

# A Cyaphide Transfer Reagent

Daniel W. N. Wilson, Stephanie J. Urwin, Eric S. Yang, and Jose M. Goicoechea\*



Cite This: *J. Am. Chem. Soc.* 2021, 143, 10367–10373



Read Online

ACCESS |



Metrics & More

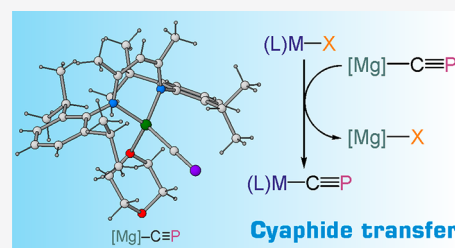


Article Recommendations



Supporting Information

**ABSTRACT:** The cyanide ion plays a key role in a number of industrially relevant chemical processes, such as the extraction of gold and silver from low grade ores. Metal cyanide compounds were arguably some of the earliest coordination complexes studied and can be traced back to the serendipitous discovery of Prussian blue by Diesbach in 1706. By contrast, heavier cyanide analogues, such as the cyaphide ion,  $C\equiv P^-$ , are virtually unexplored despite the enormous potential of such ions as ligands in coordination compounds and extended solids. This is ultimately due to the lack of a suitable synthesis of cyaphide salts. Herein we report the synthesis and isolation of several magnesium–cyaphido complexes by reduction of  ${}^iPr_3SiOCP$  with a magnesium(I) reagent. By analogy with Grignard reagents, these compounds can be used for the incorporation of the cyaphide ion into the coordination sphere of metals using a simple salt-metathesis protocol.



## INTRODUCTION

Along with the halide ions, cyanide ( $C\equiv N^-$ ) is one of the most ubiquitous anions in chemistry. Its salts are routinely used in industrial applications including bulk chemical synthesis, electroplating, metallurgy, tanning, manufacturing of paper and plastics, photography, and as fumigants and insecticides.<sup>1</sup> In organic chemistry, it is an important functional group in nitriles ( $R-C\equiv N$ ) and isonitriles ( $R-N\equiv C$ ), many of which are produced on an industrial scale (e.g., adiponitrile,  $NC(CH_2)_4CN$ , which is used to produce nylon).<sup>2,3</sup> By contrast, and despite the valence isoelectronic relationship between nitrogen and phosphorus, stable phosphorus-containing analogues of cyanides are much rarer; nitrile analogues, so-called phosphalkynes ( $R-C\equiv P$ ), have been known for almost 40 years and are highly reactive compounds due to the weak nature of  $C-P$   $\pi$  bonds.<sup>4,5</sup> Isocyanide analogues ( $R-P\equiv C$ ) remain unknown.<sup>6</sup> Unlike cyanide, which forms a multitude of stable salts, the cyaphide ion,  $C\equiv P^-$ , cannot be obtained as a simple  $A(CP)$  or  $Ae(CP)_2$  salt (where  $A$  = alkali and  $Ae$  = alkaline-earth metal). To date, the  $C\equiv P^-$  ion has only ever been isolated in the coordination sphere of three metals (platinum, ruthenium, and uranium; e.g., *trans*-[Ru(*dppe*)<sub>2</sub>(H)(CP)] where *dppe* = bis(1,2-diphenylphosphinoethane))<sup>7–12</sup> and an electrophilic borane.<sup>13</sup> While these studies demonstrate that the ion is accessible, the resulting compounds are of limited synthetic utility due to their inertness. Alkali/alkaline-earth metal salts of the cyaphide ion are a more attractive target inasmuch as they should allow for the incorporation of  $C\equiv P^-$  into novel molecules and solids, making use of salt metathesis protocols, a procedure that is well established for cyanides.<sup>14</sup> Herein we show that well-defined alkaline-earth complexes of the cyaphide ion are readily accessible and can be used as anion transfer reagents for the synthesis of novel cyaphido complexes.

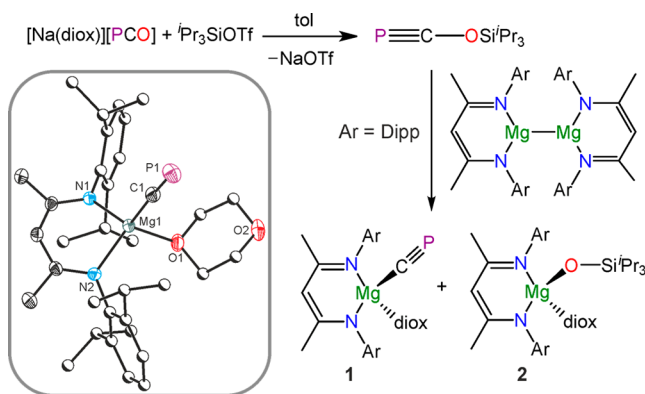
## RESULTS AND DISCUSSION

The two-electron chemical reduction of the 2-phosphaethynolate ion,  $PCO^-$ ,<sup>15</sup> to afford a uranium cyaphide complex was recently demonstrated by Meyer.<sup>11</sup> We reasoned that functionalization of  $PCO^-$  to afford a phosphaethynolate compound ( $R-O-C\equiv P$ ) would facilitate this reduction step, allowing for the straightforward generation of the cyaphide ion. A major limitation is that oxygen-functionalized phosphaethynolate compounds are rare and largely ionic in character.<sup>11,16–21</sup> To date, only one species with significant covalent character has been structurally authenticated.<sup>22</sup> *In situ* silylation of the  $[Na(\text{dioxane})_x]PCO$  with tris(isopropyl)silyl trifluoromethanesulfonate in nonpolar aromatic solvents (benzene or toluene) favors silylation at the oxygen atom to afford the kinetic product  ${}^iPr_3SiOCP$  (Figure 1), which ultimately rearranges to give the  $\kappa$ -P isomer.<sup>23</sup> Reduction of the former species using Jones' magnesium(I) reagent  $[Mg-(\text{DippNacNac})_2]$ <sup>24,25</sup> cleanly affords an equimolar mixture of  $[Mg(\text{DippNacNac})(CP)(\text{dioxane})]$  (**1**) and  $[Mg(\text{DippNacNac})(OSi^iPr_3)(\text{dioxane})]$  (**2**) where  $\text{DippNacNac} = CH\{C(CH_3)N(\text{Dipp})\}_2$  and  $\text{Dipp} = 2, 6$ -di(isopropyl)phenyl (Figure 1). Density functional theory (DFT) calculations predicted this reaction to be exergonic (at 298.15 K) by 52.2 kcal mol<sup>-1</sup> with an overall energy barrier of 12.5 kcal mol<sup>-1</sup>. The reaction proceeds via an unobserved dimagnesiated intermediate (a metalla-phosphaalkene) which rearranges by siloxyl group transfer (energy barrier of 4.4 kcal mol<sup>-1</sup>) to afford **1** and **2**.

Received: April 28, 2021

Published: June 30, 2021





**Figure 1.** Synthesis of **1** and **2** from reduction of  ${}^i\text{Pr}_3\text{SiOCP}$ . Inset: single crystal X-ray structure of **1** (anisotropic displacement ellipsoids set at 50% probability; hydrogen atoms omitted for clarity; carbon atoms of Dipp and dioxane are pictured as spheres of arbitrary radius).

(see the [Supporting Information](#) for the full computational analysis). Cleavage of the C–O bond in the phosphacetylonate ion necessitates a highly oxophilic two-electron reductant and significant steric protection (for example, when the less sterically encumbered magnesium(I) dimer  $[\text{Mg}(\text{Mes}^{\text{NacNac}})]_2$  (Mes = mesityl) was employed, the analogous reaction gave rise to a mixture of products including cyaphide oligomers).

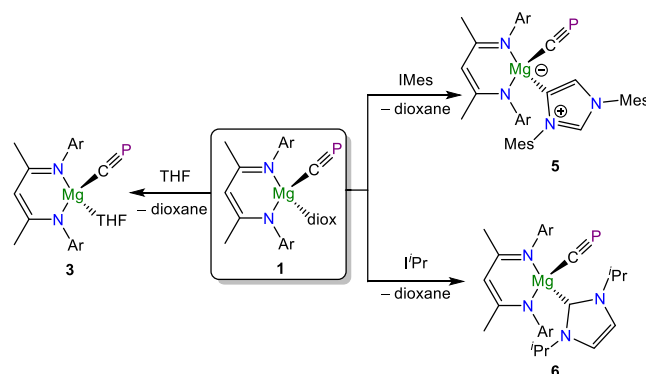
The magnesium–cyaphido complex (**1**) exhibits a resonance in its  ${}^{31}\text{P}\{^1\text{H}\}$  NMR spectrum at 177.2 ppm and a diagnostic singlet resonance in the  ${}^1\text{H}$  NMR spectrum corresponding to the  ${}^{\text{Dipp}}\text{NacNac}$   $\gamma$ -proton at 4.78 ppm. A doublet resonance corresponding to the cyaphide ligand was observed in the  ${}^{13}\text{C}\{^1\text{H}\}$  NMR spectrum at 270.97 ppm ( ${}^1J_{\text{C-P}} = 34.0$  Hz). Fractional crystallization of the reaction mixture allowed for the isolation and structural determination of compounds **1** and **2**.

The crystal structure of **1** ([Figure 1](#), inset) revealed a linear arrangement of the  $\text{Mg}-\text{C}\equiv\text{P}$  moiety ( $177.37(15)^\circ$ ), with an  $\text{Mg}-\text{C}$  bond length of 2.118(2) Å, which is similar to that observed for other related compounds, such as  $[\text{Mg}(\text{Dipp}^{\text{NacNac}})({}^n\text{Bu})(\text{THF})]$  (2.127(2) Å).<sup>26</sup> The C–P bond length in **1** is 1.553(2) Å, in line with the predicted value for a carbon–phosphorus triple bond (1.54 Å),<sup>27</sup> and similar to reported values for other metal–cyaphide complexes (cf. 1.573(2) Å in *trans*- $[\text{Ru}(\text{dppe})_2(\text{H})(\text{CP})]$ ).<sup>9</sup> The crystal structure of **2** can be found in the [Supporting Information](#).

*In situ* generated mixtures of **1** and **2** can be used to transfer the cyaphide ion to metal complexes (*vide infra*) via a salt metathesis protocol, in a manner reminiscent of Grignard reagents.<sup>28</sup> However, because of the similar solubility of **1** and **2** in common laboratory solvents, the isolation of compositionally pure samples of **1** is only possible in low yields (~20%).

Thus, we sought strategies to modify the solubility of **1**. Quantitative dioxane displacement was achieved by using  $\text{THF-}d_8$  to form  $[\text{Mg}(\text{Dipp}^{\text{NacNac}})(\text{CP})(\text{THF-}d_8)]$  (**3**; see [Scheme 1](#)); however, this adduct is equally difficult to separate from the siloxymagnesium side-product. In addition, it was observed for both solvent adducts **1** and **3** that exposure to vacuum initiated decomposition of the target compounds, evidenced by broadening of NMR spectra ([Figure S11](#)). We hypothesize that initial cleavage of the  $\text{Mg}$ –solvent interaction

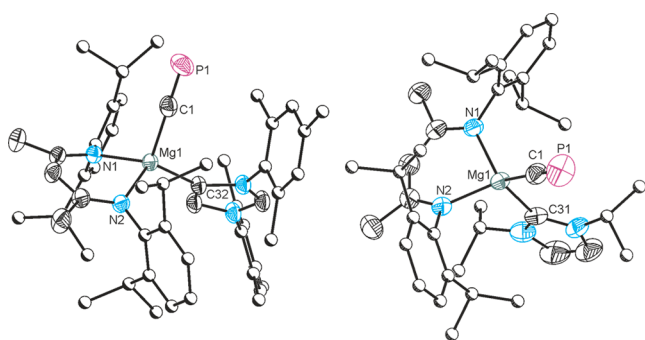
### Scheme 1. Reactivity of **1** toward Lewis Bases (Ar = Dipp)



forms the base-free analogue  $[\text{Mg}(\text{Dipp}^{\text{NacNac}})(\text{CP})]_x$  (**4**), which then rapidly decomposes. Employing dioxane-free  $\text{Na}(\text{OCP})$  during the generation of  ${}^i\text{Pr}_3\text{SiOCP}$  subsequently led to the specific formation of solvent-free analogue **4**, evidenced by a  ${}^{31}\text{P}\{^1\text{H}\}$  NMR singlet resonance at 246.7 ppm. The solubility of this desolvated analogue is sufficiently lower than **2** to facilitate efficient separation by precipitation; however, in the solid state **4** is unstable, decomposing rapidly once isolated (see the [Supporting Information](#) for further details). The structure of **4** is currently unknown, but the downfield shifted  ${}^{31}\text{P}$  NMR resonance suggests it is oligomeric; the related solvent-free cyanido complex,  $[\text{Mg}(\text{Dipp}^{\text{NacNac}})(\text{CN})]_3$ , is a cyclic trimer.<sup>29</sup> Addition of dioxane or  $\text{THF-}d_8$  to solutions of **4** resulted in the formation of the corresponding solvated adducts **1** or **3**, respectively.

To circumvent problematic cleavage of the coordinated base under vacuum, our attention turned to nonvolatile Lewis donors. Addition of excess pyridine or 4-(dimethylamino)pyridine (DMAP) to a  $\text{C}_6\text{D}_6$  solution of **1** did not result in displacement of the dioxane molecule. Addition of *N*-heterocyclic carbenes (NHCs) IMes and I'Pr (IMes = 1,3-dimesitylimidazol-2-ylidene; I'Pr = 1,3-diisopropylimidazol-2-ylidene) successfully afforded carbene adducts  $[\text{Mg}(\text{Dipp}^{\text{NacNac}})(\text{CP})(\text{IMes})]$  (**5**) and  $[\text{Mg}(\text{Dipp}^{\text{NacNac}})(\text{CP})(\text{I'Pr})]$  (**6**), which unlike solvent adducts **1** and **3** can both be isolated as compositionally pure solids in moderate yields (**5**: 54%; **6**: 48%) and can be bottled and stored for several weeks under a nitrogen atmosphere without degradation ([Scheme 1](#)). No reaction was observed between the NHCs and the siloxy byproduct **2**.

Spectroscopically **5** and **6** do not differ greatly from compound **1** and exhibit comparable NMR shifts [e.g.,  ${}^{31}\text{P}\{^1\text{H}\}$  NMR: 162.9 (**4**); 174.9 ppm (**5**)]. Both NHC adducts were structurally authenticated by single-crystal X-ray diffraction ([Figure 2](#)) and confirm the expected association of the NHC with the magnesium metal center. The  $\text{Mg}-\text{CP}$  (**5**: 2.166(2); **6**: 2.144(3) Å) and C–P bonds (**5**: 1.550(2); **6**: 1.531(3) Å) for both compounds are in line with those observed for **1**. Interestingly, it was found that while the IMes carbene associated with the magnesium metal center in an “abnormal” fashion (i.e., through the alkenic backbone), the I'Pr carbene adduct coordinates as expected in the solid state, an observation we put down to the increased steric bulk of IMes.<sup>30</sup> However, in solution the I'Pr moiety of **6** fluctuates between normal and abnormal coordination. The  ${}^{31}\text{P}\{^1\text{H}\}$  NMR spectrum of **6** at room temperature features a particularly broad singlet signal ( $\nu_{1/2} \approx 224$  Hz) which when



**Figure 2.** Single-crystal X-ray structures of **5** (left) and **6** (right). Anisotropic displacement ellipsoids set at 50% probability. Hydrogen atoms are omitted for clarity. Carbon atoms of Dipp and <sup>i</sup>Pr groups are pictured as spheres of arbitrary radius.

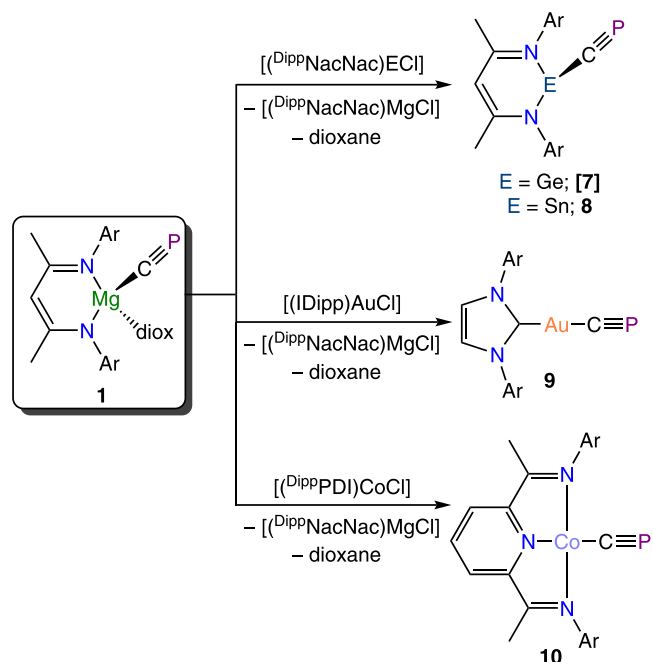
cooled below  $-20\text{ }^{\circ}\text{C}$  gives rise to two sharper singlet signals at 173.3 ppm (major) and 167.7 ppm (minor) (Figure S19). These correspond to the normal and abnormal coordination mode of the <sup>i</sup>Pr moiety, respectively, in good agreement with the DFT calculated chemical shifts (175.4 and 172.3 ppm; Table S6). Calculations further indicate that the difference in energy between these two isomers is negligible. **1** does not react with IMes<sup>Me</sup> and <sup>i</sup>Pr<sup>Me</sup>, analogous NHCs featuring methylated backbones where abnormal coordination is blocked.

Compound **5** cocrystallizes with one stoichiometric equivalent of IMes as a cocrystal, which is also seen in the <sup>1</sup>H NMR spectrum of the bulk product. Probing further, we calculated no energy payoff for the displacement of the dioxane by IMes ( $1\text{--}3\text{ kcal mol}^{-1}$ , within error), with neither compound being thermodynamically favored between  $-100$  and  $100\text{ }^{\circ}\text{C}$ . The calculated thermodynamic data are indicative of an equilibrium. However, even when just one equivalent of IMes is added to a solution of **1**, **5**-IMes can be isolated from the reaction mixture by crystallization (albeit in lower yields). This indicates that the additional molecule of IMes present in the lattice is critical to isolate crystalline samples of **5**.

Given the ionic nature of the Mg–CP bond in **1**, we reasoned that salt metathesis reactions between this species and main-group or metal halides would allow for cyaphide group transfer. This hypothesis was probed by addition of chlorotrimethylsilane to a C<sub>6</sub>D<sub>6</sub> solution of **1** formed *in situ*. The <sup>31</sup>P{<sup>1</sup>H} NMR spectrum showed a single resonance at 97.9 ppm, corresponding to the known phosphalkyne Me<sub>3</sub>SiCP.<sup>31</sup> This clean, quantitative transfer of the CP<sup>−</sup> ion is, to our knowledge, the first instance of such reactivity. Encouraged by this finding, we targeted novel cyaphide–metal complexes. It is worth noting at this stage that comparable cyaphide transfer reactions are also possible with compounds **5** and **6**.

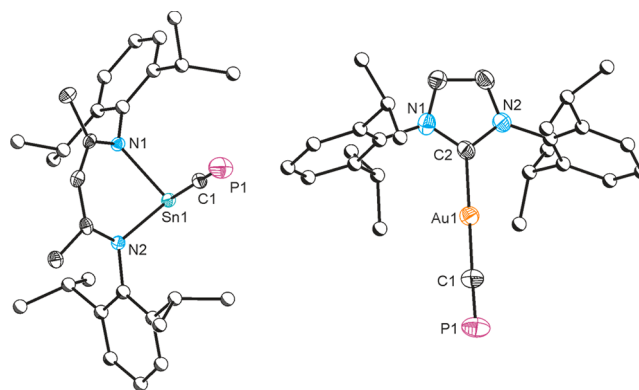
Moving to heavier group 14 elements, addition of [Ge(<sup>Dipp</sup>NacNac)Cl] to an *in situ* generated mixture of **1** and **2** leads to rapid consumption of **1** and a new <sup>31</sup>P{<sup>1</sup>H} NMR signal at 106.4 ppm (Scheme 2). A new singlet signal in the corresponding <sup>1</sup>H NMR spectrum at 5.08 ppm, within the characteristic region for  $\gamma$ -H protons, indicates a new <sup>Dipp</sup>NacNac environment. Also evident was that siloxy byproduct **2** remained unreacted (Figure S20). Over the course of a few hours, this deep-red solution, presumably containing [Ge(<sup>Dipp</sup>NacNac)(CP)] (**7**), changed to a dark-green color, and NMR spectroscopy showed decomposition of the metal–

**Scheme 2.** Reactivity of **1** toward Metal Halides (Ar = Dipp)



cyaphide complex into multiple phosphorus-containing compounds, a process which was accelerated by any physical manipulation.

Reaction of **1** with [Sn(<sup>Dipp</sup>NacNac)Cl] led to the formation of [Sn(<sup>Dipp</sup>NacNac)(CP)] (**8**), which can be isolated by fractional crystallization. Cyaphide transfer was first indicated by <sup>31</sup>P{<sup>1</sup>H} NMR spectroscopy which revealed a new resonance with P–Sn coupling satellites at 122.4 ppm (<sup>2</sup>J<sub>P–Sn</sub> = 69.8 Hz) and confirmed in the solid-state structure (Figure 3). The C≡P bond is intact and comparable (1.542(4) Å) to



**Figure 3.** Single-crystal X-ray structures of **8** (left) and **9** (right). Anisotropic displacement ellipsoids set at 50% probability. Hydrogen atoms are omitted for clarity. Carbon atoms of Dipp groups are pictured as spheres of arbitrary radius.

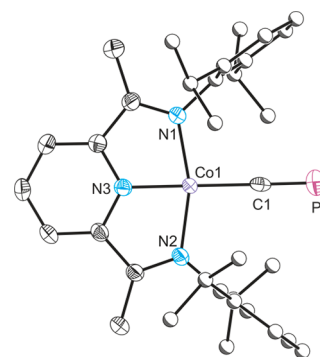
those of **1**, **5**, and **6**. At 2.216(4) Å, the Sn–C bond is relatively long, and the Sn–C≡P unit is practically linear ( $179.16^{\circ}$ ). No resonance could be found in the <sup>13</sup>C NMR spectrum of **8** corresponding to the cyaphide group which we attribute to broadening due to coupling to two adjacent NMR active nuclei. A weak band was observed in the IR spectrum of **8** at  $1321\text{ cm}^{-1}$ , which is consistent with the predicted value ( $1327$



$\text{cm}^{-1}$ ), but partially masked by a band arising from a Dipp  $\text{C}=\text{C}$  stretching mode.

Having demonstrated intermetallic cyaphide transfer through halide metathesis, our next target was to prepare transition metal–cyaphide complexes. Reaction of an *in situ* generated mixture of **1** and **2** with  $[\text{Au}(\text{IDipp})\text{Cl}]$  resulted in the formation of the gold–cyaphido complex  $[\text{Au}(\text{IDipp})(\text{CP})]$  (**9**) which exhibits a singlet resonance in its  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum at 84.1 ppm (Scheme 2). This is at a significantly lower frequency than observed for compound **1** (177.2 ppm) and slightly lower than **7** and **8** (106.4 and 122.4 ppm), consistent with an increase in the covalent character of the Au–CP bond.<sup>32–34</sup> The  $^{13}\text{C}\{^1\text{H}\}$  resonance observed for the cyaphide group in **8**, 247.70 ppm ( $^1J_{\text{C-P}} = 6.1$  Hz), is also at a lower frequency compared to **1** (270.97 ppm). The single-crystal X-ray structure of **9** (Figure 3) reveals a linear two-coordinate gold center ( $\text{C}-\text{Au}-\text{C} = 178.2(2)^\circ$ ;  $\text{Au}-\text{C}-\text{P} = 178.0(5)^\circ$ ) with  $\text{Au}-\text{C}_{\text{carbene}}$  and  $\text{Au}-\text{CP}$  distances of 2.034(6) and 1.972(6) Å, respectively. The former of these is slightly elongated compared to that observed in the  $[(\text{IDipp})\text{AuCl}]$  starting material (1.942(3) Å) due to the stronger  $\sigma$ -donor ability of the cyaphide ion.<sup>35</sup> This distance is more comparable with NHC gold acetylene or cyanido complexes such as  $[\text{Au}(\text{IDipp})(\text{C}\equiv\text{CPh})]$  (2.018(7) Å) or  $[\text{Au}(\text{IDipp})(\text{CN})]$  (1.985(15) Å).<sup>36</sup> The C–P bond distance in **9** is 1.552(6) Å, which is comparable to the other cyaphide complexes discussed thus far (cf. 1.553(2) Å for **1**). The IR spectrum of compound **9** reveals a band at  $1342\text{ cm}^{-1}$ , which is higher than the value reported for *trans*- $[\text{Ru}(\text{dppe})_2(\text{H})(\text{CP})]$  ( $1229\text{ cm}^{-1}$ ) and thus indicative of little  $\pi$ -back-bonding; however, it is worth noting that this vibrational mode is heavily coupled with the  $\text{Au}-\text{C}_{\text{carbene}}$  stretch on account of the linear coordination geometry of **9**.

Finally, in an effort to illustrate the broad synthetic utility of the cyaphide transfer reagent **1**, we sought to synthesize the first example of a 3d metal–cyaphide complex. For this purpose we reacted a mixture of **1** and **2** with  $[(^{\text{Dipp}}\text{PDI})\text{CoCl}]$  ( $^{\text{Dipp}}\text{PDI} = 2,6\text{-}\{2,6\text{-}^i\text{Pr}_2\text{C}_6\text{H}_3\text{NCMe}\}_2\text{C}_5\text{H}_3\text{N}$ ). The reaction results in the clean quantitative formation of a new product,  $[(^{\text{Dipp}}\text{PDI})\text{Co}(\text{CP})]$  (**10**), which exhibits a single resonance in its  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum at 345.4 ppm. This is notably downfield from all of the other known cyaphide complexes, presumably due to a greater paramagnetic contribution to the NMR shielding constant ( $\sigma$ ). Our calculations support this, predicting a  $\delta$  value of 341 ppm for the  $^{31}\text{P}$  NMR chemical shift. The  $^1\text{H}$  and  $^{13}\text{C}\{^1\text{H}\}$  NMR spectra for **10** are in line with the presence of a single  $^{\text{Dipp}}\text{PDI}$  ligand. Notably, we were unable to observe the NMR resonance for the cyaphide ligand in the  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum due to coupling with the  $^{31}\text{P}$  and quadrupolar  $^{59}\text{Co}$  nuclei.  $[(\text{PDI})\text{Co}(\text{R})]$  complexes have previously been attributed biradical character which explains anomalous  $^1\text{H}$  NMR shifts, which we also see in  $[\text{Co}(^{\text{Dipp}}\text{PDI})(\text{CP})]$  (e.g., the imine  $\text{NCCH}_3$  protons are upfield shifted to  $-0.23$  ppm).<sup>37</sup> The IR spectrum of compound **10** reveals a band at  $1306\text{ cm}^{-1}$ , in between the values observed for **9** ( $1342\text{ cm}^{-1}$ ) and *trans*- $[\text{Ru}(\text{dppe})_2(\text{H})(\text{CP})]$  ( $1229\text{ cm}^{-1}$ ), suggesting a moderate degree of  $\pi$ -backbonding (as expected for a first row transition metal). Extremely air- and moisture-sensitive blue crystals of **10** were obtained from a concentrated toluene solution at  $-35^\circ\text{C}$ . The structure of **10** was unequivocally confirmed by single-crystal X-ray diffraction (Figure 4) which reveals a square-planar cobalt(I) compound bonded to a cyaphide ligand.



**Figure 4.** Single-crystal X-ray structure of **10**. Anisotropic displacement ellipsoids set at 50% probability. Hydrogen atoms are omitted for clarity. Carbon atoms of Dipp groups are pictured as spheres of arbitrary radius.

## CONCLUSION

The reductive deoxygenation of  $^i\text{Pr}_3\text{SiOCP}$  offers an efficient route to cyaphide generation at a magnesium center. This reactive salt is the first example of a cyaphide transfer reagent, allowing for the synthesis of novel metal–cyaphido complexes using Grignard-like reactivity (including the first examples of square-planar, trigonal pyramidal and linear complexes of the cyaphide ligand). This new reagent will undoubtedly open up new avenues in the coordination chemistry of metal complexes and may ultimately be used for the synthesis of novel extended solids featuring the cyaphide ion such as, for example, Prussian Blue analogues.

## EXPERIMENTAL SECTION

**General Procedures.** All reactions and product manipulations were performed under an inert atmosphere of argon or dinitrogen by using standard Schlenk-line or glovebox techniques (MBraun UNILab glovebox maintained at  $<0.1$  ppm of  $\text{H}_2\text{O}$  and  $<0.1$  ppm of  $\text{O}_2$ ). Generation of  $^i\text{Pr}_3\text{SiOCP}$  was adapted from the previously reported synthesis.<sup>23</sup>  $\text{Na}[\text{PCO}(\text{dioxane})_{5,6}]$ ,<sup>38</sup>  $[\text{Mg}(^{\text{Dipp}}\text{NacNac})_2]$ ,<sup>39</sup>  $\text{IMes}$ ,<sup>40</sup>  $^i\text{Pr}$ ,<sup>41</sup>  $[\text{Ge}(^{\text{Dipp}}\text{NacNac})\text{Cl}]$ ,<sup>42</sup>  $[\text{Sn}(^{\text{Dipp}}\text{NacNac})\text{Cl}]$ ,<sup>42</sup>  $[(\text{IDipp})\text{AuCl}]$ ,<sup>35</sup> and  $[\text{Co}(^{\text{Dipp}}\text{PDI})\text{Cl}]$ <sup>43</sup> were synthesized according to previously reported synthetic procedures. Triisopropylsilyl trifluoromethanesulfonate (Sigma-Aldrich) and chlorotrimethylsilane (Sigma-Aldrich) were used as received. Hexane (hex; Sigma-Aldrich, HPLC grade) and toluene (Sigma-Aldrich, HPLC grade) were purified by using an MBraun SPS-800 solvent system.  $\text{C}_6\text{D}_6$  (Aldrich, 99.5%) was dried over  $\text{CaH}_2$  and degassed prior to use. THF (Sigma-Aldrich, HPLC grade) and  $\text{THF-}d_6$  (Sigma-Aldrich, 99.5%) were distilled over sodium/benzophenone. All dry solvents were stored under argon in gastight ampules. Additionally, solvents were stored over activated 3 Å molecular sieves.

**Characterization Techniques.** NMR spectra were acquired on Bruker AVIII 500 MHz ( $^1\text{H}$  500 MHz,  $^{13}\text{C}$  126 MHz) and Bruker AVIII 400 MHz NMR spectrometers ( $^{31}\text{P}$  162 MHz) at 295 K unless otherwise stated.  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were referenced to residual protic solvent resonance ( $^1\text{H}$  NMR  $\text{C}_6\text{D}_6$ :  $\delta = 7.16$  ppm;  $^{13}\text{C}$  NMR  $\text{C}_6\text{D}_6$ :  $\delta = 188.06$  ppm).  $^{31}\text{P}$  and  $^{119}\text{Sn}$  were externally referenced to an 85% solution of  $\text{H}_3\text{PO}_4$  in  $\text{H}_2\text{O}$  and  $\text{SnMe}_4$ , respectively. Elemental analyses were performed by Elemental Microanalyses Ltd. (Devon, UK). Samples ( $\sim 5$  mg) were submitted in sealed glass vials.

**Synthesis of  $[\text{Mg}(^{\text{Dipp}}\text{NacNac})(\text{CP})(\text{dioxane})]$  (**1**) and  $[\text{Mg}(^{\text{Dipp}}\text{NacNac})(\text{OSi}^i\text{Pr}_3)(\text{dioxane})]$  (**2**).** Inside a glovebox,  $^i\text{Pr}_3\text{SiOTf}$  (90 mg, 0.29 mmol) was dissolved in toluene (ca. 0.5 mL) and added to a vial containing  $[\text{Na}(\text{dioxane})_{5,6}]\text{PCO}$  (167 mg, 0.29 mmol). The resulting suspension was stirred for 4 h to generate  $^i\text{Pr}_3\text{SiOCP}$ , with occasional washing of the walls of the vial to ensure complete consumption of the starting materials. The resulting mixture was

filtered through a glass paper filter, and the solids were washed with a small amount of toluene.  $[\text{Mg}(\text{D}^{\text{ipp}}\text{NacNac})]_2$  (195 mg, 0.22 mmol) was added as a solid to the resulting yellow solution, causing it to darken to orange. Reaction completion was confirmed by  $^{31}\text{P}\{^1\text{H}\}$  NMR spectroscopy. The solution can be used as an *in situ* supply of **1** with an equimolar amount of **2** also present; a representative  $^1\text{H}$  NMR of such a solution can be found in Figure S1. Concentration of the solution (taking care to avoid evaporation to dryness) afforded a red oil. The residue was extracted into hexane (1 mL) and filtered. Cooling the orange solution to  $-35\text{ }^\circ\text{C}$  overnight yielded **1** as yellow crystals suitable for X-ray diffraction (29 mg, 22% yield). Further concentrating the solution, or cooling for longer periods, resulted in mixtures of **1** and **2**.

**[Mg(D<sup>ipp</sup>NacNac)(CP)(dioxane)] (1).** Anal. Calcd (%) for  $\text{C}_{34}\text{H}_{49}\text{MgN}_2\text{O}_2\text{P}$ : C, 71.26; H, 8.62; N, 4.89. Found: 71.35; H, 9.15; N, 4.82.  $^1\text{H}$  NMR (500 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  (ppm) = 7.11–7.09 (br m, 6H; Dipp ArH), 4.78 (s, 1H; NacNac  $\gamma$ -H), 3.34–3.16 (br m, 12H; Dipp  $\text{CH}(\text{CH}_3)_2$  and dioxane  $\text{CH}_2$ ), 1.63 (s, 6H; NacNac  $\text{NCCH}_3$ ), 1.38 (d,  $^3J_{\text{H-H}} = 6.9$  Hz, 6H; Dipp  $\text{CH}(\text{CH}_3)_2$ ), 1.24–1.17 (m, 14H\*; Dipp  $\text{CH}(\text{CH}_3)_2$ ), 0.88 (d,  $^3J_{\text{H-H}} = 7.9$  Hz, 6H; Dipp  $\text{CH}(\text{CH}_3)_2$  [\*should integrate as 12H; however, the fluxionality of coordinated dioxane prevents an accurate integration of this region.])  $^{13}\text{C}$  NMR (126 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  (ppm) = 270.97 (d,  $^1J_{\text{C-P}} = 34.0$  Hz; CP), 169.19 (NacNac  $\text{NCCH}_3$ ), 145.21 (Dipp ArC), 142.81 (Dipp ArC), 142.11 (Dipp ArC), 136.43 (Dipp ArC), 125.63 (Dipp ArC), 124.17 (Dipp ArC), 94.85 (NacNac  $\gamma$ -C), 67.26 (Dipp  $\text{CH}(\text{CH}_3)_2$ ), 27.98 (NacNac  $\text{NCCH}_3$ ), 25.98 (dioxane), 24.67 (Dipp  $\text{CH}(\text{CH}_3)_2$ ), 24.13 (Dipp  $\text{CH}(\text{CH}_3)_2$ ), 18.98 (unknown impurity).  $^{31}\text{P}$  NMR (162 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  (ppm) = 246.7\*, 177.2. [\*solvent-free  $[\text{Mg}]\text{CP} \sim 10\%$ .] IR: The  $\text{C}\equiv\text{P}$  bond stretch was calculated to be  $1327\text{ cm}^{-1}$ . It was not possible to resolve the peak in the IR spectrum as it is masked by the aromatic C–C bond stretches which also appear this region.

**[Mg(D<sup>ipp</sup>NacNac)(OSiPr<sub>3</sub>)(dioxane)] (2).** Anal. Calcd (%) for  $\text{C}_{42}\text{H}_{70}\text{MgN}_2\text{O}_3\text{Si}$ : C, 71.72; H, 10.03; N, 3.98. Found: 71.99; H, 10.50; N, 4.01.  $^1\text{H}$  NMR (500 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  (ppm) = 7.15 (m, overlap with  $\text{C}_6\text{D}_6$  prevents integration; Dipp ArH), 4.73 (s, 1H; NacNac  $\gamma$ -H), 3.83 (s, 6H; dioxane), 3.21 (br sept,  $^3J_{\text{H-H}} = 6.9$  Hz, 4H; Dipp  $\text{CH}(\text{CH}_3)_2$ ), 1.59 (s, 6H; NacNac  $\text{NCCH}_3$ ), 1.38 (d,  $^3J_{\text{H-H}} = 6.8$  Hz, 12H; Dipp  $\text{CH}(\text{CH}_3)_2$ ), 1.21 (d,  $^3J_{\text{H-H}} = 6.9$  Hz, 12H; Dipp  $\text{CH}(\text{CH}_3)_2$ ), 0.90 (two overlapping s, 18H; Si(C(H)CH<sub>3</sub>)<sub>3</sub>) 0.80 (m, 3H; Si(C(H)CH<sub>3</sub>)<sub>3</sub>).  $^{13}\text{C}$  NMR (126 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  (ppm) = 170.08 (NacNac  $\text{NCCH}_3$ ), 145.28 (Dipp ArC), 142.04 (Dipp ArC), 125.72 (Dipp ArC), 124.19 (Dipp ArC), 94.91 (NacNac  $\gamma$ -C), 67.95 (dioxane), 31.97 (Dipp  $\text{CH}(\text{CH}_3)_2$ ), 28.35 (Dipp  $\text{CH}(\text{CH}_3)_2$ ), 25.31 (NacNac  $\text{NCCH}_3$ ), 24.43 (NacNac  $\text{NCCH}_3$ ), 18.96 (Si(CH<sub>3</sub>)<sub>2</sub>)<sub>3</sub>, 14.65 (Si(CH<sub>3</sub>)<sub>2</sub>)<sub>3</sub>).

**Synthesis of [Mg(D<sup>ipp</sup>NacNac)(CP)(THF-d<sub>8</sub>)] (3).** Generated *in situ* by addition of THF-d<sub>8</sub> to a solution of **1** in  $\text{C}_6\text{D}_6$ .  $^1\text{H}$  NMR (500 MHz,  $\text{C}_6\text{D}_6$ )  $\delta$  (ppm) = 7.16–7.12 (m, 6H; Dipp ArH), 4.79 (s, 1H; NacNac  $\gamma$ -H), 3.53 (s; THF), 3.46 (sept,  $^3J_{\text{H-H}} = 6.8$  Hz, 4H; Dipp  $\text{CH}(\text{CH}_3)_2$ ), 3.36 (s, 8H, free dioxane), 1.64 (s, 6H; NacNac  $\text{NCCH}_3$ ), 1.37 (d,  $^3J_{\text{H-H}} = 6.8$  Hz, 12H; Dipp  $\text{CH}(\text{CH}_3)_2$ ), 1.21 (d,  $^3J_{\text{H-H}} = 6.8$  Hz, 12H; Dipp  $\text{CH}(\text{CH}_3)_2$ ), 0.94–0.84 (m, 3H; unknown impurity).  $^{13}\text{C}$  NMR (126 MHz,  $\text{C}_6\text{D}_6$ )  $\delta$  (ppm) = 271.14 (d,  $^1J_{\text{C-P}} = 33.5$  Hz; CP), 168.87 (NacNac  $\text{NCCH}_3$ ), 145.34 (Dipp ArC), 142.95 (Dipp ArC), 125.49 (Dipp ArC), 124.04 (Dipp ArC), 94.75 (NacNac  $\gamma$ -C), 67.18 (free dioxane), 67.02 (THF), 28.05 (NacNac  $\text{NCCH}_3$ ), 25.77 (Dipp  $\text{CH}(\text{CH}_3)_2$ ), 24.76 (Dipp  $\text{CH}(\text{CH}_3)_2$ ), 24.61 (THF), 24.09 (Dipp  $\text{CH}(\text{CH}_3)_2$ ).  $^{31}\text{P}$  NMR (162 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  = 175.0.

**Synthesis of [Mg(D<sup>ipp</sup>NacNac)(CP)(IMes)] (5).** **1** (~129.5 mg, 0.22 mmol) was generated *in situ*, as outlined above. To this, IMes (143.9 mg, 0.47 mmol, 2.1 equiv) was added as a solution in toluene (0.5 mL), and the resulting mixture was stirred overnight. The volatiles were removed, and the residue was extracted with pentane (5 mL). After filtration, the solution was concentrated to 1 mL and recrystallized in a single crop over several days at  $-35\text{ }^\circ\text{C}$ . The product was isolated as a pale orange solid (134.4 mg, 0.12 mmol, 54% yield). Anal. Calcd (%) for  $\text{C}_{72}\text{H}_{89}\text{MgN}_6\text{P}$ : C, 79.06; H, 8.20; N, 7.68. Found: C, 78.10; H, 8.18; N, 7.28.  $^1\text{H}$  NMR (400 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  (ppm) = 7.22 (dd,  $^3J_{\text{H-H}} = 7.7$ , 1.6 Hz, 2H; Dipp ArH), 7.08 (t,

$^3J_{\text{H-H}} = 7.6$  Hz, 2H; Dipp ArH), 7.05–6.95 (m, 2H; Dipp ArH), 6.79 (s, 4H; free IMes ArH), 6.73 (s, 2H; coord IMes ArH), 6.52 (s, 2H; coord IMes ArH), 6.44 (s, 2H; free IMes {NCH<sub>2</sub>}), 5.86 (d,  $^3J_{\text{H-H}} = 1.4$  Hz, 1H, coord IMes CH), 5.61 (d,  $^3J_{\text{H-H}} = 1.5$  Hz, 1H; coord IMes CH), 4.99 (s, 2H; NacNac  $\gamma$ -H), 4.35 (sept,  $^3J_{\text{H-H}} = 6.8$  Hz, 2H; Dipp  $\text{CH}(\text{CH}_3)_2$ ), 3.52 (sept,  $^3J_{\text{H-H}} = 6.9$  Hz, 2H; Dipp  $\text{CH}(\text{CH}_3)_2$ ), 2.20 (s, 3H; free IMes *para*-CH<sub>3</sub>), 2.15 (s, 6H; NacNac  $\text{NCCH}_3$ ), 2.10 (s, 12H; free IMes *ortho*-CH<sub>3</sub>), 1.94 (s, 3H; coord IMes *para*-CH<sub>3</sub>), 1.78 (s, 6H; coord IMes *ortho*-CH<sub>3</sub>), 1.67 (s, 3H; coord IMes *para*-CH<sub>3</sub>), 1.57 (s, 6H; IMes *ortho*-CH<sub>3</sub>), 1.43 (d,  $^3J_{\text{H-H}} = 6.8$  Hz, 6H; Dipp  $\text{CH}(\text{CH}_3)_2$ ), 1.22 (dd,  $^3J_{\text{H-H}} = 6.8$ , 2.0 Hz, 12H; Dipp  $\text{CH}(\text{CH}_3)_2$ ), 1.15 (d,  $^3J_{\text{H-H}} = 6.9$  Hz, 6H; Dipp  $\text{CH}(\text{CH}_3)_2$ ).  $^{13}\text{C}$  NMR (126 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  (ppm) = 218.62 (free IMes carbene C), 167.02 (NacNac  $\text{CCH}_3$ ), 163.31 (coord IMes  $\text{NC}=\text{C}(\text{H})\text{N}$ ), 147.54 (Dipp *ipso*-ArC), 144.57 (coord IMes *ipso*-ArC), 141.59 (Dipp *ipso*-ArC), 139.29 (coord IMes *para*-ArC), 138.84 (free IMes *ortho*-ArC), 138.73 (Dipp *ortho*-ArC), 136.91 (coord IMes *ortho*-ArC), 135.42, 135.06 (coord IMes CH), 130.97 (coord IMes CH), 128.88 (coord IMes *meta*-ArC), 128.80 (coord IMes *meta*-ArC), 128.75 (free IMes *meta*-ArC), 124.00 (Dipp ArC), 123.76 (Dipp ArC), 122.67 (Dipp ArC), 120.14 (free IMes {NCH<sub>2</sub>}), 94.70 (NacNac  $\gamma$ -C), 27.80 (Dipp  $\text{CH}(\text{CH}_3)_2$ ), 27.35 (Dipp  $\text{CH}(\text{CH}_3)_2$ ), 27.19 (Dipp  $\text{CH}(\text{CH}_3)_2$ ), 24.89 (Dipp  $\text{CH}(\text{CH}_3)_2$ ), 24.43 (Dipp  $\text{CH}(\text{CH}_3)_2$ ), 24.37 (Dipp  $\text{CH}(\text{CH}_3)_2$ ), 24.31 (coord IMes *ortho*-CH<sub>3</sub>), 24.14 (coord IMes *ortho*-CH<sub>3</sub>), 20.73 (coord IMes *para*-CH<sub>3</sub>), 20.67 (free IMes *para*-CH<sub>3</sub>), 20.52 (NacNac  $\text{CCH}_3$ ), 17.64 (coord IMes *para*-CH<sub>3</sub>), 17.45 (free IMes *ortho*-CH<sub>3</sub>), 16.47 (coord IMes *para*-CH<sub>3</sub>) [no cyaphide carbon observed].  $^{31}\text{P}\{^1\text{H}\}$  NMR (162 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  (ppm) = 162.9. IR  $\nu_{(\text{CP})} = 1316\text{ cm}^{-1}$  (calcd  $1311\text{ cm}^{-1}$ ).

**Synthesis of [Mg(D<sup>ipp</sup>NacNac)(CP)(I<sup>Pr</sup>)] (6).** **1** (~80.2 mg, 0.14 mmol) was generated *in situ*, as described above. To this, I<sup>Pr</sup> (21.6 mg, 0.14 mmol, 1.0 equiv) was added as a solution in toluene (0.5 mL), and the resulting solution was stirred for 2 h. The volatiles were removed, and the residue was washed with pentane (5 mL) and dried. The product was isolated as a beige solid (41.5 mg, 0.065 mmol, 48% yield). Anal. Calcd (%) for  $\text{C}_{39}\text{H}_{57}\text{MgN}_4\text{P}$ : C, 73.51; H, 9.02; N, 8.79. Found: C, 72.16; H, 9.12; N, 7.59.  $^1\text{H}$  NMR (400 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  (ppm) = 7.30 (d,  $^3J_{\text{H-H}} = 6.0$  Hz, 2H; Dipp ArH), 7.19–7.13 (m, overlap with  $\text{C}_6\text{D}_6$  prevents integration), 7.09 (d,  $^3J_{\text{H-H}} = 6.0$  Hz, 2H; Dipp CH), 6.23 (s, 2H; I<sup>Pr</sup> {NCH<sub>2</sub>}), 4.84 (s, 1H; NacNac  $\gamma$ -H), 4.08–3.75 (br m, 2H; Dipp  $\text{CH}(\text{CH}_3)_2$ ), 3.25–3.05 (m, 1H, overlap with adjacent signal prevents total integration; I<sup>Pr</sup>  $\text{CH}(\text{CH}_3)_2$ ), 3.08–2.90 (br m, 2H; Dipp  $\text{CH}(\text{CH}_3)_2$ ), 1.77 (d,  $^3J_{\text{H-H}} = 6.5$  Hz, 2H; I<sup>Pr</sup>  $\text{CH}(\text{CH}_3)_2$ ), 1.68 (s, 6H; NacNac  $\text{NCCH}_3$ ), 1.34 (d,  $^3J_{\text{H-H}} = 6.8$  Hz, 6H; Dipp  $\text{CH}(\text{CH}_3)_2$ ), 1.14 (d,  $^3J_{\text{H-H}} = 6.8$  Hz, 6H; Dipp  $\text{CH}(\text{CH}_3)_2$ ), 0.73 (d,  $^3J_{\text{H-H}} = 6.5$  Hz, 6H; I<sup>Pr</sup>  $\text{CH}(\text{CH}_3)_2$ ).  $^{13}\text{C}$  NMR (126 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  (ppm) = 181.54 (I<sup>Pr</sup> carbene C), 167.71 (NacNac  $\text{NCCH}_3$ ), 145.58 (Dipp *ipso*-ArC), 143.2 (Dipp *ortho*-ArC), 141.7 (Dipp *ortho*-ArC), 124.72 (Dipp *para*-ArC, overlaps with solvent), 124.14 (Dipp *meta*-ArC), 122.91 (Dipp *meta*-ArC), 116.26 (broad, I<sup>Pr</sup> {NCH<sub>2</sub>}), 93.49 (NacNac  $\gamma$ -C), 28.42 (NacNac  $\text{CH}(\text{CH}_3)_2$ ), 28.18 (NacNac  $\text{NCCH}_3$ ), 27.12 (broad, I<sup>Pr</sup>  $\text{CH}(\text{CH}_3)_2$ ), 24.94 (I<sup>Pr</sup>  $\text{CH}(\text{CH}_3)_2$ ), 24.80 (I<sup>Pr</sup>  $\text{CH}(\text{CH}_3)_2$ ), 24.55 (Dipp  $\text{CH}(\text{CH}_3)_2$ ), 23.91 (NacNac  $\text{NCCH}_3$ ), 23.87 (Dipp  $\text{CH}(\text{CH}_3)_2$ ), 23.51 (Dipp  $\text{CH}(\text{CH}_3)_2$ ), 19.34 (broad, I<sup>Pr</sup>  $\text{CH}(\text{CH}_3)_2$ ).  $^{31}\text{P}\{^1\text{H}\}$  NMR (162 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  (ppm) = 174.9 (br s).  $^{31}\text{P}\{^1\text{H}\}$  NMR (162 MHz,  $\text{C}_6\text{D}_6$ , 233 K):  $\delta$  (ppm) = 173.3 (major) and 167.7 (minor). IR  $\nu_{(\text{CP})} = 1325\text{ cm}^{-1}$  (calcd  $1312\text{ cm}^{-1}$ ).

**In Situ Generation of [Ge(D<sup>ipp</sup>NacNac)(CP)] (7).** **1** (~70 mg, 0.15 mmol) was generated *in situ*, as outlined above. To this toluene solution,  $[\text{Ge}(\text{D}^{\text{ipp}}\text{NacNac})\text{Cl}]$  (39.5 mg, 0.075 mmol) was added as a solid with stirring. NMR spectroscopy showed immediate formation of a new  $^{31}\text{P}$ -containing compound. Over a few hours, the solution changed color from red to dark green, indicating decomposition. Despite efforts, no pure sample of **7** could be isolated.  $^1\text{H}$  NMR (400 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  (ppm) = 5.08 (s, 1H; NacNac  $\gamma$ -H), 4.15 (sept,  $^3J_{\text{H-H}} = 6.7$  Hz, 2H; Dipp { $\text{CH}(\text{CH}_3)_2$ }), 3.42 (sept; Dipp { $\text{CH}(\text{CH}_3)_2$ }) overlapping with **2**), 1.56 (s;  $\text{CCH}_3$  overlapping with **2**), 1.44 (d,  $^3J_{\text{H-H}} = 6.7$  Hz, 12H), 1.28 (d,  $^3J_{\text{H-H}} = 6.8$  Hz, 12H), 1.23 (d,  $^3J_{\text{H-H}} = 6.9$  Hz, 10H, overlap with **2** prevents precise integration), 1.07 (d,



$^3J_{\text{H-H}} = 6.8$  Hz, 12H). Specific aromatic proton signals could not be identified due to overlap with resonance arising from **2**.  $^{31}\text{P}\{^1\text{H}\}$  NMR (162 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  (ppm) = 106.4.

**Synthesis of  $[\text{Sn}^{\text{Dipp}}\text{NacNac}(\text{CP})]$  (**8**).** **1** (~91.7 mg, 0.16 mmol) was generated *in situ*, as outlined above. To this toluene solution,  $[\text{Sn}^{\text{Dipp}}\text{NacNac}(\text{Cl})]$  (82.3 mg, 0.14 mmol) was added as a solid with stirring. Over ~2 h, the solution turned burgundy. The solvent was removed, and the residue was extracted with hexane (5 mL) and filtered. The solution was concentrated to ~1 mL and cooled to  $-35$  °C for 18 h to form yellow crystals of **8** (28.0 mg, 0.048 mmol, 34% yield). Anal. Calcd (%) for  $\text{C}_{30}\text{H}_{41}\text{N}_2\text{SnP}$ : C, 62.19; H, 7.13; N, 4.84. Found: C, 60.87; H, 7.35; N, 4.70.  $^1\text{H}$  NMR (400 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  (ppm) = 7.18–7.09 (m, overlap with residual solvent signal prevents integration), 7.07 (d,  $^3J_{\text{H-H}} = 2.1$  Hz, 1H; Dipp CH), 7.06 (d,  $^3J_{\text{H-H}} = 2.1$  Hz, 1H; Dipp CH), 5.04 (s, 1H; NacNac  $\gamma$ -H), 4.12 (sept,  $^3J_{\text{H-H}} = 6.7$  Hz, 2H; Dipp  $\text{CH}(\text{CH}_3)_2$ ), 3.28 (sept,  $^3J_{\text{H-H}} = 6.9$  Hz, 2H; Dipp  $\text{CH}(\text{CH}_3)_2$ ), 1.60 (s, 6H; NacNac  $\text{NCCH}_3$ ), 1.44 (d,  $^3J_{\text{H-H}} = 6.7$  Hz, 6H; Dipp  $\text{CH}(\text{CH}_3)_2$ ), 1.31 (d,  $^3J_{\text{H-H}} = 6.8$ , 6H; Dipp  $\text{CH}(\text{CH}_3)_2$ ), 1.22 (d,  $^3J_{\text{H-H}} = 6.9$ , 6H; Dipp  $\text{CH}(\text{CH}_3)_2$ ), 1.11 (d,  $^3J_{\text{H-H}} = 6.8$  Hz, 6H; Dipp  $\text{CH}(\text{CH}_3)_2$ ).  $^{13}\text{C}$  NMR (126 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  (ppm) = 166.34 (NacNac  $\text{NCCH}_3$ ), 145.49 (Dipp *ortho*-CH), 142.65 (Dipp *ortho*-CH), 142.31 (Dipp *ipso*-CH), 136.07 (Dipp *ipso*-CH), 126.80 (Dipp *para*-CH), 124.67 (Dipp *meta*-CH), 123.78 (Dipp *meta*-CH), 100.59 (NacNac  $\gamma$ -CH), 28.89 (Dipp  $\text{C}(\text{CH}_3)_2$ ), 28.74 (Dipp  $\text{C}(\text{CH}_3)_2$ ), 27.76 (Dipp  $\text{C}(\text{CH}_3)_2$ ), 24.51 (Dipp  $\text{C}(\text{CH}_3)_2$ ), 24.15 (Dipp  $\text{C}(\text{CH}_3)_2$ ), 23.64 (NacNac  $\text{NCCH}_3$ ), 23.18 (Dipp  $\text{C}(\text{CH}_3)_2$ ). Cyaphide carbon not observed up to 350 ppm, likely due to broadening by the two adjacent nuclei.  $^{31}\text{P}\{^1\text{H}\}$  NMR (162 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  (ppm) = 122.4 ( $^2J_{\text{P-Sn}} = 69.8$  Hz, CP).  $^{119}\text{Sn}$  NMR (186 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  =  $-245.6$ . IR  $\nu_{(\text{CP})} = 1321$   $\text{cm}^{-1}$  (calcd 1327  $\text{cm}^{-1}$ ).

**Synthesis of  $[\text{Au}(\text{IDipp})(\text{CP})]$  (**9**).** **1** (~106 mg, 0.22 mmol) was generated *in situ* as described above. This toluene solution was added dropwise to a stirred solution of  $[\text{Au}(\text{IDipp})(\text{Cl})]$  (75.0 mg, 0.12 mmol) in toluene (1 mL). The reaction was stirred for 2 h and filtered through a glass paper filter. The solvent was removed to dryness, and the yellow solids were washed with hexane ( $3 \times 2$  mL) [NB: the hexane fraction can be collected and concentrated to afford **2**]. The resulting white solid was taken into toluene (2 mL) and filtered to remove the remaining  $[\text{Mg}^{\text{Dipp}}\text{NacNac}(\text{Cl})]$  (dioxane). Crystals were obtained by slow diffusion of hexane into a concentrated toluene solution at  $-35$  °C (41 mg, 54% yield). Anal. Calcd (%) for  $\text{C}_{28}\text{H}_{36}\text{AuN}_2\text{P}$ : C, 53.51; H, 5.77; N, 4.46. Found: 54.14; H, 5.87; N, 4.32.  $^1\text{H}$  NMR (500 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  (ppm) = 7.15 (m, 2H; Dipp *para*-CH), 7.01 (d,  $^3J_{\text{H-H}} = 7.7$  Hz, 4H; Dipp *meta*-CH), 6.21 (s, 2H;  $\{\text{NCH}\}_2$ ), 2.49 (sept,  $^3J_{\text{H-H}} = 6.9$  Hz, 4H; Dipp  $\{\text{CH}(\text{CH}_3)_2\}$ ), 1.40 (d,  $^3J_{\text{H-H}} = 6.9$  Hz, 12H; Dipp  $\{\text{CH}(\text{CH}_3)_2\}$ ), 1.04 (d, 12H,  $^3J_{\text{H-H}} = 6.9$  Hz; Dipp  $\{\text{CH}(\text{CH}_3)_2\}$ ), 0.30 (s, < 1H; unknown impurity).  $^{13}\text{C}$  NMR (126 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  (ppm) = 247.70 (d,  $^1J_{\text{C-P}} = 6.1$  Hz; CP), 193.02 (d,  $^3J_{\text{C-P}} = 5.0$  Hz; carbene C), 145.29 ( $\{\text{NCH}\}_2$ ), 144.72 (ArC), 134.02 (ArC), 130.49 (ArC), 123.94 (ArC), 122.57 (ArC), 28.65 (Dipp  $\{\text{CH}(\text{CH}_3)_2\}$ ), 24.45 (Dipp  $\{\text{CH}(\text{CH}_3)_2\}$ ), 23.53 (Dipp  $\{\text{CH}(\text{CH}_3)_2\}$ ).  $^{31}\text{P}\{^1\text{H}\}$  NMR (162 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  (ppm) = 84.1. IR  $\nu_{(\text{CP})} = 1342$   $\text{cm}^{-1}$  (calcd 1332  $\text{cm}^{-1}$ ).

**Synthesis of  $[\text{Co}^{\text{Dipp}}\text{PDI}(\text{CP})]$  (**10**).** **1** (~65 mg, 0.11 mmol) was generated *in situ* as described above. To this toluene solution was added  $[\text{Co}^{\text{Dipp}}\text{PDI}(\text{Cl})]$  (33 mg, 0.06 mmol) as a solid with stirring. The reaction was stirred for 4 days. The solvent was removed, and the residue was washed with hexane ( $2 \times 5$  mL) and then extracted with toluene (1.5 mL). After filtration, the resulting deep blue solution was concentrated and stored at  $-35$  °C for 1 week to form blue crystals of **10**. The supernatant solution was concentrated and stored at  $-35$  °C to yield a second crop of crystals (17 mg, 0.03 mmol, 51% yield).  $^1\text{H}$  NMR (400 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  (ppm) = 9.76 (t,  $^3J_{\text{H-H}} = 7.7$  Hz, 1H; pyridine *para*-CH), 7.51 (t,  $^3J_{\text{H-H}} = 7.7$  Hz, 2H; Dipp *para*-CH), 7.36 (d,  $^3J_{\text{H-H}} = 7.7$  Hz, 4H; Dipp *meta*-CH), 7.03 (d,  $^3J_{\text{H-H}} = 7.7$  Hz, 2H; pyridine *meta*-CH), 3.10 (sept,  $^3J_{\text{H-H}} = 6.8$  Hz, 4H; Dipp  $\{\text{CH}(\text{CH}_3)_2\}$ ), 1.21 (d,  $^3J_{\text{H-H}} = 6.8$  Hz, 11H; Dipp  $\{\text{CH}(\text{CH}_3)_2\}$ ), 1.04 (d,  $^3J_{\text{H-H}} = 6.8$  Hz, 12H; Dipp  $\{\text{CH}(\text{CH}_3)_2\}$ ),  $-0.23$  (s, 6H;  $\text{NCCH}_3$ ).  $^{13}\text{C}$  NMR (151 MHz,  $\text{C}_6\text{D}_6$ )  $\delta$  169.06 (imine  $\text{NCCH}_3$ ),

155.03 (Dipp *ipso*-ArC), 153.78 (Dipp *ortho*-ArC), 140.95 (Dipp *para*-ArC), 123.75 (Dipp *meta*-ArC), 123.60 (pyridine *meta*-ArC), 120.07 (pyridine *para*-ArC), 28.96 (Dipp  $\{\text{CH}(\text{CH}_3)_2\}$ ), 24.11 (Dipp  $\{\text{CH}(\text{CH}_3)(\text{CH}_3)\}$ ), 23.75 (Dipp  $\{\text{CH}(\text{CH}_3)(\text{CH}_3)\}$ ), 22.22 ( $\text{NCCH}_3$ ).  $^{31}\text{P}\{^1\text{H}\}$  NMR (162 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  (ppm) = 345.4. IR  $\nu_{(\text{CP})} = 1306$   $\text{cm}^{-1}$  (calcd 1283  $\text{cm}^{-1}$ ).

## ■ ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/jacs.1c04417>.

Figures S1–S41 and Tables S1–S6 (PDF)

### Accession Codes

CCDC 2078056–2078062 and 2086971 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

Jose M. Goicoechea – Department of Chemistry, Chemistry Research Laboratory, University of Oxford, Oxford OX1 3TA, U.K.; [orcid.org/0000-0002-7311-1663](https://orcid.org/0000-0002-7311-1663); Email: [jose.goicoechea@chem.ox.ac.uk](mailto:jose.goicoechea@chem.ox.ac.uk)

### Authors

Daniel W. N. Wilson – Department of Chemistry, Chemistry Research Laboratory, University of Oxford, Oxford OX1 3TA, U.K.

Stephanie J. Urwin – Department of Chemistry, Chemistry Research Laboratory, University of Oxford, Oxford OX1 3TA, U.K.; [orcid.org/0000-0002-9092-0200](https://orcid.org/0000-0002-9092-0200)

Eric S. Yang – Department of Chemistry, Chemistry Research Laboratory, University of Oxford, Oxford OX1 3TA, U.K.

Complete contact information is available at:

<https://pubs.acs.org/doi/10.1021/jacs.1c04417>

### Notes

The authors declare no competing financial interest.

## ■ ACKNOWLEDGMENTS

We thank the University of Oxford, the EPSRC, and OxICFM CDT for financial support of this research (DWNW: DTA studentship; SJU: EP/T010681/1; ESY: EP/S023828/1). Dr. Stefan Mitzinger is acknowledged for optimizing the conditions for the formation of  $^i\text{Pr}_3\text{SiOCP}$ . The University of Oxford is also acknowledged for access to Chemical Crystallography facilities.

## ■ REFERENCES

- Gail, E.; Gos, S.; Kulzer, R.; Loroesch, J.; Sauer, M.; Kellens, R.; Reddy, J.; Steier, N.; Haspenpusch, W. Cyano compounds, inorganic. In *Ullmann's Encyclopedia of Industrial Chemistry*; Wiley-VCH: Weinheim, 2011; pp 673–704.
- Pollak, P.; Romeder, G.; Hagedorn, F.; Gelbke, H.-P. Nitriles. In *Ullmann's Encyclopedia of Industrial Chemistry*; Wiley-VCH: Weinheim, 2000; pp 363–376.
- Palmer, R. J. Polyamides, Plastics. In *Encyclopedia of Polymer Science and Technology*; Wiley: Hoboken, NJ, 2001; pp 618–643.
- Becker, G.; Gresser, G.; Uhl, W. Acyl- and alkylidene phosphines, XV [1] 2,2-dimethylpropylidene phosphine, a stable compound with a

phosphorus atom of coordination Number 1. *Z. Naturforsch., B: J. Chem. Sci.* **1981**, *36*, 16–19.

(5) Regitz, M. Phosphaalkynes: New Building Blocks in Synthetic Chemistry. *Chem. Rev.* **1990**, *90*, 191–213.

(6) Weber, L. The quest for isophosphaalkynes (isophosphocyanides)  $C\equiv P-R$  — Still an elusive class of compounds. *Eur. J. Inorg. Chem.* **2003**, *2003*, 1843–1856.

(7) Jun, H.; Young, V. G., Jr.; Angelici, R. J. Phosphorus analogue ( $C\equiv P^-$ ) of a bridging cyanide ( $C\equiv N^-$ ) ligand: Synthesis and structure of  $(Cl)(PEt_3)_2Pt(\mu-C\equiv P)Pt(PEt_3)_2$ . *J. Am. Chem. Soc.* **1992**, *114*, 10064–10065.

(8) Jun, H.; Angelici, R. J. Bridging Cyaphide ( $C\equiv P^-$ ) and Bridging Aryl Isocyanide ( $C\equiv P-R$ ) Ligands: Synthesis and Characterization of  $(X)(PEt_3)_2Pt(\mu-C\equiv P)Pt(PEt_3)_2$  and  $(X)(PEt_3)Pt(\mu-C\equiv P-R)Pt(PEt_3)_2(X)$  ( $X = Cl, Br; R = 2,4,6$ -tri-*tert* butylphenyl). *Organometallics* **1994**, *13*, 2454–2460.

(9) Cordaro, J. G.; Stein, D.; Rügger, H.; Grützmacher, H. Making the true “CP” ligand. *Angew. Chem., Int. Ed.* **2006**, *45*, 6159–6162.

(10) Trathen, N.; Leech, M. C.; Crossley, I. R.; Greenacre, V. K.; Roe, S. M. Synthesis and electronic structure of the first cyaphide-alkynyl complexes. *Dalton Trans.* **2014**, *43*, 9004–9007.

(11) Hoerger, C. J.; Heinemann, F. W.; Louyriac, E.; Maron, L.; Grützmacher, H.; Meyer, K. Formation of a uranium-bound  $\eta^1$ -cyaphide ( $CP^-$ ) ligand via activation and C–O bond cleavage of phosphoethynolate ( $OCP^-$ ). *Organometallics* **2017**, *36*, 4351–4354.

(12) Levis, M. C.; Pearce, K. G.; Crossley, I. R. Controlled Reactivity of Terminal Cyaphide Complexes: Isolation of the 5-Coordinate  $[Ru(dppe)_2(C\equiv P)]^+$ . *Inorg. Chem.* **2019**, *58*, 14800–14807.

(13) Finze, M.; Bernhardt, E.; Willner, H.; Lehmann, C. W.  $[(CF_3)_3BCP]^-$  and  $[(CF_3)_3BCAs]^-$ : Thermally stable phosphoethynyl and arsaethynyl complexes. *Angew. Chem., Int. Ed.* **2004**, *43*, 4160–4163.

(14) Nauth, A. M.; Opatz, T. Non-toxic cyanide sources and cyanating agents. *Org. Biomol. Chem.* **2019**, *17*, 11–23.

(15) For a recent review see: Goicoechea, J. M.; Grützmacher, H. The chemistry of the 2-phosphaethynolate anion. *Angew. Chem., Int. Ed.* **2018**, *57*, 16968–16994.

(16) Westerhausen, M.; Schneiderbauer, S.; Piotrowski, H.; Suter, M.; Nöth, H. Synthesis of alkaline earth metal bis(2-phosphaethynolates). *J. Organomet. Chem.* **2002**, *643–644*, 189–193.

(17) Camp, C.; Settineri, N.; Lefevre, J.; Jupp, A. R.; Goicoechea, J. M.; Maron, L.; Arnold, J. Uranium and thorium complexes of the phosphaethynolate ion. *Chem. Sci.* **2015**, *6*, 6379–6384.

(18) Gilliard, R. J.; Heift, D.; Benkö, Z.; Keiser, J. M.; Rheingold, A. L.; Grützmacher, H.; Protasiewicz, J. D. An isolable magnesium diphosphaethynolate complex. *Dalton Trans.* **2018**, *47*, 666–669.

(19) Bestgen, S.; Chen, Q.; Rees, N.; Goicoechea, J. M. Synthesis and reactivity of rare-earth metal phosphaethynolates. *Dalton Trans.* **2018**, *47*, 13016–13024.

(20) Grant, L. N.; Pinter, B.; Manor, B. C.; Grützmacher, H.; Mindiola, D. J. A Scandium-Stabilized Diisophosphaethynolate Ligand:  $[OCPPCO]_4^-$ . *Angew. Chem., Int. Ed.* **2018**, *57*, 1049–1052.

(21) Mei, Y.; Borger, J. E.; Wu, D. J.; Grützmacher, H. Salen supported  $Al-O-C\equiv P$  and  $Ga-P=C=O$  complexes. *Dalton Trans.* **2019**, *48*, 4370–4374.

(22) Wilson, D. W. N.; Hinz, A.; Goicoechea, J. M. An isolable phosphaethynolatoborane and its reactivity. *Angew. Chem., Int. Ed.* **2018**, *57*, 2188–2193.

(23) Heift, D.; Benkö, Z.; Grützmacher, H. Is the phosphaethynolate anion, ( $OCP^-$ ), an ambident nucleophile? A spectroscopic and computational study. *Dalton Trans.* **2014**, *43*, S920–S928.

(24) Green, S. P.; Jones, C.; Stasch, A. Stable Magnesium(I) Compounds with Mg–Mg Bonds. *Science* **2007**, *318*, 1754–1757.

(25) Jones, C. Dimeric magnesium(I)  $\beta$ -diketiminates: a new class of quasi-universal reducing agent. *Nat. Rev. Chem.* **2017**, *1*, 0059.

(26) Chisholm, M. H.; Choojun, K.; Gallucci, J. C.; Wambua, P. M. Chemistry of magnesium alkyls supported by 1,5,9-trimesityldipyrromethene and 2-[(2,6-diisopropylphenyl)amino]-4-[(2,6-

diisopropylphenyl)imino]pent-2-ene. A comparative study. *Chem. Sci.* **2012**, *3*, 3445–3457.

(27) Pyykkö, P.; Riedel, S.; Patzschke, M. Triple-Bond Covalent Radii. *Chem. - Eur. J.* **2005**, *11*, 3511–3520.

(28) Rappoport, Z.; Marek, I., Eds.; *The Chemistry of Organomagnesium Compounds*; Wiley-VCH: Weinheim, 2008.

(29) Ma, M.; Stasch, A.; Jones, C. Magnesium(I) Dimers as Reagents for the Reductive Coupling of Isonitriles and Nitriles. *Chem. - Eur. J.* **2012**, *18*, 10669–10676.

(30) For related activation/rearrangement reactions of NHCs with  $\beta$ -diketiminato magnesium compounds see: Yuvaraj, K.; Carpentier, A.; Smith, C. D.; Maron, L.; Jones, C. C–N and C–H Activation of an N-Heterocyclic Carbene by Magnesium(II) Hydride and Magnesium(I) Complexes. *Inorg. Chem.* **2021**, *60*, 6065–6072.

(31) Appel, R.; Westerhaus, A.  $(CH_3)_3Si-C\equiv P$ , ein silylfunktionelles phospha-alkin. *Tetrahedron Lett.* **1981**, *22*, 2159–2160.

(32) Pyykkö, P. Theoretical Chemistry of Gold. *Angew. Chem., Int. Ed.* **2004**, *43*, 4412–4456.

(33) Wang, X.-B.; Wang, Y.-L.; Yang, J.; Xing, X.-P.; Li, J.; Wang, L.-S. Evidence of Significant Covalent Bonding in  $Au(CN)_2^-$ . *J. Am. Chem. Soc.* **2009**, *131*, 16368–16370.

(34) Liu, H.-T.; Xiong, X.-G.; Dau, P. D.; Wang, Y.-L.; Huang, D.-L.; Li, J.; Wang, L.-S. Probing the nature of gold–carbon bonding in gold–alkynyl complexes. *Nat. Commun.* **2013**, *4*, 2223.

(35) Fructos, M. R.; Belderrain, T. R.; de Frémont, P.; Scott, N. M.; Nolan, S. P.; Diaz-Requejo, M. M.; Pérez, P. J. A Gold Catalyst for Carbene-Transfer Reactions from Ethyl Diazoacetate. *Angew. Chem., Int. Ed.* **2005**, *44*, 5284–5288.

(36) Gaillard, S.; Slawin, A. M. Z.; Nolan, S. P. A N-heterocyclic carbene gold hydroxide complex: a golden synthon. *Chem. Commun.* **2010**, *46*, 2742–2744.

(37) Knijnenburg, Q.; Hettterscheid, D.; Kooistra, T. M.; Budzelaar, P. H. M. The Electronic Structure of (Diiminopyridine)Cobalt(I) Complexes. *Eur. J. Inorg. Chem.* **2004**, *2004*, 1204–1211.

(38) Heift, D.; Benkö, Z.; Grützmacher, H. Coulomb repulsion versus cycloaddition: formation of anionic four-membered rings from sodium phosphaethynolate,  $Na(OCP)$ . *Dalton Trans.* **2014**, *43*, 831–840.

(39) Hicks, J.; Juckel, M.; Paparo, A.; Dange, D.; Jones, C. Multigram Syntheses of Magnesium(I) Compounds Using Alkali Metal Halide Supported Alkali Metals as Dispersible Reducing Agents. *Organometallics* **2018**, *37*, 4810–4813.

(40) Arduengo, A. J., III; Dias, H. V. R.; Harlow, R. L.; Kline, M. Electronic stabilization of nucleophilic carbenes. *J. Am. Chem. Soc.* **1992**, *114*, 5530–5534.

(41) Burling, S.; Paine, B. M.; Nama, D.; Brown, V. S.; Mahon, M. F.; Prior, T. J.; Pregosin, P. S.; Whittlesey, M. K.; Williams, J. M. J. C–H Activation Reactions of Ruthenium N-Heterocyclic Carbene Complexes: Application in a Catalytic Tandem Reaction Involving C–C Bond Formation from Alcohols. *J. Am. Chem. Soc.* **2007**, *129*, 1987–1995.

(42) Ding, Y.; Roesky, H. W.; Noltemeyer, M.; Schmidt, H.; Power, P. P. Synthesis and Structures of Monomeric Divalent Germanium and Tin Compounds Containing a Bulky Diketiminato Ligand. *Organometallics* **2001**, *20*, 1190–1194.

(43) Hojilla Atienza, C. C.; Milsmann, C.; Lobkovsky, E.; Chirik, P. J. Synthesis, Electronic Structure, and Ethylene Polymerization Activity of Bis(Imino)Pyridine Cobalt Alkyl Cations. *Angew. Chem., Int. Ed.* **2011**, *50*, 8143–8147.