Inorganic Chemistry
Article
pubs.acs.org/IC

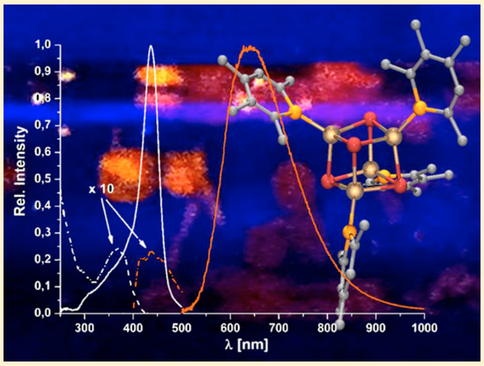
Synthesis and Photoluminescence Properties of an Unprecedented Phosphinine–Cu_4Br_4 Cluster

Philipp Roesch,[†] Jörn Nitsch,[‡] Martin Lutz,[§] Jelena Wiecko,[†] Andreas Steffen,*[,‡] and Christian Müller*[,†]

[†]Institut für Chemie und Biochemie, Freie Universität Berlin, Fabeckstraße 34/36, 12167 Berlin, Germany
[‡]Institut für Anorganische Chemie, Julius-Maximilians-Universität Würzburg, Am Hubland, 97074 Würzburg, Germany
[§]Crystal and Structural Chemistry, Utrecht University, Padualaan 8, 3584 CH Utrecht, The Netherlands

Supporting Information

ABSTRACT: A hitherto unprecedented polynuclear phosphinine–Cu(I) complex has been prepared and crystallographically characterized. The molecular structure in the crystal verifies the presence of the heterocubane-type tetrameric cluster $[LCuBr]_4$ (L = 2,4-diphenyl-5-methyl-6-(2,3-dimethylphenyl)phosphinine), which unexpectedly shows in the solid state temperature-independent orange phosphorescence solely from an ^{3}XMLCT state, in clear contrast to the well-established dual-emissive-state model for luminescent $Cu_4X_4L_4$ clusters.



■ INTRODUCTION

Since the first successful preparation of 2,4,6-triphenylphosphinine by Märkl in 1966, this low-coordinate phosphorus compound has been regarded as an aromatic heterocycle with significantly different electronic properties in comparison to its nitrogen counterpart (pyridine), as well as classical trivalent P(III) species.[1] Due to an inversion of the π- and n-orbital sequence between phosphinine and pyridine and the presence of an energetically low-lying LUMO, phosphinines usually act as weak σ-donor but rather strong π-acceptor ligands, which can stabilize efficiently metal centers in low oxidation states.[2] Because phosphinines are also ambidentate ligands with a range of possible coordination modes, their coordination chemistry is particularly versatile and has been explored during the last few decades.[2b,3] Recent attempts by our group to stabilize even transition-metal centers in medium to high oxidation states by chelating phosphinines have led to the development of a whole new range of coordination compounds based on phosphinines with potential application in molecular materials.[4] Although monodentate phosphinines prefer σ coordination through the phosphorus lone pair to rather electron rich metal centers, it is surprising that the coordination chemistry of such compounds with Cu(I) has been limited so far to only a few examples.

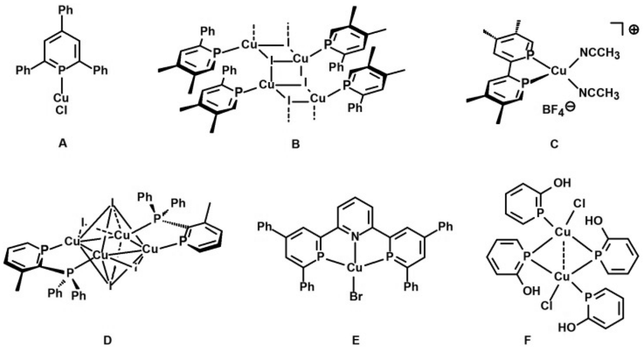


Figure 1. Phosphinine-based Cu complexes.

Kanter and Dimroth reported on spectroscopic data of 2,4,6-triphenylphosphinine–CuCl (**A**; Figure 1).[5] Matsuda et al. investigated the coordination chemistry of 2-phenyl-3,4-dimethylphosphinine (dmppn) with Cu–halides and could isolate and structurally characterize the infinite stepped straight structure of $[Cu(dmppn)I]_\infty$ (**B**).[6] Later on, also the solid-state structures of the corresponding CuCl and CuBr complexes were explored by CP/MAS $^{31}P\{^1H\}$ NMR spectroscopy.[7] The same group described that 2,4,6-triphenylphosphinine reacts with $[Cu(CH_3CN)_4]ClO_4$ to give an unusual cofacial oxidative coupling product with destruction of the aromatic system.[8] On the other hand, Le Floch and Mathey demonstrated that 2,2′-bisphosphinine reacts with $[Cu(CH_3CN)_4]BF_4$ to form the cationic monochelate **C**.[9] In the presence of 1 equiv of 2,2′-bipyridine, the formation of an infinite helical polymeric structure was observed. The same group reported on the tetranuclear $[CuI]_4$ cluster **D**, containing the chelating 2-diphenylphosphino-3-methylphosphinine ligand.[10] This cluster may be described as an octahedron having a nearly square planar Cu_4 base. Our group has reported on a diphosphinine

Received: June 18, 2014
Published: August 26, 2014

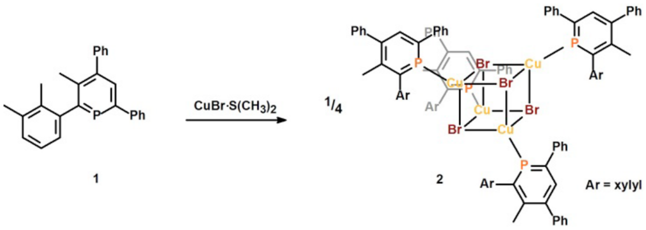
dx.doi.org/10.1021/ic5014472 | *Inorg. Chem.* 2014, 53, 9855–9859

derivative of terpyridine reacting with CuBr·SMe$_2$ to form an unusual Cu(I) complex with a distorted-tetrahedral coordination geometry of the metal center (**E**).[11] More recently, Mathey et al. described the dimeric [LCuCl]$_2$ complex **F**, with L (2-phosphaphenol) acting both as an η^1-P terminal and a μ_2-P bridging phosphinine ligand.[12]

■ RESULTS AND DISCUSSION

Because the structures of 1:1 adducts of copper(I) halides with monodentate Lewis bases, such as amines, pyridines, and phosphines, strongly depends on the steric and electronic parameters of the metal, halide, and Lewis base, we decided to further explore the coordination chemistry of especially bulky phosphinines with copper(I) bromide.[13] We anticipated that in this way the formation of different structural motifs, other than the known infinite step structure **B** (Figure 1), might be feasible. A racemic mixture of the axially chiral phosphinine **1**, which exists as R_a and S_a enantiomers due to restricted rotation around a C−C bond, was thus reacted with a stoichiometric amount of CuBr·SMe$_2$ in dichloromethane, according to Scheme 1.[14] After workup, a yellow solid was obtained in 59% isolated yield from a concentrated solution in THF. Recrystallization from THF/pentane afforded bright yellow crystals, suitable for X-ray diffraction. The compound crystallizes in the triclinic space group $P\bar{1}$ (No. 2), and the molecular structure is depicted in Figure 2, along with selected bond lengths and angles.

Scheme 1. Synthesis of 2



Interestingly, it turned out that the reaction of **1** with CuBr·SMe$_2$ led to the formation of a heterocubane-type cluster of the type [(**1**)CuBr]$_4$ (**2**). Intriguingly, this structural motif is so far unprecedented in phosphinine chemistry and represents the first tetrameric Cu(I) cluster containing an aromatic phosphorus heterocycle. The synthesis of **2** is fully reproducible, as the formation of the heterocubane cluster could be verified in independent syntheses and crystallographic characterizations.

A detailed look at the stereochemistry of the four axially chiral phosphinines in **2** reveals that one pair of the R_a and one pair of the S_a enantiomer is present in each cluster. The molecular structure of **2** can further be compared with the [LCuBr]$_4$ cluster, in which L = 2-methylpyridine.[15] In that symmetric compound the Cu−Br distances were found to be 2.589(7), 2.425(1), and 2.625(2) Å, respectively, and thus are very similar in comparison to **2**.

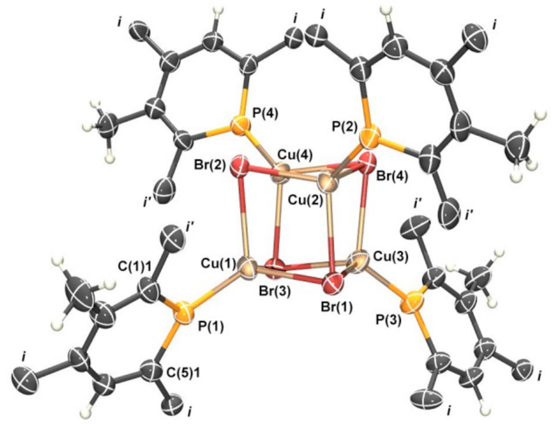


Figure 2. Molecular structure of **2** in the crystal. Displacement ellipsoids are shown at the 50% probability level. Disordered solvent molecules and the aromatic phenyl and 2,3-dimethylphenyl rings are omitted for clarity, and only the corresponding ipso carbon atoms *i* (phenyl) and *i*′ (2,3-dimethylphenyl) are shown. See also the Supporting Information. Selected bond lengths (Å) and angles (deg): Cu(1)−P(1), 2.1846(17); Cu(2)−P(2), 2.1716(16); Cu(3)−P(3), 2.1758(17); Cu(4)−P(4), 2.1758(17); Cu(1)−Br(1), 2.5155(10); Cu(1)−Br(2), 2.5446(9); Cu(1)−Br(3), 2.5378(9); Cu(2)−Br(1), 2.5160(9); Cu(2)−Br(2), 2.4825(9); Cu(2)−Br(4), 2.5617(9); Cu(3)−Br(1), 2.4810(9); Cu(3)−Br(3), 2.5638(10); Cu(3)−Br(4), 2.5280(9); Cu(4)−Br(2), 2.5403(10); Cu(4)−Br(3), 2.5171(9); Cu(4)−Br(4), 2.4943(9); C(1)1−P(1)−C(5)1, 103.6(3).

We recently started a program to investigate phosphinines as novel ligands in coordination compounds with potential photoluminescent properties and reported on the first homoleptic cyclometalated phosphinine−Ir(III) complex *fac*-[Ir(C^P)$_3$], which was prepared by C−H activation of 2,4,6-triphenylphosphinine with [Ir(acac)$_3$].[16] Interestingly, multinuclear Cu(I) compounds have also attracted considerable interest, due to their unusual photophysical properties.[17] Tetrameric copper(I) clusters composed of a Cu$_4$X$_4$ core have previously been reported to show luminescence, with [Cu$_4$I$_4$py$_4$] being the most extensively studied example, and many of them show a high-energy (HE) and a low-energy (LE) emission band varying in intensity depending on the temperature.[18] The dual emission has been rationalized by phosphorescence occurring from two different states, a cluster-centered ^{3}CC and a ^{3}XMLCT state, which can thermally interconvert depending on the nature of the halide and the ligands.[18,19] Inspired by those coordination compounds, we started to explore the photoluminescent properties of **2** and were intrigued by the fact that the tetrameric cluster **2** exhibits an intense orange luminescence (λ_{max} 640 nm) at room temperature when irradiated with UV light in the solid state. A detailed photophysical study shows an intense excitation band with a maximum at λ_{ex} 430 nm, and the broad emission between λ 500 and 1000 nm is phosphorescent in nature, with an average emission lifetime of τ_{298} = 171 μs, which is increased at T = 77 K to ca. τ_{77} = 1516 μs (Figure 3 and Supporting Information). Interestingly, a weak high-energy emission (λ_{max} 450 nm) is observable, of which the excitation is different than for λ_{max} 640 nm.

It should be mentioned here that the photophysically active pyridine-based clusters mentioned above are characterized by cuprophilic interactions (d_{CuCu} < 2.8 Å). These are absent in **2** (Figure 2; d_{CuCu} = 3.1304(12)−3.3087(11) Å), presumably due to the steric demand of the phosphinine ligands. Moreover, lowering the temperature to T = 77 K does not change the emission color: i.e., we do not observe the typical thermochromic behavior of Cu$_4$X$_4$L$_4$ clusters (Figure 4).[18,19] This makes the contribution of a ^{3}CC state to the emission highly unlikely and cannot serve as an explanation for the weak HE band shown in Figure 3.

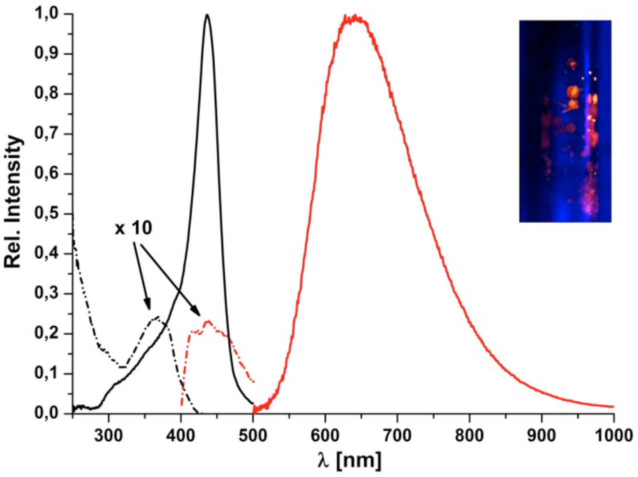


Figure 3. Excitation (black dashed line, corresponding λ_{em} 465 nm; black solid line, corresponding λ_{em} 620 nm) and emission (red dashed line, corresponding λ_{ex} 350 nm, red solid line, corresponding λ_{ex} 350 or 410 nm) spectra of **2** in the solid state at room temperature. The photo shows the luminescence of **2** under the UV lamp.

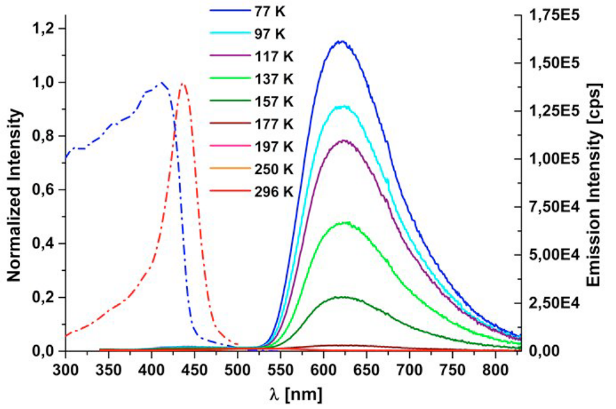


Figure 4. Excitation (dashed lines, corresponding λ_{em} 620 nm) at 296 K (red) and 77 K (blue) and temperature-dependent emission spectra (solid lines, corresponding λ_{ex} 266 nm) spectra of **2** in the solid state.

Indeed, DFT calculations (PBE0/LANL2DZ) suggest the HOMO to HOMO-8 to be combinations of Cu(d) and Br(p) orbitals, while the LUMO to LUMO+7 are all phosphinine-centered (Figure 5 and the Supporting Information).

Consequently, TD-DFT studies confirm the lowest energy excitation $S_0 \rightarrow S_1$ at λ 410 nm ($f = 0.004$), the value of which is in excellent agreement with the experiment, and the following 12 excitations between λ 408 and 352 nm to be of XMLCT character (Figures 3–5 and the Supporting Information): i.e., charge transfer from Cu and Br occurs to the phosphinine ligand. These results are similar to calculations on structurally related $Cu_4I_4L_4$ clusters (L = py, PR_3 with R = H, cpent, Ph) performed by De Angelis et al. as well as Perruchas and Boilot et al., who described those transitions as XLCT although the copper atom is strongly involved in their case as well.[19]

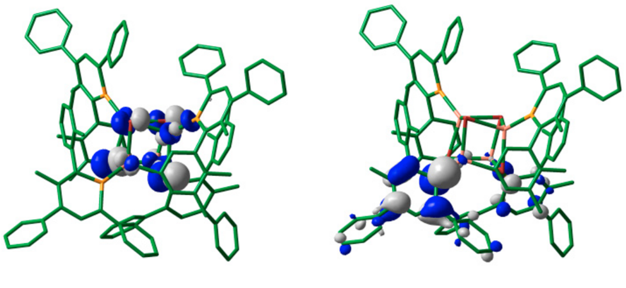


Figure 5. HOMO (left) and LUMO (right) of the optimized ground state S_0 of **2** (isovalue 0.035).

The same assignment as for S_1 in **2** is also true for the lowest triplet state T_1, with the spin density mainly being delocalized over one of the phosphinine ligands with a minor contribution of a copper and a bromine atom (Figure 6).

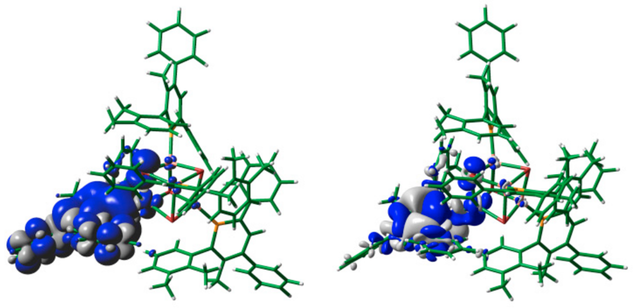


Figure 6. Spin density distribution of optimized T_1 (left) and electron density change upon emission $T_1 \rightarrow S_0$ (right) (isovalue 0.005) of **2**.

However, this is in clear contrast to the characterization of the lowest triplet state in the aforementioned clusters as ^{3}CC by photophysical and theoretical studies.[18,19] Furthermore, a comparison of the photophysical data of **2** with those of 2,6-bis(2-thienyl)-4-phenylphosphinine, which exhibits HE fluorescence (λ_{max} 450 nm) and LE phosphorescence (λ_{max} 601 nm, $\tau_{80} \approx 1000$ μs) as well, shows a very close resemblance, leading us to investigate the photophysics of the free ligand **1**.[20] The solid-state emission and excitation spectra of **1** at room temperature and at 77 K are shown in Figure 7.

The free phosphinine **1** exhibits intense fluorescence in the solid state, both at room temperature and at T = 77 K with average emission lifetimes of 1.38 and 1.56 ns, respectively (see also the Supporting Information). However, we did not observe any phosphorescence at those temperatures, although the

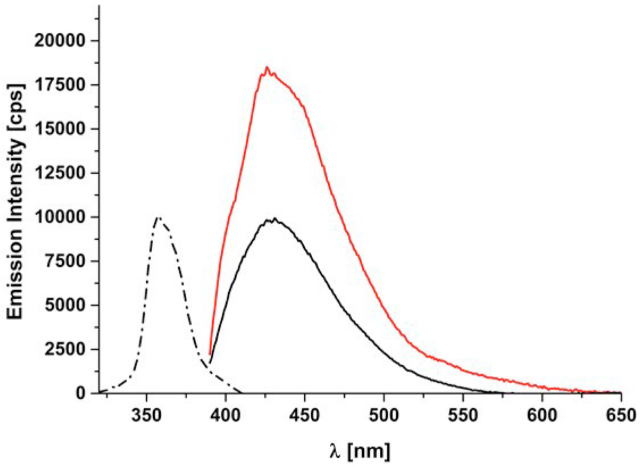


Figure 7. Excitation (dashed, corresponding λ_{em} 430 nm) and emission (solid, corresponding λ_{ex} 365 nm) spectra of phosphinine **1** in the solid state at room temperature (black) and at 77 K (red).

fluorescence intensity is increased. Therefore, we assign the weak HE band in **2** to residual fluorescence originating from ligand **1**, which is mostly quenched by the spin−orbit coupling (SOC) originating from the $\{Cu_4Br_4\}$ cluster core.

During the preparation of our paper, Moussa and Amouri et al. found a similar strong influence of the SOC mediated by Pt on a phosphinine ligand. The phosphinine displays weak fluorescence at room temperature, which is accompanied by a more intense phosphorescence (τ = 18.7 ms) at T = 77 K.[21] However, the SOC leads to quenching of the fluorescence, and phosphorescence in $[Pt(ppy)(phosphinine)_2]$ is only observed at 77 K in a glass matrix (τ = 230 μs), while at room temperature no emission is detected at all. This is in stark contrast to the case for our copper phosphinine cluster **2**, which does emit even at room temperature, while its photoluminescence spectra and assignments can be compared with those of the phosphinine−platinum complex.[21] Due to the fact that no quantum yields have been reported, a comparison with the lifetime of **2** is, however, difficult.

In conclusion, coordination compound **2** appears to be a rare example of a phosphinine-based $Cu_4X_4L_4$ cluster, which exhibits orange phosphorescence solely from a ^{3}XMLCT state. No ^{3}CC is present due to the steric demand of the phosphinine ligand, which inhibits Cu−Cu interactions. To the best of our knowledge, **2** is the first example of a phosphinine-based coordination compound showing phosphorescence even at room temperature. Further investigations in exploring these aromatic heterocycles in such molecular materials are currently being performed in our laboratories.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Text, figures, tables, and a CIF file giving details of the syntheses and characterization data for the compounds prepared in this paper, additional experimental data, crystallographic data for **2**, and details of the calculations and Cartesian coordinates for the calculated structures. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Authors

*A.S.: e-mail, andreas.steffen@uni-wuerzburg.de; fax, +49 931 318 5514; tel, +49 931 318 6180.

*C.M.: e-mail, c.mueller@fu-berlin.de; fax, +49 30 838 454004; tel, +49 30 838 54004.

Author Contributions

All authors have given approval to the final version of the manuscript.

Funding

Financial support from the DFG (STE1834/4-1) and the Bavarian State Ministry of Science, Research, and the Arts for the Collaborative Research Network "Solar Technologies go Hybrid" (A.S.) is gratefully acknowledged. C.M. thanks the European Initial Training Network Network SusPhos (317404) for financial support.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

A.S. thanks Prof. Marder (Würzburg) for his generous support. C.M. thanks B.Sc. Sebastian Brühl and M.Sc. Massimo Rigo for their synthetic input.

■ REFERENCES

(1) (a) Märkl, G. *Angew. Chem.* **1966**, *78*, 907. (b) Ashe, A. J., III *J. Am. Chem. Soc.* **1971**, *93*, 3293.

(2) (a) Waluk, J.; Klein, H.-P.; Ashe, A. J., III; Michl, J. *Organometallics* **1989**, *8*, 2804. (b) Mézailles, N.; Mathey, F.; Le Floch, P. *Prog. Inorg. Chem.* **2001**, 455.

(3) (a) Müller, C.; Broeckx, L. E. E.; de Krom, I.; Weemers, J. J. M. *Eur. J. Inorg. Chem.* **2013**, 187. (b) Müller, C.; Vogt, D. In *Catalysis and Material Science Applications*; Peruzzini, M., Gonsalvi, L., Eds.; Springer: Berlin, 2011; Vol. 36, Chapter 6. (c) Müller, C. In *Phosphorus Ligand Effects in Homogeneous Catalysis: Design and Synthesis*; Kamer, P. C. J., van Leeuwen, P. W. N. M.; Wiley-VCH: Weinheim, Germany, 2012. (d) Le Floch, P.; Mathey, F. *Coord. Chem. Rev.* **1998**, *179*, 771. (e) Le Floch, P. *Coord. Chem. Rev.* **2006**, *250*, 627. (f) Müller, C.; Vogt, D. *Dalton Trans.* **2007**, 5505.

(4) (a) de Krom, I.; Broeckx, L. E. E.; Lutz, M.; Müller, C. *Chem. Eur. J.* **2013**, *19*, 3676. (b) Broeckx, L. E. E.; Güven, S.; Heutz, F. J. L.; Lutz, M.; Vogt, D.; C. *Chem. Eur. J.* **2013**, *19*, 13087. (c) Broeckx, L. E. E.; Lutz, M.; Vogt, D.; Müller, C. *Chem. Commun.* **2011**, *47*, 2003.

(5) Kanter, H.; Dimroth, K. *Tetrahedron Lett.* **1975**, *8*, 541.

(6) Shiotsuka, M.; Matsuda, Y. *Chem. Lett.* **1994**, 351.

(7) Shiotsuka, M.; Tanamachi, T.; Urakawa, T.; Munakata, M.; Matsuda, Y. *J. Supramol. Chem.* **2002**, *2*, 211.

(8) Kojima, T.; Ishioka, Y.; Matsuda, Y. *Chem. Commun.* **2004**, 366.

(9) Le Floch, P.; Ricard, L.; Mathey, F. *Bull. Soc. Chim. Fr.* **1996**, *133*, 691.

(10) Mézailles, N.; Le Floch, P.; Waschbüsch, K.; Ricard, L.; Mathey, F.; Kubia, C. P. *J. Organomet. Chem.* **1997**, *541*, 277.

(11) Müller, C.; Pidko, E. A.; Lutz, M.; Spek, A. L.; Vogt, D. *Chem. Eur. J.* **2008**, *14*, 8803.

(12) Mao, Y.; Lim, K. M. H.; Li, Y.; Ganguly, R.; Mathey, F. *Organometallics* **2013**, *32*, 3562.

(13) Ford, P. C.; Cariati, E.; Bourassa, J. *Chem. Rev.* **1999**, *99*, 3625.

(14) (a) Müller, C.; Pidko, E. A.; Staring, A. J. P. M.; Lutz, M.; Spek, A. L.; van Santen, R. A.; Vogt, D. *Chem. Eur. J.* **2008**, *14*, 4899. (b) Müller, C.; Pidko, E. A.; Lutz, M.; Spek, A. L.; van Santen, R. A.; Vogt, D. *Dalton Trans.* **2007**, *46*, 5372−5375.

(15) Engelhardt, L. M.; Healy, P. C.; Kildea, J. D.; White, A. H. *Aust. J. Chem.* **1989**, *42*, 107.

(16) Broeckx, L. E. E.; Delaunay, W.; Latouche, C.; Lutz, M.; Boucekkine, A.; Hissler, M.; Müller, C. *Inorg. Chem.* **2013**, *52*, 10738.

(17) See for example: (a) Zhan, S.-Z.; Li, M.; Ng, S. W.; Li, D. *Chem. Eur. J.* **2013**, *19*, 10217. (b) Lapprand, A.; Dutartre, M.; Khiri, N.; Levert, E.; Fortin, D.; Rousselin, Y.; Soldera, A.; Juge, S.; Harvey, P. D. *Inorg. Chem.* **2013**, *52*, 7958. (c) Liu, Z.; Qayyum, M. F.; Wu, C.; Whited, M. T.; Djurovich, P. I.; Hodgson, K. O.; Hedman, B.; Solomon, E. I.; Thompson, M. E. *J. Am. Chem. Soc.* **2011**, *133*, 3700. (d) Omary, M. A.; Mohamed, A. A.; Rawashdeh-Omary, M. A.; Fackler, J. P. *Coord. Chem. Rev.* **2005**, *249*, 1372. (e) Dias, H. V. R.; Diyabalanage, H. V. K.; Eldabaja, M. G.; Elbjeirami, O.; Rawashdeh-Omary, M. A.; Omary, M. A. *J. Am. Chem. Soc.* **2005**, *127*, 7489. (f) Lo, W.-Y.; Lam, C.-H.; Yam, V. W.-W.; Zhu, N.; Cheung, K.-K.; Fatallah, S.; Messaoudi, S.; Le Guennic, B.; Kahlal, S.; Halet, J.-F. *J. Am. Chem. Soc.* **2004**, *126*, 7300.

(18) (a) Knorr, M.; Guyon, F.; Khatyr, A.; Strohmann, C.; Allain, M.; Aly, S. M.; Lapprand, A.; Fortin, D.; Harvey, P. D. *Inorg. Chem.* **2012**, *51*, 9917. (b) Liu, Z.; Djurovich, P. I.; Whited, M. T.; Thompson, M. E. *Inorg. Chem.* **2012**, *51*, 230. (c) Knorr, M.; Pam, A.; Khatyr, A.; Strohmann, C.; Kubicki, M. M.; Rousselin, Y.; Aly, S. M.; Fortin, D.; Harvey, P. D. *Inorg. Chem.* **2010**, *49*, 5834. (d) Ryu, C. K.; Vitale, M.; Ford, P. C. *Inorg. Chem.* **1993**, *32*, 869. (e) Ford, P. C.; Vogler, A. *Acc. Chem. Res.* **1993**, *26*, 220.

(19) (a) Perruchas, S.; Tard, C.; Le Goff, X. F.; Fargues, A.; Garcia, A.; Kahlal, S.; Saillard, J.-Y.; Gacoin, T.; Boilot, J.-P. *Inorg. Chem.* **2011**, *50*, 10682. (b) De Angelis, F.; Fantacci, S.; Sgamellotti, A.; Cariati, E.; Ugo, R.; Ford, P. C. *Inorg. Chem.* **2006**, *45*, 10576.

(20) Müller, C.; Wasserberg, D.; Weemers, J. J. M.; Pidko, E. A.; Hoffmann, S.; Lutz, M.; Spek, A. L.; Meskers, S. C. J.; Janssen, R. A. J.; van Santen, R. A.; Vogt, D. *Chem. Eur. J.* **2007**, *13*, 4548.

(21) Moussa, J.; Cheminel, T.; Freeman, G. R.; Chamoreau, L.-M.; Williams, J. A. G.; Amouri, H. *Dalton Trans.* **2014**, *43*, 8162.