (0.5 equivalents), dropwise, THF, −cod; c) $[Ni(cod)_2]$ (0.25 equivalents), THF, −2 cod; d) TlOTf (1.0 equivalents), Et_2O; e) $NaBAr^F_4$ Et_2O, −NaOTf; f) $CNAr^{Mes_2}$ (1.05 equivalents), C_6H_6, −cod; g) KI (1.0 equivalents), THF, −TlI, −KOTf; h) CO (1.0 equivalents), THF; i) $[Cp_2Fe]OTf$ (1.05 equivalents), C_6H_6, $-[Cp_2Fe]$.

$(CNAr^{Mes_2})_2]^+$ unit can be strengthened upon removal of the OTf^- counter ion. Thus treatment of $[TlNi(cod)(CNAr^{Mes_2})_2]OTf$ with $Na[BAr^F_4]$ ($Ar^F = 3,5\text{-}(CF_3)_2C_6H_3$) produced cherry red $[TlNi(cod)(CNAr^{Mes_2})_2]BAr^F_4$ after removal of NaOTf. X-ray structural characterization of $[TlNi(cod)(CNAr^{Mes_2})_2]BAr^F_4$ (Figure 2) revealed discrete ionic components where the closest $Tl\text{–}[BAr^F_4]$ contact was 5.456 Å. Notably, the Ni–Tl distance of 2.853(2) Å in $[TlNi(cod)(CNAr^{Mes_2})_2]BAr^F_4$ had contracted from that in the OTf^- species, indicating an augmentation of the interaction. Indeed, $[TlNi(cod)(CNAr^{Mes_2})_2]BAr^F_4$ gave rise to $\upsilon(CN)$ stretches of 2056 and 2103 cm^{-1}, which were further shifted to higher energy than for the OTf^- derivative.

Most revealing however, was the chemical shift exhibited by $[TlNi(cod)(CNAr^{Mes_2})_2]BAr^F_4$ ($\delta = 4430$ ppm) in solution (C_6D_6) ^{205}Tl NMR spectroscopy, which is significantly downfield of that found for $[TlNi(cod)(CNAr^{Mes_2})_2]OTf$ (2069 ppm). This downfield progression is consistent with an increase in the paramagnetic component (σ_{para}) of the ^{205}Tl shielding tensor as is expected upon lowering the coordination number of Tl.[12] Accordingly, the bonding interaction from Ni was enhanced to compensate for the removal of counterion-based electron density from the Tl center. We therefore contend that, in these isocyanide complexes, Ni provides a reverse-dative σ interaction to Tl (Ni→Tl).[13] This notion finds credence in the well-precedented ability of Tl^I centers to form closed-shell interactions with the heavy, late transition elements.[14,15] However, to our knowledge, $[TlNi(cod)(CNAr^{Mes_2})_2]BAr^F_4$ represents a unique example of an unsupported bond between a first row transition metal and a one-coordinate Tl center.[16]

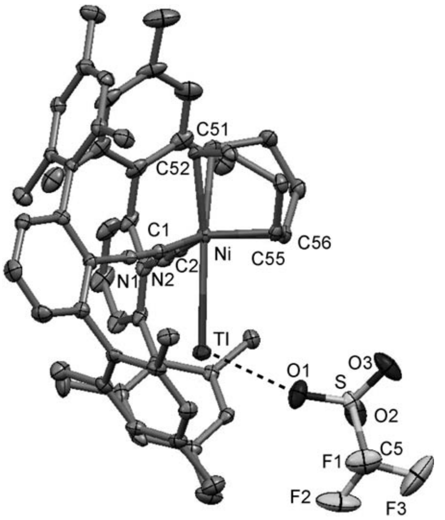

Figure 1. Molecular structure of [TlNi(cod)(CNAr^{Mes_2})$_2$]OTf. Thermal ellipsoids are set at 50% probability. Hydrogen atoms are omitted for clarity.

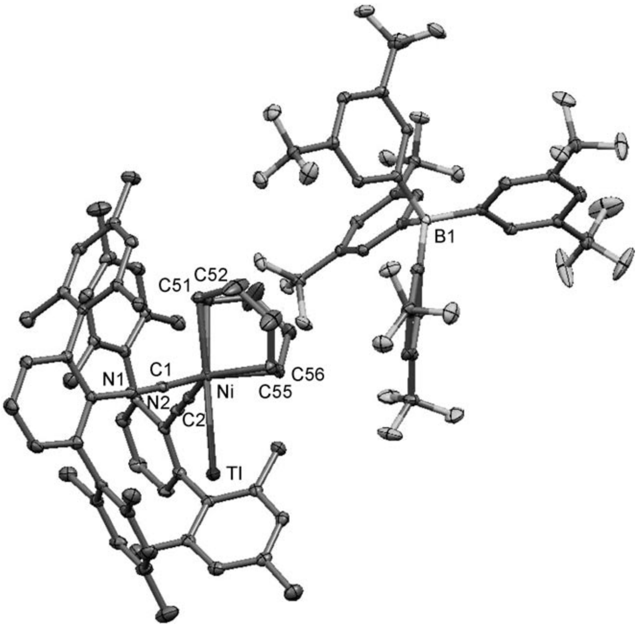

Figure 2. Molecular structure of [TlNi(cod)(CNAr^{Mes_2})$_2$]BAr$^F_4$. Thermal ellipsoids are set at 50% probability. Hydrogen atoms are omitted for clarity.

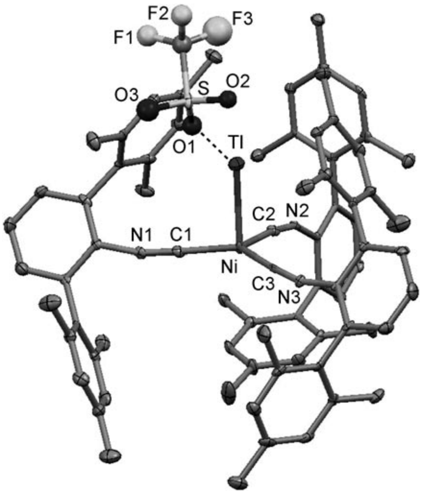

Figure 3. Molecular structure of [TlNi(CNAr^{Mes_2})$_3$]OTf. Thermal ellipsoids are set at 50% probability. Hydrogen atoms are omitted for clarity.

Whereas the Ni–Tl interaction was preserved upon anion exchange, it was also maintained during ligand-substitution processes. Thus treatment of the triflate derivative [TlNi(cod)(CNAr^{Mes_2})$_2$]OTf with additional CNAr^{Mes_2} led exclusively to the displacement of the cod unit, affording the tris-isocyanide complex [TlNi(CNAr^{Mes_2})$_3$]OTf. Single-crystal X-ray analysis of [TlNi(CNAr^{Mes_2})$_3$]OTf (Figure 3) revealed a four-coordinate complex in which the Tl atom remained coordinated to the Ni center. Whereas [TlNi(CNAr^{Mes_2})$_3$]OTf also had a long Tl–OTf$^-$ contact of 2.693(5) Å, the Ni–Tl bond length of 2.6105(11) Å was contracted in comparison to those in the cod derivatives, presumably owing to the removal of the ligand *trans* to the Tl unit.[17] Most importantly however, addition of excess CNAr^{Mes_2} to [TlNi(CNAr^{Mes_2})$_3$]OTf did not displace the ligated Tl center, thus establishing that the latter can indeed function as a coordination-site protection agent.

Removal of the Tl ligand was readily achieved by addition of an external halide source. Addition of KI to [TlNi(CNAr^{Mes_2})$_3$]OTf in THF induced the precipitation of yellow TlI, producing the burgundy tris-isocyanide complex [Ni(CNAr^{Mes_2})$_3$] along with KOTf (Scheme 1). Removal of ligated Tl by addition of halide is notable in that the reverse reaction, namely halide abstraction by soluble Tl^{I} sources, is typically employed to generate a coordinatively unsaturated metal fragment. Structural characterization of [Ni(CNAr^{Mes_2})$_3$] (Figure 4) confirmed its trigonal planar nature ($\Sigma_{(\measuredangle \text{C-Ni-C})} = 359.06^{\circ}$) in accordance with predictions[1] for zero-valent group 10 metals ligated by three strongly π-acidic ligands. Density functional (DFT) calculations (ADF 2007.01, BP86/ZORA-TZ2P) on the model [Ni(CNAr^{Ph_2})$_3$]

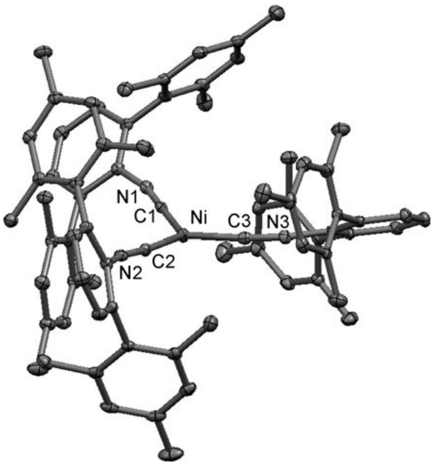

Figure 4. Molecular structure of [Ni(CNAr^{Mes_2})$_3$]. Thermal ellipsoids are set at 50% probability. Hydrogen atoms are omitted for clarity.

revealed a LUMO which is Ni pz in character as expected for a planar three-coordinate d^{10} metal center.[18] In contrast however, the corresponding HOMO is exclusively of Ni d$_{z^2}$ parentage (a$_1'$ in D_{3h} symmetry, Figure 5) owing to the fact that both the d$_{x^2-y^2}$/d$_{xy}$ (e′) and d$_{xz}$/d$_{yz}$ (e″) orbital sets are energetically stabilized by π back-donation to the cylindrically symmetric CNAr^{Mes_2} units. Thus [Ni(CNAr^{Mes_2})$_3$] bares an isolobal relationship to σ-type Lewis bases, such as phosphines (PR$_3$) and amines (NR$_3$). Accordingly, this electronic structure attribute provides a rationale for Tl binding by the Ni center in [TlNi(CNAr^{Mes_2})$_3$]OTf.

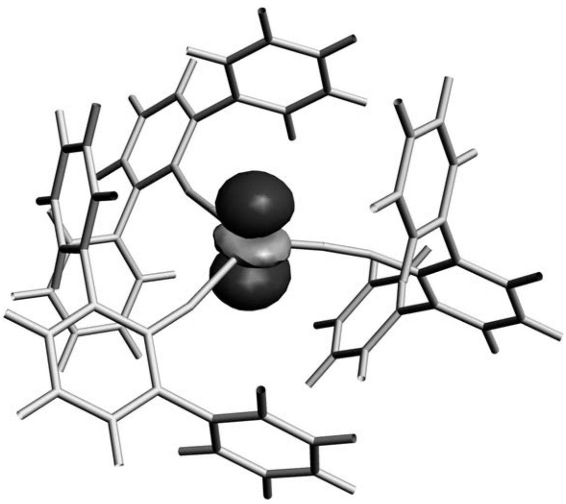
Figure 5. DFT-calculated HOMO for the model complex [Ni(CNAr^{Ph_2})$_3$].

Consistent with its coordinatively unsaturated nature, [Ni(CNAr^{Mes_2})$_3$] also reacted with nucleophilic substrates. Addition of one equivalent of carbon monoxide to [Ni(CNAr^{Mes_2})$_3$] readily generated the tetrahedral monocarbonyl complex [(OC)Ni(CNAr^{Mes_2})$_3$] (Scheme 1). The tetrakis-isocyanide complex [Ni(CNAr^{Mes_2})$_4$] was also formed upon addition of one equivalent of CNAr^{Mes_2} to [Ni(CNAr^{Mes_2})$_3$]. Indeed, this latter reaction lends credence to the suggestion that [Ni(CNAr^{Mes_2})$_3$] is a plausible intermediate in the reaction between [Ni(cod)$_2$] and three CNAr^{Mes} ligands. The tris-isocyanide platform additionally allows access to the monovalent state.[19] Thus, treatment of [Ni(CNAr^{Mes_2})$_3$] with [Cp$_2$Fe]OTf in C$_6$H$_6$ afforded the four-coordinate triflate complex, [(OTf)Ni(CNAr^{Mes_2})$_3$]. The latter is a rare example of a monovalent Ni center supported exclusively by monodentate ligands[20] and is of further note given that it does not to date have a monovalent tricarbonyl counterpart (i.e. [XNi(CO)$_3$]). In addition, [OTfNi(CNAr^{Mes_2})$_3$] is resistant to disproportionation in moderately polar organic solvents such as THF or upon removal of the triflate unit from the Ni center. This latter fact is demonstrated by the isolation and structural characterization of the salt [(thf)$_2$Ni(CNAr^{Mes_2})$_3$]OTf, which is obtained by either preparation (see Supporting Information) or crystallization of [OTfNi(CNAr^{Mes_2})$_3$] in THF solution. Further investigations into the one and two-electron chemistry accessible to [Ni(CNAr^{Mes_2})$_3$] are underway with an aim toward the activation of small-molecule substrates.

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