Diazoalkanes react with a bis(phosphino)borate copper(i) source to generate [Ph2BPtBu2]Cu(N2CR2), [Ph2BPtBu2]Cu(CPh2), and [Ph2BPtBu2]Cu–N(CPh2)(NCPh2)

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Received (in Berkeley, CA, USA) 6th September 2007, Accepted 14th December 2007

First published as an Advance Article on the web 17th January 2008

DOI: 10.1039/b713687k

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=CR2), 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 z-heteroatom stabilized copper carbens are well known,3 only two examples of non-heteroatom stabilized copper carbens 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-diketimino Cu=CH2 complex.5 Both of these systems mediate catalytic cyclopropanation reactions and employ diazoalkane precursors to generate the carbens 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 ligand7 Ph2BPtBu2 to generate unusual diazoalkane adducts, a terminal carbene, and an N1-azine adduct.

The synthesis of copper(i) species of the type [Ar2BP2]CuL (L = e.g. CH2CN, PR3, CO) was reported recently.8 Preliminary group transfer studies with diazoalkanes suggested the necessity of a [Ar2BP2]CuL precursor with a sufficiently labile L ligand to expose reactions of interest. The aniline adduct [Ph2BPtBu2]Cu(NH2Mes) (Mes = 2,4,6-trimethylphenyl) proved key in this regard. Its synthesis (Scheme 1) proceeded from the neutral pyridine adduct [Ph2BPtBu2]Cu(pyridine) (1). Reaction of LiNHMes and excess 12-crown-4 with yellow 1 provided the anionic colorless amido complex ([Ph2BPtBu2]Cu(NHMes){Li(12-crown-4)} (2). Protonation of 2 with HBF4 (toluene, –90 °C) produced the colorless aniline adduct [Ph2BPtBu2]Cu(NH2Mes) (3). Recrystallization of 3 from a THF–petroleum ether mixture provided the THF adduct [Ph2BPtBu2]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 = 1BuPCH2CH2P(1Bu)2) has an appreciably shorter Cu–N distance of 1.890(6) Å.9

When either 3 or 4 were mixed with N2C(SiMe3)2 or N2CMSes2, the stable diazoalkane adducts yellow [Ph2BPtBu2]Cu(N1-azaC(SiMe3)2) (5) and red [Ph2BPtBu2]Cu(N1-azaCMSes2) (6) formed rapidly and could be readily isolated (Scheme 1).
angles (180.000(7))

The Cu–N–N angle of 6 for Cu

and N–N distances (1.237(9) Å for

for Cu

Similar energy and intensity in the related

and N–C angles (180.000(7)°

and 176.50(6)°

Non-phosphorus atoms of the [Ph2BP(C6H5)]

and for Cu


The Cu center in 7 is best described as trigonal planar, as the Cu–Nproximal distance (2.7649(3) Å) is much longer than the Cu–Ndistal distance (1.3962(3) Å) in 7 is consistent with the azide N–N single bond formulation. The Cu center in 7

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–CR2 bond formation was detected. The diazoalkane complex (dtbpe)Ni(η2−N2CPh2) has been isolated by Hillhouse and co-workers and was shown to extrude N2 and form

dtbpe)Ni(η2−N2CPh2) upon thermolysis in the presence of catalytic Sm(OTf)3. Perhaps an important distinction to note between this Ni system and the Cu-diazoalkane adducts 5 and 6 is that N2CPh2 binds in an η2−NN mode to the L2Ni0 fragment, whereas N2C(SiMe3)2 and N2C(Me3Si) bind in an η1−N fashion to the L2Cu1 fragment described here.

When the less bulky diazoalkane reagent N2CPh2 was added to 3 or 4 at ambient temperature, N2 release occurred spontaneously with concomitant formation of an inky blue solution and free NH2Mes (in the case of 3). A mixture of two Cucontaining species, ultimately assigned as [Ph2BP(C6H5)]

Cu–N(—CPh2)NCPh2 (7, δ 39.9) and [Ph2BP(C6H5)]Cu—CPh2 (8, δ 64.8), could be detected by 31P{1H} NMR (Scheme 1). Quantitative conversion to 7 exclusively was achieved by the use of 2 equiv. or more of N2CPh2, 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.

Under dilute conditions, as high as 70% conversion to carbene complex 8 has been achieved. This species features an intense band at λmax = 583 nm (ε (est.) 12 000 M−1 cm−1) that likely arises from MLCT charge transfer into the Cu—CPh2 unit. Warren has observed an optical transition of similar energy and intensity in the related β-diketiminate Cu—CPh2 species. To cement the assignment of 8, solutions of [Ph2BP(C6H5)]Cu=13CPh2 (8,13C) were generated using N2=13CPh2 in place of unlabelled diphenyl diazomethane. A diagnostic triplet at δ 331.5 was clearly visible in the 13C{1H} NMR spectrum (Jpc = 41 Hz) (Fig. 3), and the 31P{1H} NMR spectrum of 8,13C featured a corresponding sharp doublet (δ 64.8, 2JPC = 41 Hz). A slightly larger value for δJPC was observed for Hillhouse’s (dtbpe)Ni(η2−N2CPh2) with 13C{1H} NMR chemical shift in 8,13C is considerably further downfield than for other reported copper carbene species, 3−5
though it is certainly within the range typically observed for terminal metal carbene complexes.\textsuperscript{5,14} As further evidence for the presence of the “CPhz” carbene functionality in 8, we observed quantitative carbene transfer to CO to generate ketene Ph2C=O and [Ph2BP(Bu)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.\textsuperscript{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 Ph2C=CPh2 even at \(-30^\circ\text{C}\). This fact has thus far precluded its crystalization from solution. The β-diketiminato Cu=CPh2 species degrades similarly upon thermal degradation.\textsuperscript{5}

A computational study of 8 was undertaken to probe the Cu-C distance by DFT methods.\textsuperscript{15} A diphenylcarbene unit was attached to the [Ph2BP(Bu)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. 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.

This work was funded by BP (MC\(^2\) program) and the NSF (CHE-0132216). N. P. M. is grateful for an NSF Graduate Research Fellowship. J. Christopher Thomas is acknowledged for preliminary reaction screening. John Keith gave useful advice regarding DFT calculations, and Larry Henling provided crystallographic assistance. DFT calculations were done at the Materials and Process Simulation Center at the California Institute of Technology.

### Notes and references

1. Details of the X-ray diffraction studies: 1, C\textsubscript{18}H\textsubscript{28}BCuNP\textsubscript{2} : orthorrhombic, Fdd2, \(a = 16.5848\text{(13)}\), \(b = 30.917\text{(2)}\), \(c = 13.3863\text{(10)}\) Å, \(V = 6863.8\text{(9)}\) Å\(^3\), \(Z = 8\), \(\mu\text{(Mo-Kα)} = 0.729 \text{mm}^{-1}\), 8664 total reflections, 2460 independent \((R_{int} = 0.0409)\) with \(I > 2\sigma(I)\); 2, C\textsubscript{6}H\textsubscript{12}CuLiNO\textsubscript{2}P\textsubscript{2}: monoclinic, \(P2_1/c\), \(a = 11.9146\text{(9)}\), \(b = 21.3858\text{(16)}\), \(c = 24.4619\text{(18)}\), \(\beta = 92.5560\text{(10)}\), \(V = 6226.8\text{(8)}\) Å\(^3\), \(Z = 8\), \(\mu\text{(Mo-Kα)} = 0.905 \text{mm}^{-1}\), 7262 total reflections, 14800 independent \((R_{int} = 0.0841)\) with \(I > 2\sigma(I)\); 3, C\textsubscript{9}H\textsubscript{24}BCuNP\textsubscript{2}: monoclinic, \(P2_1/c\), \(a = 10.186\text{(5)}\), \(b = 17.079\text{(5)}\), \(c = 22.083\text{(7)}\), \(\alpha = 98.24\text{(4)}\), \(V = 3802\text{(3)}\) Å\(^3\), \(Z = 4\), \(\mu\text{(Mo-Kα)} = 0.685 \text{mm}^{-1}\), 31590 total reflections, 7306 independent \((R_{int} = 0.0990)\) with \(I > 2\sigma(I)\); 4, C\textsubscript{6}H\textsubscript{12}BCuOP\textsubscript{2}: orthorrhombic, Fdd2, \(a = 17.548\text{(3)}\), \(b = 30.533\text{(5)}\), \(c = 12.818\text{(3)}\), \(V = 6823\text{(2)}\) Å\(^3\), \(Z = 8\), \(\mu\text{(Mo-Kα)} = 0.758 \text{mm}^{-1}\), 3639 total reflections, 2005 independent \((R_{int} = 0.0385)\) with \(I > 2\sigma(I)\); 5, C\textsubscript{5}H\textsubscript{12}BCuNP\textsubscript{2}: trigonal, \(R3c\), \(a = 21.4508\text{(3)}\), \(c = 47.633\text{(3)}\), \(V = 18981\text{(2)}\) Å\(^3\), \(Z = 15\), \(\mu\text{(Mo-Kα)} = 0.561 \text{mm}^{-1}\), 3767 total reflections, 3067 independent \((R_{int} = 0.0834)\) with \(I > 2\sigma(I)\); 6, C\textsubscript{9}H\textsubscript{24}BCuOP\textsubscript{2}: monoclinic, \(P2_1/c\), \(a = 11.6975\text{(16)}\), \(b = 17.9555\text{(2)}\), \(c = 23.035\text{(3)}\), \(\beta = 91.7074\text{(4)}\), \(V = 4836.1\text{(12)}\) Å\(^3\), \(Z = 4\), \(\mu\text{(Mo-Kα)} = 0.550 \text{mm}^{-1}\), 22763 total reflections, 6798 independent \((R_{int} = 0.1309)\) with \(I > 2\sigma(I)\); 7, C\textsubscript{9}H\textsubscript{24}BCuNP\textsubscript{2}: monoclinic, \(P2_1/c\), \(a = 12.0749\text{(1)}\), \(b = 22.347\text{(2)}\), \(c = 19.241\text{(2)}\), \(\alpha = 104.625\text{(2)}\), \(V = 5023\text{(8)}\) Å\(^3\), \(Z = 4\), \(\mu\text{(Mo-Kα)} = 0.536 \text{mm}^{-1}\), 42567 total reflections, 11402 independent \((R_{int} = 0.0617)\) with \(I > 2\sigma(I)\).

For crystallographic data in CIF or other electronic format see DOI: 10.1039/b113768k.