


 Cite this: *Chem. Commun.*, 2020, 56, 13359

 Received 21st August 2020,
 Accepted 30th September 2020

DOI: 10.1039/d0cc05694d

rsc.li/chemcomm

The first ring-expanded NHC–copper(i) phosphides as catalysts in the highly selective hydrophosphination of isocyanates†

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A range of N-heterocyclic carbene-supported copper diphenylphosphides (NHC = IPr, 6-Dipp, SIMes and 6-Mes) were synthesised. These include the first reports of ring-expanded NHC–copper(i) phosphides. The compounds were characterised by NMR spectroscopy and X-ray crystallography. Reaction of (6-Dipp)CuPPh₂ with isocyanates, isothiocyanates and carbon disulfide results in the insertion of the heterocumulene into the Cu–P bond. The NHC–copper phosphides were found to be the most selective catalysts yet reported for the hydrophosphination of isocyanates. They provide access to a broad range of phosphinocarboxamides in excellent conversion and good yield.

The exploitation of metal phosphides is a widespread route to organophosphorus compounds.^{1–4} Beyond their stoichiometric application, catalytic intermediates of the form L_nM_nPR₂ have been integral to a green revolution in organophosphorus chemistry, especially when the metals concerned are Earth-abundant first row transition metals (*i.e.*, Fe, Co). These mid-d-block systems, however, are prone to redox-switching and single-electron transfer reactions which, coupled with the stability of phosphorus centred radicals, often result in undesirable side reactions.^{5–7}

The propensity of copper(i) towards the well-defined isohypsic reaction steps of σ -bond metathesis, and insertion of unsaturated substrates should allow copper(i) phosphides to overcome such issues. Despite this appeal, copper phosphides often form only as complex oligomers, with a concomitant reduction in reactivity.^{8–17} Low-coordinate copper phosphides

supported by sterically demanding ligands are far less common, as evidenced by the small number of structurally characterised (NHC)CuPR₂ (NHC = N-heterocyclic carbene) complexes hitherto reported.¹⁸ Despite their relative rarity, such species hint at the potential of low-molecularity copper(i) phosphides. For example, [(NHC)CuPPh₂]₃ complexes (NHC = I^tPr, 1,3-bis(isopropyl)-imidazol-2-ylidene; I^tBu, 1,3-bis(*tert*-butyl)-imidazol-2-ylidene), mediate the hydrophosphination of terminal alkynes at elevated temperature.¹⁹

In contrast to the formation of alkyl and alkenyl phosphines from alkenes and alkynes, hydrophosphination of isocyanates has been far less well-studied. Often, significant competing side-reactivity⁶ or poor substrate scope²⁰ hamper access to, and thus exploitation of, phosphinocarboxamide products. These products are potential synthetic intermediates and, particularly, ligands owing to their polydentate nature comprising both hard and soft donor atoms.^{21–23}

Ring expanded N-heterocyclic carbenes (RE-NHCs) can offer increased stability and reduced molecularity to reactive metal species through their significant steric demand.^{24–26} RE-NHC–copper(i) complexes such as copper(i) halides and copper(i) alkoxides have been established as having enhanced catalytic activity over their five-membered ring counterparts.^{27–29}

We thus set out to synthesise and characterise a range of low-coordinate copper phosphide species supported by both 5- and 6-membered NHCs in order to evaluate their potential as catalytic intermediates. Herein we report the rational synthesis of four (NHC)CuPPh₂ compounds (NHC = IPr, 6-Dipp, SIMes and 6-Mes), including the first examples of RE-NHC copper phosphides. These compounds were fully characterised by NMR spectroscopy and X-ray crystallography and investigated for their onward reactivity towards heterocumulenes. This access to well-defined putative reaction intermediates allows us to report the most selective catalytic hydrophosphination of isocyanates found to date.

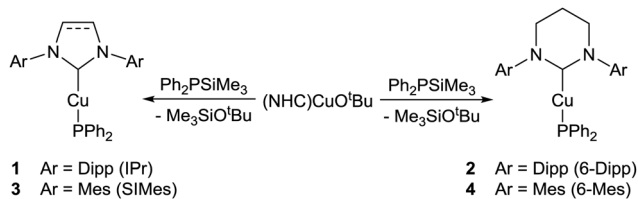
Addition of 1 equivalent of Ph₂PSiMe₃ to a colourless benzene solution of (IPr)CuO^tBu resulted in the instantaneous

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† Electronic supplementary information (ESI) available: General synthetic experimental details, NMR spectra, X-ray analysis of compounds 1–7. DOSY experiments, details of the computational analysis and atomic coordinates of the DFT computed structures. CCDC 2014370–2014376. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/d0cc05694d



Scheme 1 Synthesis of (NHC)CuPPh₂ complexes.

appearance of a yellow colouration and the emergence of new peaks in the ¹H and ³¹P NMR spectra. (IPr)CuPPh₂, **1**, was isolated from this solution (Scheme 1) in 81% yield, and characterised by the presence of a ³¹P{¹H} NMR resonance at δ –26.1 ppm, consistent with the data previously reported by Nolan and co-workers.³⁰ Application of these conditions to (NHC)CuOtBu (NHC = 6-Dipp, SIMes and 6-Mes) yielded (6-Dipp)CuPPh₂, **2**, as a yellow solid, as well as (SIMes)CuPPh₂, **3**, and (6-Mes)CuPPh₂, **4**, as orange solids (Scheme 1). Compounds **2**, **3** and **4** each exhibit a single ³¹P{¹H} NMR resonance at δ –23.8, –32.0 and –23.5 ppm respectively. The presence of peaks attributed to ^tBuOSiMe₃ in the ¹H NMR spectra of each of these reactions was interpreted as an indication that the formation of compounds **1–4** occurs *via* a Cu–O/P–Si σ-bond metathesis.

Crystals suitable for single crystal X-ray diffraction analysis of **1–4** were grown from benzene/hexane solutions at room temperature. Compounds **1** (Fig. S1, ESI†) and **2** (Fig. 1a), featuring bulky diisopropylphenyl groups on the flank of the NHC, exhibit monomeric structures with a near-linear geometry at the copper centre (**1**: C1–Cu1–P1 177.09(6)°; **2**: C1–Cu1–P1 177.51(6)°). Compounds **3** (Fig. 1b) and **4** (Fig. S2, ESI†), containing less sterically-encumbering mesityl groups, adopt dimeric crystal structures in which the copper centres are three-coordinate, bonding to two bridging phosphorus atoms to give approximately rhomboid four-membered rings (**3**: P1–Cu1–P1ⁱ 88.712(16)°, Cu1–P1–Cu1ⁱ 91.286(16)°; **4**: P1–Cu1–P2 85.61(3)°, Cu1–P2–Cu2 94.66(3)°). Previous reports of dimeric NHC–copper(i) complexes supported by less bulky NHCs feature short Cu···Cu distances of 2.23–2.31 Å, which were interpreted as indicating the presence of copper–copper interactions. The longer Cu···Cu interatomic distances of compounds **3** (3.3502(7) Å) and **4** (3.4852(5) Å) suggest there is no significant interaction between the metal centres in these two cases. Comparatively, the only other structurally characterised (NHC)CuPPh₂, [(^tBu)CuPPh₂]₃, adopts a trimeric structure in the solid state.¹⁹

The Cu–C_{NHC} bond distances of compounds **1–4** range between 1.90–1.97 Å. The monomeric complexes, **1** (1.9037(17) Å) and **2** (1.9272(18) Å), possess shorter bonds than in **3** (1.9234(15) Å) and **4** (1.969(3), 1.965(3) Å), an observation attributed to the increased steric demand provided by two bridging phosphides. These compare with the even longer Cu–C_{NHC} bonds of 1.990–1.997 Å observed in trimeric [(^tBu)CuPPh₂]₃.¹⁹ Complexes **2** and **4**, featuring ring-expanded NHCs, have noticeably longer Cu–C_{NHC} bonds than **1** and **3** respectively, likely due to the enhanced steric demand of the flanking aryl groups resulting from the increased N–C–N bond angle of the NHC. These trends are conserved in the Cu–P bond

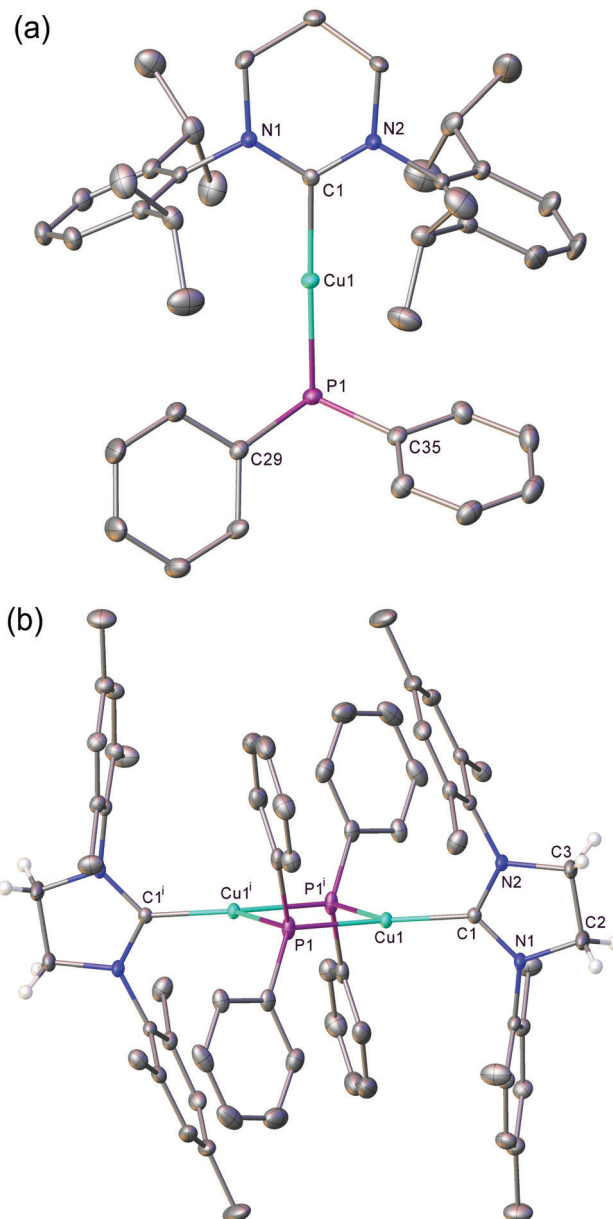


Fig. 1 ORTEP representations (30% probability ellipsoids) of (a) compound **2** and (b) compound **3**. Hydrogen atoms except those on the NHC backbone of **3** are omitted for clarity. Selected bond lengths (Å) and angles (°): (**2**) Cu1–P1 2.2113(5), Cu1–C1 1.9272(18), P1–C29 1.835(2), P1–C35 1.836(2), C1–Cu1–P1 177.51(6), Cu1–P1–C29 107.31(6), Cu1–P1–C35 102.92(6), C29–P1–C35 105.12(9); (**3**) Cu1–P1 2.3298(5), Cu–P1ⁱ 2.3558(5), Cu1–C1 1.9234(15), P1–C22 1.824(2), P1–C28 1.8208(18), C1–Cu1–P1 137.59(5), C1–Cu1–P1ⁱ 133.14(4), P1–Cu1–P1ⁱ 88.712(16), Cu1–P1–Cu1ⁱ 91.286(16), Cu1–P1–C22 110.55(5), Cu1–P1–C28 121.30(6).

distances which are longer for the RE–NHC containing compounds, **2** and **4**, compared to their respective 5-membered counterparts, **1** and **3**, (**1**: 2.2079(5) Å, *versus* **2**: 2.2113(5) Å; **3** 2.3298(5) Å, *versus* **4** 2.3803(9), 2.3908(8) Å) and wherein the dimeric species **3** and **4** show greater Cu–P distances than the monomeric compounds, **1** and **2**.

In order to investigate the persistence of the observed solid-state structures in solution, the compounds were interrogated



by diffusion ordered ^1H NMR spectroscopy (DOSY). Compounds **1** and **2** were found to have hydrodynamic radii that corresponded to their crystallographically derived monomeric structures (**1**: $r_{\text{DOSY}} = 5.40 \text{ \AA}$, $r_{\text{comp}} = 5.31 \text{ \AA}$; **2**: $r_{\text{DOSY}} = 5.27 \text{ \AA}$, $r_{\text{comp}} = 5.52 \text{ \AA}$). The hydrodynamic radius observed by DOSY for compound **3** showed a close correlation with that calculated for its dimeric structure seen in the solid state (**3**: $r_{\text{DOSY}} = 6.03 \text{ \AA}$, $r_{\text{comp}} = 6.50 \text{ \AA}$). This interpretation is corroborated by the low-temperature (235 K) $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **3** which shows a broad triplet for the carbenic carbon from a $^2J_{^{13}\text{C}-^{31}\text{P}}$ coupling to the two bridging but equivalent phosphorus atoms. Compound **4**, however, was found to have a hydrodynamic radius that was more consistent with it existing in solution as a monomer, not the dimer observed in the solid state (**4**: $r_{\text{DOSY}} = 5.29 \text{ \AA}$, $r_{\text{comp}} = 5.21 \text{ \AA}$ for monomer, $r_{\text{comp}} = 6.55 \text{ \AA}$ for dimer).

Addition of a slight excess of isopropyl isocyanate to a yellow C_6D_6 solution of **2** resulted in a loss of colour. Analysis by $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy revealed the attenuation of the resonance assigned to **2**, and the appearance of a single major resonance at δ 2.2 ppm. Comparison to the $^{31}\text{P}\{^1\text{H}\}$ NMR signal of δ -4.0 ppm observed for the free phosphorene $\text{Ph}_2\text{PC}(\text{O})\text{NH}(\text{tPr})$ was interpreted as implying that insertion of the isocyanate into the Cu-P bond had occurred (Scheme 2).⁶ The corresponding ^1H NMR spectrum exhibited a new set of peaks consistent with a complex incorporating the 6-Dipp ligand and the isopropyl isocyanate.

The formation of $(6\text{-Dipp})\text{Cu}[\text{N}(\text{tPr})\text{C}(\text{O})\text{PPh}_2]$, **5**, was confirmed by X-ray diffraction analysis, performed on colourless single crystals which grew from the reaction solution when left to stand at room temperature (Fig. 2). In contrast to previously reported phosphoreneates which comprise a $\kappa^2\text{-}(\text{N},\text{O})$ coordination mode and delocalised π -bonding,²¹⁻²³ **5** features κ^1 -coordination of the nitrogen to the copper atom. This results in a relatively short Cu-N bond length (1.9053(11) \AA), with C-N (1.3314(19) \AA) and C=O (1.2383(17) \AA) bond lengths consistent with localised single and double bonds respectively. Evidence for the persistence of this bonding mode in solution can be inferred from the $^{31}\text{P}\{^1\text{H}\}$ NMR signal at 2.2 ppm. This value is significantly downfield of known Zr(IV) and Y(III) compounds which feature a delocalised $\kappa^2\text{-}(\text{N},\text{O})$ bonding mode in the solid state and solution $^{31}\text{P}\{^1\text{H}\}$ NMR spectra containing resonances at δ -12.1 and -20.1 ppm respectively.^{21,22}

The facile insertion of an isocyanate into the Cu-P bond of **2** prompted a study of other electrophiles. Reactions with excesses of phenyl isothiocyanate and carbon disulfide resulted in insertion of the respective heterocumulene into the Cu-P bond to give new compounds, **6** and **7** (Scheme 2). X-Ray diffraction

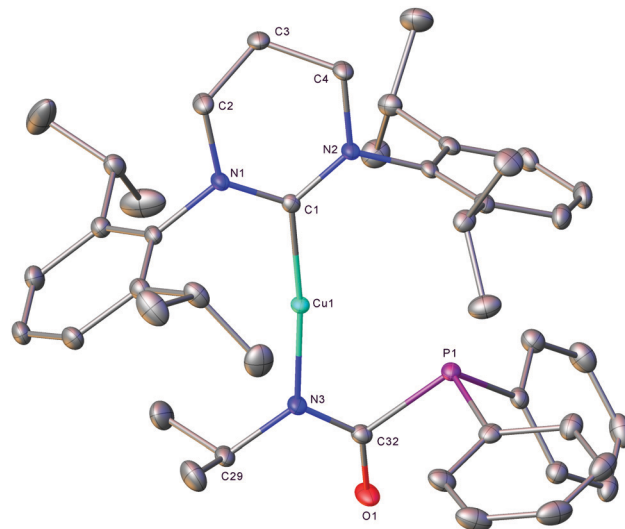
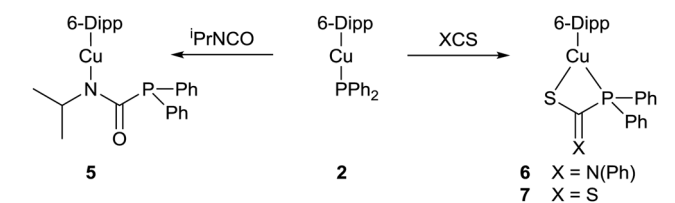


Fig. 2 ORTEP representations (30% probability ellipsoids) of compound **5**. Hydrogen atoms are omitted for clarity. Selected bond lengths (\AA) and angles ($^\circ$): Cu1-N3 1.9053(11), Cu1-C1 1.9283(13), N3-C29 1.4871(18), N3-C32 1.3314(19), O1-C32 1.2383(17), P1-C32 1.8826(14), C1-Cu1-N3 173.90(5), Cu1-N3-C29 124.19(9), Cu1-N3-C32 120.92(9), N3-C32-O1 128.34(13), N3-C32-P1 109.84(9), O1-C32-P1 121.76(11).

analysis performed on colourless crystals of **6** (Fig. S3, ESI[†]) and red crystals of **7** (Fig. S4, ESI[†]) reveal that the copper centre is bonded to the sulfur atom in both cases. In contrast to the phosphoreneate **5**, the phosphorus atoms in compounds **6** and **7** also coordinate to the metal centre resulting in CuSCP four-membered rings in both cases. The $^{31}\text{P}\{^1\text{H}\}$ NMR spectra of **6** and **7** each reveal a single major resonance, at δ 28.8 and 45.2 ppm respectively.

Addition of 1 equivalent of diphenylphosphine to a colourless solution of compound **5** resulted immediately in yellow colouration, and inspection of the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum suggested that $\text{Ph}_2\text{PC}(\text{O})\text{NH}(\text{tPr})$ had been liberated with the regeneration of complex **2**. These stoichiometric reactions could be assembled into a catalytic manifold (Fig. 3) to hydrophosphinate a range of isocyanates with diphenylphosphine in C_6D_6 in the presence of 1 mol% of **1-4** (Table 1).

Whilst catalyst-free hydrophosphination of isocyanates can be conducted under strictly neat conditions, the reactivity was limited to a range of small aromatic isocyanates;²⁰ cyclohexyl



Scheme 2 Reactivity of $(6\text{-Dipp})\text{CuPPh}_2$, **2**, with $^t\text{PrNCO}$, PhNCS and CS_2 .

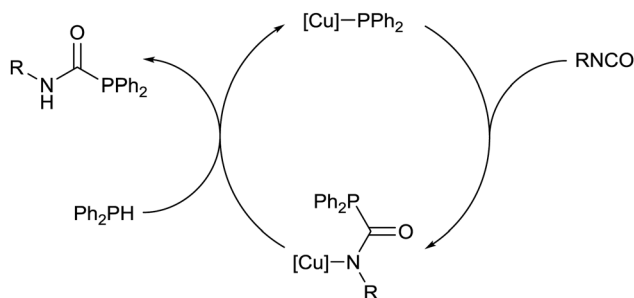


Fig. 3 Proposed mechanism for the copper-catalysed hydrophosphination of isocyanates.



Table 1 Catalytic hydrophosphination of isocyanates (0.20 mmol) with Ph₂PH (35 μL, 0.20 mmol) and 1 mol% **1–4** in C₆D₆ (0.5 mL)

Entry	R	Catalyst	Time (h)	Conversion ^a (%)	I:II
1	ⁱ Pr	1	0.5	90	100:0
2		2	5	96	100:0
3		3	0.5	> 99 (70) ^b	100:0
4		4	0.5	> 99	100:0
5	^t Bu	1	2	94	100:0
6		2	4	81	100:0
7		3	2	91 (67) ^b	100:0
8		4	2	96	100:0
9	Ph	1	0.5	> 99	100:0
10		2	0.5	48	92:8
11		3	0.5	> 99 (77) ^b	95:5
12		4	0.5	> 99	100:0
13	Cy	3	0.5	> 99 (79) ^b	100:0
14		4	0.5	> 99	100:0

^a Conversions based on relative ¹H and ³¹P NMR spectroscopic integrations of starting material and product. ^b Isolated yields of **I** from a preparative scale reaction in toluene, see ESI.

isocyanate exhibited no reactivity under such conditions. In contrast, 1 mol% of complexes **3** and **4** brought about full conversion of both cyclohexyl and isopropyl isocyanate within 30 minutes, and even the very sterically-congested *tert*-butyl isocyanate reached excellent conversions (>90%) within 2 hours. **2** was found to catalyse the reaction more slowly than **1**, **3**, and **4**, attributable to the greater steric demands of the 6-Dipp ligand.

In contrast to the iron-catalysed hydrophosphination of isocyanates,⁶ only very limited amounts of double insertion of the N=C bond were observed for phenyl isocyanate when catalysed by **2** or **3**, and none was observed when **1** or **4** were the precatalyst. In all other cases, the reaction was specific for single insertion, and in no case was the formation of Ph₂PPP₂ observed.

In conclusion, the synthesis of a series of NHC-copper(I) phosphides was accomplished by reaction of alkoxide precursors with Ph₂PSiMe₃. Complexes **1–4**, including the first reports of RE-NHC copper(I) phosphides (compounds **2** and **4**), were found to be either monomeric or dimeric in the solid- and solution-state depending on the steric bulk of the NHC ligand. Reaction of **2** with isocyanates, isothiocyanates and carbon disulfide resulted in the insertion of the heterocumulene into the Cu–P bond to give compounds **5–7**. Compounds **1–4** were found to be highly active and selective precatalysts for the hydrophosphination of isocyanates. We continue to investigate the nature and scope of this catalytic reactivity, including its application in the hydrophosphination of other heterocumulenes.

This research made use of the Balena High Performance Computing (HPC) Service at the University of Bath. DJL thanks the Royal Society for the support of a University Research

Fellowship. We acknowledge financial support from the EPSRC Centre for Doctoral Training in Catalysis (EP/L016443/1) for JWH.

Conflicts of interest

There are no conflicts to declare.

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