**Tuning the Photophysical Properties of
Amidophosphine Complexes of Copper**
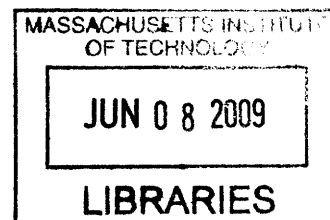
by

Seth F. Mickenberg

B.S., Chemistry (2007)

University of California, Berkeley

Submitted to the Department of Chemistry
in Partial Fulfillment of the Requirements for the Degree of
Master of Science in Chemistry

at the

Massachusetts Institute of Technology

June 2009

© 2009 Massachusetts Institute of Technology
All rights reserved

Signature of Author........

Department of Chemistry
May 22, 2009

Certified by.

Jonas C. Peters
Professor of Chemistry
Thesis Supervisor

Accepted by.........................................................................

Robert W. Field
Chairman, Departmental Committee on Graduate Students

# Tuning the Photophysical Properties of Amidophosphine Complexes of Copper

by

Seth F. Mickenberg

Submitted to the Department of Chemistry
on May 22, 2009 in Partial Fulfillment of the
Requirements for the Degree of
Master of Science in Chemistry

## ABSTRACT

A series of monomeric copper complexes that allow for the tuning of the emission properties is reported. Luminescence lifetimes up to 150 μs are observed in benzene solution at ambient temperature, which are comparable to the lifetimes of the longest-lived previously reported copper luminophores. These complexes also exhibit quantum yields up to $\phi = 0.70$ at 298 K. The results of time-dependent density functional theory (TDDFT) calculations indicate emission from a triplet state in all cases. The calculations also successfully correlate the energy of the transition from this triplet state to the energy of the observed emission. Such luminescence from a first-row metal is highly unusual, especially when considering the phosphine-based ligand framework used.

Thesis Supervisor: Jonas C. Peters
Title: Professor of Chemistry

## Introduction.

Transition metal complexes exhibiting highly efficient and long-lived luminescence have been widely studied[1] due to their possible uses in the fields of photochemical catalysis,[2] solar cell dye sensitizers,[3] light-driven fuel production,[4] and OLEDs.[5] However, most luminescent complexes make use of second- or third-row metals,[5b,6] and are therefore relatively expensive for practical uses. On the other hand, copper is relatively inexpensive, and a versatile series of copper-based luminophores could greatly expand the scope of applications for luminescent transition metal complexes.[7]

Recently, our group reported a series of monomeric, four-coordinate amidophosphine complexes of copper supported by two ancillary tertiary phosphine donors which exhibited the longest lifetimes and highest quantum yields yet reported for luminescent monomeric copper complexes.[8] The properties exhibited by these complexes are significantly more favorable than any previously reported copper luminophores.[9] Modifications to both the amidophosphine and ancillary phosphine ligands were shown to change the luminescence properties of the resulting complexes. We have also reported dimeric copper complexes using a similar bis(phosphino)amide ligand, which adopt a diamond-core structure and are also highly luminescent.[10] While transition metal complexes that exhibit long-lived luminescence at room temperature are common for second- and third-row metals, they are rare for those metals in the first row, due to weak spin-orbit coupling. Of the known luminescent first-row metal complexes, most are limited to complexes of chromium and copper clusters,[9,11] or relatively simple copper phosphine complexes,[12] all of which exhibit significantly lower quantum yields than those from our group mentioned above, and are usually studied in the solid state, rather than in solution. The cost-effectiveness of the metal and unprecedented properties at room temperature in solution therefore motivated us to attempt to further tune the emission properties of these monocopper complexes, as well as to better understand the electronic properties leading to their luminescence.

We now report a series of monomeric amidophosphine [PN] complexes of copper with a wide range of emission maxima that exhibit quantum yields and lifetimes comparable to those previously reported.[8] While these compounds differ only in the nature and position of a single substituent on the [PN] ligand (Chart 1), the corresponding bis(triphenylphosphine) copper complexes have emission maxima in a range of over 70 nm, and lifetimes ranging from ~2 μs to over 150 μs.
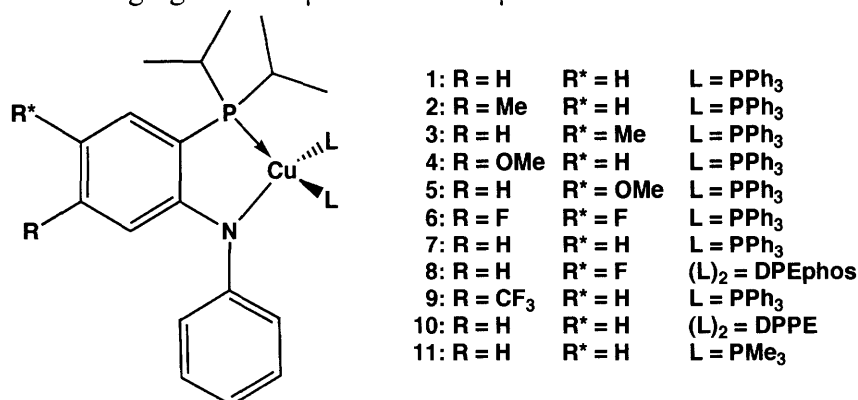


| 1: R = H | R* = H | L = PPh₃ |
|---|---|---|
| 2: R = Me | R* = H | L = PPh₃ |
| 3: R = H | R* = Me | L = PPh₃ |
| 4: R = OMe | R* = H | L = PPh₃ |
| 5: R = H | R* = OMe | L = PPh₃ |
| 6: R = F | R* = F | L = PPh₃ |
| 7: R = H | R* = H | L = PPh₃ |
| 8: R = H | R* = F | (L)₂ = DPEphos |
| 9: R = CF₃ | R* = H | L = PPh₃ |
| 10: R = H | R* = H | (L)₂ = DPPE |
| 11: R = H | R* = H | L = PMe₃ |

**Chart 1.**

Furthermore, a copper complex of the parent [PN] with the chelating phosphine bis[2-(diphenylphosphino)-phenyl] ether (DPEphos, also referred to elsewhere in the literature as POP) was able to effect a red-shift of the emission maximum of nearly 50 nm compared to the bis(triphenylphosphine) complex.

Additionally, time-dependent density functional theory (TDDFT) calculations were undertaken to assist in determining the nature of the excited states involved in the observed luminescence. These calculations successfully correlated the emission wavelengths and absorption spectra with the measured values; there is literature precedent for such studies.[13,14] Moreover, the calculations also provided insight into the structure of the orbitals responsible for the emissive excited state and the resulting long lifetime of this state. Indeed, the calculations confirmed the nature of the emission to be phosphorescence, rather than fluorescence.

Such a combination of synthetic and computational methods is thus shown to be a complimentary approach for the understanding of these luminescent copper systems. Slight modifications to both the amidophosphine [PN] ligand as well as the ancillary phosphine allowed for the adjustment of the photophysical properties of the resulting copper complexes. Consequently, the computational studies were able to give results that correlated with the experimental data, indicating that this technique might be useful as a screening method to identify additional goals for synthesis. Working in concert, these two methods provide for a more detailed understanding of these systems than previously existed, such as the phosphorescent nature of the emission and possible reasons for the stability of the long-lived excited state.

**Results and Discussion.**

After our previous communication detailing the use of simple substituents to tune the emission of [PN]Cu(L)$_2$ complexes,[8] we decided to expand on this result by using additional substituents and varying their positions. Initial DFT calculations indicated that the HOMO and LUMO are both localized on the aryl ring comprising the backbone of the [PN] ligand, and therefore we attempted to perturb the relative energies of these orbitals by changing the substituents on this ring system. Since the LUMO and the HOMO had been calculated to be localized on different carbon atoms in the ring, it was also hypothesized that changing the location of the substituent would have a large effect on its photophysical properties. Throughout this manuscript, the ligands referred to as [$^R$PN] contain the substituent R *para* to the diisopropylphosphino group, whereas the ligands referred to as [$^{R*}$PN] contain the substituent R *para* to the amide nitrogen (see Chart 1, above).

The substituted amidophosphine ligands were synthesized by a variety of methods. The methyl-substituted ligand [$^{Me*}$PN]Li was prepared analogously to those [PN] ligands previously reported,[8] via nucleophilic attack of LiP$^i$Pr$_2$ on the appropriate fluorinated diarylamine (Scheme 1).[15]
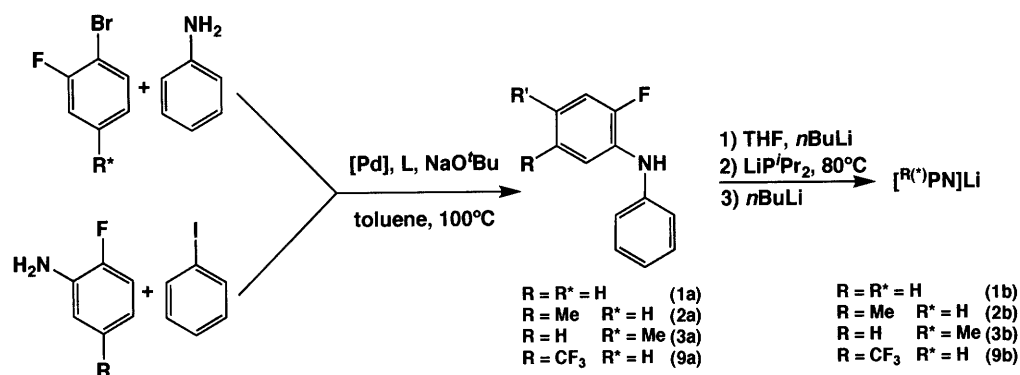
**Scheme 1.** Reaction conditions: **1** [Pd] = Pd$_2$dba$_3$ (dba = dibenzylideneacetone),
L = DPPF (DPPF = 1,1'-Bis(diphenylphosphino)-ferrocene); **2** and **9** [Pd] = Pd$_2$dba$_3$,
L = 2-(dicyclohexylphosphino)-biphenyl; **3** [Pd] = Pd(OAc)$_2$, L = DPEphos

The fluoro- and methoxy-substituted ligands were synthesized from 2-bromodiarylamines, using a method adapted from Harkins,[16] in a manner similar to that recently reported by Mindiola.[17] These ligands were synthesized by coupling the appropriate 2-bromoaniline with phenylboronic acid using Cu(OAc)$_2$,[18] followed by lithiation of the aryl bromide and reaction with ClP$^i$Pr$_2$ (Scheme 2).
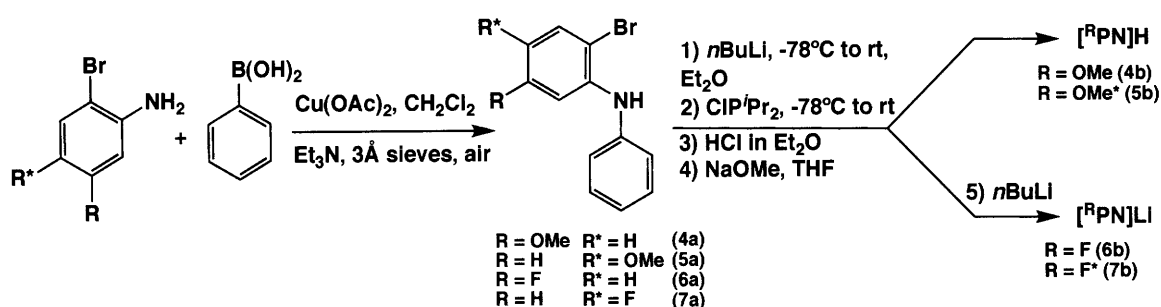


**Scheme 2.**

It should be noted that the conversions (and therefore isolated yields) on the Cu(OAc)$_2$ reactions are often rather low, but the unreacted aniline can be collected upon purification and reused. Furthermore, since the exclusion oxygen has been shown to reduce the efficiency of the reaction, these reactions were performed in air.[18a] However, this synthetic pathway allows for the coupling of a bromoaniline with an arylboronic acid to form a bromine-substituted diarylamine, which would be difficult at best utilizing the more common cross-coupling methods involving Pd.[19] Additionally, the use of a brominated starting material removes the need for a selective bromination,[17] which would reduce the number and variety of possible ligands.

The fluoro-substitued ligands were isolated as lithium amides, while those with methoxy substituents were used in their crude form. Addition of a solution in diethyl ether of a lithium salt of one of the amidophosphine ligands to a slurry of CuBr•SMe$_2$ and the appropriate tertiary phosphine provided a ready synthetic route to the corresponding complexes. Alternatively, for the ligands that are isolated as the free amine, as opposed to the lithium amide, addition of a diethyl ether solution of the amine to a stirring solution of mesitylcopper and the appropriate phosphine also allowed for the synthesis of the desired complex. Both of these synthetic routes afforded complexes of the type

[$^R$PN]Cu(PPh$_3$)$_2$ (**2** R = Me; **3** R = Me*; **4** R = OMe; **5** R = OMe*; **6** R = F; **7** R = F*) or [PN]Cu(L)$_2$ (**8** (L)$_2$ = DPEphos, and the previously reported **11** L = PMe$_3$) as orange to yellow solids. All of these complexes exhibit NMR data similar to those of the monomeric complexes previously reported by our group,[8] with two peaks in the $^{31}$P NMR spectra (between +10 and -15 ppm), exhibiting an integration ratio of 1:2. Via these two methods, methyl, methoxy, and fluoro substituents have been installed in positions on the arene backbone, both *para* to the nitrogen and *para* to the phosphorus, providing a wide range of electronic perturbations to the ligand.

All of the complexes discussed herein exhibit similar absorption spectra. They each include a minimum of two peaks, with one around 430 nm ($\varepsilon$ = 1500-2500 M$^{-1}$ cm$^{-1}$) and another around 350 nm ($\varepsilon$ = 8000-15000 M$^{-1}$ cm$^{-1}$), which is sometimes manifested as a shoulder of a larger, higher-energy feature, rather than a distinct peak. However, for every complex, no features are exhibited above 500 nm. The absorption spectra are also essentially identical when measured in either benzene or THF, indicating that solvent is not coordinating to the metal or interacting directly with the complexes in solution in any other way.

Excitation of solutions of each of the complexes **1 – 8** in benzene leads to sharp but featureless emission at 298 K. The complexes can be excited at wavelengths across their absorbing region to give qualitatively the same spectrum (Figure 1).
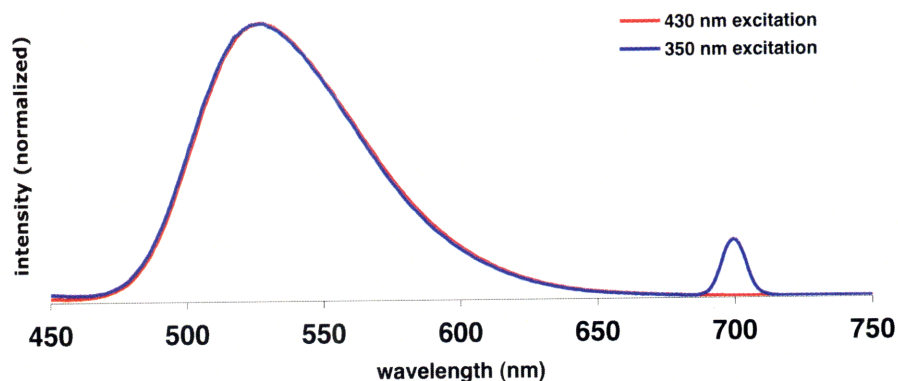


**Figure 1.** Normalized emission spectra of **5**. The small peak at 700 nm resulting from 350 nm excitation is an artifact from the instrument grating.

Solutions of complexes **1 – 8** in benzene are uniformly yellow, and glow green to some extent under visible light. Luminescence is also observed for these compounds in the solid state. The quantum yields of these complexes in benzene solution were measured at 298 K by exciting at either 430 nm or 350 nm (see Tables 1 and 2), and similar data were obtained at either excitation wavelength, indicating efficient energy transfer into the emissive state regardless of excitation.

The emission profile of these complexes can be varied significantly by varying both the [PN] ligand as well as the (L)$_2$ ancillary phosphine(s), even though neither the [PN] ligand nor the ancillary phosphine is a classic luminophores itself. The change in

emission of [PN]Cu(L)$_2$ complexes across a range of nearly 60 nm caused by varying the phosphine(s) from (PMe$_3$)$_2$ (**11**) to DPEphos (**8**), is shown in Figure 2 and Table 1.

| complex | phosphine | $\lambda_{em}$ (nm) | $\phi_{em}$ (430 nm) | $\phi_{em}$ (350 nm) | $\tau$ (µs) |
|---|---|---|---|---|---|
| **1** | PPh$_3$ | 504 | 0.56 | 0.52 | 20.2(1) |
| **8** | DPEphos | 555 | 0.45(1) | 0.49(1) | 2.6(2) |
| **10** | DPPE | 534 | 0.31 | 0.36 | 16.3(3) |
| **11** | PMe$_3$ | 497 | 0.21 | 0.17 | 22.3(7) |

**Table 1.** Quantum yield (with excitation wavelength) and lifetime data of [PN]Cu(L)$_2$ complexes. All measurements were taken in benzene. Data for **1**, **10**, and **11** from Ref.
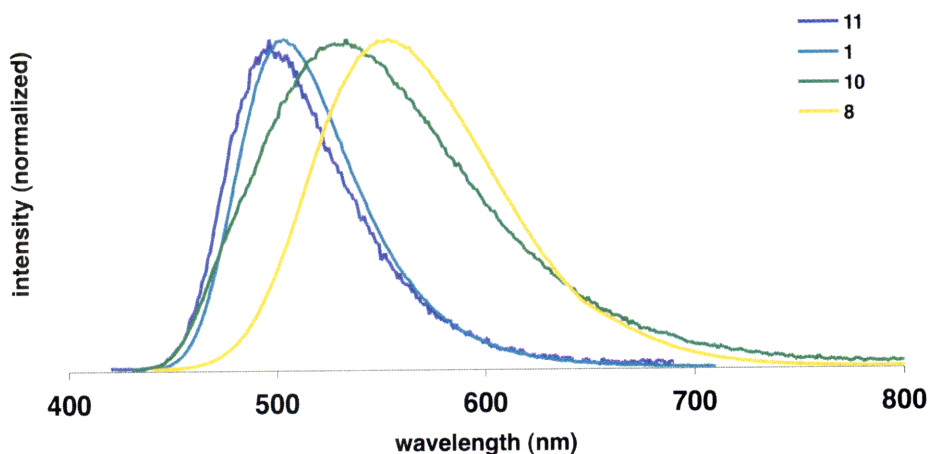


**Figure 2.** Normalized emission spectra of [PN]Cu(L)$_2$ complexes in order of increasing wavelength: L = PMe$_3$ (**11**), L = PPh$_3$ (**1**), (L)$_2$ = DPPE (**10**), (L)$_2$ = DPEphos (**8**). Data for **1**, **10**, and **11** from Ref. 8.

The PMe$_3$ and PPh$_3$ complexes qualitatively show nearly the same emission spectra, but the efficiency is strongly attenuated in **11**. Additionally, the use of chelating bisphosphines shifts the emission to lower energy, especially in light of the fact that DPEphos is essentially two PPh$_3$ moities with an ether linkage, though this small change causes a shift of approximately 50 nm in the emission.

As mentioned above, modification of the amidophosphine [PN] ligand also allows for the tuning of the emission properties of the respective complex. A variety of substituents were used in the positions both *para* to the amide nitrogen and *para* to the phosphorus. In each case, the remainder of the molecule was held constant, including the use of PPh$_3$ as the ancillary phosphine, L. However, even such a small perturbation

effected a shift in emission of nearly 70 nm, from 481 nm in the case of **6** to 552 in the case of **9**. Furthermore, differing the substituents makes possible the tuning of emission wavelength across the entire range of wavelengths between those exhibited by **6** (481 nm) and **9** (552 nm), as shown in Figure 3 and Table 2.
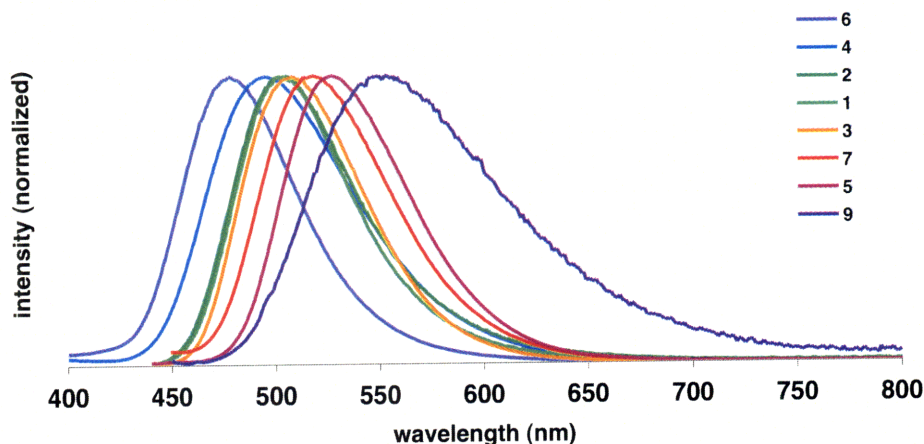


**Figure 3.** Normalized emission spectra of [$^R$PN]Cu(PPh$_3$)$_2$ complexes, in order of increasing emission wavelength: R = F (**6**), R = OMe (**4**), R = Me (**2**), R = H (**1**), R = Me* (**3**), R = F* (**7**), R = OMe* (**5**), R = CF$_3$ (**9**). Data for **1**, **2**, and **9** from Ref. 8.

| complex | substituent | $\lambda_{em}$ (nm) | $\phi_{em}$ (430 nm) | $\phi_{em}$ (350 nm) | $\tau$ ($\mu$s) |
|---|---|---|---|---|---|
| **1** | H | 504 | 0.56 | 0.52 | 20.2(1) |
| **2** | Me | 498 | 0.70 | n/a | 6.7(1) |
| **3** | Me* | 508 | 0.70(2) | 0.58(8) | 44(1) |
| **4** | OMe | 496 | 0.59(2) | 0.43(6) | 2.2(1) |
| **5** | OMe* | 528 | 0.24(1) | 0.32(4) | 154(6) |
| **6** | F | 481 | 0.51(3) | 0.41(6) | 4.6(3) |
| **7** | F* | 520 | 0.58(3) | 0.27(2) | 147(11) |
| **9** | CF$_3$ | 552 | 0.16 | n/a | 150(3) |

**Table 2.** Quantum yield (with excitation wavelength) and lifetime data of [$^R$PN]Cu(PPh$_3$)$_2$ complexes. All measurements were taken in benzene. Data for **1**, **2**, and **9** from Ref. 8.

The luminescence lifetimes of benzene solutions of complexes **1 – 8** taken at 298 K are also exceptionally long (see Tables 1 and 2). Previously, the longest lifetime that we reported was for the complex [$^{CF3}$PN]Cu(PPh$_3$)$_2$ (**9**), at 150 μs.[8] Both **5** and **7** also exhibit luminescence lifetimes of approximately this length, while also exhibiting shorter wavelength emission. Among the complexes with L = PPh$_3$ (**1 – 7, 9**), longer wavelength emission corresponds to longer lifetimes. This trend is specific to the ancillary phosphine L, however, since **8** has the longest emission wavelength but one of the shortest lifetimes (2.6 μs, which is still long compared to nearly all of the previously reported copper luminophores), and the complex [PN]CuDPPE (**10**, DPPE = 1,2-

bis(diphenylphosphino)ethane) also has a much shorter lifetime than the $PPh_3$ complexes with similar emission wavelengths.

The $^{31}P$ NMR chemical shifts of the amidophosphine phosphorus in the copper complexes utilizing $PPh_3$ as the ancillary phosphine exhibit a trend that is correlated to the wavelength of the observed phosphorescence. As indicated in Table 3, a blue-shift in the emission corresponds to an upfield shift in the $^{31}P$ NMR signal.

| | complex | $\lambda_{em}$ (nm) | $^{31}P$ $\delta$ (ppm) |
|---|---|---|---|
| 6 | [$^F$PN]Cu(PPh$_3$)$_2$ | 481 | -4.60 |
| 4 | [$^{OMe}$PN]Cu(PPh$_3$)$_2$ | 496 | -4.63 |
| 2 | [$^{Me}$PN]Cu(PPh$_3$)$_2$ | 498 | -3.9 |
| 1 | [PN]Cu(PPh$_3$)$_2$ | 504 | -3.7 |
| 3 | [$^{Me*}$PN]Cu(PPh$_3$)$_2$ | 508 | -3.42 |
| 7 | [$^{F*}$PN]Cu(PPh$_3$)$_2$ | 520 | -3.32 |
| 5 | [$^{OMe*}$PN]Cu(PPh$_3$)$_2$ | 528 | -3.26 |

**Table 3.** Comparison of emission wavelengths with $^{31}P$ NMR chemical shift. $^{31}P$ NMR chemical shifts are measured in benzene and reported relative to 85% $H_3PO_4$. Data for **1** and **2** from Ref. **8**.

Although the change in the $^{31}P$ NMR resonance is small, and these resonances are also fairly broad due to the quadrupolar nature of the coordinated copper nucleus, the emission wavelength and chemical shift both exhibit a clear trend, as stated above. Such a correlation of $^{31}P$ NMR chemical shift with emission wavelength is not unknown: the same trend is exhibited by complexes of the type [(dppb)CuX]$_2$ (dppb = 1,2-bis(diphenylphosphino)benzene, X = Cl, Br, I).[12] The data in Table 3 indicate that it is the position of the ligand substituent, rather than the functional group, that has a dominant effect on the emission of the final complex. The complexes that contain substituents *para* to the amide all exhibit lower-energy emission than the unsubstituted [PN] complex **1**; conversely, complexes with substituents *para* to the diisopropylphosphino group are shifted to higher energy. Within each grouping based on substituent position, the relationship between the fluoro- and methoxy-substituted complexes confirms expectations: the electron-withdrawing fluoro group has a higher-energy emission and a $^{31}P$ NMR signal equivalent to or upfield of the electron-donating methoxy group. It is surprising, given the intermediate electronic nature of the substituent, that neither of the methyl-substituted complexes fall in between the values exhibited by the fluoro- and methoxy-substituted complexes. Instead, they are closest to the unsubstituted complex **1**. This is a direct manifestation of the relationship between the electronics of the [PN] ligands and the photophysical properties of the resulting copper complexes.

Time-dependent density functional theory (TDDFT) calculations were conducted to further probe the nature of the observed luminescence. In order to maximize the correlation between calculated and experimental parameters, the complete molecules were used. The structures were set up starting from the crystal structure coordinates of **1**, and were then optimized using the B3LYP hybrid functional[20,21] and 6-31G(d) basis set,

followed by time-dependent calculations using the same functional and 6-31G(d) on the light atoms, and the LANL2DZ basis set[22] on Cu and P, with the addition of diffuse and polarization functions to phosphorus.[23]

The results of the TDDFT calculations provided a good correlation to the observed absorption spectra. The results of these parts of the calculations are summarized in Table 4. The calculations consistently overestimate the wavelengths of the lowest-energy transitions, though not by more than 25 nm (except in the case of **4**). There is also reasonable correlation with the higher-energy transitions, although no pattern is immediately evident in errors in these cases. However, it has been documented that TDDFT sometimes performs poorly for higher-energy transitions as well as for charge-transfer excitations over long distances.[24,25] Furthermore, it is difficult to include the effects of singlet-triplet excitations, since these transitions are formally forbidden and therefore do not have a calculated oscillator strength.

In multiple cases with the B3LYP functional, there are predicted transitions of significantly high oscillator strengths that are not observed experimentally. These transitions involve similar orbitals in each of the complexes in which they occur. To interrogate the nature of these transitions, the calculation on **1** was performed a second time, changing only the functional to PBE1PBE.[26] Not only was a transition exhibiting a comparatively high oscillator strength with a similar energy not predicted when using the hybrid PBE1PBE functional, there was no evidence for any transitions involving similar orbitals in the range calculated. However, the major transitions listed in Table 4 that correlate with those experimentally observed are also present in the PBE1PBE calculation, although with an increase in energy of ~0.2 eV, and are predicted to arise from similar transitions as in the B3LYP calculation. From this, it is clear that either of these

| complex | $\lambda_{calc}$ (nm) | $f$ | $\lambda_{expt}$ (nm) |
|---|---|---|---|
| **1** | 452.39 | 0.0118 | 434 |
| | *362.31* | *0.0162* | |
| | 338.75 | 0.0137 | 339 |
| **2** | 456.79 | 0.0114 | 433 |
| | *367.23* | *0.0153* | |
| | 347.90 | 0.0115 | 342 |
| | 339.74 | 0.0139 | |
| **3** | 466.45 | 0.0126 | 449 |
| | *368.61* | *0.0213* | |
| | 332.58 | 0.0943 | 341 |
| | 331.70 | 0.0197 | |
| **4** | 450.70 | 0.0108 | 412 |
| | 346.08 | 0.0101 | 341(sh) |
| | 330.95 | 0.0145 | |
| **5** | 466.76 | 0.0131 | 463 |
| | 384.06 | 0.0155 | |
| | 372.23 | 0.0158 | 345 |
| | 334.75 | 0.0887 | |
| **6** | 435.74 | 0.0109 | 413 |
| | 349.17 | 0.0133 | |
| | 335.03 | 0.0093 | 338(sh) |
| | 333.82 | 0.0164 | |
| **7** | 462.10 | 0.0122 | 454 |
| | *383.64* | *0.0165* | |
| | 332.77 | 0.0768 | 334(sh) |
| **8** | 452.34 | 0.0052 | 430 (sh) |
| | *362.67* | *0.0162* | |
| | 346.08 | 0.0110 | 345 |
| | 341.36 | 0.0130 | |

**Table 4.** Comparison of calculated (TDDFT/B3LYP) and observed (UV-Vis) absorbance peaks, including calculated oscillator strengths (*f*). Values in italics are transitions with high oscillator strengths around 370 nm that do not appear experimentally.

11

hybrid functionals can be utilized with these systems, although it does seem that B3LYP gives a better correlation with experimental data.

The TDDFT calculations indicate that the lowest excited state of all of the complexes is a triplet. Additionally, the energy predicted in each case for the lowest-energy transition from the ground state to this excited state corresponds well with the experimental value of the emission, within 0.15 eV, and often correlating even better (Table 5). At these wavelengths, that corresponds to a difference of 35 nm for **8** (with DPEphos), and 21 nm or less for **1-7** and **10**. The calculated energy of the emission is uniformly overestimated. One reason is that the calculations do not take into account structural reorganization of the excited state; this reorganization would cause the emitted photon to have a lower energy than otherwise calculated.[13] It is also possible that the calculated energies are systematically overestimated: since the calculations overestimate both absorption and emission energies, and these energies were derived from the same calculations, a systematic error is likely. Furthermore, the calculations indicate that the electron involved in this singlet-triplet transition comes from the HOMO of the ground state and is excited to the lowest-energy excited state. It is conceivable that there might be one or more radiative decay pathways from a higher excited state, but in fact the observed luminescence is simply the reverse of the process mentioned directly above, in accordance with Kasha's rule.[27] As is to be expected given the length of the lifetime, this triplet-singlet emission should be classified as phosphorescence. Less expected is the fact that the orbital populated during the long-lived excited state is actually concentrated almost exclusively on the ancillary phosphine.

| | complex | $\lambda_{em}$ (nm) | $\lambda_{calc}$ (nm) | $\Delta$ (nm) | $\Delta$ (eV) |
|---|---|---|---|---|---|
| **1** | [PN]Cu(PPh$_3$)$_2$ | 504 | 492 | 12 | 0.06 |
| **2** | [$^{Me}$PN]Cu(PPh$_3$)$_2$ | 498 | 495 | 3 | 0.02 |
| **3** | [$^{Me*}$PN]Cu(PPh$_3$)$_2$ | 508 | 506 | 2 | 0.01 |
| **4** | [$^{OMe}$PN]Cu(PPh$_3$)$_2$ | 496 | 489 | 7 | 0.03 |
| **5** | [$^{OMe*}$PN]Cu(PPh$_3$)$_2$ | 528 | 507 | 21 | 0.10 |
| **6** | [$^{F}$PN]Cu(PPh$_3$)$_2$ | 481 | 469 | 12 | 0.07 |
| **7** | [$^{F*}$PN]Cu(PPh$_3$)$_2$ | 520 | 506 | 14 | 0.07 |
| **8** | [PN]Cu(DPEphos) | 552 | 517 | 35 | 0.15 |
| **10** | [PN]CuDPPE | 534 | 518 | 16 | 0.07 |

**Table 5.** Comparison of experimentally observed (spectrofluorometry) and calculated (TDDFT/B3LYP) emission wavelengths, including the difference between them. The calculated wavelength is that of the transition from the ground state to the lowest (triplet) excited state.

The orbital calculated by DFT as the HOMO is qualitatively the same for each of the complexes, and is centered on the [PN] ligand, with very little interaction with the Cu or the ancillary phosphine(s). As shown in Figure 4 (which is representative of all of the complexes), it is essentially a mixture of the π-system of the arene backbone and a p-orbital on the amide. Furthermore, it should be noted that the phenyl group attached to

the amide is not coplanar with the arene backbone π-system, but is in fact perpendicular, prohibiting any significant π-orbital interaction between the two arenes.
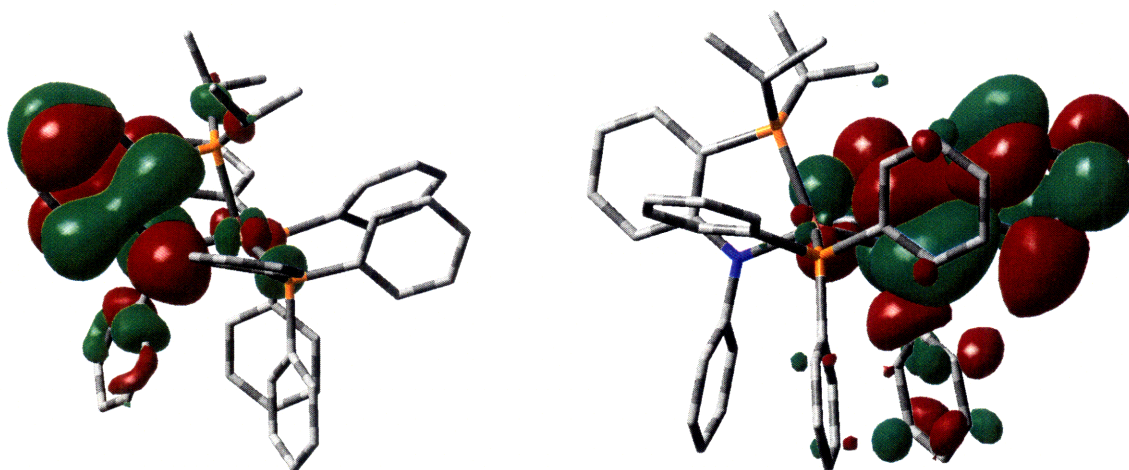


**Figure 4.** Left: The HOMO of **1** as determined by DFT. The orbital is almost entirely located on the [PN] ligand. Right: The LUMO of **1** as determined by DFT. The orbital is almost entirely located on the $PPh_3$. For both, the [PN] ligand is at left, the isodensity is 0.02, and hydrogen atoms have been omitted for clarity.

The DFT calculations indicate that the HOMO and the LUMO are both almost completely ligand-based. However, there is a large spatial separation between them since the ligand is not the same (i.e., the [PN] ligand versus the $PPh_3$). This gives some insight into the reason for the exceptionally long lifetimes of these complexes. In the first (triplet) excited state, the electron density is highly delocalized across the phosphine, which increases the stability of the excited state, and therefore the lifetime.[6] The correct formulation of this emission is therefore as a triplet ligand-to-ligand (interligand) charge transfer ($^3$LLCT).

This finding is somewhat contradictory to what we reported previously as the LUMO, centered on the [PN] ligand.[8] However, an orbital with essentially the same form as previously reported is also present in these calculations. Furthermore, this orbital is the lowest unoccupied [PN]-based orbital (see Figure 5). All of the unoccupied orbitals that are lower in energy than this one are based purely on the ancillary phosphine, and the large quantity of these orbitals is due to the high level of symmetry exhibited by the phenyl groups.

The TDDFT calculations also indicate that the orbital pictured in Figure 5 is involved in the transitions that lead to the absorption peak around 340 nm that is observed for all of
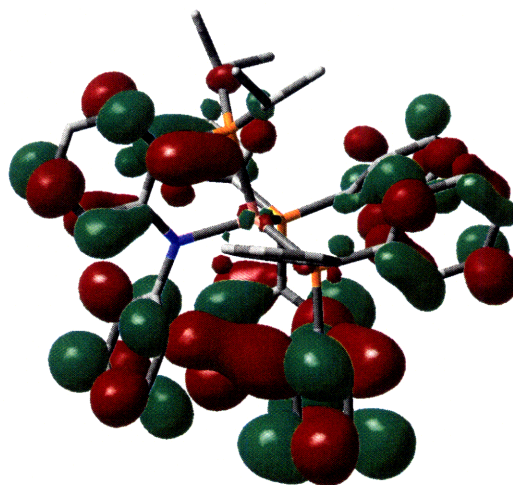


**Figure 5.** The LUMO+11 of **1** as determined by DFT. This is the first unoccupied orbital with character on the [PN] ligand, which is at left. The isodensity is 0.02 and hydrogen atoms have been removed for clarity.

13

the complexes. Since this orbital has significant character on both the [PN] and the ancillary phosphine ligands, it allows for the direction of excited electrons into the manifold of orbitals on the ancillary phosphine, leading to the emissive triplet state. However, excitation into this orbital is not necessary for efficient emission, as is evidenced by the similarity of emission for excitations at both 430 nm and 350 nm. The calculations indicate that the absorption band at 430 nm corresponds to another LLCT transition directly into one of the mid-level orbitals of the ancillary phosphine manifold. A representation of the excitation and emission of 1 is shown in Figure 6.
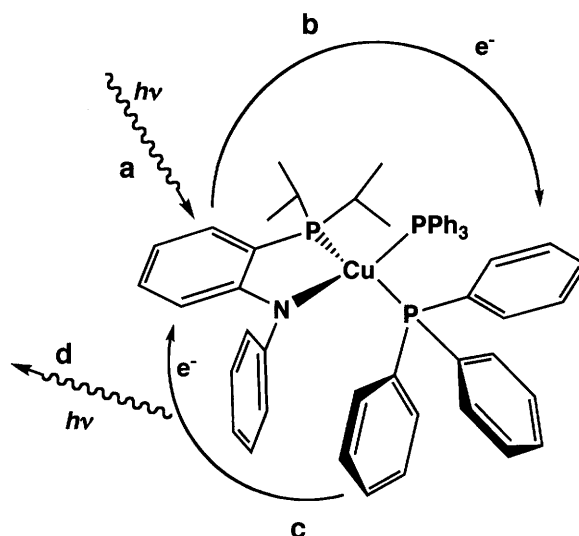


**Figure 6.** A schematic representation of excitation and emission: a photon excites an electron from the HOMO into a singlet excited state (a), which rapidly converts into a triplet. The electron is transferred to the ancillary phosphine (b), with mediation by the Cu center, where it relaxes to the long-lived excited state. The excited state relaxes to the ground state (c), transferring the electron back to the [PN] ligand ($^3$LLCT) and emitting a photon (d).

The high quantum yields indicate an efficient funneling of excitons into the long-lived triplet state. Without this so-called "triplet harvesting," such efficiencies would be impossible to achieve.[6] The similarities that exist in the quantum yields regardless of excitation energy also indicate that intersystem crossing into the triplet manifold is efficient regardless of the initial excited state, and is, at a minimum, highly competitive with singlet emission. Figure 7 gives a simplified description of the photophysics displayed by these complexes. Excitation of a molecule in the singlet ground state leads to an excited singlet, which rapidly converts through an intersystem crossing into a triplet and relaxes into the lowest triplet state, $T_1$. The $T_1$ state is the long-lived excited state, which is stabilized by the large spatial separation between the orbitals contributing to these two states, which prevents facile
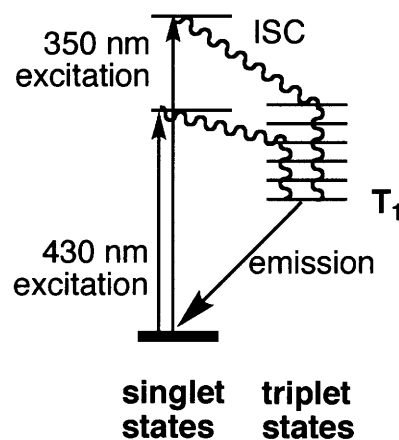


**Figure 7.** Representative diagram of the excitation and emission of [$^R$PN]CuL$_2$ complexes, showing singlet excitation, intersystem crossing to the triplet manifold, and the long-lived emissive triplet state.

relaxation to the singlet ground state. This state eventually does relax, however, leading to the observed emission.

**Conclusion.**

The amidophosphine [PN] ligand system has proven to be an extremely versatile framework for the synthesis of luminescent copper complexes. We have shown that a single substituent on the arene ligand backbone has the ability to tune the luminescence of the copper complexes by up to 70 nm. Furthermore, the luminescence properties are also tunable over a range of nearly 60 nm solely by differing the ancillary phosphine ligand(s) while using the same amidophosphine ligand. Additionally, even across this wide range of perturbations affecting the luminescence properties of the complexes, they continue to retain their remarkably efficient and long-lived characteristics.

The nature of the excited state has been probed using time-dependent DFT calculations, which have been shown to successfully predict the wavelength of emission. The emissive state is a triplet state (the lowest triplet state, as would be expected from Kasha's rule), which therefore classifies the luminescence of all members of this class of compounds as phosphorescence. This is in agreement with the length of the luminescence lifetimes, as well. Thus, it has been shown that a series of structurally related amidophosphine complexes of copper exhibits unprecedented phosphorescence and lifetime length at room temperature in solution.

**Acknowledgement.**

## Experimental Section

All manipulations were carried out using standard Schlenk or glove-box techniques under a dinitrogen atmosphere, unless otherwise indicated. Except for those used for reactions that take place in air, solvents were deoxygenated and dried by thorough sparging with $N_2$ followed by passage through an activated alumina column, and were stored over 3Å molecular sieves. Solvents other than acetonitrile were tested with a standard purple solution of sodium benzophenone ketyl in tetrahydrofuran in order to confirm removal of oxygen and moisture. Deuterated solvents were degassed, dried until purple over sodium and benzophenone, and vacuum transferred before being stored over sieves. LiP($^i$Pr)$_2$,[28] 2-bromo-4-methoxyaniline,[29] 2-bromo-5-methoxyaniline,[29] mesityl-Cu,[30] and [PN]Li (Lithium 2-(diisopropylphosphino)diphenyl amide)[8] were prepared according to literature procedures. Celite (Celite® 545) was dried at 300°C under vacuum for 48 hours. Silica gel ('BAKER' Silica Gel 40 μm Flash Chromatography Packing, 60Å pore diameter) was purchased from J.T. Baker and used as received. All other reagents were purchased from commercial sources and used without further purification, unless explicitly stated. Elemental analyses were carried out at Columbia Analytics, Tucson, Arizona, or Midwest Microlab, Indianapolis, Indiana. NMR spectra were recorded at ambient temperature on a Varian Mercury 300 MHz or Inova 500 MHz spectrometer. $^1$H and $^{13}$C chemical shifts were referenced to residual solvent. $^{31}$P chemical shifts are reported relative to an external standard of 85% $H_3PO_4$ ($\delta = 0$ ppm), and $^{19}$F chemical shifts are reported relative to an external standard of $C_6F_6$ ($\delta = -165$ ppm). UV-Vis measurements were taken on a Varian Cary 50 UV-Vis Spectrophotometer, using a quartz crystal cell with either a ground glass stopper or silicone-lined screw cap. High resolution mass spectra (HRMS) were obtained at the Massachusetts Institute of Technology Department of Chemistry Instrumentation Facility.

**Lifetime Measurements.** A dilute solution (optical density of less than 0.1 at the excitation wavelength) of analyte in benzene was prepared in a nitrogen-filled glovebox. Quartz cuvettes (1 cm path length) were charged with this solution and sealed with either a ground glass stopper or silicone-lined screw cap. Luminescence lifetime measurements were determined by time-resolved phosphorescence spectroscopy, as previously described.[31] The irradiation source was an Oriel nitrogen laser (Model 79111) with a 5 ns pulsewidth operating at approximately 5 Hz. The emitted light was dispersed in an Oriel MS-260i spectrograph with a 300 lines mm$^{-1}$ grating, and was detected by an Andor Technologies Intensified CCD camera (1024 x 128 pixels) with an onboard delay generator and a minimum gate width of 5 ns (gate width used was 30 μs) operating in full vertical binning mode and triggered by a TTL prepulse from the nitrogen laser. The detector was calibrated using a Hg(Ar) pencil-style calibration lamp. Measurements were performed at 298 K with at least two cuvettes of analyte solution over a variety of gate steps, with excitation at $\lambda_{ex} = 337$ nm. Data were acquired using horizontal binning of 2, using 10 accumulations per measurement, with 10 pulses per accumulation. The emission decays at the five wavelengths around the maximum ($\lambda_{em}$) were fit to an exponential function from which $k_{obs}$ and $\tau$ were determined.

**Quantum Yield Measurements.** Emission spectra were collected on a SPEX Fluorolog-τ3 fluorometer (model FL-321, 450 W Xenon lamp) using right angle detection. A solution of analyte or reference in benzene was prepared in a nitrogen filled glovebox. A minimum of two cuvettes (1 cm path length) were charged with this solution and sealed with either a ground glass stopper or silicone-lined screw cap. The absorbance of all samples was kept below 0.1 at and above the excitation wavelength in order to minimize reabsorption artifacts. Fluorescence measurements were performed at the specified wavelength at 298 K. Quantum yields were determined from an analytically pure sample of [PN]CuDPPE (DPPE = bis(diphenylphosphino)ethane),[8] calculated by the method described by Demas and Crosby.[32]

**Computational Details.** DFT and TDDFT calculations were performed on each of the copper-bis(triphenylphosphine) complexes, as well as the previously reported [PN]Cu(PPh₃)₂, [PN]Cu(PMe₃)₂, and [PN]CuDPPE,[8] using the Gaussian 03 program package.[33] The geometries of the new complexes and [PN]CuDPPE were first optimized using either the B3LYP[20,21] or PBE1PBE[26] hybrid functional and 6-31G(d) basis set, without any symmetry restrictions or truncation of the molecules. At the optimized geometries (or, in the case of [PN]Cu(PPh₃)₂ and [PN]Cu(PMe₃)₂, using the crystal structure coordinates as a starting point), TDDFT calculations were performed, again using the B3LYP functional, applying the LANL2DZ basis set[22] to Cu and P and the 6-31G(d) basis set to all other atoms. Diffuse and polarization functions were applied to phosphorus.[23] The calculations were set up to find the lowest 50 excitations (both singlet-singlet and singlet-triplet) without any symmetry restrictions. The calculations were run without using a solvation model, since the absorption spectra do not show any difference between solutions in either benzene or THF.

**2-Fluoro-4-methyl-diphenylamine (3a).** In the glovebox, a 200 mL Schlenk tube was charged with Pd(OAc)₂ (22.7 mg, 0.1 mmol), DPEphos (bis(2-[diphenylphosphino]phenyl) ether; 108 mg, 0.2 mmol), and 40 mL toluene. It was sealed with a Teflon stopper, brought out of the glovebox, and to the yellow solution was added NaOᵗBu (1.35 g, 14 mmol) under a counterflow of dinitrogen. 4-Bromo-3-fluorotoluene (1.27 mL, 1.89 g, 10 mmol) was added via syringe through a septum and the solution was stirred for 5 minutes, at which point aniline (1.12 g, 12 mmol) was also added via syringe, yielding a dark brown solution, which was stirred at 80°C. The reaction was monitored by GCMS, and was finished after approximately 17 hours. From this point, all manipulations were carried out in air. The mixture was filtered through a plug of silica and washed with copious hexanes. After evaporating the solvent and allowing the residue to stand overnight, there remained a brown oil with large colorless crystals, which were collected on a frit and washed with hexanes to give a pure off-white solid (1.73 g, 86%). ¹H NMR (C₆D₆, 300 MHz): δ 7.07 (m, 3H), 6.78 (m, 4H), 6.57 (d, 1H), 5.29 (br s, 1H), 1.98 (s, 3H). ¹⁹F NMR (C₆D₆, 282.4 MHz): δ -129.7. HRMS (ESI⁺) *m/z* calcd. for C₁₃H₁₂FN 202.1027. Found: 202.1031 [M+H].

**[Me*PN]Li (3b).**[34] A 50 mL Schlenk tube was charged with 2-Fluoro-4-methyl-diphenylamine (750 mg, 3.73 mmol) and 5 mL THF to give a pale yellow solution. To this was added a 1.6 *M* solution of *n*BuLi (2.56 mL, 4.10 mmol), and the mixture was

stirred for 30 minutes, giving an orange solution. At this point, a solution of LiP($^i$Pr)$_2$ (1.16 g, 9.33 mmol) in 15 mL THF was slowly added via cannula without a color change, and the tube was sealed with a Teflon stopper and heated to 75°C. After 3 days, the solution was greenish and luminescent under UV light, and showed complete conversion by GCMS. The reaction was quenched with 4 mL EtOH, turning the solution grey. The solvent was removed in vacuo and the vessel was brought into the glovebox, where the grey residue was extracted with pentane and filtered through silica, washing with copious pentane (ca. 150 mL total). The solvent was pulled off in vacuo and the clear oil was redissolved in 5 mL pentane. To this solution was added 1.76 $M$ nBuLi (2.33 mL, 4.10 mmol) was added and the mixture was stirred overnight, yielding a greenish, off-white powder, which was collected on a frit (786 mg, 69%). $^1$H NMR (THF-$d^8$, 300 MHz): δ 7.17 (m, 1H), 7.03 (dd, 1H), 6.84-6.70 (m, 4H), 6.59 (d, 1H), 6.18 (t, 1H), 2.18-1.96 (m, 5H), 1.12 (d, 3H), 1.07 (d, 3H), 0.99 (d, 3H), 0.95 (d, 3H). $^{31}$P NMR (THF-$d^8$, 121.5 MHz): δ -6.32. HRMS (ESI$^+$) $m/z$ calcd. for C$_{19}$H$_{26}$NP 300.1876. Found: 300.1885 [M+H].

**[$^{Me*}$PN]Cu(PPh$_3$)$_2$ (3).** Separate diethyl ether solutions of 3 mL each of [$^{Me*}$PN]Li (76 mg, 0.25 mmol), CuBr•SMe$_2$ (51.4 mg, 0.25 mmol), and PPh$_3$ (131 mg, 0.50 mmol) were cooled to -35°C. The Cu and PPh$_3$ solutions were mixed and stirred for 5 minutes at ambient temperature, giving a white opaque mixture, to which was added the cold yellow [$^{Me*}$PN]Li solution dropwise, causing the mixture to clear. The resulting yellow solution was stirred for 3 hours, at which point the solvent was removed in vacuo. The residue was extracted with benzene, which was filtered through Celite and lyophilized to yield a bright yellow, analytically pure powder. $^1$H NMR (C$_6$D$_6$, 500 MHz): δ 7.5-7.4 (m, 13H), 7.19-7.13 (m, 3H), 7.05-6.96 (m, 17H), 6.85 (t, 1H), 2.28 (s, 3H), 2.06 (m, 2H), 1.07 (d, 3H), 1.03 (d, 3H), 1.00 (d, 3H), 0.97 (d, 3H). $^{13}$C NMR (C$_6$D$_6$, 125 MHz): δ 136.03 (d, J$_{PC}$ = 12.6 Hz), 134.56 (d, J$_{PC}$ = 16.6 Hz), 133.43, 133.15, 129.86, 129.71, 129.18 (d, J$_{PC}$ = 8.6 Hz), 128.92, 128.68, 125.74, 119.17, 23.87 (d, J$_{PC}$ = 12.6 Hz), 21.15, 20.24 (d, J$_{PC}$ = 10.9 Hz), 19.11. $^{31}$P NMR (C$_6$D$_6$, 202.5 MHz): δ 0.92 (2P), -3.42 (1P). Anal. calcd. for C$_{55}$H$_{55}$CuNP$_3$: C, 74.52; H, 5.47; N, 1.35; Found: C, 74.25; H, 5.85; N, 1.28.

**2-Bromo-5-methoxy-diphenylamine (4a).** 2-Bromo-5-methoxyaniline (130 mg, 0.64 mmol), phenylboronic acid (127 mg, 1.29 mmol), copper(II) acetate (129 mg, 0.71 mmol), and 3Å molecular sieves were added to a 10 mL round bottom flask in air. 5 mL dichloromethane and triethylamine (130 mg, 180 μL, 1.29 mmol) were added and the flask was stoppered with a rubber septum and stirred for 20 hours, at which point the reaction was shown to be complete by TLC. The solution was filtered through a plug of silica, washed with hexanes, and the solvent was evaporated to give a brown oil (170 mg, 95%). $^1$H NMR (C$_6$D$_6$, 500 MHz): δ 7.29 (d, 1H), 7.03 (t, 2H), 6.84 (m, 4H), 6.13 (dd, 1H), 5.97 (br s, 1H), 3.14 (s, 3H). HRMS (ESI$^+$) $m/z$ calcd. for C$_{13}$H$_{12}$BrNO 278.0175. Found: 278.0180 [M+H], 246.1493 [M-OMe].

**[$^{OMe}$PN]H (4b) and [$^{OMe}$PN]Cu(PPh$_3$)$_2$ (4).** 2-Bromo-5-methoxy-diphenylamine (760 mg, 2.73 mmol) was dissolved in 50 mL diethyl ether in a Teflon-sealed Schlenk tube and was cooled to -78°C, giving a pale orange solution. A solution of nBuLi (1.6 $M$ in hexanes, 3.42 mL, 5.46 mmol) was added via syringed, and the resulting yellow solution

was allowed to warm to ambient temperature. After stirring for 4 hours, the solution was recooled to -78°C and chlorodiisopropylphosphine (834 mg, 5.46 mL) was added via syringe. The resulting yellow solution was stirred at ambient temperature for 16 hours, at which point a large amount of precipitate was evident. It was filtered through Celite and washed with ether, at which point 20 mL (20 mmol) of a 1.0 $M$ solution of HCl in diethyl ether was added via syringe, immediately turning the yellow solution white and causing the precipitation of the product as an HCl salt. This mixture was stirred for 3 hours and the solvent was removed in vacuo. The residue was washed with copious pentane and was then redissolved in THF, at which point excess (700 mg) NaOMe was added to the solution, which was stirred overnight. The solvent was again removed in vacuo, and the sticky residue was extracted with pentane and filtered through Celite. The filtrate was evaporated to leave a sticky white solid, [$^{OMe}$PN]H (673 mg, 78%). Although the crude solid was not pure, it could be used subsequently in the successful synthesis of the metal complex. A solution of this solid (192 mg, 0.609 mmol) in diethyl ether was added to a pale yellow solution of mesityl-Cu (111 mg, 0.609 mmol) and triphenylphosphine (319 mg, 1.22 mmol) in diethyl ether. The solution immediately turned cloudy and green-yellow, and was diluted to 15 mL and stirred for 3 hours. The solution was then filtered through Celite, washing with additional diethyl ether, and the solvent was removed in vacuo to leave a yellow-orange oil. This was dissolved in acetonitrile, layered with pentane, and cooled to -35°C. Decanting the solvent while cold yields a yellow powder (76 mg, 14%). Note: The compound is still somewhat soluble in acetonitrile at -35°C, and rapidly redissolves upon warming. The solvent must be removed while still cold to obtain any product at all. Data for [$^{OMe}$PN]H: $^{31}$P NMR ($C_6D_6$, 121.5 MHz): δ -17.3. HRMS (ESI$^+$) $m/z$ calcd. for $C_{19}H_{26}NOP$ 316.1825. Found: 316.1832 [M+H]. Data for [$^{OMe}$PN]Cu(PPh$_3$)$_2$: $^1$H NMR ($C_6D_6$, 300 MHz): δ 7.42 (m, 17H), 7.01 (m, 25H), 6.85 (t, 2H), 6.37 (dd, 1H), 3.33 (s, 3H), 2.04 (m, 2H), 1.08 (d, 3H), 1.02 (m, 6H), 0.97 (d, 3H). $^{13}$C NMR ($C_6D_6$, 75.5 MHz): δ 136.16 (d, $J_{PC}$ = 11 Hz), 134.54 (d, $J_{PC}$ = 17 Hz), 129.81, 129.18 (d, $J_{PC}$ = 8.5 Hz), 126.17, 119.80, 54.63, 23.98, 23.97, 20.35, 20.21, 18.95. $^{31}$P NMR ($C_6D_6$, 121.5 MHz): δ 0.37 (2P), -4.63 (1P). HRMS (ESI$^+$) $m/z$ calcd. for $C_{55}H_{55}CuNOP_3$ 902.2865, [M-PPh$_3$] 640.1959. Found: 640.1944 [M-PPh$_3$], 587.1109 [M-[PN]].

**2-Bromo-4-methoxy-diphenylamine (5a).** 2-Bromo-4-methoxyaniline (100 mg, 0.495 mmol), phenylboronic acid (121 mg, 0.99 mmol), copper(II) acetate (99 mg, 0.54 mmol), and 3Å molecular sieves were added to a 10 mL round bottom flask in air. 5 mL dichloromethane was added and the light brown solution was stirred, at which point triethylamine (100 mg, 138 µL, 0.99 mmol) was added via syringe, causing the solution to turn dark red-brown. The flask was stoppered with a rubber septum and stirred for 4 days, monitoring by TLC. The resulting green solution was filtered through a plug of silica and washed with copious hexanes. The solvent was evaporated to give a reddish oil, and the residue was purified on a silica column (using a gradient of hexanes to 5% ethyl acetate in hexanes as eluent) to give a yellow oil (124 mg, 90%). $^1$H NMR ($C_6D_6$, 300 MHz): δ 7.07 (m, 4H), 6.81 (t, 1H), 6.75 (d, 2H), 6.56 (dd, 1H), 5.48 (br s, 1H), 3.15 (s, 3H). HRMS (ESI$^+$) $m/z$ calcd. for $C_{13}H_{12}BrNO$ 278.0175. Found: 278.0181 [M+H].

19

**[$^{OMe*}$PN]H (5b) and [$^{OMe*}$PN]Cu(PPh$_3$)$_2$ (5).** 2-Bromo-4-methoxy-diphenylamine (1.77 g, 6.36 mmol) was dissolved in 50 mL diethyl ether in a Teflon-sealed Schlenk tube, giving a pale orange solution. The solution was cooled to -78°C and a 1.6 $M$ solution of $n$BuLi in hexanes (7.9 mL, 12.7 mmol) was syringed in. After stirring for 3.5 hour at ambient temperature, the yellow solution was recooled to -78°C, and chlorodiisopropylphosphine (1.94 g, 12.7 mL) was added via syringe and the solution was stirred overnight at ambient temperature. The solution was filtered through Celite, washing with an additional 50 mL ether, and then a 1.0 $M$ solution of HCl in diethyl ether (45 mL, 45 mmol) was added. The solvent was removed in vacuo, and the remaining orange residue was washed with 100 mL pentane before dissolving in 50 mL THF. To this solution was added excess NaOMe (1.4 g), and the resulting mixture was stirred overnight and then evaporated to dryness in vacuo, leaving a viscous orange oil. This was extracted into pentane (ca. 125 mL) and filtered through Celite. The solvent was then removed, leaving a transparent yellow-orange oil, [$^{OMe*}$PN]H. Although the crude oil was not pure, it could be used subsequently in the successful synthesis of the metal complex. A solution of this [$^{OMe*}$PN]H (77 mg, 0.244 mmol) in diethyl ether at -35°C was added dropwise to a stirring cloudy yellow solution of triphenylphosphine (128 mg, 0.488 mmol) and mesityl-Cu (44.5 mg, 0.244 mmol), which had been stirring for 5 minutes, instantly yielding a darker yellow solution and precipitate. After stirring overnight, the solution was filtered and the solvent removed in vacuo to give a yellow oil. This oil was stirred in acetonitrile and filtered again. The filtrate yielded orange crystals upon standing for 3 days (187 mg, 81%). Data for [$^{OMe*}$PN]H: $^{31}$P NMR (C$_6$D$_6$, 121.5 MHz): δ -12.9. HRMS (ESI$^+$) $m/z$ calcd. for C$_{19}$H$_{26}$NOP 316.1825. Found: 316.1838 [M+H]. Data for [$^{OMe*}$PN]Cu(PPh$_3$)$_2$: $^1$H NMR (C$_6$D$_6$, 300 MHz): δ 7.54-7.37 (m, 15H), 7.02 (m, 17H), 6.92 (dd, 1H), 6.80 (m, 2H), 3.50 (s, 3H), 1.99 (m, 2H), 1.03 (d, 3H), 0.98 (d, 3H), 0.96 (d, 3H), 0.92 (d, 3H). $^{13}$C NMR (C$_6$D$_6$, 125 MHz): δ 161.60, 161.45, 159.00, 149.35, 136.22 (d, $J_{PC}$ = 10.9 Hz), 134.53 (d, $J_{PC}$ = 17.1 Hz), 129.82, 129.73, 129.20 (d, $J_{PC}$ = 8.0 Hz), 125.21, 119.19, 118.67 (d, $J_{PC}$ = 14.4 Hz), 115.17 (d, $J_{PC}$ = 5.8 Hz), 56.35, 23.88 (d, $J_{PC}$ = 11.5 Hz), 20.13 (d, $J_{PC}$ = 11.5 Hz), 19.01 (d, $J_{PC}$ = 4.0 Hz). $^{31}$P NMR (C$_6$D$_6$, 121.5 MHz): δ 0.64 (2P), -3.26 (1P). Anal. calcd. for C$_{55}$H$_{55}$CuNOP$_3$•CH$_3$CN: C, 72.56; H, 6.20; N, 2.97; Found: C, 72.32; H, 6.08; N, 2.84.

**2-Bromo-5-fluoro-diphenylamine (6a).** In air, a 250 mL round bottom flask was charged with 2-bromo-5-fluoroaniline (3.57 g, 18.8 mmol), phenylboronic acid (4.58 g, 37.6 mmol), copper(II) acetate (3.76 g, 20.7 mmol), and 3Å molecular sieves. 100 mL dichloromethane was added, followed by triethylamine (3.80 g, 5.2 mL, 37.6 mmol). After addition of the triethylamine, the mixture became mostly homogeneous except for the sieves, and was sealed with a rubber septum and stirred. After four days, no further progress was observed via GCMS, and the mixture was filtered through a plug of silica gel, washing with copious hexanes. The filtrate was evaporated and the residue was purified on a silica column, using hexanes as eluent (485 mg, 9.7%). Note: The unreacted aniline starting material was also collected from the column, and was reused for subsequent reactions. $^1$H NMR (C$_6$D$_6$, 300 MHz): δ 7.08 (dd, 1H), 6.98 (t, 2H), 6.83 (m, 2H), 6.70 (d, 2H), 6.14 (td, 1H), 5.90 (br s, 1H). $^{19}$F NMR (C$_6$D$_6$, 282.4 MHz): δ -110.84. HRMS (ESI$^+$) $m/z$ calcd. for C$_{12}$H$_9$BrFN 265.9975. Found: 265.9980 [M+H].

20

[<sup>F</sup>PN]Li (6b).[34] 2-Bromo-5-fluoro-diphenylamine (485 mg, 1.82 mmol) was dissolved in 25 mL diethyl ether and the very pale yellow solution was cooled to -78°C, at which point a solution of $n$BuLi (1.6 $M$ in hexanes, 2.3 mL, 3.65 mmol) was added via syringe. After warming to ambient temperature and stirring for 3 hours, the solution was again cooled to -78°C and chlorodiisopropylphosphine (556 mg, 3.65 mmol) was added via syringe. The resulting solution was stirred at ambient temperature for 3 days, at which point the yellow solution was filtered through Celite. 1.0 $M$ HCl in diethyl ether (15 mL, 15 mmol) was then added via syringe, bleaching the solution and causing the precipitation of a sticky yellow solid. After stripping off the solvent in vacuo, the solid was washed with copious pentane, and then redissolved in THF. Excess NaOMe (400 mg) was added and the resulting solution was stirred overnight. The solvent was removed in vacuo, and the residue was extracted with pentane and filtered. The solvent was removed, and the residue redissolved in 20 mL pentane and cooled to -35°C, at which point $n$BuLi (1.6 $M$ in hexanes, 1.14 mL, 1.82 mmol) was added via syringe, causing the precipitation of a light brown solid, which was collected on a frit (352 mg, 63%). $^1$H NMR (THF-$d^8$, 300 MHz): δ 6.94 (m, 2H), 6.84 (m, 3H), 6.55 (br d, 1H), 6.41 (t, 1H), 5.78 (t, 1H), 2.03 (m, 2H), 1.14 (d, 3H), 1.09 (d, 3H), 1.00 (d, 3H), 0.96 (d, 3H). $^{19}$F NMR (THF-$d^8$, 282.4 MHz): δ -113.11. HRMS (ESI$^+$) $m/z$ calcd. for $C_{18}H_{23}FNP$ 304.1625. Found: 304.1638 [M+H], 291.1626 [M-Me].

[<sup>F</sup>PN]Cu(PPh₃)₂ (6). 3 mL diethyl ether solutions of CuBr•SMe₂ (108 mg, 0.524 mmol) and triphenylphosphine (275 mg, 1.05 mmol) were combined and stirred, giving a white slurry. [<sup>F</sup>PN]Li (162 mg, 0.524 mmol) was dissolved in 3 mL diethyl ether and cooled to -35°C, then the yellow solution was added dropwise to the Cu/phosphine mixture, turning the combined solution clear and dark yellow. The solution was diluted with diethyl ether to 15 mL and stirred for 3 hours, at which point the solvent was removed in vacuo. The residue was extracted with benzene, filtered through Celite, and lyophilized to give a spectroscopically pure yellow-orange powder (353 mg, 76%). $^1$H NMR (C₆D₆, 300 MHz): δ 7.39 (m, 20H), 7.30 (dd, 2H), 7.15-6.98 (m, 33H), 6.97-6.81 (m, 2H), 6.30 (td, 1H), 1.98 (m, 2H), 1.03 (d, 3H), 0.98 (d, 3H), 0.94 (d, 3H), 0.89 (d, 3H). $^{13}$C NMR (C₆D₆, 75.5 MHz): δ 136.24 (d, $J_{PC}$ = 9.5 Hz), 134.59 (d, $J_{PC}$ = 17 Hz), 129.91, 129.77, 129.14 (d, $J_{PC}$ = 8.2 Hz), 126.15, 120.64, 23.87 (d, $J_{PC}$ = 13.6 Hz), 20.15 (d, $J_{PC}$ = 10 Hz), 18.87. $^{19}$F NMR (C₆D₆, 282.4 MHz): δ -108.67. $^{31}$P NMR (C₆D₆, 121.5 MHz): δ -1.31 (2P), -4.60 (1P). HRMS (ESI$^+$) $m/z$ calcd. for $C_{54}H_{52}CuFNP_3$ 890.2665, [M-PPh₃] 628.2054. Found: 628.1980 [M-PPh₃], 587.1288 [M-[PN]].

**2-Bromo-4-fluoro-diphenylamine (7a).** In air, a 250 mL round bottom flask was charged with phenylboronic acid (6.43 g, 52.7 mmol), copper(II) acetate (5.27 g, 29.0 mmol), and 3Å molecular sieves. 150 mL dichloromethane was added, followed by 2-bromo-4-fluoroaniline (5.01 g, 3.0 mL, 26.4 mmol), and then triethylamine (5.33 g, 7.3 mL, 52.7 mmol). After addition of the triethylamine, the mixture became mostly homogeneous except for the sieves, and was sealed with a rubber septum and stirred. After two days, no further progress was observed via GCMS, and the mixture was filtered through a plug of silica gel, washing with copious hexanes. The filtrate was evaporated and the residue was purified on a silica column, using hexanes as eluent, to yield a brown oil (480 mg, 6.8%). $^1$H NMR (C₆D₆, 300 MHz): δ 7.05 (m, 3H), 6.81 (m, 2H), 6.70 (d,

2H), 6.53 (td, 1H), 5.55 (br s, 1H). $^{19}$F NMR (C$_6$D$_6$, 282.4 MHz): δ -120.06. HRMS (ESI$^+$) m/z calcd. for C$_{12}$H$_9$BrFN 265.9975. Found: 265.9986 [M+H].

[$^{F*}$PN]Li (7b).$^{34}$ 2-Bromo-4-fluoro-diphenylamine (455 mg, 1.71 mmol) was dissolved in 25 mL diethyl ether and the pale yellow solution was cooled to -78°C, at which point a solution of nBuLi (1.6 M in hexanes, 2.14 mL, 3.42 mmol) was syringed in, causing the solution to darken slightly. After warming to ambient temperature and stirring for 3 hours, the solution was again cooled to -78°C and chlorodiisopropylphosphine (522 mg, 3.42 mmol) was added via syringe. The resulting orange solution was immediately green luminescent, and was stirred at ambient temperature for 18 hours, at which point the reaction was shown to be complete by $^{19}$F NMR. The solution was filtered through Celite, and 1.0 M HCl in diethyl ether (14 mL, 14 mmol) was then added via syringe, immediately bleaching the solution and causing the precipitation of a yellow-orange solid. After removing the solvent in vacuo, the solid was washed with copious pentane, and then redissolved in THF. Excess NaOMe (400 mg) was added and the resulting solution was stirred overnight. The solvent was removed in vacuo, and the residue was extracted with pentane and filtered through Celite. The solvent was removed, and the yellow-brown residue was redissolved in 10 mL pentane and cooled to -35°C, at which point nBuLi (1.6 M in hexanes, 1.1 mL, 1.76 mmol) was added via syringe. After stirring overnight, a large amount of precipitate was evident, which was collected on a frit, yielding a light brown solid (218 mg, 41%). $^1$H NMR (THF-d$^8$, 300 MHz): δ 7.03 (m, 1H), 6.84 (t, 2H), 6.71 (m, 3H), 6.53 (t, 1H), 6.22 (t, 1H), 2.02 (m, 2H), 1.13 (d, 3H), 1.09 (d, 3H), 1.01 (d, 3H), 0.97 (d, 3H), $^{19}$F NMR (THF-d$^8$, 282.4 MHz): δ -133.68. HRMS (ESI$^+$) m/z calcd. for C$_{18}$H$_{23}$FNP 304.1625. Found: 304.1635 [M+H], 291.1624 [M-Me].

[$^{F*}$PN]Cu(PPh$_3$)$_2$ (7). 3 mL diethyl ether solutions of CuBr•SMe$_2$ (55 mg, 0.265 mmol) and triphenylphosphine (139 mg, 0.53 mmol) were combined and stirred, giving a white slurry. [$^F$PN]Li (82 mg, 0.265 mmol) was dissolved in approximately 3 mL diethyl ether and cooled to -35°C, then the yellow solution was added dropwise to the Cu/phosphine solution, causing it to turn dark orange. The solution was diluted with diethyl ether to 12 mL and stirred for 18 hours, at which point the solvent was removed in vacuo. The residue was extracted with benzene, filtered through Celite, and lyophilized to give a spectroscopically pure orange powder (206 mg, 87%). $^1$H NMR (C$_6$D$_6$, 300 MHz): δ 7.48-7.35 (br m, 18H), 7.07-6.98 (m, 24H), 1.87 (m, 2H), 0.99 (d, 3H), 0.93 (d, 3H), 0.89 (d, 3H), 0.85 (d, 3H). $^{13}$C NMR (C$_6$D$_6$, 125 MHz): δ 136.13, 134.59 (d, J$_{PC}$ = 17.1 Hz), 129.81, 129.15 (J$_{PC}$ = 8.0 Hz), 128.92, 125.67, 30.56, 23.91, 20.13, 18.93. $^{19}$F NMR (C$_6$D$_6$, 282.4 MHz): δ -133.61. $^{31}$P NMR (C$_6$D$_6$, 121.5 MHz): δ -0.69 (2P), -3.32 (1P). HRMS (ESI$^+$) m/z calcd. for C$_{54}$H$_{52}$CuFNP$_3$ 890.2665, [M-PPh$_3$] 628.2054. Found: 628.1882 [M-PPh$_3$], 587.1211 [M-[PN]].

[PN]Cu(DPEphos) (8). In the glovebox, 5 mL diethyl ether solutions of CuBr•SMe$_2$ (141 mg, 0.687 mmol) and DPEphos (bis[2-(diphenylphosphino)-phenyl] ether, 370 mg, 0.687 mmol), were cooled to -35°C. The DPEphos solution was added to the copper solution, giving a white slurry, which was stirred while a yellow solution of [PN]Li (200 mg, 0.687 mmol) in 5 mL diethyl ether was also cooled to -35°C. The [PN]Li solution

was added to the mixture of CuBr and DPEphos, and the resulting yellow solution was diluted to 40 mL with diethyl ether and stirred at ambient temperature. After 24 hours, the solvent was removed in vacuo. The remaining residue was redissolved in benzene, filtered through Celite, and lyophilized to give a bright yellow powder (514 mg, 84%). $^1$H NMR ($C_6D_6$, 500 MHz): δ 7.71 (dd, 1H), 7.57 (s, 8H), 7.41 (d, 2H), 7.13 (t, 1H), 7.04 (t, 2H), 6.97 (m, 14H), 6.85 (t, 1H), 6.69 (m, 3H), 6.54 (t, 2H), 6.43 (m, 3H), 1.60 (m, 2H), 1.22 (dd, 6H) 0.54 (dd, 6H). $^{13}$C NMR ($C_6D_6$, 125 MHz): 136.05 (d, $J_{PC}$ = 13 Hz), 134.58 (d, $J_{PC}$ = 16.6 Hz), 132.26 (d, $J_{PC}$ = 14.3 Hz), 129.87, 129.81, 129.16 (d, $J_{PC}$ = 8.5 Hz), 128.91, 128.68, 23.94, 20.08 ($J_{PC}$ = 10.9 Hz), 19.25, 17.24, 16.83. $^{31}$P NMR (202.5 MHz): δ -2.8 (1P), -14.2 (2P). Anal. calcd. for $C_{54}H_{51}CuNOP_3 \cdot C_6H_6$: C, 74.71; H, 5.96; N, 1.45; Found: C, 74.55; H, 5.93; N, 1.44.

---

[1] Vlček, A., Jr. *Coord. Chem. Rev.* **2000**, *200-202*, 933-977.

[2] Ciesla, P.; Kocot, P.; Mytych, P.; Stasicka, Z. *J. Mol. Catal., A.* **2004**, *224*, 17-33.

[3] (a) Grätzel, M. *J. Photochem. Photobiol., A*, **2004**, *164*, 3-14. (b) Nazeeruddin, Md. K.; Klein, C.; Liska, P.; Grätzel, M. *Coord. Chem. Rev.* **2005**, *249*, 1460-1467.

[4] (a) Brown, G. M.; Brunschwig, B. S.; Creutz, C.; Endicott, J. F.; Sutin, N. *J. Am. Chem. Soc.* **1979**, *101*, 1298-1300 (b) Bard, A. J.; Fox, M. A. *Acc. Chem. Res.* **1995**, *28*, 141-145.

[5] (a) Chou, P.-T.; Chi, Y. *Eur. J. Inorg. Chem.* **2006**, *2006*, 3319-3332 (b) Williams, J. A. G.; Develay, S.; Rochester, D. L.; Murphy, L. *Coord. Chem. Rev.* **2008**, *252*, 2596-2611.

[6] Yersin, H. *Top. Curr. Chem.* **2004**, *241*, 1-26.

[7] Armaroli, N. *Chem. Soc. Rev.* **2001**, *30*, 113-124.

[8] Miller, A. J. M.; Dempsey, J. L.; Peters, J. C. *Inorg. Chem.* **2007**, *46*, 7244-7246.

[9] (a) Yam, V. W.-W.; Lo, K. K.-W.; Wang, C.-R.; Cheung, K.-K. *J. Phys. Chem., A*, **1997**, *101*, 4666-4672. (b) Cuttell, D. G.; Kuang, S.-M.; Fanwick, P. E.; McMillin, D. R.; Walton, R. A. *J. Am. Chem. Soc.* **2002**, *124*, 6-7.

[10] Harkins, S. B.; Peters, J. C. *J. Am. Chem. Soc.* **2005**, *127*, 2030-2031.

[11] Evans, R. C.; Douglas, P.; Winscom, C. J. *Coord. Chem. Rev.* **2006**, *250*, 2093-2126.

[12] Tsuboyama, A.; Kuge, K.; Furugori, M.; Okada, S.; Hoshino, M.; Ueno, K. *Inorg. Chem.* **2007**, *46*, 1992-2001.

[13] (a) De Angelis, F.; Fantacci, S.; Evans, N.; Klein, C.; Zakeeruddin, S. M.; Moser, J.-E.; Kalyanasundaram, K.; Bolink, H. J.; Grätzel, M.; Nazeeruddin, Md. K. *Inorg. Chem.* **2007**, *46*, 5989-6001 (b) De Angelis, F.; Fantacci, S.; Sgamellotti, A.; Cariati, E.; Ugo, R.; Ford, P. C. *Inorg. Chem.* **2006**, *45*, 10576-10584.

[14] Zgierski, M. Z. *J. Chem. Phys.* **2003**, *118*, 4045-4051.

[15] Sadighi, J. P.; Harris, M. C.; Buchwald, S. L. *Tetrahedron Lett.* **1998**, *39*, 5327-5330.

[16] Harkins, S. B. Ph.D Thesis, California Institute of Technology, Pasadena, CA, 2005.

[17] Tran, B. L.; Pink, M.; Mindiola, D. J.; *Organometallics* **2009**, *28*, 2234-2243.

[18] (a) Thomas, A. W.; Ley, S. V. *Angew. Chem. Int. Ed.* **2003**, *42*, 5400-5449. (b) Chan, D. M. T.; Monaco, K. L.; Wang, R.-P.; Winters, M. P. *Tetrahedron Lett.* **1998**, *39*, 2933-2936.

[19] (a) Miyaura, N.; Suzuki, A. *Chem. Rev.* **1995**, *95*, 2457-2483. (b) Hartwig, J. F. *Angew. Chem. Int. Ed.* **1998**, *37*, 2046-2067.

[20] Becke, A. D., *J. Chem. Phys.* **1993**, *98*, 5648-5652.

[21] Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785-789.

[22] (a) Hay, P. J.; Wadt, W. R. *J. Chem. Phys.* **1985** *82*, 270-283. (b) Hay, P. J.; Wadt, W. R. *J. Chem. Phys.* **1985** *82*, 284-298. (c) Hay, P. J.; Wadt, W. R. *J. Chem. Phys.* **1985** *82*, 299-310.

[23] Check, C. E.; Faust, T. O.; Bailey, J. M.; Wright, B. J.; Gilbert, T. M.; Sunderlin, L. S. *J. Phys. Chem., A*, **2001**, *105*, 8111-8116.

[24] (a) Dreuw, A.; Head-Gordon, M. *J. Am. Chem. Soc.* **2004**, *126*, 4007-4016. (b) Dreuw, A.; Head-Gordon, M. *Chem. Rev.* **2005**, *105*, 4009-4037.

[25] Zyubin, A. S.; Mebel, A. M. *J. Comput. Chem.* **2003**, *24*, 692-700.

[26] (a) Perdew J. P.; Burke, K.; Ernzerhof, M. *Phys. Rev. Lett.* **1996**, *77*, 3865-3868. (b) Perdew J. P.; Burke, K.; Ernzerhof, M. *Phys. Rev. Lett.* **1997**, *78*, 1396.

[27] Kasha, M. *Discuss. Faraday Soc.* **1950**, *9*, 14-19.

[28] Cowely, A. H.; Jones, R. H.; Mardones, M. A.; Nunn, C. M. *Organometallics* **1991**, *10*, 1635-1637.

[29] Tidwell, J. H.; Buchwald, S. L. *J. Am. Chem. Soc.* **1994**, *116*, 11797-11810.

[30] Tsuda, T.; Yazawa, T.; Watanabe, K.; Fujii, T.; Saegusa, T. *J. Org. Chem.* **1981**, *46*, 192-194.

[31] Thomas, S. L.; Yagi, S.; Swager, T. M.; *J. Mater. Chem.* **2005**, *15*, 2829-2835.

[32] Demas, J. N.; Crosby, G. A.; *J. Phys. Chem.* **1971**, *75*, 991-1024.

[33] Gaussian 03, Revision E.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, and J. A. Pople, Gaussian, Inc., Wallingford CT, 2004.

[34] Protonolysis of lithium amides **3b**, **6b**, and **7b** with EtOH yielded the corresponding amines, which were analyzed by HRMS.

**Appendix:**

**Curriculum Vitae**

# Seth Mickenberg

Massachusetts Institute of Technology
Cambridge, MA 02139 USA

Bldg. 18-143
sfm@mit.edu

| | | |
|---|---|---|
| **Education** | **Massachusetts Institute of Technology** | Cambridge, MA |

**Education**

**Massachusetts Institute of Technology**      Cambridge, MA
M.Sc. in June 2009. Graduate Student and Research Assistant. Department of Chemistry.
Research on new luminescent copper complexes with unprecedented lifetimes and quantum yields.

**University of California, Berkeley**      Berkeley, CA
B.Sc. in Chemistry with Honors with a minor in German, May 2007. Coursework in inorganic,
organic, physical, and nuclear chemistry, including labs, as well as three years of German.

**Technische Universität Berlin**      Berlin, Germany
Studied abroad in Germany at the Technische Universität in Berlin in academic year 2005-06.
Courses in chemistry, German language, and German history, taught in German.

**Research**

**MIT, Department of Chemistry** (Advisor: Jonas Peters)      Cambridge, MA
Probed the electronic effects of various substituents on the luminescent properties of
amidophosphine-copper complexes synthetically and computationally.      (Dec. 2007 – June 2009)

**UC Berkeley, Department of Chemistry** (Advisor: John Arnold)      Berkeley, CA
Synthesis of a new tetradentate-monoanionic ligand for use with various transition metal centers,
including characterization of complexes with all first-row metals.      (Sep. 2006 – May 2007)

**TU Berlin, Department of Chemistry** (Advisor: Andreas Grohmann)      Berlin, Germany
Work with various ligands exhibiting reversible bond cleavage and agostic interactions.

**Teaching**

**MIT, Department of Chemistry**      Cambridge, MA
Introductory Inorganic and Organic Chemistry Laboratory
Taught two semesters of the first lab classes taken by chemistry majors. The first semester was the
first time these "modules" had been taught, and the various kinks inherent in a new class had to be
worked out on the go. 30 students over two semesters.      (Aug. 2007 – May 2008)

**Employment**

**Apple Computer** (Mac Specialist)      Emeryville, CA
Sales of computers, iPods, and accessories at one of the busiest Apple retail stores in the Bay
Area.      (Oct. 2004 – April 2005)

**Publications**

S. F. Mickenberg and J. C. Peters. Inorganic Chemistry. Manuscript in Preparation.
W. A. Chomitz, S. F. Mickenberg, and J. Arnold. Inorganic Chemistry. 2008, 47, 373-380.

**Activities**

**Language**
- Fluent in German (speaking, reading, writing), 3+ years of study.

**Travel**
- Traveled extensively in the following countries: Germany, UK, Netherlands, Switzerland, Australia, New Zealand, Thailand, and throughout the US.
- Shorter visits to: France, Poland, Italy, Canada, Myanmar, and Laos.

**Study Abroad**
- Studied in Berlin during third year of university, living independently.
- Acted as a mentor to a visiting student from Germany after returning.
- Partook in various panel discussions put on by the study abroad office.

**Awards**

Stipend from the DAAD (German Academic Exchange Service) for study in Berlin (2005-06).