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Sequential Addition of Phosphine to Alkynes for the Selective Synthesis of 1,2-Diphosphinoethanes under Catalysis. Well-Defined NHC-Copper Phosphides vs in Situ $CuCl_2$/NHC Catalyst

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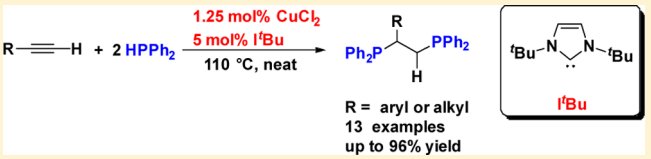
Supporting Information

ABSTRACT: The well-defined NHC-copper phosphides $[(NHC)CuPPh_2]_3$ (**1**, NHC = 1,3-diisopropyl-4,5-dimethylimidazol-2-ylidene (I^iPr); **2**, NHC = *N*,*N*-di-*tert*-butylimidazol-2-ylidene (I^tBu)) have been prepared by the reaction of simple copper halides with $HPPh_2$ in the presence of N-heterocyclic carbenes (NHCs). Complexes **1** and **2** enabled catalytic double hydrophosphination of alkyl and aryl terminal alkynes to yield 1,2-diphosphinoethanes selectively in good yields. On the basis of these results, the most efficient and pratical in situ $CuCl_2$/NHC catalyst has been developed. It catalyzes the selective double hydrophosphination of the alkynes with high efficiency and a wide substrate scope and exhibits even better performance than the well-defined NHC-Cu phosphides. The mechanistic studies disclosed that the formation of a copper acetylide in the catalytic cycle played an important role in the acceleration of the catalytic process.



INTRODUCTION

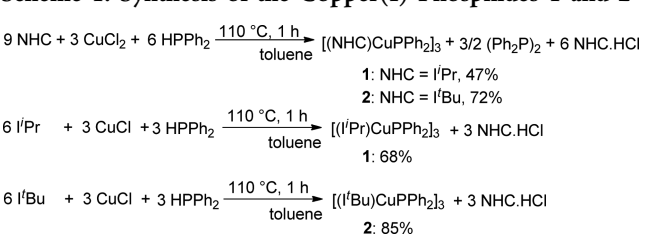
Bidentate organophosphines are immensely important ligands in coordination chemistry and transition-metal catalysis because of their relatively rigid coordination environments and collaborative electronic effects.[1] However, the modification of a desired backbone with different substituents is impeded by the use of strong bases and multistep synthesis.[2−4] Thus, the efficient and concise synthesis of various bidentate phosphines is of crucial importance for their wide and practical applications in catalysis and related fields.

In the past several years, metal-catalyzed addition of phosphines to unsaturated organic compounds has emerged as the most straightforward and atom-economical strategy for the construction of organophosphines.[5,6] To access bidentate phosphines, double addition of organophosphines to conjugated dienes and alkynes presents the most powerful and concise approach. However, double hydrophosphination of alkynes is very difficult, partially because of the steric hindrance of the resulting single hydrophosphination product. On the other hand, the chelating effects of the formed diphosphinoethanes may result in their strong bonding to the active metals, leading to catalyst poisoning.[4−7] As such, only a few well-defined catalysts based on iron, rhodium, and zirconium have been reported. However, these catalysts suffered from long reaction times (3−7 days) and limited substrate scopes or side reactions.[7,8]

To develop more efficient and practical catalysts, strongly electron donating ligands that are compatible with base metals may be considered to overcome the aforementioned chelating effects of the resulting bidentate phosphines. In the past several decades, NHC-copper complexes have been extensively studied as catalysts for diverse reactions due to the strongly electron donating character and structural diversity of NHC ligands.[9] With regard to hydrophosphination catalysts, metal phosphido complexes have been postulated as the key intermediates.[6] However, there are only very limited reports on the synthesis of well-defined copper phosphido complexes, since they tend to form large aggregates in the solid state in the absence of suitable supporting ligands.[10,11] Nolan and co-workers reported the synthesis of an NHC-Cu(I) phosphide by the reaction of an NHC-copper hydroxide with $HPPh_2$, but its structure and reactions have not been studied.[12]

Herein, we report the straightforward synthesis of NHC-copper phosphides by reaction of a simple copper halide with $HPPh_2$ in the presence of NHC ligands (Scheme 1). These phosphides enabled the catalytic double hydrophosphination of alkynes to yield 1,2-diphosphinoethanes selectively. On the

Scheme 1. Synthesis of the Copper(I) Phosphides 1 and 2



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basis of these results, the most practical and efficient in situ $CuCl_2$/NHC catalytic system for the sequential addition of a phosphine to aryl- and alkyl-substituted terminal alkynes has been rationally developed. This system enabled stepwise addition of a phosphine to alkynes and exhibited noticeably better activity in comparison to the well-defined copper phosphides. In addition, the mechanistic studies indicated that the formation of a copper acetylide from a terminal alkyne plays an important role in the acceleration of the catalytic process.

RESULTS AND DISCUSSION

Synthesis of NHC-Cu(I) Phosphide Complexes. The synthesis of the NHC-Cu(I) phosphides **1** and **2** was furnished in good yield by reaction of $CuCl_2$ with $HPPh_2$ in the presence of NHCs (NHC = 1,3-diisopropyl-4,5-dimethylimidazol-2-ylidene (I^iPr), 1,3-di-*tert*-butylimidazol-2-ylidene (I^tBu)) at 110 °C in toluene, along with the formation of $(Ph_2P)_2$ and the imidazolium chloride (Scheme 1).[11−13] Alternatively, complexes **1** and **2** could be similarly prepared by the reaction of CuCl with $HPPh_2$. However, a similar reaction in the presence of the more bulky NHC IDipp (1,3-bis(2,6-ispropylphenyl)imidazol-2-ylidene) did not occur, indicating the pronounced steric effects on the reaction.

Complexes **1** and **2** have been fully characterized by NMR spectroscopy and elemental analysis. The ^{13}C NMR spectra of the phosphides **1** and **2** exhibit C_{NHC} resonances at δ 188.5 and 188.2 ppm, respectively. The ^{31}P NMR spectra of **1** and **2** show singlets at δ −35.6 and −30.4 ppm, respectively. Single crystals of **2** suitable for an X-ray diffraction study were obtained from toluene/*n*-hexane at −40 °C. As shown in Figure 1, the

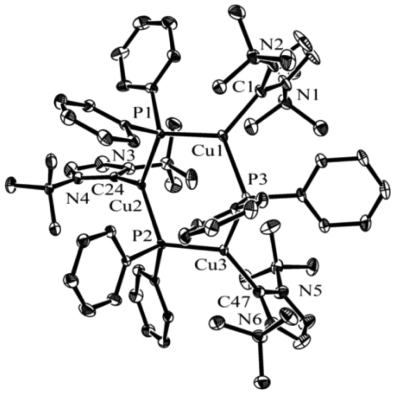
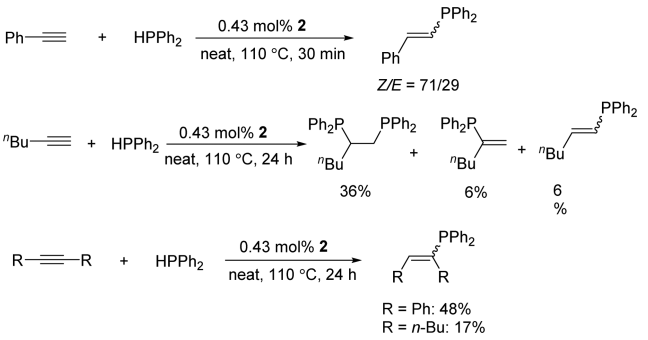


Figure 1. ORTEP drawing of **2** with 30% probability ellipsoids. Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (deg): Cu1−C1 1.997(3), Cu1−P1 2.3062(9), Cu1−P3 2.3323(9), Cu2−C24 1.993(3), Cu2−P2 2.3183(9), Cu2−P1 2.3393(8), Cu3−C47 1.990(4), Cu3−P3 2.3211(9), Cu3−P2 2.3225(8); P1−Cu1−P3 116.37(3); P2−Cu2−P1 114.30(3), P3−Cu3−P2 114.93(3), Cu1−P1−Cu2 116.17(3), Cu2−P2−Cu3 117.23(3), Cu3−P3−Cu1 117.50(4).

phosphide **2** is a trimer with the bridged PPh_2 ligand. The lengths of the six Cu−P bonds range from 2.3062 to 2.3393(8) Å, much longer than those observed in the tetrameric phosphides $Cu_4[P(^tBu)_2]_4$ (2.203(5)−2.214(4) Å).[11a] The three Cu−C_{NHC} bond lengths of 1.997(3), 1.993(3), and 1.990(4) Å are in the reported range for the NHC-Cu(I) silylphosphido complexes.[10a] Complex **2** represents a rare well-defined NHC-Cu(I) phosphide.[10,11]

Hydrophosphinaiton of Alkynes with NHC-Cu(I) Phosphide Complexes. With complexes **1** and **2** in hand, their potentials for the hydrophosphination of alkynes with $HPPh_2$ have been examined. As shown in Scheme 2, with 0.43

Scheme 2. Hydrophosphination of Alkynes with $HPPh_2$ Catalyzed by 2



mol % loading of complex **2**, the catalytic reaction of phenylacetylene with 1 equiv of $HPPh_2$ was complete at 110 °C in 30 min under solvent-free conditions, leading to the formation of the regioselective products as a mixture of *Z* and *E* isomers (*Z*:*E* = 71:29). The reaction in toluene also gave the products in 93% yield under similar conditions. Remarkably, the reaction of hex-1-yne with 1 equiv of $HPPh_2$ catalyzed by **2** gave the double-hydrophosphination product as a major product in 36% yield with the almost complete consumption of $HPPh_2$, along with the formation of single-addition products in 12% yield. However, the reactions of 1,2-diphenylethyne and dec-5-yne only gave the corresponding single hydrophosphination products in 48% and 17% yields, respectively. The results indicated that the hydrophosphination reaction is more efficient for terminal alkenes, and the double hydrophosphination of alkynes is possible. The successful double hydrophosphination of the alkyl-substituted terminal alkyne is especially noteworthy, since $CpFe(CO)_2Me$-catalyzed double hydrophosphination is only viable for aryl-substituted terminal alkynes and required 3 days at 110 °C.[7]

The double hydrophosphination of phenylacetylene with $HPPh_2$ has been studied as a model reaction for the optimization of catalysts and reaction conditions. In addition to complexes **1** and **2**, $IDippCuPPh_2$ (**3**)[12] was also prepared by following the route developed by Nolan for the investigation of steric effects of NHCs. When 2 molar equiv of $HPPh_2$ was employed for the reaction of phenylacetylene at 110 °C, complexes **1**−**3** resulted in the highly selective formation of double-addition products in comparable yields under the same conditions (Scheme 3). Complex **2** exhibits slightly higher activity and thus was chosen for further studies.

Since complex **2** was prepared by the reaction of $CuCl_2$ with $HPPh_2$ in the presence of I^tBu, we reasoned that the catalytic double-addition reaction might also proceed with the in situ $CuCl_2/I^tBu$ system without the prior isolation of **2**. Indeed, when the reaction was catalyzed by 1.25 mol % of $CuCl_2$ in the presence of ca. 5 mol % of I^tBu under similar conditions, the double hydrophosphination proceeded more conveniently to give the expected product in 96% yield. The vinylphosphine produced by the single addition of phenylacetylene was tested for the second addition catalyzed by the same catalysts. The results showed that the vinylphosphine can be converted to the same double-phosphination product in good yields, indicating

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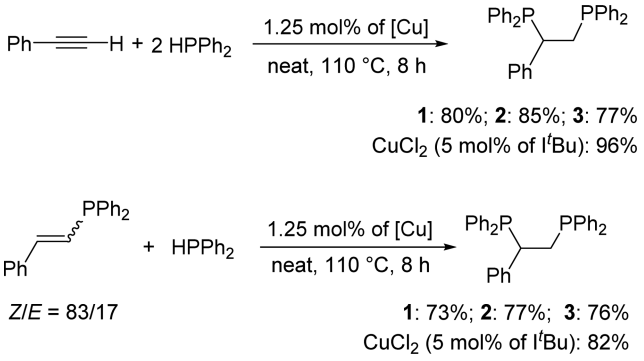
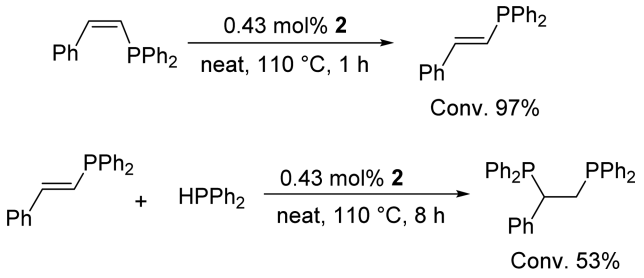
Scheme 3. Comparison of $CuCl_2$/NHC Catalytic System and NHC-Copper Phosphide Complexes 1−3 for the Double Hydrophosphination of Phenylacetylene and the Single Hydrophosphination of Vinylphosphine



that the double hydrophosphination occurred in a stepwise manner. This in situ catalytic system not only is user friendly but also exhibits an improved catalytic activity in comparison to complex **2**.

It is noteworthy that the transformation of the (*Z*)-vinylphosphine to the (*E*)-vinylphosphine was observed when the (*Z*)-vinylphosphine was heated at 110 °C in the presence of a catalytic amount of **2** (Scheme 4).[14] The catalytic

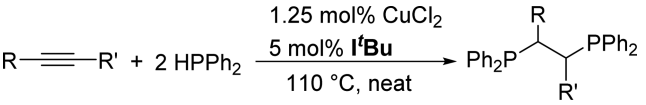
Scheme 4. Conversion of (*Z*)-Phenylvinylphosphine to the *E* Isomer Catalyzed by 2 and the Hydrophosphination of the *E* Isomer



hydrophosphination of the (*E*)-vinylphosphine with $HPPh_2$ in the presence of 0.43 mol % of the phosphide **2** for 8 h only led to the formation of the desired product in 53% yield, suggesting that the *E* isomer is less reactive than the *Z* isomer in the second addition reaction (Scheme 4).

Double Hydrophosphination of Alkynes. With the optimized conditions using $CuCl_2$/I^{t}Bu as catalyst, a range of alkynes was examined with 2 molar equiv of $HPPh_2$ (Table 1). Most of the alkynes were converted into the corresponding double-hydrophosphination products in high yields (86−96%) in 4−24 h (Table 1, entries 1−8). The reaction is tolerant to aromatic halides (F, Cl, Br; Table 1, entries 6−8). Alkynes substituted with 4-dimethylaminophenyl, pyridinyl, and thiophenyl groups were also effective, albeit in modest yields (Table 1, entries 9−11). It is noted that the unactivated 1-hexyne and *N*,*N*-dimethylprop-2-yn-1-amine were also successful in the double hydrophosphination to give the products in 79% and 85% yields, respectively (Table 1, entries 12 and 13). However, trimethyl(prop-2-yn-1-yloxy)silane (Table 1, entry 14) and ethynylcyclopentane (Table 1, entry 15) only gave the expected double-hydrophosphination products in very low yields. 5-Chloropent-1-yne only gave the single hydrophosphination

Table 1. Catalytic Double Phosphination of Different Alkynes with $HPPh_2$ under the Optimized Conditions[a]



entry	R	R′	*t* (h)	yield (%)[b]	TON	TOF (h^{-1})
1	C_6H_5	H	8	96 (95)	76.8	9.6
2	4-MeC_6H_4	H	24	91 (88)	72.8	3.0
3	4-$MeOC_6H_4$	H	12	91 (89)	72.8	6.1
4	2-$MeOC_6H_4$	H	24	86 (82[c])	68.8	2.9
5	4-^{t}BuC_6H_4	H	24	91 (88)	72.8	3.0
6	4-FC_6H_4	H	4	96 (93)	76.8	19.2
7	4-ClC_6H_4	H	4	91 (88)	72.8	18.2
8	4-BrC_6H_4	H	12	86 (82[c])	68.8	5.7
9	4-$Me_2NC_6H_4$	H	24	79 (72)	63.2	2.6
10	2-py	H	24	65 (58[c])	52	2.2
11	2-C_4H_3S	H	24	40 (36[c])	32	1.3
12	*n*-Bu	H	24	79 (75[c])	63.2	2.6
13	Me_2NCH_2	H	24	85 (82)	68	2.8
14	Me_3SiOCH_2	H	24	8		
15	cyclopentyl	H	24	<2		
16	$ClCH_2(CH_2)_2$	H	24	0		
18	^{t}Bu	H	24	0		
19	Ph	Ph	24	0		
20	Ph	Et	24	0		

[a]Reaction conditions: Ph_2PH (2.0 mmol), alkynes (1.0 mmol), I^{t}Bu (0.05 mmol), and $CuCl_2$ (0.0125 mmol), 110 °C. [b]NMR yield (isolated yield). [c]Isolated yield after oxidation.

product in ca. 5% yield (Table 1, entry 16). The reactions with the bulky terminal alkyne 3,3-dimethylbut-1-yne (Table 1, entry 18) and internal alkynes 1,2-diphenylethyne (Table 1, entry 19) and 1-phenyl-1-butyne (Table 1, entry 20) only gave the single hydrophosphination products in 30%, 12%, and 32% yields, respectively, indicating that the steric factors of the substrates have significant effects on the reaction. The double hydrophosphination of phenylacetylene with Cy_2PH was also tested. However, the reaction only gave the single-hydrophosphination product with ca. 12% conversion and the double-addition product was not observed.

Mechanistic Studies. Monitoring the reaction of **2** with 1 equiv of PhCCH in C_6D_6 by NMR spectroscopy showed the generation of $HPPh_2$ and the copper acetylide I^{t}BuCuCCPh (**4**) (details are given in the Supporting Information) with the formation of a small amount of single-hydrophosphination product as a mixture of *Z* and *E* isomers at room temperature in 30 min (Figure S6 in the Supporting Information), indicating that the copper acetylide is also involved in the catalytic cycle. Indeed, it was found that complex **4** also exhibited catalytic activity comparable with that of **2**. Monitoring the reaction of **4** with $HPPh_2$ by ^{1}H and ^{31}P NMR spectroscopy in C_6D_6 (Figure S7 in the Supporting Information) indicated the formation of phenylacetylene and **2** with a small amount of single-hydrophosphination product as a mixture of *Z* and *E* isomers under the same conditions. These results supported that complexes **2** and **4** are interconvertible in the catalytic cycle.

To understand the interconversion process, the relative energy profiles for the possible intermediates **A**−**D** were obtained by DFT calculations (Figure 2). The coordination of $HPPh_2$ to complex **4** and the subsequent hydrogen transfer in the intermediate **A** to form **B** only require a free energy of 6.03

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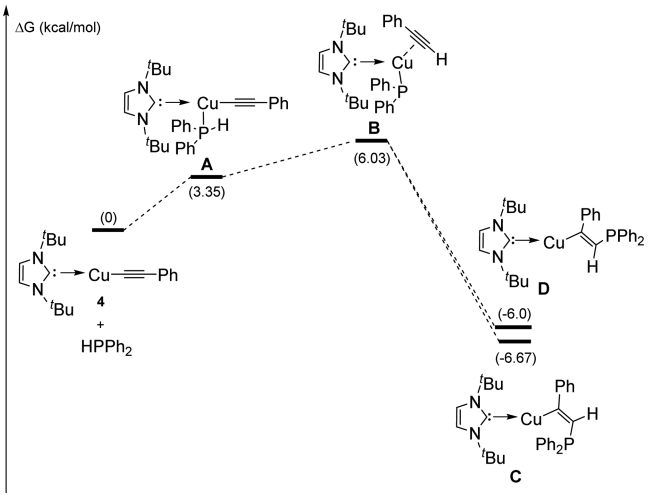
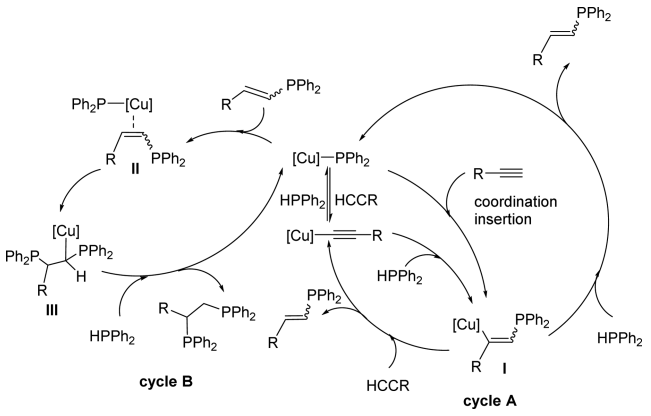


Figure 2. Relative energy profiles for the possible intermediates **A**–**D** obtained by DFT calculations. The values in parentheses are Gibbs free energies in kcal/mol. The optimized structures of **A**–**D** are given in Figures S1–S5 in the Supporting Information.

kcal/mol. The following migration–insertion of the coordinated alkyne into the Cu–P bond led to the formation of intermediates **C** and **D**, which have a very small energy difference of 0.67 kcal/mol.

DFT calculations disclosed the important roles of the copper acetylide **4** in the acceleration of the single-addition reaction, in line with the experimental observations. The inability for double hydrophosphination of internal alkynes is very likely due to steric effects. This notion is supported by the experimental observation that the *E* isomer obtained by the single addition encounters much more difficulty in undergoing the second hydrophosphination in comparison to the corresponding *Z* isomer. On the basis of the experimental results and DFT calculations, a tentative mechanism is given in Scheme 5. Initially, the copper phosphide Cu-PPh_2 and

Scheme 5. Tentative Mechanism for the Double Hydrophosphination of Alkynes



acetylide Cu-CCR reacted with an alkyne and $HPPh_2$ via migration–insertion to yield the copper alkenyl intermediate **I**, which subsequently underwent protonolysis with HCCPh and $HPPh_2$ to liberate the single-hydrophosphination product as a mixture of *Z*- and *E* isomers to complete cycle A. The acetylide Cu-CCR and copper phosphide Cu-PPh_2 are interconvertible in catalytic cycle A. After the single addition was complete, the formed vinylphosphine underwent coordination and migration–insertion reactions with the Cu-PPh_2 to yield the intermediates **II** and **III**. Cleavage of the Cu–C bond by $HPPh_2$ yielded the double-hydrophosphination product with the regeneration of the catalyst.

CONCLUSIONS

In summary, we have developed a straightforward method for the synthesis of well-defined NHC-copper phosphides by reactions of copper halides with $HPPh_2$ in combination with N-heterocyclic carbenes. The NHC-Cu phosphides have been proven to be highly efficient and selective catalysts for double hydrophosphination of aryl- and alkyl-subsituted terminal alkynes. Interestingly, the catalytic reaction can be more conveniently and practically performed with the in situ $CuCl_2$/NHC system, which exhibits better performance than the well-defined copper catalysts. The easy availability of diverse NHC ligands, including chiral ligands, and copper halides renders the catalytic system to be the most practical and tunable. This system might also be amenable to wide applications in the catalytic addition reactions as well as stereoselective double hydrophosphinations.

EXPERIMENTAL SECTION

Further details of the synthesis and characterization of complexes **1**, **2**, and **4** and typical procedures for catalytic double hydrophosphination of alkynes are given in the Supporting Information.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.organomet.6b00854.

Experimental details, characterization data, and crystallographic data (PDF)

Crystallographic data (CIF)

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Notes

The authors declare no competing financial interest.

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REFERENCES

(1) (a) Quin, L. D. *A Guide to Organophosphorus Chemistry*; Wiley-Interscience: New York, 2000. (b) Clarke, M. L.; Williams, J. M. J. In *Organophosphorus Reagents. A Practical Approach in Chemistry*; Murphy, P. J., Ed.; Oxford University Press: Oxford, U.K., 2004; Chapter 2. (c) Parshall, G. W.; Ittel, S. D. *Homogeneous Catalysis*; Wiley: New York, 1992.

(2) (a) King, R. B.; Kapoor, P. N. *J. Am. Chem. Soc.* **1969**, *91*, 5191–5192. (b) Treichel, P. M.; Wong, W. K. *J. Organomet. Chem.* **1978**, *157*, C5–C9. (c) Bookham, J. L.; Smithies, D. M.; Wright, A.; Thornton-Pett, M.; McFarlane, W. *J. Chem. Soc., Dalton Trans.* **1998**,

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Organometallics XXXX, XXX, XXX–XXX

811−818. (d) Bookham, J. L.; McFarlane, W.; Thornton-Pett, M.; Jones, S. *J. Chem. Soc., Dalton Trans.* **1990**, 3621−3627.
(3) (a) Kovacik, I.; Scriban, C.; Glueck, D. S. *Organometallics* **2006**, *25*, 536−539. (b) Mizuta, T.; Miyaji, C.; Katayama, T.; Ushio, J.; Kubo, K.; Miyoshi, K. *Organometallics* **2009**, *28*, 539−546. (c) Allen, A., Jr.; Ma, L.; Lin, W. *Tetrahedron Lett.* **2002**, *43*, 3707−3710. (d) Stone, J. J.; Stockland, R. A., Jr.; Reyes, J. M., Jr.; Kovach, J.; Goodman, C. C.; Tillman, E. S. *J. Mol. Catal. A: Chem.* **2005**, *226*, 11−21. (d1) Pullarkat, S. A.; Yi, D.; Li, Y.; Tan, G.-K.; Leung, P.-H. *Inorg. Chem.* **2006**, *45*, 7455−7463.
(4) Kondoh, A.; Yorimitsu, H.; Oshima, K. *J. Am. Chem. Soc.* **2007**, *129*, 4099−4104.
(5) (a) Delacroix, O.; Gaumont, A.-C. *Curr. Org. Chem.* **2005**, *9*, 1851−1882. (b) Tanaka, M. *Top. Curr. Chem.* **2004**, *232*, 25−54.
(6) (a) Rosenberg, L. *ACS Catal.* **2013**, *3*, 2845−2855. (b) Alonso, F.; Beletskaya, I. P.; Yus, M. *Chem. Rev.* **2004**, *104*, 3079−3160. (c) Koshti, V.; Gaikwad, S.; Chikkali, S. H. *Coord. Chem. Rev.* **2014**, *265*, 52−73. (d) Hu, H.; Cui, C. *Organometallics* **2012**, *31*, 1208−1211. (e) Yuan, J.; Hu, H.; Cui, C. *Chem. - Eur. J.* **2016**, *22*, 5778−5785.
(7) (a) Kamitani, M.; Itazaki, M.; Tamiya, C.; Nakazawa, H. *J. Am. Chem. Soc.* **2012**, *134*, 11932−11935. (b) Itazaki, M.; Katsube, S.; Kamitani, M.; Nakazawa, H. *Chem. Commun.* **2016**, *52*, 3163−3166.
(8) (a) Di Giuseppe, A.; De Luca, R.; Castarlenas, R.; Pérez-Torrente, J. J.; Crucianelli, M.; Oro, L. A. *Chem. Commun.* **2016**, *52*, 5554−5557. (b) Bange, C. A.; Waterman, R. *ACS Catal.* **2016**, *6*, 6413−6416.
(9) (a) Lazreg, F.; Nahra, F.; Cazin, C. S. J. *Coord. Chem. Rev.* **2015**, *293−294*, 48−79. (b) Gaillard, S.; Cazin, C. S. J.; Nolan, S. P. *Acc. Chem. Res.* **2012**, *45*, 778−787. (c) Hopkinson, M. N.; Richter, C.; Schedler, M.; Glorius, F. *Nature* **2014**, *510*, 485−496.
(10) (a) Khalili Najafabadi, B.; Corrigan, J. F. *Dalton Trans.* **2015**, *44*, 14235−14241. (b) Abdellah, I.; Bernoud, E.; Lohier, J.-F.; Alayrac, C.; Toupet, L.; Lepetit, C.; Gaumont, A.-C. *Chem. Commun.* **2012**, *48*, 4088−4090.
(11) (a) Cowley, A. H.; Giolando, D. M.; Jones, R. A.; Nunn, C. M.; Power, J. M. *J. Chem. Soc., Chem. Commun.* **1988**, 208−209. (b) Brauer, D. J.; Hessler, G.; Knüppel, P. C.; Stelzer, O. *Inorg. Chem.* **1990**, *29*, 2370−2375. (c) Eichhöfer, A.; Fenske, D.; Holstein, W. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 242−245. (d) Fenske, D.; Holstein, W. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 1290−1292. (e) Brauer, D. J.; Knüppel, P. C.; Stelzer, O. *J. Chem. Soc., Chem. Commun.* **1988**, 551−552. (f) Mankad, N. P.; Harkins, S. B.; Antholine, W. E.; Peters, J. C. *Inorg. Chem.* **2009**, *48*, 7026−7032. (g) Mankad, N. P.; Rivard, E.; Harkins, S. B.; Peters, J. C. *J. Am. Chem. Soc.* **2005**, *127*, 16032−16033.
(12) Fortman, G. C.; Slawin, A. M. Z.; Nolan, S. P. *Organometallics* **2010**, *29*, 3966−3972.
(13) (a) Cain, M. F.; Hughes, R. P.; Glueck, D. S.; Golen, J. A.; Moore, C. E.; Rheingold, A. L. *Inorg. Chem.* **2010**, *49*, 7650−7662. (b) Zhang, S.-L.; Bie, W.-F.; Huang, L. *Organometallics* **2014**, *33*, 5263−5271.
(14) (a) Ohara, K.; Inokuma, Y.; Fujita, M. *Angew. Chem., Int. Ed.* **2010**, *49*, 5507−5509. (b) Yu, J.; Gaunt, M. J.; Spencer, J. B. *J. Org. Chem.* **2002**, *67*, 4627−4629. (c) Bai, X.-F.; Xu, L.-W.; Zheng, L.-S.; Jiang, J.-X.; Lai, G.-Q.; Shang, J.-Y. *Chem. - Eur. J.* **2012**, *18*, 8174−8179. (d) Kim, I. S.; Dong, G. R.; Jung, Y. H. *J. Org. Chem.* **2007**, *72*, 5424−5426. (e) Gauthier, D.; Lindhardt, A. T.; Olsen, E. P. K.; Overgaard, J.; Skrydstrup, T. *J. Am. Chem. Soc.* **2010**, *132*, 7998−8009.

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