Organic LETTERS

Letter

pubs.acs.org/OrgLett

# Light Mediated Preparation of Palladium Nanoparticles as Catalysts for Alkyne *cis*-Semihydrogenation

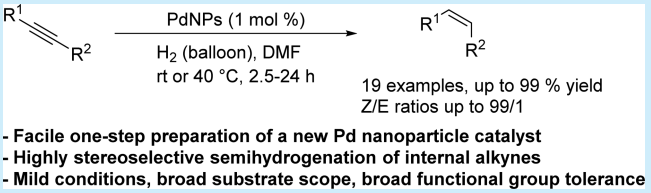
Florian Mäsing,[†] Harald Nüsse,[‡] Jürgen Klingauf,[‡] and Armido Studer*[,†]

[†]Institute of Organic Chemistry, University of Münster, Corrensstrasse 40, 48149 Münster, Germany

[‡]Institute of Medical Physics and Biophysics, University of Münster, Robert-Koch-Strasse 31, 48149 Münster, Germany

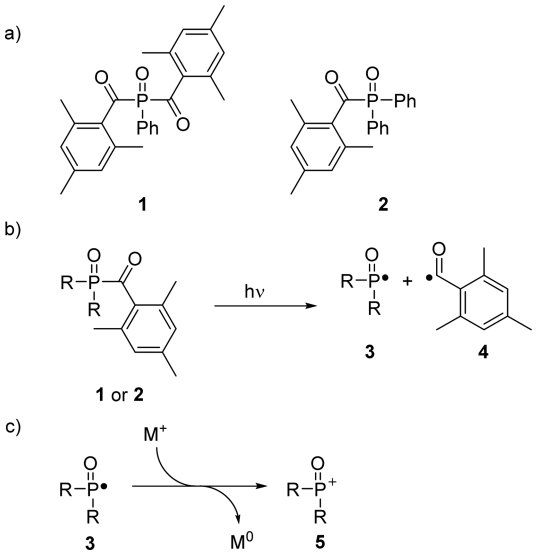
Supporting Information

**ABSTRACT:** A bisacylphosphine oxide photoinitiator was used for the light mediated preparation of palladium nanoparticles (PdNPs) with a small diameter of 2.8 nm. All starting materials are commercially available, and PdNP synthesis is experimentally very easy to conduct. The PdNP-hybrid material was applied as catalyst for the semihydrogenation of various internal alkynes to provide the corresponding alkenes in excellent yields (up to 99%) and *Z*-selectivities (*Z*/*E* ratios up to 99/1).




Phenylbis(2,4,6-trimethylbenzoyl)phosphine oxide (**1**, BAPO) and diphenyl(2,4,6-trimethylbenzoyl)phosphine oxide (**2**, TMDPO) are well established and widely used photoinitiators for radical polymerization in industry that have found applications in various processes such as UV-curing of coatings, adhesives, inks, or dental fillings (Scheme 1).[1] Moreover, the application of BAPO **1** for the photochemical preparation of AgNP- or AuNP-polymer hybrid materials was reported.[2] In these processes, BAPO **1** plays a dual role: first, BAPO **1** engages in a photomediated Norrish type 1 P−C bond homolysis to form a phosphinoyl/benzoyl (**3**/**4**) radical pair.[2,3] The phosphinoyl radical **3** then acts as a one-electron reductant for the Ag/Au-metal salts to generate metal nanoparticles (Scheme 1).[2,3] Second, the photochemically formed BAPO-fragments **3** and **4** can initiate the polymerization of monomers that are present in the reaction mixture as cosolvents. These in situ formed polymers then prevent the aggregation of the generated Ag/Au-nanoparticles.[2,3] However, to our knowledge commercial P-based radical photoinitiators have not been used for Pd-nanoparticle preparation to date.

**Scheme 1. (a) Photoinitiators Investigated for the Light Mediated Preparation of PdNPs; (b) Norrish Type 1 Photolysis of Photoinitiators 1 and 2; (c) Phosphinoyl Radical As Reductant for Metal Ions**




Metal nanomaterials are well-known for their unique reactivity. For instance, Pd, Fe, Ni, or Au based nanoparticles have been applied as catalysts for alkyne semihydrogenation to form *Z*-alkenes.[4] These new nanomaterials may replace in future Lindlar's catalyst, the current standard semihydrogenation catalyst in synthesis. It is well-known that the Lindlar catalyst suffers from several drawbacks: toxic $Pb(OAc)_2$ and large amounts of quinoline are required to suppress over-hydrogenation of the target alkenes to alkanes.

Furthermore, low *Z*-selectivity due to *Z*/*E*-isomerization, irreproducibility, and a limited substrate scope are challenging factors.[4i−k,5] Considering metal nanocatalysts for alkyne semihydrogenation as alternatives, they generally have to be prepared by a complex multistep procedure including the use of noncommercial chemicals. Furthermore, many of them operate under harsh reaction conditions limiting their applicability.[6]

Recently, our group introduced a light mediated process for the preparation of polymer coated Au and Pd nanoparticles by using well-defined but noncommercial homo- and copolymers bearing photoactive α-hydroxyalkyl ketone (HAK) substituents.[4l,7] During irradiation with UV-light the HAK moieties undergo Norrish type 1 cleavage to generate ketyl radicals able

**Received:** April 3, 2017

DOI: 10.1021/acs.orglett.7b00999
*Org. Lett.* XXXX, XXX, XXX−XXX

to reduce metal ions to form metal nanoparticles. The photochemically modified polymers formed as byproducts then stabilize the metal nanoparticles.[4l,7] Inspired by these results, we decided to investigate PdNP preparation using acylphosphine oxide photoinitiators **1** and **2** as Norrish type 1 active species. In contrast to the photoactive polymers used before,[4l,7] initiators **1** and **2** are commercially available and cheap, offering an easy and valuable entry to palladium nanomaterials. Herein, we present first results along those lines.

For nanoparticle preparation, phenylbis(2,4,6-trimethylbenzoyl)phosphine oxide (**1**) or diphenyl(2,4,6-trimethylbenzoyl)phosphine oxide (**2**) was diluted in DMF and $Pd(OAc)_2$ was added. The ratio of photoactive moieties to $Pd(OAc)_2$ was set as 20:1. Irradiation under an argon atmosphere in a photoreactor ($\lambda$ = 254 nm) for 10 min using bisacylphosphine oxide **1** provided a deep brown solution indicating Pd nanoparticle formation. Indeed, TEM investigations revealed successful preparation of Pd nanoparticles (Pd@**1***) with a diameter of 2.8 ± 1.0 nm (Figure 1a). By

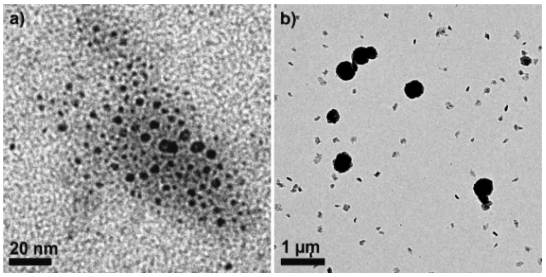
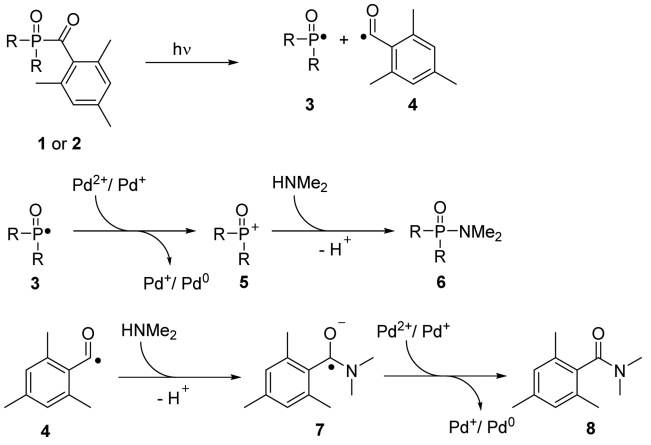



**Figure 1.** TEM images of the prepared palladium nanoparticles: (a) Pd@**1*** and (b) Pd@**2***.

switching to acylphosphine oxide **2** under otherwise identical conditions, polydisperse Pd nanoparticles (Pd@**2***) between 40 and 900 nm (mean diameter: 177 ± 126 nm) were obtained, documenting the large effect of the initiator structure on nanoparticle formation (Figure 1b). The Pd oxidation state in the hybrid material was investigated by powder X-ray diffraction (see the Supporting Information). Only the broad diffraction signals characteristic for $Pd^0$ nanoparticles were detected proving full photochemical reduction of the Pd-salt within the 10 min of irradiation.[8]

By mass spectrometric analysis of the irradiated PdNP solutions, phosphinic acid amide **6** and amide **8** were identified along with unreacted **1** or **2** revealing that the photochemical decomposition of the initiators was not complete within 10 min of irradiation (Scheme 2). Considering the experimentally identified fragmentation products, the following mechanism for PdNP formation is suggested. Phosphinoyl/benzoyl (**3**/**4**) radical pairs are generated by Norrish Type 1 homolysis.[9] The P-radical **3** then acts as a one-electron donor to reduce Pd-ions thereby being oxidized to an oxophosphonium cation **5**, which is eventually trapped by dimethylamine derived from DMF to amide **6**.[3] The concomitantly generated benzoyl radical **4** is trapped with dimethylamine to give after deprotonation a ketyl radical anion **7**, which is able to act as a one-electron donor for Pd salt reduction explaining the formation of amide **8** as a second byproduct (Scheme 2).[4l,10] We do not assume that DMF and the trace amounts of dimethylamine are the reductants for Pd-ions in this system, since the formation of PdNPs was significantly slower in a control experiment in the absence of photoinitiators **1** and **2**.[11] It is likely that amides **6**, **8**,

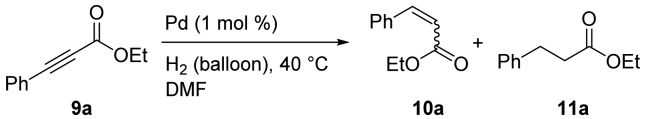
**Scheme 2. Proposed Mechanism of the Light Mediated PdNP Formation**




and unreacted Norrish initiators (**1** and **2**) stabilize the thus generated PdNPs. Isolation of the PdNP-hybrid material as a black solid material was achieved by evaporation of DMF, and this hybrid was then used directly in catalysis as is.

As a first reaction the hydrogenation of ethyl 3-phenylpropiolate (**9a**) in DMF at 40 °C with $H_2$ (1 atm, balloon) as a reductant was investigated. Pleasingly, with nanoparticles prepared from BAPO **1** (Pd@**1***, 1 mol %) the semihydrogenation product **10a** was obtained in near-quantitative yield (99%) and excellent *Z*/*E* selectivity (99/1) after 3 h (Table 1, entry 1). The corresponding overhydrogenation

**Table 1. Semihydrogenation of Ethyl 3-Phenylpropiolate (9a) Using Various Pd Catalysts**




| entry | Pd source | *t* (h) | conv **9a** (%)[a] | yield **10a** (%) (*Z*/*E*)[a] | yield **11a** (%)[a] |
|---|---|---|---|---|---|
| 1 | Pd@**1*** | 3 | >99 | 99 (99/1) | <1 |
| 2 | Pd@**1*** | 8 | >99 | 99 (99/1) | <1 |
| 3[b] | Pd@**1*** | 2.5 | >99 | 93 (97/3) | 6 |
| 4 | Pd@**2*** | 8 | 1 | 1 (n.d.) | 0 |
| 5 | Pd/C | 1.5 | 98 | 33 (91/9) | 65 |
| 6 | Pd/C | 2 | >99 | 0 | 99 |
| 7 | $Pd(OAc)_2$ | 3 | >99 | 25 (91/9) | 74 |
| 8 | $Pd(OAc)_2$ | 4 | >99 | 0 | 99 |

[a]Conversion of alkyne **9a**, yield and *Z*/*E* ratio of alkene **10a**, and yield of alkane **11a** determined by GC-FID using an internal standard. GC peaks assigned by GC-MS. Structure of **10a** confirmed by NMR spectroscopy. [b]Catalyst recycling, reaction performed at room temperature. n.d. = not determined.

product **11a** was identified in traces only (<1%) by gas chromatography. Extending the reaction time to 8 h did not change the outcome, clearly showing that *Z*/*E* isomerization and overhydrogenation are kinetically disfavored processes under the applied conditions (Table 1, entry 2).

The Pd@**1*** catalyst was recycled via removal of the solvent and all reaction products by distillation. Pd@**1*** remaining in the reaction flask was applied to the next cycle by recharging with DMF, alkyne **9a**, and $H_2$. Interestingly, the recycled catalyst was found to be more active and the reaction was

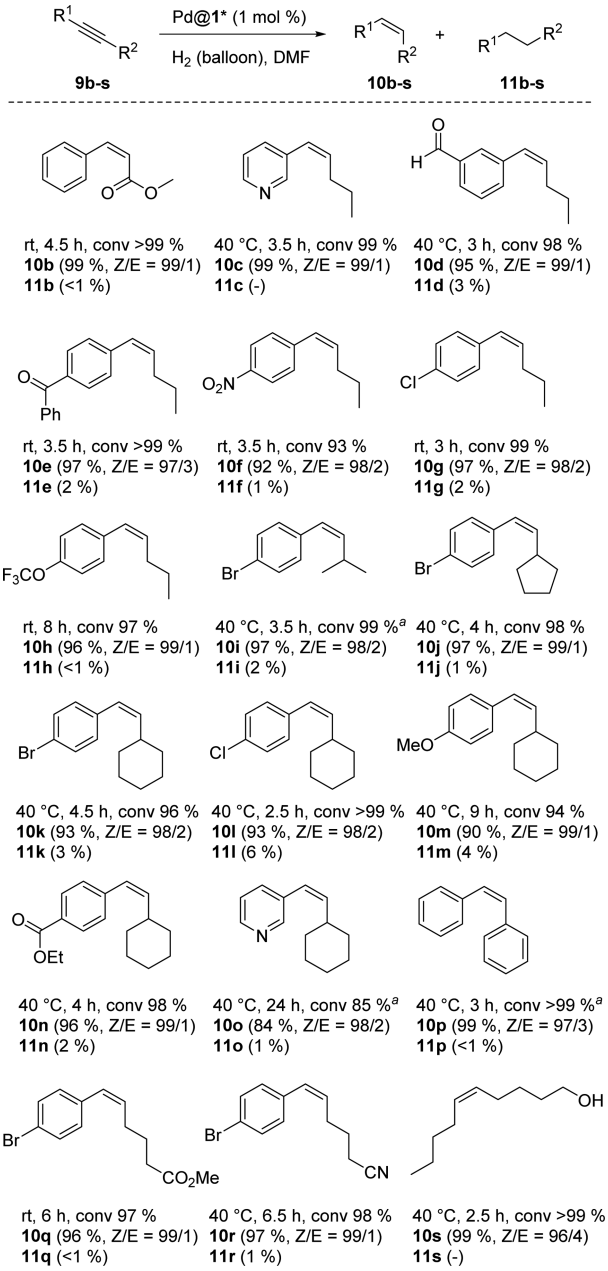

DOI: 10.1021/acs.orglett.7b00999
Org. Lett. XXXX, XXX, XXX−XXX

completed within 2.5 h at room temperature. The desired alkene **10a** was obtained in a good yield (93%) (Table 1, entry 3). However, selectivity slightly dropped (97/3) and over-hydrogenated alkane **11a** was formed in 6% yield, revealing that the original catalyst performs better.

PdNPs prepared with TMDPO **2** (Pd@**2***) are not active semihydrogenation catalysts, and only 1% conversion was achieved after 8 h under otherwise identical conditions (Table 1, entry 4). This change in reactivity may be explained considering the large diameter differences of the hybrids (see Figure 1) or by ligand effects.[12] To document the unique reactivity of Pd@**1*** exerted by the ligands **1**, **6**, and **8**, semihydrogenation of alkyne **9a** was repeated with Pd/C and $Pd(OAc)_2$ under otherwise identical conditions. Pd/C was found to be more active than Pd@**1***, and complete conversion was obtained within 1.5 h (Table 1, entry 5). However, the yield of alkene **10a** was low (33%) and the *Z*/*E*-selectivity was only 91/9. In this case, alkane **11a** was formed as the major product in 65% yield. Extending the reaction time to 2 h afforded alkane **11a** in a quantitative yield (Table 1, entry 6). A similar result was achieved with $Pd(OAc)_2$ as a precatalyst (Table 1, entries 7, 8).[13]

We next tested the substrate scope using alkynes **9b–s** as substrates (Scheme 3). Reactions were followed by GC analysis, and the reaction time was adapted individually according to the alkyne reactivity. Conversion, yields, and *Z*/*E* ratios of alkenes **10b–s** and yields of alkanes **11b–s** were determined by GC-FID using an internal standard. GC peaks were assigned by GC-MS, and structures of *Z*-alkenes **10b–s** were confirmed by NMR spectroscopy. Isolated yields for *Z*-alkenes **10a–s** that are provided in the Supporting Information are slightly lower. For methyl 3-phenylpropiolate (**9b**) full conversion was achieved at room temperature within 4.5 h to give **10b** in quantitative yield (99%) and excellent *Z*/*E* ratio (99/1). Various arylpropyl alkynes **9c–h** were investigated, and electronic effects exerted by the aryl substituent studied. The 3-pyridyl derivate **9c** was fully converted at 40 °C for 3.5 h to the alkene **10c** (99%, *Z*/*E* = 99/1). Arylpropyl alkynes **9d–h** bearing formyl-, keto-, nitro-, chloro-, or trifluormethoxy-substituents were smoothly converted to the corresponding alkenes **10d–h** in good to excellent yields (92–97%) with excellent *Z*/*E* ratios (97/3–99/1) in 3–8 h. Importantly, functional groups such as formyl, keto, or nitro, which are readily reduced using classical Pd-catalysts, are tolerated.[14] In these reactions, up to 3% of the undesired alkanes **11d–h** were identified. We then tested more sterically shielded alkynes and found the aryl isopropyl congener **9i** to be converted in 3.5 h at 40 °C to **10i** in excellent yield (97%) and *Z*/*E* selectivity (98/2). However, the catalyst loading had to be increased to 2 mol %. The cyclopentyl derivate **9j** was readily transferred to alkene **10j** (97% yield, *Z*/*E* ratio 99/1) in 4 h at 1 mol % catalyst loading. Arylcyclohexyl alkynes also turned out to be good substrates. Various substituents such as bromo, chloro, methoxy, or ethoxycarbonyl (**9k–n**) are tolerated, and the corresponding alkenes **10k–n** were obtained in 2.5–9 h in good yields (90–96%) and excellent *Z*/*E* ratios (98/2 or 99/1). For these substrates, 2–6% of the overhydrogenated alkanes **11k–n** were formed as byproducts. The 3-pyridylcyclohexyl congener **9o** was a very unreactive substrate and an 85% conversion at 2% catalyst loading was noted after 24 h. The alkene **10o** was formed in 84% yield with excellent *Z*/*E* selectivity (98/2). Under the same conditions, diphenylacetylene (**9p**) was reduced to stilbene **10p** (99%, *Z*/*E* ratio = 97/3).

**Scheme 3. Scope**




[a]Reaction performed with 2 mol % of the catalyst.

Arylalkyl alkynes bearing a methylester or nitrile functionality at the alkyl terminus were successfully semihydrogenated to give **10q** and **10r** in good yields (96%, 97%) and excellent *Z*/*E* ratios (99/1). We studied the semihydrogenation of bisalkyl alkyne **9s** and obtained alkene **10s** within 2.5 h in a quantitative yield (99%) and high selectivity (*Z*/*E* = 96/4). Finally, we performed the semihydrogenation of alkyne **9a** at 1 mmol scale and the desired *Z*-alkene (*Z*/*E* = 99/1) was obtained after 1 h in 90% isolated yield.

In summary, a new method for the photochemical preparation of Pd nanoparticles using cheap and commercially available photoinitiators **1** and **2** was developed. Simple mixing of the photoinitiator and $Pd(OAc)_2$ in DMF and subsequent irradiation with UV-light leads to the formation of PdNPs that are stabilized by unreacted photoinitiator and amide byproducts **6** and **8** derived therefrom. PdNP-hybrids obtained are



DOI: 10.1021/acs.orglett.7b00999
Org. Lett. XXXX, XXX, XXX–XXX

characterized by TEM, XRD, and mass spectrometry. Importantly, PdNP preparation is very easy to conduct and reliably provides small PdNPs within a few minutes. Whereas PdNPs derived from **2** turned out to be not active in the reduction of alkynes, Pd@**1*** is a highly efficient catalyst for the highly stereoselective semihydrogenation of various internal alkynes to provide Z-alkenes in excellent yields (up to 99%) and *Z*/*E* ratios (up to 99/1). The semihydrogenation is very robust, scalable and exhibits a broad substrate scope.

## ■ ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.7b00999.

Detailed experimental procedures, spectroscopic data for all products (PDF)

## ■ AUTHOR INFORMATION


### Corresponding Author

*E-mail: studer@uni-muenster.de.

### ORCID

Armido Studer: 0000-0002-1706-513X


### Notes

The authors declare no competing financial interest.

## ■ ACKNOWLEDGMENTS

Dr. Xi Wang (Institute of Organic Chemistry, University of Münster) is acknowledged for preparing some of the alkynes used. Dr. Uta Rodehorst (Münster Electrochemical Energy Technology Institute, University of Münster) is acknowledged for performing the XRD measurements. We thank the Deutsche Forschungsgemeinschaft (SFB 858) for funding this work.

## ■ REFERENCES


(1) (a) Müller, G.; Zalibera, M.; Gescheidt, G.; Rosenthal, A.; Santiso-Quinones, G.; Dietliker, K.; Grützmacher, H. *Macromol. Rapid Commun.* **2015**, *36*, 553−557. (b) Chibac, A. L.; Melinte, V.; Buruiana, T.; Buruiana, E. C. *J. Polym. Sci., Part A: Polym. Chem.* **2014**, *52*, 728−738. (c) Dietliker, K.; Braig, A.; Ricci, A. *Photochemistry* **2010**, *38*, 344−368.

(2) (a) Cook, W. D.; Nghiem, Q. D.; Chen, Q.; Chen, F.; Sangermano, M. *Macromolecules* **2011**, *44*, 4065−4071. (b) Balan, L.; Melinte, V.; Buruiana, T.; Schneider, R.; Vidal, L. *Nanotechnology* **2012**, *23*, 415705. (c) Buruiana, E. C.; Chibac, A. L.; Buruiana, T.; Melinte, V.; Balan, L. *J. Nanopart. Res.* **2013**, *15*, 1335.

(3) (a) Yagci, Y.; Tasdelen, M. A.; Jockusch, S. *Polymer* **2014**, *55*, 3468−3474. (b) Jockusch, S.; Turro, N. J. *J. Am. Chem. Soc.* **1998**, *120*, 11773−11777. (c) El-Zaatari, B. M.; Shete, A. U.; Adzima, B. J.; Kloxin, C. J. *Phys. Chem. Chem. Phys.* **2016**, *18*, 25504−25511.

(4) For selected publications, see: (a) Zhao, M. *Chem. - Asian J.* **2016**, *11*, 461−464. (b) Gieshoff, T. N.; Welther, A.; Kessler, M. T.; Prechtl, M. H. G.; von Wangelin, A. J. *Chem. Commun.* **2014**, *50*, 2261−2264. (c) Mitsudome, T.; Yamamoto, M.; Maeno, Z.; Mizugaki, T.; Jitsukawa, K.; Kaneda, K. *J. Am. Chem. Soc.* **2015**, *137*, 13452−13455. (d) Alonso, F.; Osante, I.; Yus, M. *Adv. Synth. Catal.* **2006**, *348*, 305−308. (e) Liang, S.; Hammond, G. B.; Xu, B. *Chem. Commun.* **2016**, *52*, 6013−6016. (f) Vasilikogiannaki, E.; Titilas, I.; Vassilikogiannakis, G.; Stratakis, M. *Chem. Commun.* **2015**, *51*, 2384−2387. (g) Yang, S.; Cao, C.; Peng, L.; Zhang, J.; Han, B.; Song, W. *Chem. Commun.* **2016**, *52*, 3627−3630. (h) Evangelisti, C.; Panziera, N.; D'Alessio, A.; Bertinetti, L.; Botavina, M.; Vitulli, G. *J. Catal.* **2010**, *272*, 246−252. (i) Mitsudome, T.; Takahashi, Y.; Ichikawa, S.; Mizugaki, T.; Jitsukawa, K.; Kaneda, K. *Angew. Chem., Int. Ed.* **2013**, *52*, 1481−1485. (j) Slack, E. D.; Gabriel, C. M.; Lipshutz, B. H. *Angew. Chem., Int. Ed.* **2014**, *53*, 14051−14054. (k) Verho, O.; Zheng, H.; Gustafson, K. P. J.; Nagendiran, A.; Zou, X.; Bäckvall, J.-E. *ChemCatChem* **2016**, *8*, 773−778. (l) Mäsing, F.; Wang, X.; Nüsse, H.; Klingauf, J.; Studer, A. *Chem. - Eur. J.* **2017**, *23*, 6014−6018.

(5) (a) Lindlar, H. *Helv. Chim. Acta* **1952**, *35*, 446−450. (b) Oger, C.; Balas, L.; Durand, T.; Galano, J.-M. *Chem. Rev.* **2013**, *113*, 1313−1350. (c) Molnár, Á.; Sárkány, A.; Varga, M. *J. Mol. Catal. A: Chem.* **2001**, *173*, 185−221. (d) Hauwert, P.; Maestri, G.; Sprengers, J. W.; Catellani, M.; Elsevier, C. J. *Angew. Chem., Int. Ed.* **2008**, *47*, 3223−3226.

(6) Witte, P. T.; Boland, S.; Kirby, F.; van Maanen, R.; Bleeker, B. F.; de Winter, D. A. M.; Post, J. A.; Geus, J. W.; Berben, P. H. *ChemCatChem* **2013**, *5*, 582−587.

(7) Mäsing, F.; Mardyukov, A.; Doerenkamp, C.; Eckert, H.; Malkus, U.; Nüsse, H.; Klingauf, J.; Studer, A. *Angew. Chem., Int. Ed.* **2015**, *54*, 12612−12617.

(8) (a) Luo, C.; Zhang, Y.; Wang, Y. *J. Mol. Catal. A: Chem.* **2005**, *229*, 7−12. (b) Lee, D.-W.; Jin, M.-H.; Lee, Y.-J.; Park, J.-H.; Lee, C.-B.; Park, J.-S. *Sci. Rep.* **2016**, *6*, 26474.

(9) Jockusch, S.; Koptyug, I. V.; McGarry, P. F.; Sluggett, G. W.; Turro, N. J.; Watkins, D. M. *J. Am. Chem. Soc.* **1997**, *119*, 11495−11501.

(10) Kawamoto, T.; Sato, A.; Ryu, I. *Chem. - Eur. J.* **2015**, *21*, 14764−14767.

(11) (a) Storr, T. E.; Baumann, C. G.; Thatcher, R. J.; De Ornellas, S.; Whitwood, A. C.; Fairlamb, I. J. S. *J. Org. Chem.* **2009**, *74*, 5810−5821. (b) Reay, A. J.; Fairlamb, I. J. S. *Chem. Commun.* **2015**, *51*, 16289−16307.

(12) (a) Wilson, O. M.; Knecht, M. R.; Garcia-Martinez, J. C.; Crooks, R. M. *J. Am. Chem. Soc.* **2006**, *128*, 4510−4511. (b) Chen, J.; Zhang, Q.; Wang, Y.; Wan, H. *Adv. Synth. Catal.* **2008**, *350*, 453−464.

(13) Henglein, A. *J. Phys. Chem. B* **2000**, *104*, 6683−6685.

(14) Mori, A.; Miyakawa, Y.; Ohashi, E.; Haga, T.; Maegawa, T.; Sajiki, H. *Org. Lett.* **2006**, *8*, 3279−3281.




DOI: 10.1021/acs.orglett.7b00999
*Org. Lett.* XXXX, XXX, XXX−XXX