

# Generation of a Ni<sub>3</sub> Phosphinidene Cluster from the Ni(0) Synthons, Ni( $\eta^3$ -CPh<sub>3</sub>)<sub>2</sub>

Alexander J. Touchton, Guang Wu, and Trevor W. Hayton\*

Cite This: <https://dx.doi.org/10.1021/acs.organomet.0c00095>

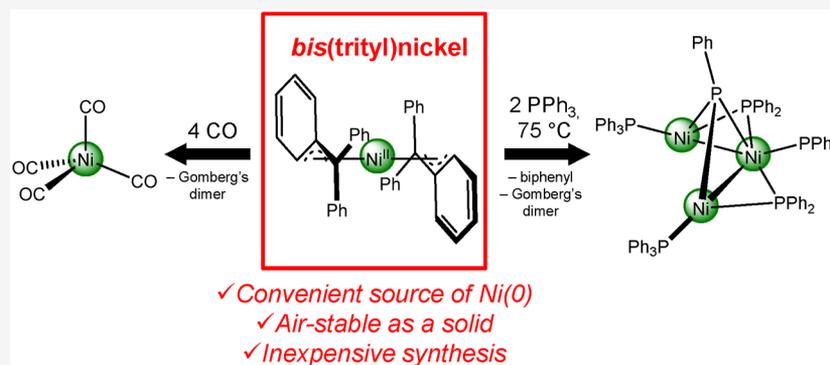
Read Online

ACCESS |

Metrics & More

Article Recommendations

Supporting Information



**ABSTRACT:** Reaction of NiCl<sub>2</sub> in THF with 2 equiv of Li(CPh<sub>3</sub>) at −25 °C results in formation of Ni( $\eta^3$ -CPh<sub>3</sub>)<sub>2</sub> (**1**) in moderate yield. Complex **1** was fully characterized, which included analysis by X-ray crystallography. In the solid state, **1** features an  $\eta^3$  binding mode of its trityl ligands, resulting in a structure that is reminiscent of the archetypal Ni(II) organometallic, bis( $\eta^3$ -allyl)nickel. In addition, complex **1** has proved to be an excellent Ni(0) synthon. For example, reaction of **1** with excess CO resulted in formation of Ni(CO)<sub>4</sub> along with Gomberg's dimer. Similarly, reaction of **1** with 4 equiv of PPh<sub>3</sub> resulted in formation of Ni(PPh<sub>3</sub>)<sub>4</sub> (**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<sub>3</sub>, in an attempt to form a larger Ni cluster, resulted in formation of [Ni<sub>3</sub>( $\mu_3$ -PPh)( $\mu$ -PPh<sub>2</sub>)<sub>2</sub>(PPh<sub>3</sub>)<sub>3</sub>] (**3**) in moderate yield. Its phosphide and phosphinidene ligands are derived from the formal reduction of the PPh<sub>3</sub> ligand.

## INTRODUCTION

The field of atomically precise nanoclusters (APNCs) has experienced a rapid expansion in the past decade.<sup>1</sup> However, most of this work has been restricted to APNCs of the coinage metals (Cu, Ag, Au).<sup>1</sup> In contrast, limited progress has been made toward 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.<sup>1b,2</sup> 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<sub>4</sub>, 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<sub>2</sub> with PhCH<sub>2</sub>CH<sub>2</sub>SH and excess NaBH<sub>4</sub> resulted in formation of the Co(II)-containing cluster, [Co<sub>10</sub>(SCH<sub>2</sub>CH<sub>2</sub>Ph)<sub>16</sub>Cl<sub>4</sub>], as the only isolated product.<sup>2</sup> Similarly, reaction of NiCl<sub>2</sub> with PhCH<sub>2</sub>CH<sub>2</sub>SH and excess NaBH<sub>4</sub> results only in isolation of a Ni(II) thiolate cluster.<sup>1b,3</sup> 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<sub>3</sub>)<sub>2</sub>, 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<sub>3</sub>) with NiBr<sub>2</sub> in diethyl ether at −78 °C.<sup>5d</sup> Importantly, Wilke demonstrated its utility as a Ni(0) synthon by reaction with 4 equiv of PPh<sub>3</sub>, which resulted in formation of Ni(PPh<sub>3</sub>)<sub>4</sub>. Presumably, Ni(CPh<sub>3</sub>)<sub>2</sub> 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 other transition

Received: February 10, 2020

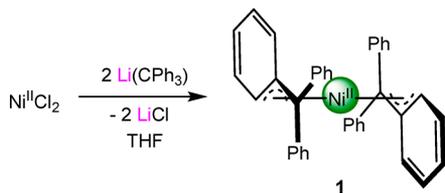
metal trityl complexes have also proven to be good sources of metal-centered radicals, including  $\text{Re}(\text{CO})_4(\eta^3\text{-CPh}_3)$  and  $\text{L}^{\text{Me}}\text{Fe}(\eta^1\text{-CPh}_3)$  ( $\text{L}^{\text{Me}} = \{(2,6\text{-}^i\text{Pr}_2\text{C}_6\text{H}_3)\text{NC}(\text{Me})_2\text{CH}\}$ ), providing further support for this concept.<sup>4</sup> However,  $\text{Ni}(\text{CPh}_3)_2$  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 binding mode of the trityl ligand in  $\text{Ni}(\text{CPh}_3)_2$ , with Wilke suggesting an  $\eta^1$  binding mode and other authors suggesting an  $\eta^3$  binding mode.<sup>5</sup>

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

## RESULTS AND DISCUSSION

Reaction of a suspension of  $\text{NiCl}_2$  in THF with 2 equiv of  $\text{Li}(\text{CPh}_3)$  at  $-25^\circ\text{C}$  resulted in formation of  $\text{Ni}(\eta^3\text{-CPh}_3)_2$  (**1**), which was isolated as a purple powder in 46% yield after work-up (Scheme 1). While similar yields were reported by

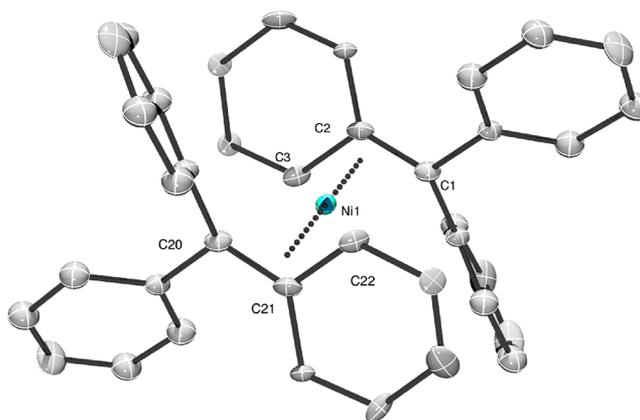
### Scheme 1. Synthesis of $\text{Ni}(\eta^3\text{-CPh}_3)_2$ (**1**)



Wilke and Schott in their preparation of **1**, we found it necessary to modify the reported work-up. In particular, the low solubility of **1** 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  $\text{H}_2\text{O}$ , gave suitably pure material in acceptable yields.

As a solid, **1** is stable in air for several months. However, solutions of **1** in THF or  $\text{CH}_2\text{Cl}_2$  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 ( $\sim 1$  mg/mL in each). The highest solubility of **1** is observed in  $\text{CH}_2\text{Cl}_2$  and  $\text{CHCl}_3$  ( $\sim 2$  mg/mL). However, it does slowly decompose in these solvents, concomitant with formation of Gombert's dimer and small amounts of triphenylmethane.

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  $\eta^3$  binding mode, resulting in a structure that is reminiscent of the archetypal Ni(II) organometallic, bis( $\eta^3$ -allyl)nickel.<sup>6</sup> Its Ni–C distances range from 2.01(2) to 2.10(1) Å (av. Ni–C = 2.05 Å), while the C–C bonds within the allyl unit range from 1.40(2) to 1.48(2) Å (av.  $\text{C}_{\text{allyl}}\text{--C}_{\text{allyl}}$  = 1.44 Å). These values are similar to those reported for the only other structurally characterized Ni(trityl) complex,  $\text{CpNi}(\eta^3\text{-trityl})$ , as well as  $(\text{acac})\text{Pd}(\eta^3\text{-trityl})$ .<sup>5b,7</sup> A handful of other trityl complexes

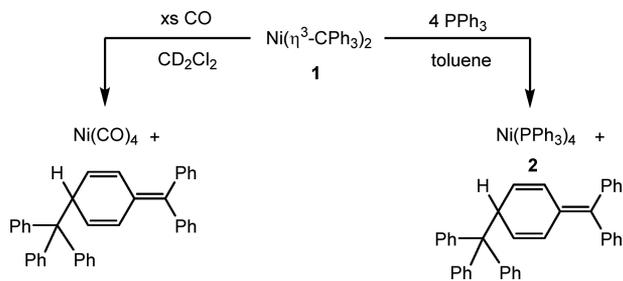


**Figure 1.** ORTEP drawing of one independent molecule of **1**. Shown with 50% probability thermal ellipsoids. All hydrogen atoms are omitted for clarity. Selected bond lengths (Å): Ni1–C1 = 2.05(2), Ni1–C2 = 2.01(2), Ni1–C3 = 2.10(2), Ni1–C20 = 2.08(2), Ni1–C21 = 2.03(2), Ni1–C22 = 2.04(2).

have also been structurally characterized, including recently  $\text{L}^{\text{Me}}\text{Fe}(\eta^1\text{-CPh}_3)$ , which features an  $\eta^1$  trityl binding mode,<sup>4b</sup> and  $[\text{Ti}(\text{CO})_4(\eta^5\text{-CPh}_3)]^-$ , which features an  $\eta^5$  trityl binding mode.<sup>8</sup>

The  $^1\text{H}$  NMR spectrum of **1** in  $\text{CD}_2\text{Cl}_2$  at room temperature exhibits several very broad resonances in the aromatic region, indicative of a fluxional  $\eta^3$ -trityl ligand (Supporting Information, Figure S1).<sup>5b</sup> On cooling the NMR sample to  $-40^\circ\text{C}$ , however, these resonances sharpen considerably, decoalescing into five distinct peaks (Supporting Information, Figures S2 and S3). Doublets at 6.24 and 6.57 ppm are assignable to the ortho protons of the Ni-coordinated and free phenyl groups, respectively. A triplet at 6.99 ppm is assignable to the para protons of the Ni-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 imply that interconversion of coordinated and free phenyl groups via an  $\eta^1$ -trityl intermediate is slower than the NMR time scale at this temperature.<sup>4a,9</sup> However, the observation that the two ortho protons of the Ni-coordinated phenyl group are still magnetically equivalent at this temperature suggests that suprafacial exchange of the  $\eta^3$ -trityl ligand is still occurring.<sup>5b,9,10</sup> Cooling the sample to  $-79^\circ\text{C}$  led to only 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  $\text{CD}_2\text{Cl}_2$  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  $2040\text{ cm}^{-1}$  (Supporting Information, Figure S21), which is assignable to the  $\text{T}_2$  stretching mode of  $\text{Ni}(\text{CO})_4$  (cf.  $\nu(\text{C}=\text{O}) = 2043\text{ cm}^{-1}$ ).<sup>11</sup> Moreover, a  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of this sample featured a resonance at 192 ppm, matching the reported value for  $\text{Ni}(\text{CO})_4$ .<sup>12</sup> Finally, examination of  $^1\text{H}$  NMR spectrum confirmed the presence of Gombert's dimer, as indicated by the presence of diagnostic multiplets at 6.22 and 5.96 ppm, along with a singlet at 5.11 ppm (Supporting Information, Figure S5).<sup>13</sup> Small amounts of

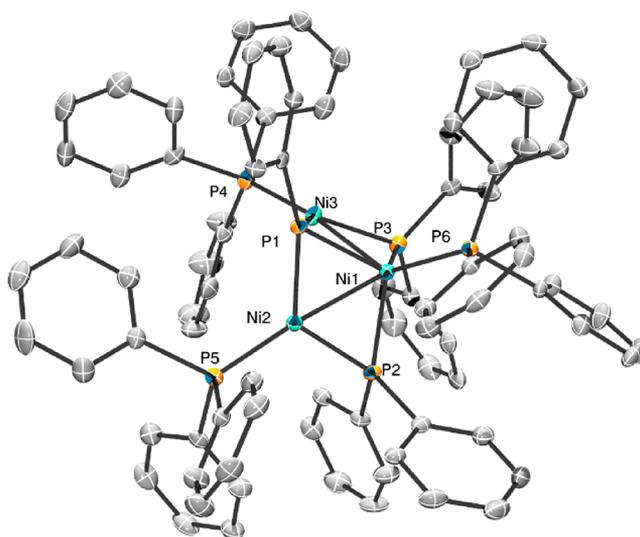
Scheme 2. Reaction of **1** with CO and  $\text{Ph}_3\text{P}$ 

$\text{Ph}_3\text{CH}$ , as indicated by a singlet at 5.55 ppm, are also present in the reaction mixture.<sup>14</sup>

Similarly, addition of 4 equiv of  $\text{PPh}_3$  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  $\text{Ni}(\text{PPh}_3)_4$  (**2**) as a brown microcrystalline solid in 70% yield. Similar results were reported by Wilke.<sup>5d</sup> A  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum of **2** features a single broad resonance at 18 ppm, consistent with the spectrum previously reported for this material (Supporting Information, Figure S8).<sup>15</sup> In addition, the generation of Gombert's dimer during the formation of **2** was confirmed by *in situ* spectroscopic monitoring of the reaction of **1** with 4 equiv of  $\text{PPh}_3$  in toluene- $d_8$  (Supporting Information, Figure S9).<sup>13</sup>

After establishing the suitability of **1** as an Ni(0) synthon, we explored its ability to generate an APNC. Previously, we demonstrated that changes to the metal: $\text{Ph}_3\text{P}$  ratio used in the synthesis APNCs has a profound effect on cluster speciation.<sup>16</sup> Thus, we reacted **1** with only 2 equiv of  $\text{PPh}_3$  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 phosphinidene complex,  $[\text{Ni}_3(\mu_3\text{-PPh})(\mu\text{-PPh}_2)_2(\text{PPh}_3)_3]$  (**3**), was 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  $\text{Ni}_{12}$  cluster,  $[\text{Ni}_{12}(\text{PMe})_{10}(\text{PET}_3)_8]$ , which is formed by reaction of  $\text{Ni}(1,5\text{-cod})_2$  with  $(\text{PMe})_5$  and  $\text{PET}_3$ .<sup>17</sup>

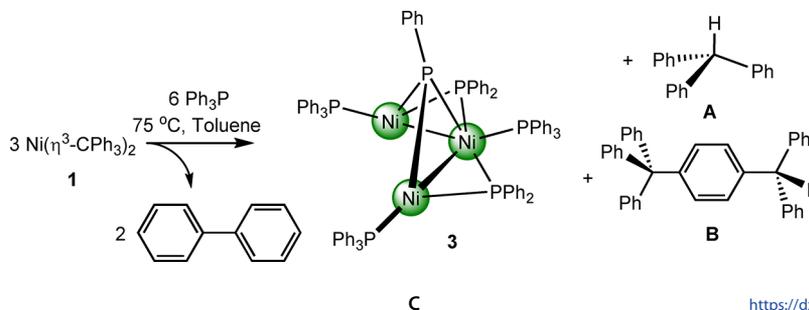
Complex **3** crystallizes in the triclinic space group  $P\bar{1}$  as a toluene solvate,  $3 \cdot 2\text{C}_7\text{H}_8$ . Its solid-state molecular structure is shown in Figure 2. In the solid state, **3** features three Ni centers ligated by a triply bridged phosphinidene ligand, two doubly bridged phosphide ligands, and three phosphine ligands (one bound to each Ni center). The phosphinidene and phosphide ligands are evidently derived from reduction of  $\text{PPh}_3$  (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

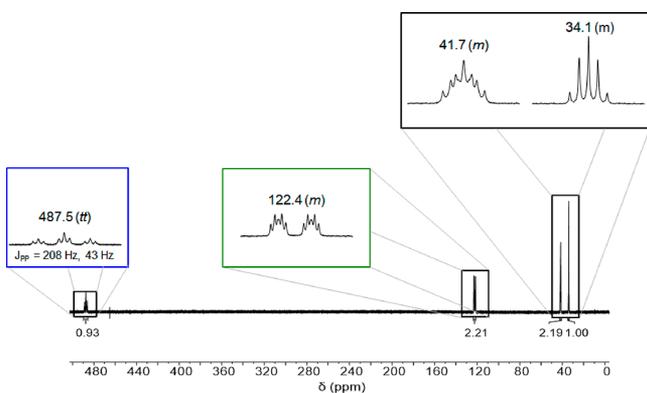


**Figure 2.** ORTEP drawing of  $3 \cdot 2\text{C}_7\text{H}_8$ . Shown with 50% probability thermal ellipsoids. Hydrogen atoms and toluene solvate molecules are omitted for clarity. Selected bond distance (Å) and angles (deg): Ni1–Ni2 = 2.451(1), Ni1–Ni3 = 2.4442(9) Å, av. Ni– $\text{PPh}_2$  = 2.18, av. Ni– $\text{PPh}$  = 2.16,  $\sum(\angle\text{P–Ni}_2\text{–P}) = 359.3^\circ$ ,  $\sum(\angle\text{P–Ni}_3\text{–P}) = 360.0^\circ$ .

ratio = 0.99 and 0.98, respectively).<sup>18</sup> 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  $[\text{RP}]^{2-}$  or  $[\text{R}_2\text{P}]^-$  ligands.<sup>19</sup> For example, the Ni phosphinidene complex,  $[\text{Ni}_8(\text{CO})_8(\mu_4\text{-PPh})_6]$ , features an average Ni–P bond length of 2.183 Å,<sup>19c</sup> while the Ni phosphide complex,  $[\text{Ni}_2(\mu\text{-PPh}_2)_2(\text{PCy}_3)_2]$ , features an average Ni–P bond length of 2.16 Å.<sup>19j</sup> If the Ni–Ni bonds are ignored, the central Ni center features a tetrahedral geometry ( $\tau_4 = 0.96$ ),<sup>20</sup> whereas the two outer Ni centers display trigonal planar geometries ( $\sum(\angle\text{P–Ni}_2\text{–P}) = 359.3^\circ$ ,  $\sum(\angle\text{P–Ni}_3\text{–P}) = 360.0^\circ$ ). 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.

The  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum of **3** in benzene- $d_6$  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  $\text{Ph}_3\text{P}$  environments, the phosphide environment, and the phosphinidene environment, respectively. The phosphinidene resonances appears as a triplet of triplets ( $^2J_{\text{PP}} = 208$  Hz, 43 Hz) due to coupling to two equivalent phosphide ligands and two

Scheme 3. Formation of  $[\text{Ni}_3(\mu_3\text{-PPh})(\mu\text{-PPh}_2)_2(\text{PPh}_3)_3]$  (**3**) upon Thermolysis of  $\text{Ni}(\eta^3\text{-CPh}_3)_2$  (**1**) and  $\text{PPh}_3$ 



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

equivalent  $\text{PPh}_3$  ligands. The other  $^{31}\text{P}$  resonances are complicated multiplets. The  $^{31}\text{P}$  chemical shifts for the  $\mu_3$ - $\text{PPh}$  and  $\mu$ - $\text{PPh}_2$  ligands in **3** are similar to those observed for other clusters bearing bridging  $[\text{PPh}]^{2-}$  ligands<sup>19e</sup> or  $[\text{PPh}_2]^-$  ligands.<sup>19i,21</sup> The  $^1\text{H}$  NMR spectrum of **3** in benzene- $d_6$  features multiplets at 7.45 and 7.25 ppm, which are assignable to the *ortho* protons of the inequivalent phenyl groups of the  $[\text{PPh}_2]^-$  ligands (one phenyl group is below the  $\text{Ni}_3$  plane and one phenyl group is above the  $\text{Ni}_3$  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  $[\text{M}]^+$  (calcd 1440.1964  $m/z$ ) and  $[\text{M} - \text{PPh}_3]^+$  (calcd 1178.1052  $m/z$ ), respectively (Supporting Information, Figures S22–S24).

To better understand the reaction stoichiometry, we sought to identify the organic byproducts present in the reaction mixture. A  $^1\text{H}$  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 and Supporting Information, Figure S14). This conclusion was further confirmed by inspection of the  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of the same sample (Supporting Information, 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  $^1\text{H}$  NMR spectrum, which can be ascribed to triphenylmethane (**A**) and 1-(diphenylmethyl)-4-(trityl)benzene (**B**). These assignments were further corroborated by the  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of this sample (Supporting Information, Figure S15). Both **A** and **B** are known Gomberg's dimer decomposition products.<sup>22</sup> Also observed in the  $^1\text{H}$  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 subsequent thermal decomposition.

To rationalize our observations and explain the formation of **3**, we propose that **1** initially reacts with  $\text{PPh}_3$  to form  $\text{Ni}(\text{PPh}_3)_n$  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,  $[\text{Ni}_2(\mu_2\text{-PPh}_2)_2(\text{PPh}_3)_3]$  (**4**).<sup>19g</sup> Addition of another equivalent of  $\text{Ni}(\text{PPh}_3)_n$  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  $\text{PPh}_3$  at  $\text{Ni}(0)$ , with elimination of biphenyl, has been reported previously.<sup>23</sup> The conversion of a  $\text{PPh}_2$  ligand to a  $\text{PPh}$  ligand, via P–C oxidative addition, is also known.<sup>19b</sup> To further support our proposed mechanistic sequence, we monitored the thermolysis of **2** by  $^1\text{H}$  and  $^{31}\text{P}\{^1\text{H}\}$  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  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum revealed resonances tentatively assigned to complex **4** (Supporting Information, Figure S16). However, upon further heating, these signals disappear, concomitant with the appearance of signals assignable to **3**. Significantly, this experiment confirms that  $\text{Ni}(\text{PPh}_3)_4$  is a viable precursor to complex **3**.

## CONCLUSIONS

In summary, we have completed the characterization of  $\text{Ni}(\text{CPh}_3)_2$ , confirming that it features an  $\eta^3$  binding mode of its trityl ligands. Moreover, we have demonstrated that  $\text{Ni}(\text{CPh}_3)_2$  is a good source of  $\text{Ni}(0)$  via its reactions with CO and  $\text{PPh}_3$ . Indeed,  $\text{Ni}(\text{CPh}_3)_2$  offers several attractive features that are not found in other common  $\text{Ni}(0)$  synthons,<sup>24</sup> such as  $\text{Ni}(1,5\text{-cod})_2$  and  $\text{Ni}(\text{CO})_4$ . For example,  $\text{Ni}(1,5\text{-cod})_2$  is highly air-sensitive and somewhat light-sensitive,<sup>25</sup> while CO displacement reactions in  $\text{Ni}(\text{CO})_4$  become more difficult as the total number of CO ligands decreases.<sup>25a</sup> In contrast,  $\text{Ni}(\text{CPh}_3)_2$  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  $\text{Ni}(\text{CPh}_3)_2$  will be a good precursor for not only APNC formation but also  $\text{Ni}(0)$ -catalyzed cross couplings.<sup>26</sup> That said, we note that our efforts to form large Ni APNCs using  $\text{Ni}(\text{CPh}_3)_2$  were thwarted by the facile oxidative addition of the P–C bonds of  $\text{PPh}_3$ . This result demonstrates the high reactivity of the “ $\text{Ni}(0)$ ” formed from  $\text{Ni}(\text{CPh}_3)_2$  and also suggests that successful formation of large,  $\text{Ni}(0)$ -containing APNCs will require the use of co-ligands that are particularly resistant to reduction.

## ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.organomet.0c00095>.

Experimental, spectroscopic, and crystallographic details for complexes **1** and **3** (PDF)

### Accession Codes

CCDC 1982483 and 1982484 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif), or by emailing [data\\_request@ccdc.cam.ac.uk](mailto:data_request@ccdc.cam.ac.uk), or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

## AUTHOR INFORMATION

### Corresponding Author

Trevor W. Hayton – Department of Chemistry and Biochemistry, University of California, Santa Barbara, California 93106, United States; [orcid.org/0000-0003-4370-1424](https://orcid.org/0000-0003-4370-1424); Email: [hayton@chem.ucsb.edu](mailto:hayton@chem.ucsb.edu)

### Authors

Alexander J. Touchton – Department of Chemistry and Biochemistry, University of California, Santa Barbara, California 93106, United States

Guang Wu – Department of Chemistry and Biochemistry,  
University of California, Santa Barbara, California 93106,  
United States

Complete contact information is available at:  
<https://pubs.acs.org/10.1021/acs.organomet.0c00095>

## Notes

The authors declare no competing financial interest.

## ACKNOWLEDGMENTS

We thank the National Science Foundation (CHE 1764345) for financial support of this work. This research made use of the 400 MHz NMR spectrometer of the UCSB Chemistry Department, supported by an NIH SIG (1S10OD012077-01A1). The MRL Shared Experimental Facilities are supported by the MRSEC Program of the National Science Foundation under award NSF DMR 1720256, a member of the NSF-funded Materials Research Facilities Network. A.J.T. thanks the Mellichamp Academic Initiative in Sustainability at UCSB for a summer fellowship.

## REFERENCES

- (1) (a) Jin, R.; Zeng, C.; Zhou, M.; Chen, Y. Atomically Precise Colloidal Metal Nanoclusters and Nanoparticles: Fundamentals and Opportunities. *Chem. Rev.* **2016**, *116*, 10346. (b) Cook, A. W.; Hayton, T. W. Case Studies in Nanocluster Synthesis and Characterization: Challenges and Opportunities. *Acc. Chem. Res.* **2018**, *51*, 2456. (c) Du, X.; Jin, R. Atomically Precise Metal Nanoclusters for Catalysis. *ACS Nano* **2019**, *13*, 7383. (d) Fang, J.; Zhang, B.; Yao, Q.; Yang, Y.; Xie, J.; Yan, N. Recent advances in the synthesis and catalytic applications of ligand-protected, atomically precise metal nanoclusters. *Coord. Chem. Rev.* **2016**, *322*, 1. (e) Jin, R. Atomically precise metal nanoclusters: stable sizes and optical properties. *Nanoscale* **2015**, *7*, 1549. (f) Zeng, C.; Chen, Y.; Das, A.; Jin, R. Transformation Chemistry of Gold Nanoclusters: From One Stable Size to Another. *J. Phys. Chem. Lett.* **2015**, *6*, 2976.
- (2) Cook, A. W.; Wu, G.; Hayton, T. W. A Re-examination of the Synthesis of Monolayer-Protected  $\text{Co}_2(\text{SCH}_2\text{CH}_2\text{Ph})_m$  Nanoclusters: Unexpected Formation of a Thiolate-Protected Co(II) T3 Super-tetrahedron. *Inorg. Chem.* **2018**, *57*, 8189.
- (3) Kagalwala, H. N.; Gottlieb, E.; Li, G.; Li, T.; Jin, R.; Bernhard, S. Photocatalytic hydrogen generation system using a nickel-thiolate hexameric cluster. *Inorg. Chem.* **2013**, *52*, 9094.
- (4) (a) Crocker, L. S.; Mattson, B. M.; Heinekey, D. M.; Schulte, G. K. Synthesis and characterization of ( $\eta^3$ -trityl)tetracarbonylrhenium thermal precursor for generation of the pentacarbonylrhenium radical. *Inorg. Chem.* **1988**, *27*, 3722. (b) MacLeod, K. C.; DiMucci, I. M.; Zovinka, E. P.; McWilliams, S. F.; Mercado, B. Q.; Lancaster, K. M.; Holland, P. L. Masked Radicals: Iron Complexes of Trityl, Benzophenone, and Phenylacetylene. *Organometallics* **2019**, *38*, 4224.
- (5) (a) Jolly, P. W.; Wilke, G. Nickel Hydride, Nickel Alkyl, and Nickel Aryl Complexes. In *The Organic Chemistry of Nickel*; Jolly, P. W., Wilke, G., Eds.; Academic Press: 1974; Chap. IV, p 139. (b) Sonoda, A.; Mann, B. E.; Maitlis, P. M. Preparation and fluxional behaviour of  $\alpha,1,2$ - $\eta$ -triphenylmethyl-palladium and -platinum complexes. *J. Chem. Soc., Chem. Commun.* **1975**, 108. (c) Seyferth, D.; King, R. B. *Annual Surveys of Organometallic Chemistry*; Elsevier Publishing Company: 1967; Vol. 3. (d) Wilke, G.; Schott, H. Bistritylnickel and Tritylnickel Chloride. *Angew. Chem., Int. Ed. Engl.* **1966**, *5*, 583.
- (6) (a) Goddard, R.; Krueger, C.; Mark, F.; Stansfield, R.; Zhang, X. Effect upon the hydrogen atoms of bonding an allyl group to a transition metal. A theoretical investigation and an experimental determination using neutron diffraction of the structure of bis( $\eta^3$ -allyl)nickel. *Organometallics* **1985**, *4*, 285. (b) Wilke, G.; Bogdanović, B. Bis- $\pi$ -allyl-nickel. *Angew. Chem.* **1961**, *73*, 756. (c) Bönnemann, H.; Bogdanović, B.; Wilke, G. cis- and trans-Bis-( $\pi$ -allyl)nickel Systems. *Angew. Chem., Int. Ed. Engl.* **1967**, *6*, 804.
- (7) (a) Pasykiewicz, S.; Pietrzykowski, A.; Bukowska, L.; Słupecki, K.; Jerzykiewicz, L. B.; Urbańczyk-Lipkowska, Z. Reactions of nickelocene with diphenylmethyl- and triphenylmethyl-lithium. *J. Organomet. Chem.* **2000**, *604*, 241. (b) Sonoda, A.; Bailey, P. M.; Maitlis, P. M. Crystal and molecular structures of pentane-2,4-dionato-( $\alpha,1,2$ - $\eta$ -triphenylmethyl)-palladium and -platinum. *J. Chem. Soc., Dalton Trans.* **1979**, 346.
- (8) Fischer, P. J.; Ahrendt, K. A.; Young, V. G.; Ellis, J. E. Trityltitanium Complexes. X-ray Structural Characterization of  $[\text{Ti}(\text{CO})_4\{\eta^5\text{-C}(4\text{-C}_6\text{H}_4\text{R})_3\}]^-$  (R = H,  $\text{OCH}_3$ )<sup>1</sup>. *Organometallics* **1998**, *17*, 13.
- (9) (a) Cotton, F. A.; Marks, T. J. Stereochemically nonrigid organometallic molecules. XX. Proton nuclear magnetic resonance study of the fluxional behavior of some substituted (1,2,7-trihaptobenzyl)(pentahaptocyclopentadienyl)dicarbonyl compounds of molybdenum and tungsten. *J. Am. Chem. Soc.* **1969**, *91*, 1339. (b) Becker, Y.; Stille, J. K. The dynamic  $\eta^1$ - and  $\eta^3$ -benzylbis-(triethylphosphine)palladium(II) cations. Mechanisms of interconversion. *J. Am. Chem. Soc.* **1978**, *100*, 845.
- (10) (a) Carmona, E.; Paneque, M.; Poveda, M. L. Synthesis and characterization of some new organometallic complexes of nickel(II) containing trimethylphosphine. *Polyhedron* **1989**, *8*, 285. (b) Wasilke, J.-C.; Ziller, J. W.; Bazan, G. C. Trimethylphosphine-bis(benzyl)-nickel: Synthesis and Characterization. *Adv. Synth. Catal.* **2005**, *347*, 405.
- (11) Crawford, B. L., Jr.; Cross, P. C. The vibrational spectrum and thermodynamic properties of nickel carbonyl. *J. Chem. Phys.* **1938**, *6*, 525.
- (12) Bramley, R.; Figgis, B. N.; Nyholm, R. S. <sup>13</sup>C and <sup>17</sup>O n.m.r. spectra of metal carbonyl compounds. *Trans. Faraday Soc.* **1962**, *58*, 1893.
- (13) Lankamp, H.; Nauta, W. T.; MacLean, C. A new interpretation of the monomer-dimer equilibrium of triphenylmethyl- and alkylsubstituted-diphenyl methyl-radicals in solution. *Tetrahedron Lett.* **1968**, *9*, 249.
- (14) Attempts to quantify the amount of Gombert's dimer formed in the reaction were thwarted by the formation of several unidentified Gombert's dimer decomposition products.
- (15) Mynott, R.; Mollbach, A.; Wilke, G. A proof of the existence of  $\text{Ni}[\text{P}(\text{C}_6\text{H}_5)_3]_4$  in solution. *J. Organomet. Chem.* **1980**, *199*, 107.
- (16) Nguyen, T. A. D.; Jones, Z. R.; Goldsmith, B. R.; Buratto, W. R.; Wu, G.; Scott, S. L.; Hayton, T. W. A  $\text{Cu}_{25}$  Nanocluster with Partial Cu(0) Character. *J. Am. Chem. Soc.* **2015**, *137*, 13319.
- (17) Doud, E. A.; Butler, C. J.; Paley, D. W.; Roy, X. Nickel Phosphinidene Molecular Clusters from Organocyclophosphine Precursors. *Chem. - Eur. J.* **2019**, *25*, 10840.
- (18) (a) Pauling, L. Atomic Radii and Interatomic Distances in Metals. *J. Am. Chem. Soc.* **1947**, *69*, 542. (b) Eisenhart, R. J.; Rudd, P. A.; Planas, N.; Boyce, D. W.; Carlson, R. K.; Tolman, W. B.; Bill, E.; Gagliardi, L.; Lu, C. C. Pushing the Limits of Delta Bonding in Metal-Chromium Complexes with Redox Changes and Metal Swapping. *Inorg. Chem.* **2015**, *54*, 7579.
- (19) (a) Cook, S. L.; Evans, J.; Gray, L. R.; Webster, M. The preparation and crystal structure of  $\text{Fe}_3(\text{CO})_9(\mu_3\text{-PPh})_2$ . *J. Organomet. Chem.* **1982**, *236*, 367. (b) Maclaughlin, S. A.; Carty, A. J.; Taylor, N. J. Hydrogenation of phosphido bridged ruthenium clusters. A view of P—C bond activation and cleavage in the coordinatively unsaturated molecule  $\text{Ru}_3(\text{CO})_9(\mu_2\text{-PPh}_2)(\mu_2\text{-H})$ : conversion of  $\mu_2\text{-PPh}_2$  to  $\mu_3\text{-PPh}$ . *Can. J. Chem.* **1982**, *60*, 87. (c) Lower, L. D.; Dahl, L. F. Synthesis and structural characterization of a new type of metal cluster system, octacarbonylhexakis( $\mu_4$ -phenylphosphido)octanickel, containing a completely bonding metal cube. A transition metal analog of cubane,  $\text{C}_8\text{H}_8$ . *J. Am. Chem. Soc.* **1976**, *98*, 5046. (d) Fenske, D.; Basoglu, R.; Hachgenei, J.; Rogel, F. Novel Clusters of Cobalt and Nickel with Organophosphorus Ligands. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 160. (e) Fenske, D.; Hachgenei, J.; Rogel, F.  $[\text{Ni}_8(\mu_4\text{-PPh})_6(\text{PPh}_3)_4]$  and  $[\text{Ni}_6(\mu_4\text{-PPh})_6(\text{PPh}_3)_4]$ ; Cluster with Coordina-

tively Unsaturated Ni-Atoms. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 982. (f) Coleman, J. M.; Dahl, L. F. Molecular Structures of  $[(C_6H_5)_2PCoC_3H_5]_2$  and  $[C_6H_5)_2PNiC_3H_5]_2$ . An Assessment of the Influence of a Metal-Metal Bond on the Molecular Geometry of an Organometallic Ligand-Bridged Complex. *J. Am. Chem. Soc.* **1967**, *89*, 542. (g) Lu, Z.; Abbina, S.; Sabin, J. R.; Nemykin, V. N.; Du, G. Unexpected Formation of Chiral Pincer CNN Nickel Complexes with  $\beta$ -Diketiminato Type Ligands via C–H Activation: Synthesis, Properties, Structures, and Computational Studies. *Inorg. Chem.* **2013**, *52*, 1454. (h) Rieck, D. F.; Gavney, J. A.; Norman, R. L.; Hayashi, R. K.; Dahl, L. F. Synthesis, chromatographic separation, and stereophysical analysis of the homologous  $[Ni_{12-x}(PMe)_x(CO)_{24-3x}]^{2-}$  series ( $x = 2, 3, 4$ ) containing noncentered  $Ni_{12-x}P_x$  icosahedral cages and the  $[Ni_{10}(\mu_5-PMe)_2(\mu_4-PMe)_5(CO)_{10}]^{2-}$  dianion containing a structurally unprecedented heptacapped pentagonal prismatic metal cage: structural, spectroscopic, and electrochemical consequences due to replacement of  $Ni(CO)_3$  fragments with electronically equivalent (isolobal) PMe fragments. *J. Am. Chem. Soc.* **1992**, *114*, 10369. (i) Beck, R.; Shoshani, M.; Krasinkiewicz, J.; Hatnean, J. A.; Johnson, S. A. Synthesis and chemistry of bis(triisopropylphosphine) nickel(i) and nickel(0) precursors. *Dalton Trans.* **2013**, *42*, 1461. (j) Haehnel, M.; Hansen, S.; Schubert, K.; Arndt, P.; Spannenberg, A.; Jiao, H.; Rosenthal, U. Synthesis, Characterization and Reactivity of Group 4 Metallocene Bis(diphenylphosphino)acetylene Complexes—A Reactivity and Bonding Study. *J. Am. Chem. Soc.* **2013**, *135*, 17556. (k) Keşanlı, B.; Gardner, D. R.; Scott, B.; Eichhorn, B. W. Two new bimetallic phosphido carbonyl complexes of nickel(0):  $[Ni_2(CO)_2-(PPh_3)_2(\mu-CO)(\mu-PPh_2)]^-$  and  $[Ni_2(CO)_4(\mu-PPh_2)_2]^{2-}$ . *J. Chem. Soc., Dalton Trans.* **2000**, 1291.

(20) Yang, L.; Powell, D. R.; Houser, R. P. Structural variation in copper(i) complexes with pyridylmethylamide ligands: structural analysis with a new four-coordinate geometry index,  $\tau^4$ . *Dalton Trans* **2007**, 955.

(21) Chen, Y.; Sui-Seng, C.; Zargarian, D. Tetraphenylborate as a Novel Bridging Ligand in a Zwitterionic Nickel(I) Dimer. *Angew. Chem., Int. Ed.* **2005**, *44*, 7721.

(22) (a) Eisch, J. J.; Yu, K.; Rheingold, A. L. 6,12-Diphenyldibenzo-[b, f][1, 5]diazocine as an Electron-Capture Agent: Efficient Mechanistic Probe for SET Processes and Reagent for the Oxidative Dimerization of Benzylic Organometallics. *Eur. J. Org. Chem.* **2012**, *2012*, 3165. (b) Takeuchi, H.; Nagai, T.; Tokura, N. The Transformation of the Triphenylmethyl Radical into the Triphenylmethyl Cation in the Sulfur Dioxide - Oxygen System. *Bull. Chem. Soc. Jpn.* **1970**, *43*, 1747. (c) Chen, C.; Lee, H.; Jordan, R. F. Synthesis, Structures, and Ethylene Polymerization Behavior of Bis(pyrazolyl)-borate Zirconium and Hafnium Benzyl Complexes. *Organometallics* **2010**, *29*, 5373.

(23) Fahey, D. R.; Mahan, J. E. Reversible oxidative addition of triphenylphosphine to zero-valent nickel and palladium complexes. *J. Am. Chem. Soc.* **1976**, *98*, 4499.

(24) Nattmann, L.; Saeb, R.; Nöthling, N.; Cornella, J. An air-stable binary Ni(0)–olefin catalyst. *Nat. Catal.* **2020**, *3*, 6.

(25) (a) Tolman, C. A. Phosphorus ligand exchange equilibria on zerovalent nickel. Dominant role for steric effects. *J. Am. Chem. Soc.* **1970**, *92*, 2956. (b) Dander, J. E.; Weires, N. A.; Garg, N. K. Benchtop Delivery of Ni(cod)<sub>2</sub> using Paraffin Capsules. *Org. Lett.* **2016**, *18*, 3934.

(26) Tasker, S. Z.; Standley, E. A.; Jamison, T. F. Recent advances in homogeneous nickel catalysis. *Nature* **2014**, *509*, 299.