ACS Catalysis

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Letter

A Copper(I) Platform for One-Pot P−H Bond Formation and Hydrophosphination of Heterocumulenes

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Cite This: *ACS Catal.* 2022, 12, 8214−8219

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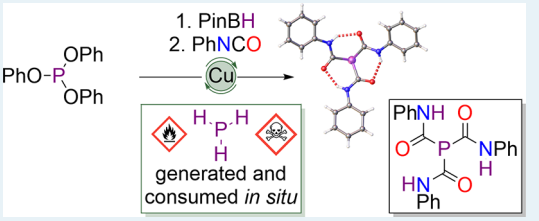
ABSTRACT: The reaction of phosphorus(III) esters with pinacolborane generates phosphines via the action of an NHC-copper(I) catalyst. This gives access, within minutes, to 12 P−H bonded species, including secondary and primary phosphines as well as PH_3, in excellent conversions. These phosphines can be subsequently applied in the copper(I)-catalyzed hydrophosphination of heterocumulenes in a telescoped, one-pot fashion. This approach yielded 12 phosphaureas, 3 phosphaguanidines, and 2 phosphathioureas in moderate to excellent yields without the need to handle toxic, pyrophoric, or gaseous P−H bond containing compounds. The crystal structures of two of the phosphaureas, $PhP(C(O)NHPh)_2$ and $P(C(O)NHPh)_3$, are presented.



KEYWORDS: *phosphine, P−H bond formation, hydrophosphination, heterocumulene, copper catalysis, homogeneous catalysis*

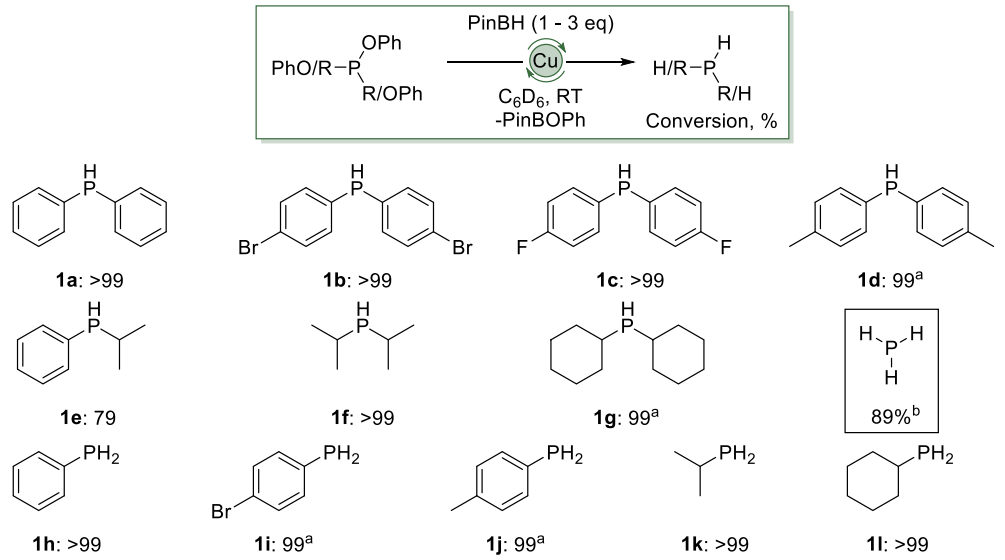
Compounds containing P−C bonds have found widespread application, and hydrophosphination has emerged as an important route to organophosphorus compounds, attractive for the high atom efficiency and versatility. Uncatalyzed hydrophosphination proceeds with the addition of heat, light, or a radical initiator but is hampered by poor selectivity.[1] First described in 1990,[2,3] metal-catalyzed hydrophosphination has emerged as the preeminent method to provide selectivity to hydrophosphination. Metals from most parts of the periodic table have now been reported to mediate this reaction, and these diverse catalysts show an unsurprising dissimilitude in mechanism.[1,4−13] In comparison to the challenging formation of alkyl and alkenyl phosphines from alkenes and alkynes, the hydrophosphination of heterocumulenes has been less well studied and for many substrates proceeds under neat, catalyst-free conditions.[14,15] Nevertheless, a number of catalytic approaches have recently been reported.[16] Despite its many attractive attributes, hydrophosphination is inherently reliant on access to molecules containing P−H bonds. This moiety often imbues molecules with several unattractive properties, such as an unpleasant, penetrating odor, profound toxicity, and sensitivity toward an ambient atmosphere.

Despite the challenges associated with handling these compounds, a number of routes to primary and secondary phosphines have been reported, driven by their utility in synthesis.[17−37] These approaches provide access to a wide library of primary and secondary phosphines but still rely on their isolation before synthetic utilization and often necessitate the handling of toxic or highly reactive compounds such as tin derivatives and alanes. The action of silanes on phosphorus(V) esters catalyzed by $B(C_6F_5)_3$ was reported to generate a small range of phosphines, including PH_3, but suffered from long reaction times and, in some cases, limited conversion.[38] Beller and co-workers used a similar methodology in a domino reaction which obviated the need to handle phosphines;[39] in their hands, the copper-catalyzed reduction of secondary phosphine oxides with a silane followed by an Ullman-type coupling with R−X bonds provided tertiary phosphines without the need to isolate the intermediate secondary phosphine. While it was limited to the monocoupling of secondary phosphine oxides, this work exemplified the attractive reductive capacity of copper systems in the presence of appropriate hydride sources. This reactivity has been widely exploited for the reduction of a large range of organic substrates.[40] Copper catalysis has also been reported to effect numerous other transformations: for example, we recently reported the hydrophosphination of isocyanates effected by N-heterocyclic carbene (NHC) supported copper(I) catalysts in a highly selective fashion.[41]

While traditional routes to phosphines occur via chlorination, attractive direct routes from P_4 to phosphorus(III) esters are increasingly of interest.[42] We thus set out to develop a general method to install P−H bonds via the copper catalyzed reduction of P^{III}−O bonds and couple it to the hydrophosphination of heterocumulenes. Herein we report the copper-catalyzed reduction of phosphite, phosphonite, and phosphinite esters to PH_3 and primary and secondary phosphines, respectively. This step can be coupled to the copper(I)-catalyzed hydrophosphination of heterocumulenes to yield tris-, bis-, and

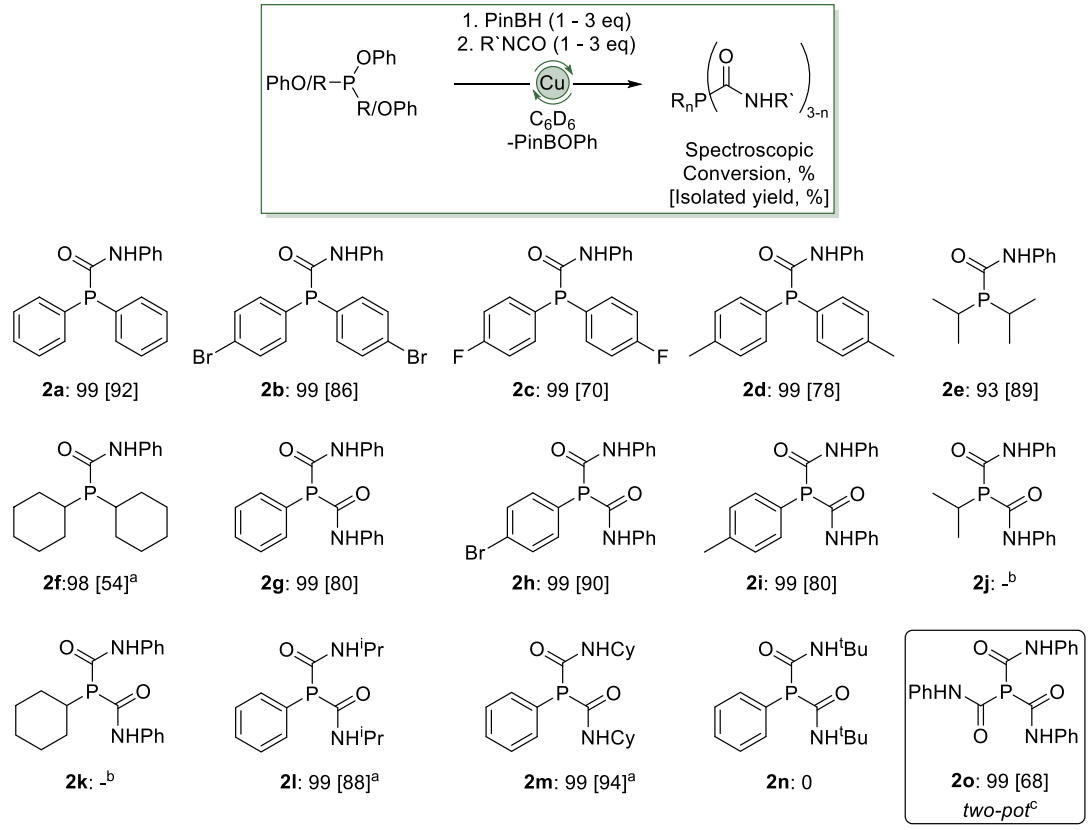
Received: May 6, 2022
Revised: June 20, 2022
Published: June 24, 2022

Scheme 1. Results of the Study of the Scope of Phosphine Formation Mediated by 2 mol % of (IPr)CuO-*t*-Bu (2 μmol) with Phosphinite/Phosphonite (100 μmol) and PinBH (1 equiv, 15.0 μL, 103 μmol; 2 equiv, 29.5 μL, 203 μmol) in C_6D_6 (0.5 mL)[a]



[a]Values shown reflect the consumption of $(PhO)_nPR_{3-n}$. Legend: in all cases, H_nPR_{3-n} is the only observable product except where noted (a), where there are trace amounts of other phosphorus-containing species; (b) see text for conditions.

Scheme 2. Catalytic Hydrophosphination of Isocyanates (1 or 2 equiv) with Phosphines Generated *In Situ* from $R_nP(OPh)_{3-n}$ (0.10 mmol) and PinBH (1 or 2 equiv) with 2 mol % of (IPr)CuO-*t*-Bu in C_6D_6 (0.5 mL)[a]



[a]Legend: (a) ^{1}H NMR spectroscopic yields calculated by use of a 1,3,5-$(MeO)_3C_6H_3$ internal standard; (b) see the Supporting Information, inconsistent results; (c) $P(OPh)_3$ (0.10 mmol) and PinBH (2.9 equiv) with 10 mol % (6-Dipp)CuO*t*-Bu allowed to react for minutes, volatile components of the reaction mixture transferred *in vacuo* onto 5 mol % of (SIMes)CuO*t*-Bu and phenyl isocyanate (3 equiv).

monophosphacarboxamide derivatives from stable, less odoriferous, relatively low toxicity starting materials in a one-pot fashion.

Seeking a rapid route to phosphines from P(III) precursors, we initially turned our attention to the generation of P–H bonds via a copper(I)-catalyzed reduction, investigating the reduction

https://doi.org/10.1021/acscatal.2c02199
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of $R_nP(OPh)_{3-n}$. The P−H-containing products of such transformations are toxic, odoriferous, and often pyrophoric. They must be handled with care under an inert atmosphere and disposed of appropriately (see the Supporting Information).

We first attempted the reduction of a range of species of the form Ph_2PX (X = Cl, OEt, OPh) with pinacolborane in the presence of (IPr)CuO-*t*-Bu. While diphenylchlorophosphine did not react, the phosphinite esters Ph_2POEt and Ph_2POPh were observed to convert to Ph_2PH within minutes. Attempts to extend this to $PhP(OR)_2$ (R = Me, Ph) indicated a further divergence; triphenylphosphonite provided conversion to $PhPH_2$, while *O*,*O*′-dimethylphenylphosphonite showed no reaction. Similarly, $P(OPh)_3$ gave limited (∼9%) conversion to PH_3, whereas $P(OMe)_3$ was inert to these conditions. A variation of the ligand at copper indicated that other NHCs (6-Dipp, 6-Mes, SIMes) had limited effects on the rate of reaction, while phosphines (dppe, Xantphos) and nitrogen-based ligands (1,10-phenanthroline, 2,2-bipyridine) provided reduced rates of reaction. This resulted in a set of standard conditions—exposure of substituted phosphorus(III) phenyl esters to an appropriate amount of pinacolborane in the presence of 2 mol % of (IPr)CuO-*t*-Bu in C_6D_6. These conditions were applied to a range of substitution patterns on the phosphorus center (Scheme 1).

There are, to date, limited routes to generate fastidiously dry PH_3 on a small scale. The application of the standard conditions shown in Scheme 1 to $P(OPh)_3$ gave poor conversions. Alteration of the ligand to 6-Dipp, however, gave 89% consumption of $P(OPh)_3$ within 30 min. The sole observable product of this reaction in the ^{31}P NMR spectrum was phosphine. This method thus provides a useful new component in the synthetic toolkit, providing access to an extensive range of phosphines on ideal scales for reaction development approaches.

Having optimized the generation of primary and secondary phosphines as well as PH_3, we investigated coupling this step to hydrophosphination. In an initial reaction, an equimolar mixture of triphenylphosphinite, pinacolborane, and phenyl isocyanate was added to a C_6D_6 solution of 2 mol % of (IPr)CuO-*t*-Bu. During this reaction, we observed the competing hydroboration of the isocyanate to PinBN(Ph)C(O)H (see the Supporting Information) and interpreted this as necessitating a temporal separation between the P−H formation and hydrophosphination steps. To validate this approach, 2 mol % of (IPr)CuO-*t*-Bu was added to an equimolar solution of Ph_2POPh and PinBH in C_6D_6 to generate diphenylphosphine, using the standard conditions. One equivalent of phenyl isocyanate was then immediately added to this mixture. Examination of the reaction mixture by NMR spectroscopy showed a mixture of $Ph_2PC(O)NHPh$ (**2a**) and PinBOPh, indicating success. Similar conditions were then applied in the hydrophosphination of phenyl isocyanate with a range of phosphines, generated *in situ* (Scheme 2). For secondary phosphines bearing aromatic substituents, an inspection of ^1H and ^{31}P NMR spectra showed that the phosphine was consumed within 30 min, to give the corresponding phosphaurea. Secondary alkyl phosphines took longer (overnight) to achieve good conversions, which might reflect the lower acidity of the P−H bonds in the aliphatic phosphines.[43]

Both $PhP(C(O)NHi\text{-}Pr)_2$ (**2l**) and $PhP(C(O)NHCy)_2$ (**2m**) could be generated from $PhPH_2$ and 2 equiv of *i*-PrNCO and CyNCO, respectively, though the reaction required a longer time to reach completion in comparison to that for $PhP(C(O)NHPh)_2$ (**2g**). No production of $PhP(C(O)NH\text{-}t\text{-}Bu)_2$ (**2n**) from *t*-BuNCO and $PhPH_2$ was observed, even after 24 h. The synthesis of compound **2g** was repeated on a preparative scale (see the Supporting Information), and the product was analyzed by XRD. The asymmetric unit of the crystal structure consists of four molecules of **2g** arranged in a crownlike structure, held together through a combination of intramolecular and intermolecular N−H···O hydrogen-bonding interactions (Figure 1a).

In contrast to aromatic primary phosphines, the reaction of their aliphatic analogues, RPH_2 (R = *i*-Pr, Cy), with phenyl isocyanate did not allow the isolation of the desired phosphaureas, **2k,j**. While resonances tentatively attributed to these species were observed in the ^{31}P NMR spectrum, these

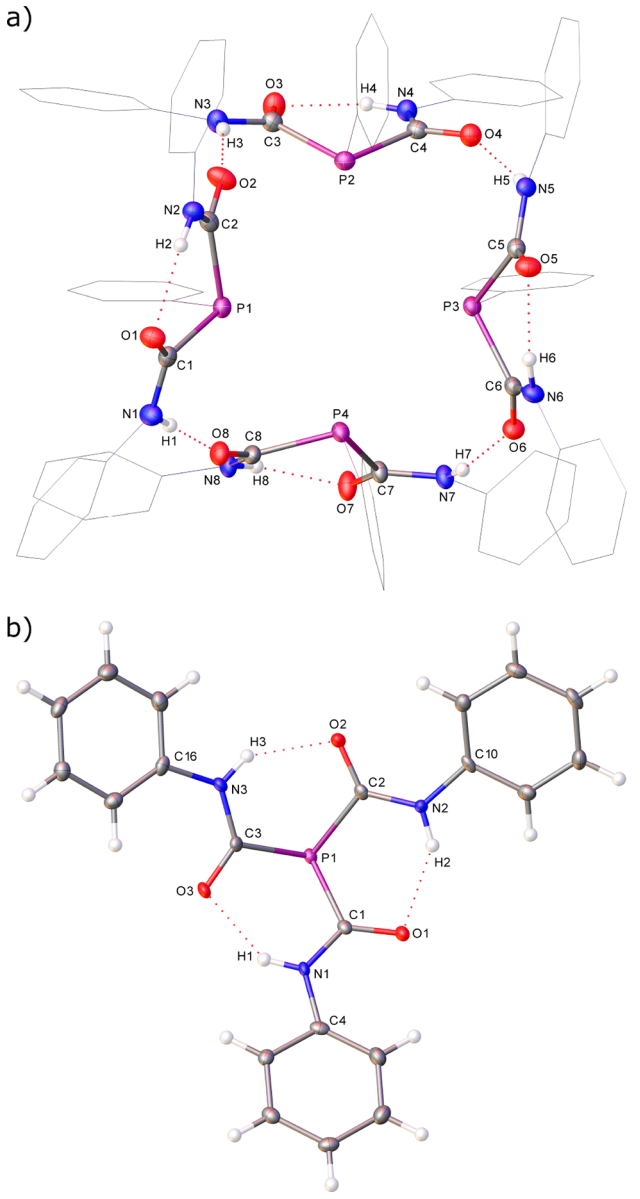

Figure 1. (a) Molecular structure (30% probability ellipsoids) of $PhP(C(O)NHPh)_2$ (**2g**). Hydrogen atoms, except those involved in hydrogen bonding, are omitted for clarity. Phenyl groups are rendered in wireframe, also for visual simplicity. (b) Molecular structure (30% probability ellipsoids) of $P(C(O)NHPh)_3$ (**2o**). Only the major disordered component is shown for clarity. For metric parameters, see the Supporting Information.

https://doi.org/10.1021/acscatal.2c02199
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were accompanied by a mixture of unattributed signals and the ratios of these products, alongside the observed reaction times, were inconsistent.

Catalytic hydrophosphination using PH_3 as a substrate was also attempted. The reaction was initially conducted on an NMR scale in C_6D_6, as detailed in Scheme 2 and examined by ^1H and ^{31}P NMR spectroscopy. Within 30 min PH_3 was no longer visible in the ^{31}P NMR spectrum, with only a single major resonance being apparent at −46.3 ppm. The reaction was repeated on a preparative scale in toluene, from which a white powder, $P(C(O)NHPh)_3$ (**2o**), was isolated in a 68% yield. The structure was confirmed by XRD conducted on crystals grown from a THF/Et_2O solution (Figure 1b). As with compound **2g**, the crystal structure features N−H···O hydrogen-bonding interactions. In this case these interactions are solely intramolecular, forming a spiral of the three amido groups about the phosphorus center. The synthesis of compound **2o** was described in 1959 by Buckler,[44] but their route provided only a 13% yield after 4 days and required storage of PH_3, indicating the utility of our approach.

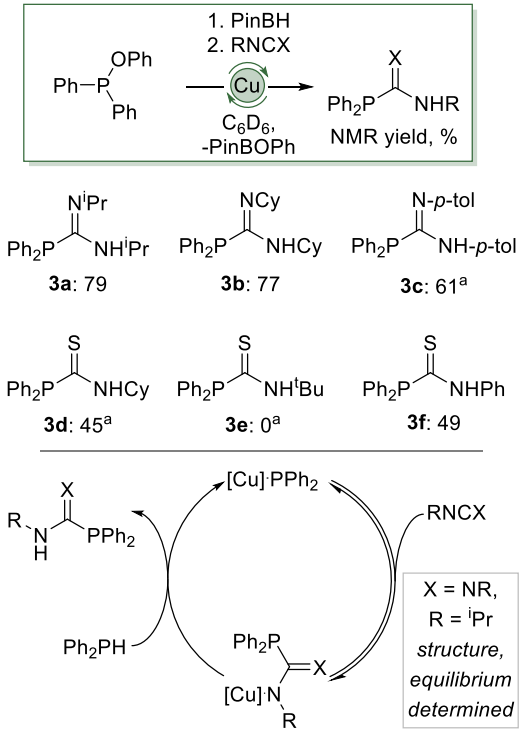
The potential for (IPr)CuO-*t*-Bu to act as a precatalyst in the hydrophosphination of other heterocumulenes, with Ph_2PH generated *in situ*, was then explored (Scheme 3). These reactions were generally slower than those to generate phosphaureas and required higher catalyst loadings, elevated temperatures, or both. Using 2.5 mol % of (IPr)CuO-*t*-Bu as the precatalyst, hydrophosphination of *i*-PrNCN-*i*-Pr and CyNCNCy gave good conversion to the phosphaguanidine overnight. With *p*-tolCNC-*p*-tol as the substrate, 3 days at 80 °C was required to achieve good conversion. We previously proposed that the hydrophosphination of isocyanates proceeded via a phosphaamidate, which we were able to structurally characterize. We thus sought to isolate an analogous phosphaguanidinate intermediate from a copper(I) phosphide and carbodiimide. The reaction of (IPr)$CuPPh_2$ with 5 equiv of isopropylcarbodiimide gave access to (IPr)CuN(*i*-Pr)C(N-*i*-Pr)PPh_2 which was characterized by SC-XRD and found to bond in a κ_1-N fashion (see the Supporting Information).

During characterization of this species by NMR spectroscopy, the insertion of the carbodiimide was found to be reversible. Thus, the Gibbs free energy change at 298 K could be estimated for the reaction of *i*-PrNCN-*i*-Pr and (IPr)$CuPPh_2$ via a van 't Hoff analysis and was found to be −7.9 kJ mol^{-1} ($\Delta H = -88.1 \pm 4.1$ kJ mol^{-1} and $\Delta S = -269 \pm 13$ J mol^{-1} K^{-1}; see the Supporting Information). This equilibrium is likely to influence the rate of reaction for carbodiimides and may account for their slower hydrophosphination in comparison to the isocyanates observed here. Nevertheless, the addition of diphenylphosphine to (IPr)CuN(*i*-Pr)C(N-*i*-Pr)PPh_2 provided evidence of compound **3a** and (IPr)$CuPPh_2$, allowing us to propose a revised mechanism (Scheme 3).

For the hydrophosphination of isothiocyanates, 5 mol % of the precatalyst was used. Even with this higher loading, after 24 h PhNCS was observed to produce only 49% of the phosphathiourea at room temperature and an elevated temperature was not found to improve the conversion. CyNCS was less reactive, requiring heating at 80 °C to achieve a modest conversion of 45% after 24 h. *t*-BuNCS exhibited no reactivity after prolonged heating, whereupon darkening of the reaction mixture was taken to indicate catalyst death.

We have thus reported a new route to generate P−H bonds from phosphite, phosphonite, and phosphinite esters via reduction with pinacolborane. This reaction tolerates an extensive range of substituents and readily generates PH_3 and primary and secondary phosphines. This novel protocol can be coupled with the hydrophosphination of a range of isocyanates, carbodiimides, and isothiocyanates to produce phosphacarboxamide derivatives without the need to handle smelly, toxic, and pyrophoric phosphines. This approach is demonstrably scaleable, providing sufficient material of two phosphaureas to allow crystallographic characterization. The isolation and characterization of (IPr)CuN(*i*-Pr)C(N-*i*-Pr)PPh_2 provided a rationale for the relative reaction rates of different heterocumulenes.

Scheme 3. (Top) Catalytic Hydrophosphination of Heterocumulenes with Ph_2PH Generated *In Situ* from Ph_2POPh (0.10 mmol) and PinBH (14.5 μL, 0.10 mmol) with Catalytic (IPr)CuO-*t*-Bu (2.5 mol % for 3a−c, 5 mol % for 3d−f) in C_6D_6 (0.5 mL)[a] and (Bottom) the Proposed Mechanism



[a] $^{31}P\{^1H\}$ NMR spectroscopic yields calculated by use of a Ph_3PO internal standard. Legend: (a) reaction at 80 °C.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acscatal.2c02199.

Characterization data for the compounds, NMR data, and crystallographic details (PDF)

Crystallographic data for $PhP(C(O)NHPh)_2$ (**2g**),$P(C(O)NHPh)_3$ (**2o**) and (IPr)CuN(*i*-Pr)C(N-*i*-Pr)PPh_2 (CIF)

https://doi.org/10.1021/acscatal.2c02199
ACS Catal. 2022, 12, 8214−8219

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Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

D.J.L. thanks the Royal Society for the support of a University Research Fellowship. We wish to thank the EPSRC for funding and the University of Bath and MC^2 for use of their analysis facilities. We thank the EPSRC UK National Crystallography Service at the University of Southampton for the collection of the crystallographic data for **2o**.[45]

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https://doi.org/10.1021/acscatal.2c02199
ACS Catal. 2022, 12, 8214−8219