Generation of a Ni_3 Phosphinidene Cluster from the Ni(o) Synthon, $Ni(\eta^3\text{-}CPh_3)_2$

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ABSTRACT: Reaction of $NiCl_2$ in THF with 2 equiv of $Li(CPh_3)$ at −25 °C results in formation of $Ni(\eta^3\text{-}CPh_3)_2$ (**1**) in moderate yield. Complex **1** was fully characterized, which included analysis by X-ray crystallography. In the solid-state, **1** features an η^3 binding mode of its trityl ligands, resulting in a structure that is reminiscent of the archetypal Ni(II) organometallic, *bis*(η^3-allyl)nickel. In addition, complex **1** has proved to be excellent Ni(0) synthon. For example, reaction of **1** with excess CO results in formation of $Ni(CO)_4$ along with Gomberg's dimer. Similarly, reaction of **1** with 4 equiv of PPh_3 results in formation of $Ni(PPh_3)_4$ (**2**). Presumably, its ability to function as a Ni(0) source is derived from the relatively high stability of the trityl radical, which results in weak Ni-C bonds that are susceptible to homolytic cleavage. Finally, reaction of **1** with 2 equiv of PPh_3, in an attempt to form a larger Ni cluster, resulted in formation of $Ni_3(\mu_3\text{-}PPh)(\mu\text{-}PPh_2)_2(PPh_3)_3$ (**3**) in moderate yield. Its phosphide and phosphinidene ligands are derived from the formal reduction of the PPh_3 ligand.

Introduction

The field of atomically precise nanoclusters (APNCs) has experienced a rapid expansion in the past decade.[1] However, most of this work has been restricted to APNCs of the coinage metals (Cu, Ag, Au).[1] In contrast, limited progress has been made towards the synthesis of APNCs of the other transition metals. Part of this shortfall can be ascribed to the high air-sensitivity that is expected for APNCs of Fe, Co, and Ni, which makes their isolation more challenging.[1b, 2] The lack of a general synthetic route to these materials also plays a role. For example, while group 11 APNCs are typically made by reaction of a metal halide precursor with a supporting ligand and a strong reducing agent, such as $NaBH_4$, similar reactions with Ni or Co have only resulted in the isolation of M(II)-containing clusters. For example, we demonstrated that reaction of $CoCl_2$ with $PhCH_2CH_2SH$ and excess $NaBH_4$ resulted in formation of the Co(II)-containing cluster, $[Co_{10}(SCH_2CH_2Ph)_{16}Cl_4]$, as the only isolated product.[2] Similarly, reaction of $NiCl_2$ with $PhCH_2CH_2SH$ and excess $NaBH_4$ results only in isolation of an Ni(II) thiolate cluster.[1b, 3] The apparent difficulty of generating M(0) in these reactions points to the need for a fundamentally new strategy for APNC formation, one in which M(0) can be easily generated under mild conditions. Accordingly, we sought to find a transition metal M(0) synthon that could reliably deliver M(0) equivalents during APNC synthesis.

A survey of the literature reveals that *bis*(trityl)nickel, $Ni(CPh_3)_2$, may serve our purposes. This complex was reported in 1966 by Wilke and Schott and was formed by reaction of 2 equiv of $Na(CPh_3)$ with $NiBr_2$ in diethyl ether at −78 °C.[5d] Importantly, Wilke demonstrated its utility as a Ni(0) synthon by reaction with 4 equiv of PPh_3, which resulted in formation of $Ni(PPh_3)_4$. Presum-

ably, $Ni(CPh_3)_2$ functions as a good Ni(0) synthon because the relatively high stability of the trityl radical results in weak Ni-C bonds, which are susceptible to homolytic cleavage. Several others transition metal trityl complexes have also proven to be good sources of metal-centered radicals, including $Re(CO)_4(\eta^3\text{-}CPh_3)$ and $L^{Me}Fe(\eta^1\text{-}CPh_3)$ ($L^{Me} = \{(2,6\text{-}^iPr_2C_6H_3)NC(Me)\}_2CH$), providing further support for this concept.[4] However, $Ni(CPh_3)_2$ was not fully characterized and its structure was never determined by X-ray crystallography. The latter point is significant because there is some uncertainty concerning the bonding mode of the trityl ligand in $Ni(CPh_3)_2$, with Wilke suggesting an η^1 binding mode, and other authors suggesting an η^3 binding mode.[5]

Herein, we report the synthesis and characterization of *bis*(η^3-trityl)nickel (**1**) and demonstrate its utility as a Ni(0) synthon during the preparation the Ni phosphinidene cluster, $[Ni_3(\mu_3\text{-}PPh)(\mu\text{-}PPh_2)_2(PPh_3)_3]$ (**3**).

Results and Discussion

Reaction of a suspension of $NiCl_2$ in THF with 2 equiv of $Li(CPh_3)$ at −25 °C results in formation of $Ni(\eta^3\text{-}CPh_3)_2$ (**1**), which can be isolated as a purple powder in 46% yield after work-up (Scheme 1). While similar yields were reported by Wilke and Schott in their preparation of **1**, we found it necessary to modify the reported work-up. In particular, its low solubility in benzene (see below) made the reported work-up (recrystallization from benzene) impractical. Instead, we found that washing the crude reaction mixture with hexanes, followed by washing with a 1:1 (v:v) solution of MeCN and H_2O, gave spectroscopically pure material in acceptable yields.
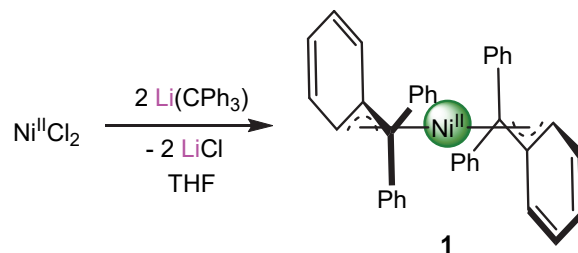
Scheme 1. Synthesis of $Ni(\eta^3\text{-}CPh_3)_2$ (**1**)

As a solid, **1** is stable in air for several months. However, solutions of **1** in THF or CH_2Cl_2 are quite sensitive, quickly losing their purple hue on exposure to air. Complex **1** is insoluble in hexanes, acetonitrile, diethyl ether, methanol, and water, and very sparingly soluble in ethyl acetate and acetone. It is somewhat more soluble in benzene, toluene, and THF (~1 mg/mL in each). The highest solubility is observed in CH_2Cl_2 and $CHCl_3$ (~2 mg/mL). However, it does slowly decompose in these solvents, concomitant with formation of Gomberg's dimer and small amounts of triphenylmethane.
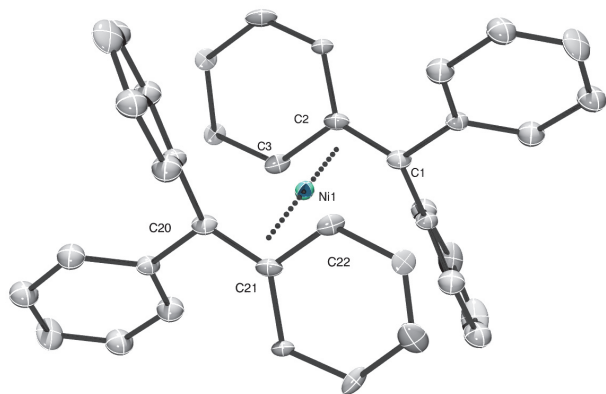
Figure 1. ORTEP drawing of one independent molecule of **1**. Shown with 50% probability thermal ellipsoids. All hydrogen atoms are omitted for clarity. Selected bond lengths (Å): Ni1-C1 = 2.05(2), Å, Ni1-C2 = 2.01(2), Ni1-C3 = 2.10(2), Ni1-C20 = 2.08(2), Ni1-C21 = 2.03(2), Ni1-C22 = 2.04(2).

Complex **1** crystallizes in the monoclinic space group, *Pn*, with two independent molecules in the asymmetric unit (Figure 1). The crystal was twinned and weakly diffracting, which reduced the precision of the resulting metrical parameters; nonetheless, the connectivity of **3** was unambiguously confirmed. Each trityl ligand in **1** adopts an η^3 binding mode, resulting in a structure that is reminiscent of the archetypal Ni(II) organometallic, *bis*(η^3-allyl)nickel.[6] Its Ni-C distances range from 2.01(2) to 2.10(1) Å (av. Ni-C = 2.05(7) Å), while the C-C bonds within the allyl unit range from 1.40(2) to 1.48(2) Å (av. C_{allyl}-C_{allyl} = 1.44(8) Å). These values are similar to those reported for the only other structurally characterized Ni(trityl) complex CpNi(η^3-trityl), as well as (acac)Pd(η^3-trityl).[5b, 7] A handful of other trityl complexes have also been structurally characterized, including recently L^{Me}Fe(η^1-CPh$_3$), which features and η^1 trityl binding mode,[4b] and [Ti(CO)$_4$(η^5-CPh$_3$)]$^-$, which features an η^5 trityl binding mode.[8]

The ^{1}H NMR spectrum of **1** in CD$_2$Cl$_2$ at room temperature exhibits several very broad resonances in the aromatic region, indicative of a fluxional η^3-trityl ligand.[5b] On cooling the NMR sample to –40 °C, however, these resonances sharpen considerably, decoalescing into five distinct peaks (Figure S2-S3). Doublets at 6.24 and 6.57 ppm are assignable to the ortho protons of the coordinated and free phenyl groups, respectively. A triplet at 6.99 ppm is assignable to the para protons of the coordinated phenyl groups, a multiplet at

7.05 ppm is assignable to overlapping meta resonances of free and bound phenyl groups, and a triplet at 7.23 ppm is assignable to the para protons of the free phenyl groups. The pattern and relative ratios of these peaks implies that interconversion of coordinated and free phenyl groups via an η^1-trityl intermediate is slower than the NMR time scale this temperature.[4a, 9] However, the observation that the two ortho protons of the coordinated phenyl group are still magnetically equivalent at this temperature suggests that suprafacial exchange of the η^3-trityl ligand is still occurring.[5b, 9-10] Cooling the sample to −79 °C only led to slight broadening of this resonance, suggesting that the barrier to suprafacial exchange is very low.

To test the efficacy of **1** as a Ni(0) synthon, we probed its reaction with CO. Thus, addition of CO (1 atm) to a CD$_2$Cl$_2$ solution of **1** resulted in an immediate color change from purple to colorless (Scheme 2). A solution-phase IR spectrum of this sample revealed the presence of a strong absorption band at 2040 cm^{-1}, which is assignable to the T$_2$ stretching mode of Ni(CO)$_4$ (cf. ν(C=O) = 2043 cm^{-1}).[11] Moreover, a ^{13}C{^{1}H} NMR spectrum of this sample featured a resonance at 192 ppm, matching the reported value for Ni(CO)$_4$.[12] Finally, examination of ^{1}H NMR spectrum confirmed the presence of Gomberg's dimer (**5**), as indicated by the presence of diagnostic multiplets at 6.22 and 5.96 ppm, along with a singlet at 5.11 ppm.[13] Small amounts of Ph$_3$CH, as indicated by a singlet at 5.55 ppm, are also present in the reaction mixture.[14]

Scheme 2. Reaction of **1** with CO and Ph$_3$P
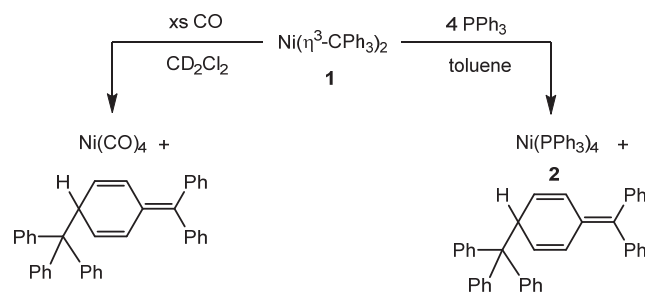
Similarly, addition of 4 equiv of PPh$_3$ to a suspension of **1** in toluene resulted in a gradual color change to red-orange (Scheme 2). Work-up of this solution resulted in the isolation of Ni(PPh$_3$)$_4$ (**2**) as a brown microcrystalline solid in 70% yield. Similar results were reported by Wilke.[5d] A ^{31}P{^{1}H} NMR spectrum of **2** features a single broad resonance at 18 ppm, consistent with the spectrum previously reported for this material.[15] In addition, the generation of Gomberg's dimer during the formation of **2** was confirmed by *in situ* spectroscopic monitoring of the reaction of **1** with 4 equiv of PPh$_3$ in toluene-d_8 (Figure S9).[13]
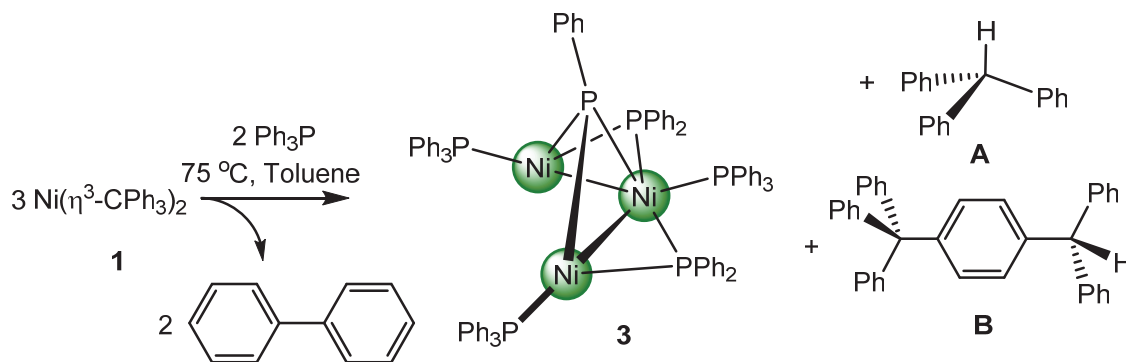
Scheme 3. Formation of Ni$_3$(μ_3-PPh)(μ-PPh$_2$)$_2$(PPh$_3$)$_3$ (**3**) upon thermolysis of Ni(η^3-CPh$_3$)$_2$ (**1**).

After establishing the suitability of **1** as an Ni(0) synthon, we explored its ability to generate an APNC. Previously, we demonstrated that lowering the metal:Ph$_3$P ratio in the synthesis of phosphine-ligated Cu APNCs resulted in isolation of larger clusters.[16]

Thus, we performed the reaction of **1** with only 2 equiv of PPh$_3$ in toluene. Heating of this reaction mixture to 75 °C for 15 h resulted in formation of a brown solution from which the novel nickel phos-

phinidine complex, [Ni$_3$(μ_3-PPh)(μ-PPh$_2$)$_2$(PPh$_3$)$_3$] (**3**), can be isolated in 38% yield as a deep brown crystalline solid after work-up (Scheme 3). Complex **3** is insoluble in hexanes, sparingly soluble in diethyl ether, and soluble in THF, toluene, and 1,2-dimethoxyethane. The synthesis of **3** mirrors that of the recently reported Ni$_{12}$ cluster, [Ni$_{12}$(PMe)$_{10}$(PEt$_3$)$_8$], which is formed by reaction of Ni(1,5-COD)$_2$ with (PMe)$_5$ and PEt$_3$.[17]

Complex **3** crystallizes in the triclinic space group P-1 as a toluene solvate, **3**·2C$_7$H$_8$. Its solid-state molecule structure is shown in Figure 2. In the solid state, **3** features three Ni centers ligated by a triply-bridged phosphinidene ligand, two doubly-bridged phosphide ligands, and three phosphine ligands (one bound to each Ni center). The phosphinidene and phosphide ligands are evidently derived from reduction of PPh$_3$ (see below). The Ni-Ni bond lengths are 2.451(1) and 2.4442(9) Å. These distances are consistent with those expected for formal single Ni-Ni bonds (formal shortness ratio = 0.99, 0.98, respectively).[18] The Ni-P bond lengths for the bridging phosphide (av. Ni-P = 2.18 Å, range = 2.139(1)-2.219(1) Å) and phosphinidene (av. Ni-P = 2.16 Å, range = 2.097(1)-2.263(1) Å) moieties are consistent with those of other clusters bearing bridging [RP]$^{2-}$ or [R$_2$P]$^-$ ligands.[19] For example, the Ni phosphinidine complex, [Ni$_8$(CO)$_8$(μ_4-PPh)$_6$] features an average Ni-P bond length of 2.183 Å,[19h] while the Ni phosphide complex, [Ni$_2$(μ-PPh$_2$)$_2$(PCy$_3$)$_2$] features an average Ni-P bond length of 2.16 Å.[19k] If the Ni-Ni bonds are ignored, the central Ni center features a tetrahedral geometry (τ_4 = 0.96),[20] whereas the two outer Ni centers display trigonal planar geometries (Σ($\angle$P-Ni2-P) = 359.3°, Σ($\angle$P-Ni3-P) = 360.0°). The average Ni oxidation state in **3** is +1.33, but given its short Ni-Ni bonds, and its diamagnetism (see below), the valence electrons are clearly strongly coupled and delocalized over all three Ni centers.
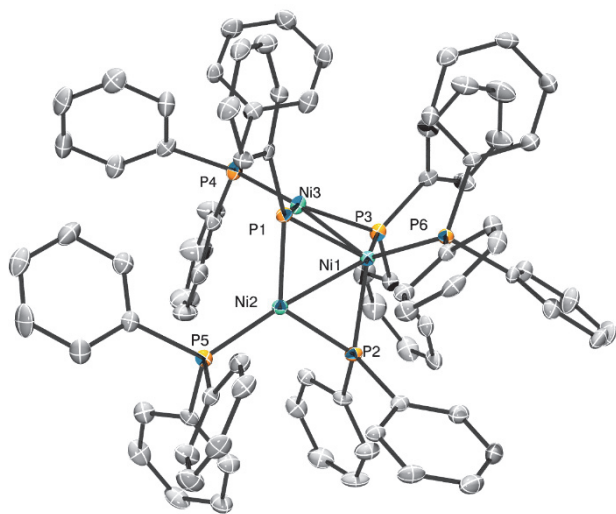

Figure 2. ORTEP drawing of **3**·2C$_7$H$_8$. Shown with 50% probability thermal ellipsoids. Hydrogen atoms and toluene solvate molecules are omitted for clarity. Selected bond distance (Å) and angles (°): Ni1-Ni2 = 2.451(1), Ni1-Ni3 = 2.4442(9) Å, av. Ni-PPh$_2$ = 2.18(6) and av. Ni-PPh = 2.16(5), Σ($\angle$P-Ni2-P) = 359.3°, Σ($\angle$P-Ni3-P) = 360.0°.

The ^{31}P{^{1}H} NMR spectrum of **3** in C$_6$D$_6$ is consistent with its solid state molecular structure. In particular, it features resonances at 34.1 (1P), 41.7 (2P), 122.4 (2P), and 487.5 ppm (1P) (Figure 3), which are assignable to the two unique Ph$_3$P environments, the phosphide environment, and phosphinidene environment, respectively. The phosphinidene resonances appears as a triplet of triplets ($^2J_{PP}$ = 208 Hz, 43 Hz) due to coupling to two equivalent phosphide

ligands and two equivalent PPh$_3$ ligands. The other ^{31}P resonances are complicated multiplets. The ^{31}P chemical shifts for the μ_3-PPh and μ-PPh$_2$ ligands in **3** are similar to those observed for other clusters bearing bridging [PPh]$^{2-}$ ligands[19e] or [PPh$_2$]$^-$ ligands.[19j, 21] The ^{1}H NMR spectrum of **3** in C$_6$D$_6$ features multiplets at 7.45 and 7.25 ppm, which are assignable to the *ortho* protons of the inequivalent phenyl groups of the [PPh$_2$]$^-$ ligands (one phenyl group is below the Ni$_3$ plane and one phenyl group is above the Ni$_3$ plane), indicating the stereochemical rigidity of the cluster skeleton. Finally, the ESI-MS of **3** in THF acquired in positive ion mode further supports the proposed formulation. The two major peaks at 1440.2716 *m/z* and 1178.1591 *m/z* are ascribable to [M]$^+$ (calcd. 1440.1964 *m/z*) and [M-PPh$_3$]$^+$, respectively (Figures S23-S25).
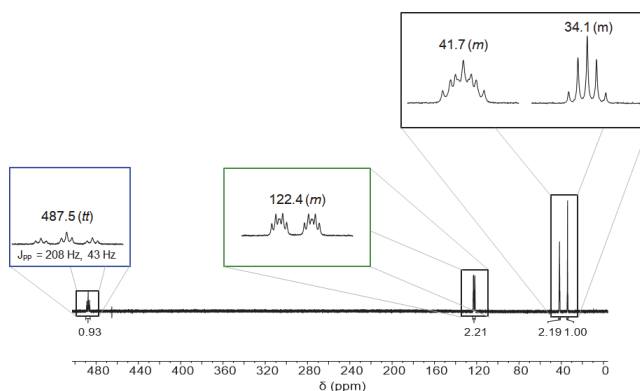

Figure 3. ^{31}P{^{1}H} NMR spectrum of **3** in benzene-d_6 at room temperature.

To better understand the reaction stoichiometry, we sought to identify the organic by-products present in the reaction mixture. A ^{1}H NMR spectrum of the crude mixture, recorded in benzene-d_6, reveals the presence of biphenyl, as indicated by resonances at 7.46, 7.21, and 7.13 ppm (Scheme 3, Figure S14). This conclusion was further confirmed by inspection of ^{13}C{^{1}H} NMR spectrum of the same sample (Figure S15). Curiously, though, we do not observe any resonances assignable to Gomberg's dimer. Instead, we observe singlets at 5.43 and 5.38 ppm in the ^{1}H NMR spectrum, which can be ascribed to triphenylmethane (**A**), and 1-(diphenylmethyl)-4-(trityl)benzene (**B**). These assignments were further corroborated by the ^{13}C{^{1}H} NMR spectrum of this sample (Figure S15). Both **A** and **B** are known Gomberg's dimer decomposition products.[22] Also observed in the ^{1}H NMR spectrum are singlets at 3.82 and 3.78 ppm, which are also likely Gomberg's dimer decomposition products, but which remain unidentified. Given the elevated temperature of this transformation it is likely that Gomberg's dimer is initially formed, but undergoes a subsequent thermal decomposition.

To rationalize our observations and explain the formation of **3**, we propose that **1** initially reacts with PPh$_3$ to form Ni(PPh$_3$)$_n$ and Gomberg's dimer. Subsequent oxidative addition of a P-C bond across the Ni center, followed by dimerization and reductive elimination of biphenyl would provide the known phosphide-bridged bimetallic, Ni$_2$(μ-PPh$_2$)$_2$(PPh$_3$)$_3$ (**4**).[19g] Addition of another equivalent of Ni(PPh$_3$)$_n$ and one more oxidative addition/reductive elimination step would provide **3**. In support of this proposed mechanism, we note that oxidative addition of a P-C bond in PPh$_3$ at Ni(0), with elimination of biphenyl, has been reported previously.[23] The conversion of a PPh$_2$ ligand to a PPh ligand, via P-C oxidative addition, is also known.[19b] To further support our proposed mechanistic sequence, we monitored the thermolysis of **2** by ^{1}H and ^{31}P{^{1}H} NMR spectroscopies in toluene-d_8 after heating at 40 °C for 19 h and then 80 °C for 25 h. After 19 h at 40 °C, the ^{31}P{^{1}H}

NMR spectrum revealed resonances tentatively assigned to complex **4** (Figure S16). However, upon further heating these signals disappear, concomitant with the appearance of signals assignable to **3**. Significantly, this experiment confirms that Ni(PPh₃)₄ is a viable precursor to complex **3**.

Conclusions

In summary, we have completed the characterization of Ni(CPh₃)₂, confirming that it features an η^3 binding mode of its trityl ligands. Moreover, we have demonstrated that Ni(CPh₃)₂ is a good source of Ni(0) via its reactions with CO and PPh₃. Indeed, Ni(CPh₃)₂ offers several attractive features that are not found in other common Ni(0) synthons,[24] such as Ni(1,5-cod)₂ and Ni(CO)₄. For example, Ni(1,5-cod)₂ is highly air-sensitive and somewhat light sensitive,[25] while CO displacement reactions in Ni(CO)₄ become more difficult as the total number of CO ligands decreases.[25a] In contrast, Ni(CPh₃)₂ is both air and water stable as a solid, while loss of both trityl ligands appears to be facile, judging by its rapid reaction with CO. Thus, we suggest that Ni(CPh₃)₂ will be a good precursor for not only APNC formation, but also for Ni(0)-catalyzed cross couplings.[26] That said, we note that our efforts to form a large Ni APNCs using Ni(CPh₃)₂ were thwarted by the facile oxidative addition of the P-C bonds of PPh₃. This result demonstrates the high reactivity of the "Ni(0)" formed from Ni(CPh₃)₂ and also suggest that successful formation of large, Ni(0)-containing APNCs will require the use of co-ligands that are particularly resistant to reduction.

ASSOCIATED CONTENT

Supporting Information

Experimental, spectroscopic, and crystallographic details for complexes **1** and **3**.

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Notes
The authors declare no competing financial interests.

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Reaction of NiCl$_2$ with 2 equiv of Li(CPh$_3$) in THF results in formation of Ni(η^3-CPh$_3$)$_2$, an air- and water-stable source of nickel(0).