Diazoalkanes react with a bis(phosphino)borate copper(I) source to generate $[Ph_2BP^{tBu}{}_2]Cu(\eta^1\text{-}N_2CR_2)$, $[Ph_2BP^{tBu}{}_2]Cu(CPh_2)$, and $[Ph_2BP^{tBu}{}_2]Cu\text{–}N(CPh_2)(NCPh_2)$†

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$[Ph_2BP^{tBu}{}_2]Cu\text{–}L$ complexes react with diazoalkanes to generate structurally unusual η^1-diazoalkane adducts, a terminal carbene, and an η^1-azine adduct.

Metal-catalyzed carbene transfer from diazoalkanes to organic substrates has become a versatile technique in synthesis, and copper catalysts have been particularly well studied in this regard.[1,2] Careful study of copper carbene complexes ($Cu{=}CR_2$), the presumed reactive intermediates in these reactions, serves to deepen understanding of these copper-catalyzed transformations. Identifying factors that affect copper carbene stability, characterizing specific decomposition pathways, and understanding the nature of copper–diazoalkane interactions prior to copper–carbene bond formation are therefore issues of fundamental interest.

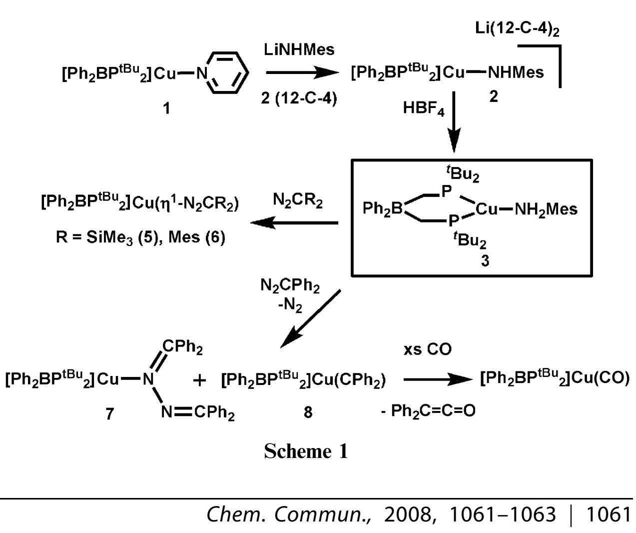
Whereas α-heteroatom stabilized copper carbenes are well known,[3] only two examples of non-heteroatom stabilized copper carbenes have been reported. Both of these derivatives are stabilized by bidentate, monoanionic N-chelates. The first such example was reported by Straub and Hofmann in 2001 and assigned using spectroscopic data.[4] Warren and co-workers later reported X-ray structural data for a β-diketiminato $Cu{=}CPh_2$ complex.[5] Both of these systems mediate catalytic cyclopropanation reactions and employ diazoalkane precursors to generate the carbenes of interest. In this context we note that the presumed diazoalkane adduct intermediates *en route* to carbene formation were not observed, and to our knowledge no such species have been previously characterized for copper systems.

Our group has had an interest in exploiting (phosphino)borate ligands to stabilize mid-to-late first-row metals featuring metal ligand multiple bonds.[6] In this paper, we describe the utility of the bulky bis(phosphino)borate ligand[7] $[Ph_2BP^{tBu}{}_2] = Ph_2B(CH_2P^tBu_2)_2$ to generate unusual diazoalkane adducts of Cu^I. In addition, we establish that N_2CPh_2 reacts to generate the copper carbene complex $[Ph_2BP^{tBu}{}_2]Cu{=}CPh_2$ as verified by NMR spectroscopy and group transfer of the carbene unit. This latter species is unstable in the presence of additional N_2CPh_2 in solution and as such generates the structurally novel azine adduct $[Ph_2BP^{tBu}{}_2]Cu\text{–}N(CPh_2)(NCPh_2)$ as a side product.

The synthesis of copper(I) species of the type $[Ar_2BP^R{}_2]CuL$ (L = *e.g.* CH_3CN, PR_3, CO) was reported recently.[8] Preliminary group transfer studies with diazoalkanes suggested the necessity of a $[Ar_2BP^R{}_2]CuL$ precursor with a sufficiently labile L ligand to expose reactions of interest. The aniline adduct $[Ph_2BP^{tBu}{}_2]Cu(NH_2Mes)$ (Mes = 2,4,6-trimethylphenyl) proved key in this regard. Its synthesis (Scheme 1) proceeded from the neutral pyridine adduct $[Ph_2BP^{tBu}{}_2]Cu(pyridine)$ (**1**). Reaction of LiNHMes and excess 12-crown-4 with yellow **1** provided the anionic colorless amido complex $\{[Ph_2BP^{tBu}{}_2]CuNHMes\}\{Li(12\text{-crown-}4)_2\}$ (**2**). Protonation of **2** with HBF_4 (toluene, –90 °C) produced the colorless aniline adduct $[Ph_2BP^{tBu}{}_2]Cu(NH_2Mes)$ (**3**). Recrystallization of **3** from a THF–petroleum ether mixture provided the THF adduct $[Ph_2BP^{tBu}{}_2]Cu(THF)$ (**4**).

The X-ray crystal structures of complexes **2** and **3**, which are related by a proton transfer, are shown in Fig. 1. The crystal structure of **3** features a longer Cu–N distance (2.0758(3) Å) and more compressed Cu–N–C angle (118.46(2)°) when compared to its conjugate base **2** (1.962(1) Å and 136.43(1)°, respectively).‡ Gunnoe and co-workers have recently reported that the structurally related but neutral complex (dtbpe)Cu(NHPh) (dtbpe = $^tBu_2PCH_2CH_2P^tBu_2$) has an appreciably shorter Cu–N distance of 1.890(6) Å.[9]

When either **3** or **4** were mixed with $N_2C(SiMe_3)_2$ or N_2CMes_2, the stable diazoalkane adducts yellow $[Ph_2BP^{tBu}{}_2]Cu(\eta^1\text{-}N_2C(SiMe_3)_2)$ (**5**) and red $[Ph_2BP^{tBu}{}_2]Cu(\eta^1\text{-}N_2CMes_2)$ (**6**) formed rapidly and could be readily isolated (Scheme 1).



Scheme 1

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† Electronic supplementary information (ESI) available: Synthetic details, crystal structure diagrams of complexes **1–7** and spectroscopic data. See DOI: 10.1039/b713687k

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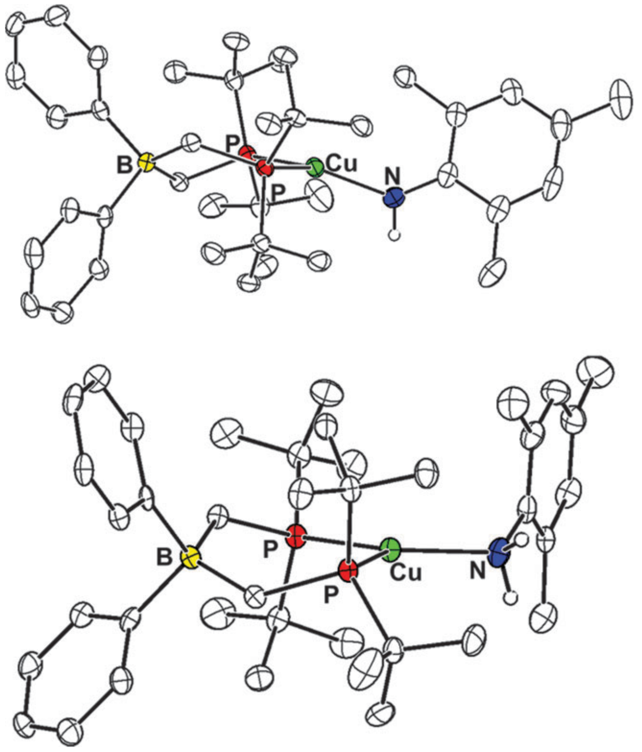

Fig. 1 Solid-state structure of {[PhBP$^{tBu}{}_2$]Cu(NH$_2$Mes)}{Li(12-crown-4)$_2$} (**2**) (top) and [PhBP$^{tBu}{}_2$]Cu(NH$_2$Mes) (**3**) (bottom). Only the anion of **2** is shown. N–H hydrogens are shown in calculated positions.

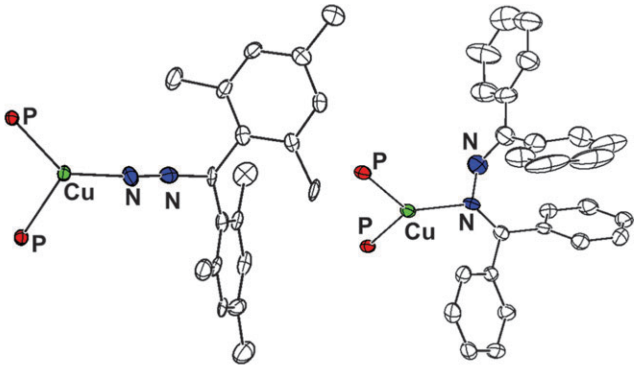

Fig. 2 Solid-state structures of [Ph$_2$BP$^{tBu}{}_2$]Cu(N$_2$CMes$_2$) (**6**) (left) and [Ph$_2$BP$^{tBu}{}_2$]Cu–N(=CPh$_2$)NCPh$_2$ (**7**) (right). Non-phosphorus atoms of the [Ph$_2$BP$^{tBu}{}_2$] ligands have been omitted for clarity.

We were surprised to find that these adducts are the only characterized examples of Cu^{I}-diazoalkane complexes to be reported, though Hofmann and co-workers have described a formally Cu^{III}-diazoalkane complex resulting from reduction of a chelating diazoalkane unit by a Cu^{I} precursor.[10] The observed N$_2$*C*R$_2$ ^{13}C{^{1}H} chemical shifts (δ 29.5 for **5** and δ 99.3 for **6**) and CN$_2$ vibrational frequencies (2108 cm^{-1} for **5** and 2041 cm^{-1} for **6**) are very similar to the corresponding values for the free diazoalkanes,[11] indicating that the diazoalkane moieties have not been significantly perturbed upon coordination to copper. The molecular structures of **5** and **6** (Fig. 2) feature N–N distances (1.200(8) Å for **5** and 1.1630(6) Å for **6**), N–C distances (1.237(9) Å for **5** and 1.3188(7) for **6**), and N–N–C angles (180.000(7)° for **5** and 176.50(6)° for **6**) that are notably similar to the corresponding parameters for the free diazoalkanes.[11] The Cu–N–N angle of **5** is linear (180.000(2)°) whereas for **6** the angle drops to 156.95(5)°.‡ For comparison, Hofmann's Cu^{III}-diazoalkane complex has severely bent Cu–N–N and N–N–C angles (123.8(2) and 134.3(3)°, respectively) owing to the reduced diazoalkane ligand.[10]

Complex **5** is stable to 110 °C in toluene solutions even in the presence of Lewis acid catalysts. Complex **6** decomposes to a complicated mixture of products when heated in hydrocarbon solutions, and though the product profile simplifies when Sm(OTf)$_3$ is added as a catalyst, no stable products were isolated from these thermolysis experiments, and no evidence for Cu=CR$_2$ bond formation was detected. The diazoalkane complex (dtbpe)Ni(η^2-N$_2$CPh$_2$) has been isolated by Hillhouse and co-workers and was shown to extrude N$_2$ and form (dtbpe)Ni=CPh$_2$ upon thermolysis in the presence of catalytic Sm(OTf)$_3$.[12] Perhaps an important distinction to note between this Ni system and the Cu-diazoalkane adducts **5** and **6** is that N$_2$CPh$_2$ binds in an η^2-NN mode to the L$_2$Ni^0 fragment, whereas N$_2$C(SiMe$_3$)$_2$ and N$_2$CMes$_2$ bind in an η^1-N fashion to the L$_2$Cu^I fragment described here.

When the less bulky diazoalkane reagent N$_2$CPh$_2$ was added to **3** or **4** at ambient temperature, N$_2$ release occurred spontaneously with concomitant formation of an inky blue solution and free NH$_2$Mes (in the case of **3**). A mixture of two Cu-containing species, ultimately assigned as [Ph$_2$BP$^{tBu}{}_2$]-Cu–N(=CPh$_2$)NCPh$_2$ (**7**, δ 39.9) and [Ph$_2$BP$^{tBu}{}_2$]Cu=CPh$_2$ (**8**, δ 64.8), could be detected by ^{31}P{^{1}H} NMR (Scheme 1). Quantitative conversion to **7** exclusively was achieved by the use of 2 equiv. or more of N$_2$CPh$_2$, and its assignment as a benzophenone azine adduct was verified by single-crystal X-ray diffraction (Fig. 2).‡ The N–N bond distance of 1.3962(3) Å in **7** is consistent with the azine N–N single bond formulation. The Cu center in **7** is best described as trigonal planar, as the Cu–N$_{distal}$ distance (2.7649(3) Å) is much longer than the Cu–N$_{proximal}$ bond length of 2.0166(2) Å. Complex **7** presumably forms from the reaction between the intermediate carbene species **8** and unreacted N$_2$CPh$_2$; such C–N bond forming reactions between isolated terminal metal carbenes and diazoalkanes have been observed for metals other than copper.[13]

Under dilute conditions, as high as 70% conversion to carbene complex **8** has been achieved. This species features an intense band at λ_{max} = 583 nm (ε = (est.) 12 000 M^{-1} cm^{-1}) that likely arises from MLCT charge transfer into the Cu=*CPh$_2$* unit. Warren has observed an optical transition of similar energy and intensity in the related β-diketiminato Cu=CPh$_2$ species.[5] To cement the assignment of **8**, solutions of [Ph$_2$BP$^{tBu}{}_2$]Cu=^{13}CPh$_2$ (**8-^{13}C**) were generated using N$_2$^{13}CPh$_2$ in place of unlabelled diphenyldiazomethane. A diagnostic triplet at δ 331.5 was clearly visible in the ^{13}C{^{1}H} NMR spectrum ($^2J_{PC}$ = 41 Hz) (Fig. 3), and the ^{31}P{^{1}H} NMR spectrum of **8-^{13}C** featured a corresponding sharp doublet (δ 64.8, $^2J_{PC}$ = 41 Hz). A slightly larger value for $^2J_{PC}$ was observed for Hillhouse's (dtbpe)Ni=CPh$_2$ species (δ 222, $^2J_{PC}$ = 51 Hz).[12] Interestingly, the Cu=*C*Ph$_2$ ^{13}C{^{1}H} NMR chemical shift in **8-^{13}C** is considerably further downfield than for other reported copper carbene species,[3–5]

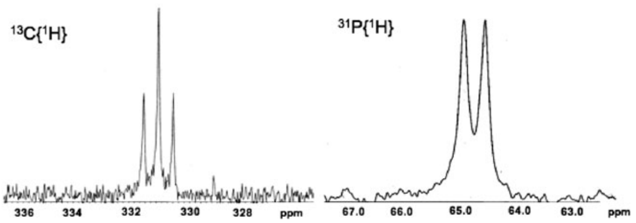

Fig. 3 $^{13}C\{^1H\}$ signal (left) and $^{31}P\{^1H\}$ signal (right) for $[Ph_2BP^{tBu}{}_2]Cu{=}^{13}CPh_2$ (**8-^{13}C**).

though it is certainly within the range typically observed for terminal metal carbene complexes.[5,14] As further evidence for the presence of the "CPh_2" carbene functionality in **8**, we observed quantitative carbene transfer to CO to generate ketene $Ph_2C{=}C{=}O$ and $[Ph_2BP^{tBu}{}_2]Cu(CO)$ upon exposure of solutions of **8** to excess carbon monoxide (Scheme 1). Carbene transfer to CO is also characteristic of the Ni and Cu carbenes of Hillhouse and Warren, respectively.[5,12] Complex **8** did not readily transfer its carbene unit to olefins such as 1-hexene or styrene.

Whereas Warren's β-diketiminato copper carbene complex is stable at room temperature, complex **8** loses $Ph_2C{=}CPh_2$ even at −30 °C. This fact has thus far precluded its crystallization from solution. The β-diketiminato $Cu{=}CPh_2$ species degrades similarly upon thermolysis.[5]

A computational study of **8** was undertaken to probe the Cu–C distance by DFT methods.[15] A diphenylcarbene unit was attached to the $[Ph_2BP^{tBu}{}_2]Cu$ fragment taken from the atomic coordinates in the solid-state structure of **1**. Geometry optimization calculations using various initial Cu–C distances all gave the same optimized geometry, featuring trigonal planar geometries at both the copper center and the carbene carbon atom, with a Cu–C distance of 1.933 Å. Significantly shorter distances have been determined experimentally for the previously reported $M{=}CR_2$ (M = Cu, Ni) complexes (1.834–1.859 Å).[5,12] It is possible that the long predicted Cu–C distance in **8** is experimentally manifested by the relatively small value for $^2J_{PC}$ and the significantly deshielded carbene carbon atom. It must however be noted that optimizing the geometry of **8** while fixing the Cu–C distance to be either 1.830 or 2.030 Å gave structures whose energies spanned a range of only 1.0 kcal mol^{-1}, indicating that the molecule's potential energy surface is quite flat with regard to the Cu–C distance.

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Notes and references

‡ Details of the X-ray diffraction studies: **1**, $C_{18}H_{28}BCuNP_2$: orthorhombic, *Fdd*2, a = 16.5848(13), b = 30.917(2), c = 13.3863(10) Å, V = 6863.8(9) Å^3, Z = 8, μ(Mo-Kα) = 0.729 mm^{-1}, 8664 total reflections, 2460 independent (R_{int} = 0.0409) with $I > 2\sigma(I)$; **2**, $C_{60}H_{106}BCuLiNO_8P_2$: monoclinic, $P2_1/c$, a = 11.9146(9), b = 21.3858(16), c = 24.4619(18) Å, β = 92.5560(10)°, V = 6226.8(8) Å^3, Z = 8, μ(Mo-Kα) = 0.905 mm^{-1}, 72625 total reflections, 14800 independent (R_{int} = 0.0841) with $I > 2\sigma(I)$; **3**, $C_{39}H_{63}BCuNP_2$: monoclinic, $P2_1/c$, a = 10.186(5), b = 17.079(8), c = 22.083(7) Å, β = 98.24(4)°, V = 3802(3) Å^3, Z = 4, μ(Mo-Kα) = 0.685 mm^{-1}, 31590 total reflections, 7306 independent (R_{int} = 0.0990) with $I > 2\sigma(I)$; **4**, $C_{34}H_{58}BCuOP_2$: orthorhombic, *Fdd*2, a = 17.548(3), b = 30.333(5), c = 12.818(3) Å, V = 6823(2) Å^3, Z = 8, μ(Mo-Kα) = 0.758 mm^{-1}, 3639 total reflections, 2005 independent (R_{int} = 0.0385) with $I > 2\sigma(I)$; **5**, $C_{34}H_{59}BCuN_2P_2Si_2$: trigonal, $R\bar{3}c$, a = 21.4508(13), c = 47.633(3) Å, V = 18981(2) Å^3, Z = 15, μ(Mo-Kα) = 0.561 mm^{-1}, 37667 total reflections, 3067 independent (R_{int} = 0.0834) with $I > 2\sigma(I)$; **6**, $C_{49}H_{72}BCuN_2P_2$: monoclinic, $P2_1/c$, a = 11.6975(16), b = 17.955(2), c = 23.035(3) Å, β = 91.707(4)°, V = 4836.1(12) Å^3, Z = 4, μ(Mo-Kα) = 0.550 mm^{-1}, 22763 total reflections, 6798 independent (R_{int} = 0.1309) with $I > 2\sigma(I)$. **7**, $C_{56}H_{70}BCuN_2P_2$: monoclinic, $P2_1/c$, a = 12.0749(11), b = 22.347(2), c = 19.2412(18) Å, β = 104.625(2)°, V = 5023.8(8) Å^3, Z = 4, μ(Mo-Kα) = 0.536 mm^{-1}, 42567 total reflections, 11402 independent (R_{int} = 0.0617) with $I > 2\sigma(I)$. CCDC 659790–659796. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b713687k

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