ORGANOMETALLICS

Article

pubs.acs.org/Organometallics

Iron(IV)-Corrole Catalyzed Stereoselective Olefination of Aldehydes with Ethyl Diazoacetate

Huai-Bo Zou,[†] Hong Yang,[†] Ze-Yu Liu,[†] Mian HR Mahmood,[†] Guang-Quan Mei,[‡] Hai-Yang Liu,*[,†] and Chi-Kwong Chang*[,§]

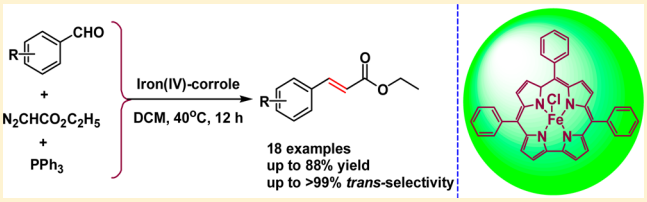
[†]Department of Chemistry, South China University of Technology, Guangzhou 510640, China

[‡]Key Laboratory of Jiangxi University for Applied Chemistry & Chemical Biology, Yichun University, Yichun 336000, China

[§]Department of Chemistry, Michigan State University, E. Lansing, Michigan 48824, United States

Supporting Information

ABSTRACT: Iron(IV)-corrole complexes were first investigated as catalysts for olefination of aldehydes with ethyl diazoacetate in the presence of triphenylphosphine. Efficient olefination of aromatic aldehydes with high *trans*-selectivity was observed, showing iron corrole is a new kind of promising catalyst for olefination reaction. Transformation of the phosphazine to ylide by iron(IV) corrole was proved to be the key step in the present system.

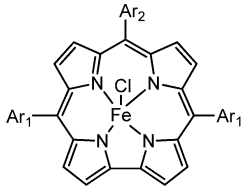


INTRODUCTION

Metallocorroles are efficient catalysts for many important organic reactions such as epoxidation,[1] asymmetric sulfoxidation,[2] hydroxylation,[3] aziridination,[4] and oxygen atom transfer reactions.[5] Iron corroles are especially proved to be effective catalysts in oxidation,[6] cyclopropanation of olefins,[7] and the insertion reactions involving −NH,[7c−e] −SH,[7e] and −CH[7f] groups by ethyl diazoacetate (EDA). Recent research revealed that iron corroles can catalyze the copolymerization of epoxides with carbon dioxide (CO_2)[8] and the [4 + 2] cycloaddition of dienes and aldehydes.[9] These examples imply that iron corroles may be potent catalysts for various other organic reactions.

Construction of C═C double bonds is one of the most important organic reactions. Wittig reaction is a practical and the most commonly used olefination method for this purpose.[10] An alternative approach is to use easily accessible EDA to generate ylide *in situ* by using metal complexes as catalysts.[11] It was observed that iron porphyrin displayed good catalytic activity for this olefination reaction in which metal-carbene is involved as the intermediate.[12] Corrole is a close analogue of porphyrin tetrapyrrolic macrocycle,[13] and we here wish to report the first investigation of iron(IV)-corrole-catalyzed olefination of aldehydes with EDA. The current catalytic olefination reaction is efficient and can afford *trans*-olefination products with high selectivity. Evidence showed that the phosphazine to ylide transformation by iron(IV) corrole is the key step for this catalytic system.

Iron-corrole complexes **1**−**4** used in this work are shown in Figure 1. These iron-corrole complexes are peripherally substituted with phenyl ($-C_6H_5$) and 2,3,4,5,6-pentafluorophenyl ($-C_6F_5$) groups at *meso*-positions of the corrole ring, which may impart different electronic features to the



1: $Ar_1 = Ar_2 = C_6H_5$
2: $Ar_1 = C_6H_5$, $Ar_2 = C_6F_5$
3: $Ar_1 = C_6F_5$, $Ar_2 = C_6H_5$
4: $Ar_1 = Ar_2 = C_6F_5$

Figure 1. Structures of iron(IV)-corrole complexes **1**−**4**.

complexes. Among them, **2** and **3** are first reported here (for characterization data, see Supporting Information).

RESULTS AND DISCUSSION

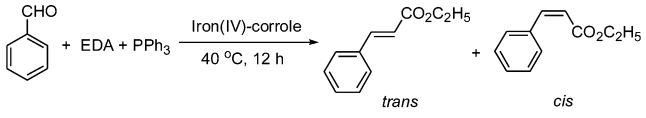
The catalytic olefination of benzaldehyde (1 equiv) with EDA (2 equiv) by iron corroles (1 mol %) were conducted in dichloromethane (DCM) at 40 °C for 12 h in the presence of triphenylphosphine (PPh_3, 1.1 equiv; Table 1). The olefination product was obtained with yield 79−88% and good *trans*-selectivity for iron corroles **1**−**4**. The control experiment gave no olefination product (entry 2), and no benzaldehyde consumption was observed in the absence of PPh_3 (entry 3), demonstrating that PPh_3 was necessary for this reaction. Of all the investigated iron corroles, **1** exhibited the highest activity. The catalytic activity gradually reduced with the enhancement of electron-withdrawing property of iron corroles.

To explore the scope of this reaction, iron corrole **1** was selected as catalyst for the olefination of various aryl aldehyde substrates (Table 2). Most aldehydes underwent olefination from moderate to high yields and with high *trans*-selectivity. Except for 4-dimethylaminobenzaldehyde which gave a low

Received: January 24, 2015
Published: May 28, 2015

DOI: 10.1021/acs.organomet.5b00069
Organometallics 2015, 34, 2791−2795

Table 1. Iron-Corrole-Catalyzed Olefination of Benzaldehyde with EDA[a]



1a

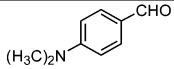
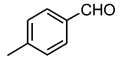
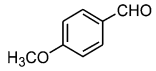
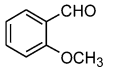
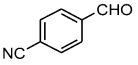
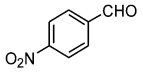
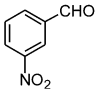
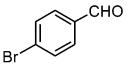
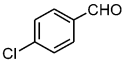
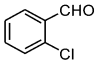
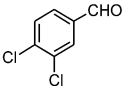
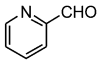
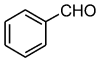
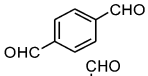
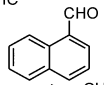
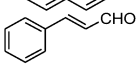
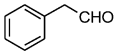
entry	catalyst	catalyst loading (mol %)	yield[b] (%)	*trans*/*cis* ratio[b]
1	**1**	1.0	88 (86)	24:1
2[c]			nd[e]	nd
3[d]	**1**	1.0	nr[e]	nd
4	**2**	1.0	82	16:1
5	**3**	1.0	81	24:1
6	**4**	1.0	79	19:1

[a]Reactions were carried out at 40 °C for 12 h in DCM under N_2, with 1.0 equiv of benzaldehyde, 2.0 equiv of EDA, and 1.0 mol % of catalyst (4.7 μmol) in the presence of 1.1 equiv of PPh_3. [b]Determined by GC. Number in parentheses is isolated yield. [c]Control reaction without catalysts. [d]Without PPh_3. [e]nd: not determined. nr: no reaction.

yield of 20% (entry 1), all other tested aryl aldehydes bearing electron-donating groups (Table 2, entries 2−4) gave the desired olefin in good to high yields (77−87%). Aryl aldehydes bearing electron-withdrawing groups were also suitable substrates for this transformation with moderate to high yields (entries 5−11). It seems electron-deficient aryl aldehydes disfavor this reaction and give lower yields. 3,4-dichlorobenzaldehyde gave significantly lower yield (63%, entry 11) than 4-chlorobenzaldehyde (88%, entry 9). And the steric hindrance at *ortho*-position of aryl aldehyde obviously lowered the *trans*-selectivity (entries 4 and 10). Interestingly, aromatic heterocyclic furfural may give moderate yield of 56% (entry 12), while 2-formylpyridine gave very low yield (7%, entry 13). The sharp drop in yield may be caused by the axial coordination of pyridyl nitrogen atom and central iron atom of the catalyst, which results in the lower catalytic activity by blocking the active center. This was confirmed by the observation that the addition of pyridine axial ligand to the reaction system will lower the yield. The olefination yield of benzaldehyde drops from 86% (Table 1, entry 1) to 60% (Table 2, entry 14) in the presence of pyridine. The lowered olefination yield of 4-dimethylaminobenzaldehyde (Table 2, entry 1) may also be rationalized by axial coordination of amino group. PPh_3 is a strong axial ligand for iron corrole, and it was found a large excess of PPh_3 would hinder the reaction also (Figure S17, Supporting Information). When using terephthalaldehyde (entry 15) as substrate, the mono-olefinated product was isolated with a yield of 83%, and diolefinated product could not be isolated. This is probably due to its low yield in the current catalytic conditions. α,β-unsaturated cinnamaldehyde (entry 17) can obtain the desired product with high yield and *trans*-stereoselectivity. Polycyclic 1-naphthalenecarboxaldehyde was also a good substrate (83%, entry 16). Aliphatic phenylacetaldehyde gave 33% yield and almost 100% *trans*-selectivity (entry 18) in the present catalytic system. As compared to iron porphyrin catalyzed olefintion of aldehyde with EDA,[12a,c,f] iron(IV) corrole although gives comparable yields, but the *trans*-selectivity are remarkably higher for a lot of substrates (Table 2, entries 11, 12, 14, 15, 17, 18).

Three possible mechanisms have been suggested for the olefination of aldehydes with EDA catalyzed by transition metal complexes (Scheme 1).[14] Most transition metal complexes

Table 2. Olefination of Aldehyde Substrates with EDA Using Iron Corrole 1 Catalyst[a]

entry	aldehyde	product	yield[b] (%)	*trans*/*cis* ratio[c]
1		**1b**	20	10:1
2		**1c**	77	19:1
3		**1d**	81	24:1
4		**1e**	87	5:1
5		**1f**	58	16:1
6		**1g**	56	16:1
7		**1h**	63	12:1
8		**1i**	74	19:1
9		**1j**	88	13:1
10		**1k**	77	6:1
11		**1l**	63	99:1
12		**1m**	56	> 99:1
13		**1n**	7	49:1
14[d]		**1a**	60	> 99:1
15		**1o**[e]	83	99:1
16		**1p**	83	16:1
17		**1q**	85	> 99:1
18		**1r**	33	> 99:1

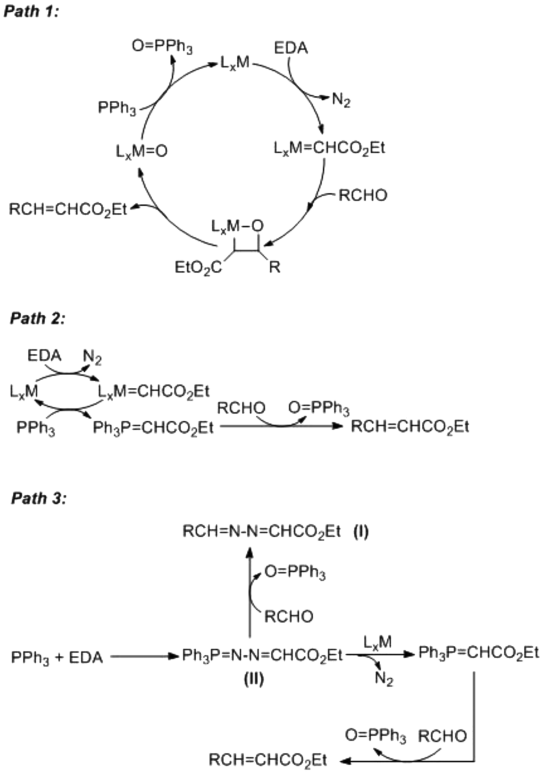
[a]Reaction conditions, see Table 1. [b]Isolated yield. [c]Determined by ^1H NMR. [d]23 μL of pyridine (0.6 equiv relative to benzaldehyde) was added into the reaction. [e]Mono-olefinated product.

catalyzed aldehyde olefination reactions proceed via path 1 or path 2; only one example was reported via the path 3 mechanism.[14a] In the current catalytic system, we found the ^1H NMR spectrum of iron corrole **1** was exactly the same in the presence and absence of EDA. This implies that iron corrole could not react with EDA to yield iron-carbene species or the formed carbene species is too reactive to be detected by ^1H NMR.

In the absence of catalyst **1** (e.g., Table 1, entry 2), no olefin could be detected, but the reaction could still go on to give azine $PhCH{=}N{-}N{=}CHCO_2Et$ (**I**) and $O{=}PPh_3$ as previously observed.[15] We also prepared azine **I** (for its

DOI: 10.1021/acs.organomet.5b00069
Organometallics 2015, 34, 2791−2795

Scheme 1. Three Mechanisms for the Olefination Catalyzed by Transition Metal Complexes



characterization, see the Supporting Information) purposely and found it did not react with iron-corrole catalyst **1** to yield olefin as detected by GC-MS. This suggests that azine **I** is not the intermediate of the present olefination reaction. It is known that PPh_3 can react rapidly with EDA to form phosphazine **II**[14a,c,16] (Scheme 1), and the formation of phosphazine can be easily monitored by the ^{31}P NMR signal at 22.39 ppm (Figure S18, Supporting Information). The direct reaction of phophazine **II** with aldehydes produces azine **I**.[14a]

Phosphazine **II** was detected as the major product in the mixture of PPh_3, EDA, and catalyst **1** (0.5 mol % relative to EDA) after 0.5 h reaction time, and PPh_3 was almost consumed. At the same time, a small amount of phosphorus ylide $Ph_3P{=}CHCO_2Et$ could also be detected in the ^{31}P NMR spectrum (Figure 2, signal B). After some time, the amount of phosphazine **II** (signal A) decreased gradually and the ylide concentration increased. This indicates that iron corrole **1** can catalyze the transformation of phosphazine **II** to phosphorus ylide. Although the aldehyde substrate is absent in the mixture, phosphine oxide (signal C) was also observable; this may result from the oxidation of ylide by oxygen. Further evidence comes from the direct reaction of prepared phosphazine **II**[17,18] and iron corrole **1** (1 mol % relative to **II**). Figure 3 shows the ^{31}P NMR changes of the reaction mixture of **II** and **1** in $CDCl_3$. Phosphazine **II** (signal A) was gradually transformed into the phosphorus ylide (signal B). The peak shape and chemical shift of signal B are identical to those of the commercial ylide sample (Figure S19, Supporting Information). The ylide then reacts with aryl aldehyde to give olefin via Wittig reaction. Interestingly, the reaction of benzaldehyde (1 equiv) and phosphazine **II** (1 equiv) in the presence of catalyst **1** (1 mol % relative to benzaldehyde) under the catalytic conditions gives the same GC olefination yield (88%) and *trans*-selectivity

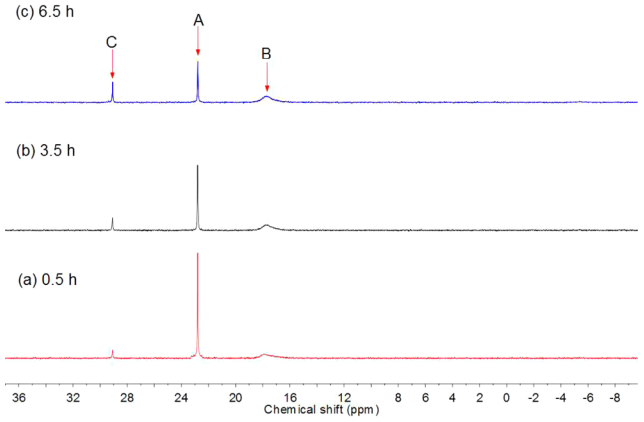


Figure 2. ^{31}P NMR changes of the reaction mixture of PPh_3, EDA, and iron corrole **1** in $CDCl_3$ at room temperature: (A) phosphazine **II** (δ = 22.80 ppm); (B) phosphorus ylide (δ = 17.65 ppm); (C) $O{=}PPh_3$ (δ = 29.08 ppm).

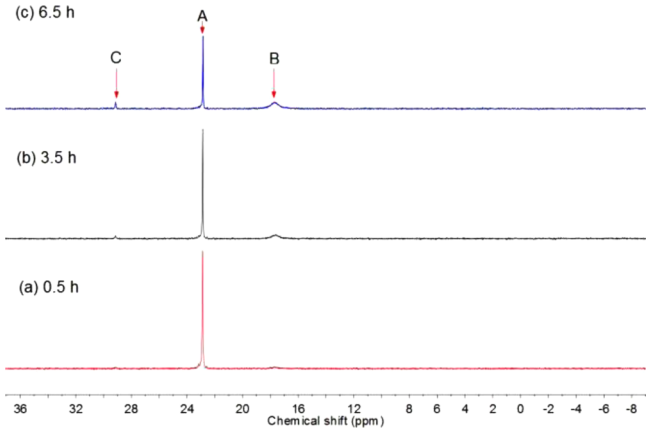


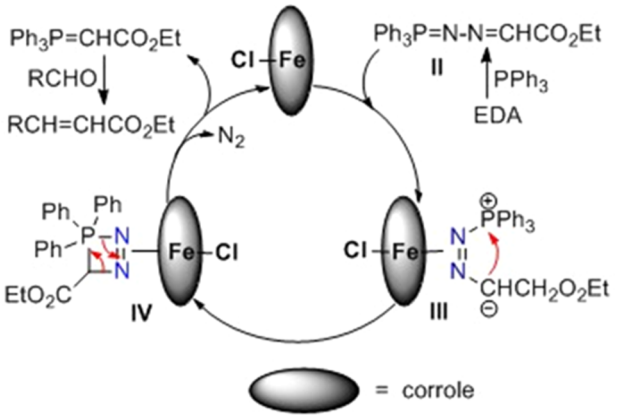
Figure 3. ^{31}P NMR changes of the reaction mixture of phosphazine **II** and iron corrole **1** in $CDCl_3$ at room temperature: (A) phosphazine **II** (δ = 22.85 ppm); (B) phosphorus ylide (δ = 17.60 ppm); (C) $O{=}PPh_3$ (δ = 29.01 ppm).

(96%) as entry 1 of Table 1 (Figure S20, Supporting Information). Thus, the current catalytic reaction is suggested to proceed via a phosphazine **II** to ylide route (path 3, Scheme 1); a similar mechanism had been suggested by Lu in the molybdenum complex mediated olefination of aldehyde.[14a]

On the basis of these observations, a proposed reaction mechanism for the olefination of aldehyde catalyzed by iron(IV) corrole is depicted in Scheme 2. First, PPh_3 reacts with EDA to form the phosphazine **II**. It then coordinates with iron corrole **1** to form intermediate **III**. The electronegative carbon atom attacks the electropositive phosphorus atom to form four-membered-ring intermediate **IV**, which gives an ylide via intramolecular rearrangement and releases an iron corrole catalyst. The ylide then reacts with aldehydes to give olefins. The *trans*-selectivity might be explained by the Wittig reaction, in which stabilized ylide $Ph_3P{=}CHCO_2Et$ reacts with aldehyde to give exclusively *trans* double bonds.[19] Interestingly, in a similar olefination reaction catalyzed by iron(II or III) porphyrin,[12] iron carbenes were suggested to be the active intermediates. The different catalytic behavior of iron(IV) corrole might be related to its higher oxidation state of the central iron atom.

DOI: 10.1021/acs.organomet.5b00069
Organometallics 2015, 34, 2791−2795

Scheme 2. Proposed Mechanism for Olefination of Aldehyde with EDA Catalyzed by Iron(IV) Corrole



CONCLUSION

In summary, we have presented the first and efficient iron-corrole-catalyzed olefination of aldehydes with EDA. The iron-corrole-catalyzed transformation of phosphazine to ylide is a plausible key step in the present system.

EXPERIMENTAL SECTION

General Considerations. Unless otherwise noted, all solvents and chemicals were reagent grade, purchased commercially, and used without further purification. The iron(IV) corroles **1**–**4** were readily prepared according to the reported procedure,[8] although they included some inseparable impurity such as hydrocarbon, and they are used for the olefination without further purification. Column chromatography was performed using 200–300 mesh silica gel. Melting points were obtained on a Büchi melting point B-545 apparatus and are uncorrected. Yields are based on the pure products isolated. All ^{1}H, ^{13}C, ^{19}F, and ^{31}P NMR spectra were recorded on a Bruker Avance III 400 MHz NMR spectrometer with tetramethylsilane (TMS) as internal reference in $CDCl_3$ at 7.25 ppm in ^{1}H NMR spectra or about 77.10 ppm in ^{13}C NMR. Chemical shifts (δ) were reported as parts per million (ppm) in δ scale downfield from TMS. Coupling constants (J) were reported in hertz (Hz). The following abbreviations are used: s = singlet, d = doublet, t = triplet, q = quartet, dd = double doublet, dt = double triplet, and m = multiplet. HR-MS (ESI) mass spectra were recorded on an Agilent 1290 LC-MS spectrometer. UV–vis spectra were recorded on a Hitachi U-2450 spectrophotometer. GC-MS analysis was conducted on a Finnigan GC-MS Trace DSQ apparatus.

General Procedure for the Preparation of the Iron(IV) Corroles 1–4.[8] A flame-dried 20 mL Schlenk tube containing a magnetic stirring bar was charged with 5,10,15-trisphenylcorrole (32 mg, 0.06 mmol), $FeCl_2{\cdot}4H_2O$ (248 mg, 1.2 mmol), and DMF (20 mL) under argon. After stirring at 140 °C for 1.5 h in the dark, the solvent was removed. The resulting residue was dissolved in diethyl ether and passed through a short pad of silica gel. After the solvent was evaporated, the residue was dissolved in CH_2Cl_2 (20 mL) and washed with 7% aqueous HCl (15 mL × 3). The organic layer was dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure to give the desired iron corrole **1**. Preparation of **2**–**4** was done according to the same method.

General Procedure for the Olefination of Aldehydes with EDA Catalyzed by Iron(IV) Corrole 1. A 0.472 mmol amount of aldehyde, 136 mg (0.52 mmol) of PPh_3, and 2.90 mg (1 mol % versus aldehyde) of the iron(IV) corrole catalyst **1** were placed into a round-bottom flask and dissolved in 3 mL of DCM at 40 °C under N_2. A solution of 98 mg (0.94 mmol) of EDA in 2 mL of DCM was added dropwise over approximately 2 min to the reaction mixture with vigorous stirring. After 12 h, the solvent was removed *in vacuo*. After column chromatography (SiO_2, 1.5 cm × 25 cm) using *n*-hexane/EtOAc, the desired target product was obtained upon evaporation of the solvent.

Procedure for the Synthesis of Azine.[14a] A mixture of benzaldehyde (100 mg, 0.94 mmol), EDA (150 mg, 1.3 mmol), and PPh_3 (300 mg, 1.1 mmol) in benzene (5 mL) was refluxed for 5 h. After removal of the solvent, the residue was separated by column chromatography (SiO_2, 1.5 cm × 25 cm) using petroleum ether/EtOAc (4:1, v/v), giving a yellow oil (154 mg, 80% yield).

Procedure for the Synthesis of Phosphazine.[17] PPh_3 (1311 mg, 5.0 mmol) was dissolved in 20 mL of *n*-pentane. EDA (57 mg, 0.5 mmol) was added to the clear mixture, and then the solution was stirred for 8 h. The resulting solid was filtered and washed three times with cold *n*-pentane, giving a white powder (1562 mg, 83% yield).

ASSOCIATED CONTENT

Supporting Information

Characterization data and copies of ^{1}H, ^{13}C, ^{19}F, and ^{31}P NMR and UV–vis spectra and HR-MS (ESI). The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.organomet.5b00069.

AUTHOR INFORMATION

Corresponding Authors

*E-mail: chhyliu@scut.edu.cn.
*E-mail: changc@msu.edu.

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

We are grateful for the financial support from the National Natural Science Foundation of China (NSFC 21171057, 21371059, 21261024).

REFERENCES

(1) Collman, J. P.; Zeng, L.; Decréau, R. A. *Chem. Commun.* **2003**, 2974–2975.
(2) Mahammed, A.; Gross, Z. *J. Am. Chem. Soc.* **2005**, *127*, 2883–2887.
(3) Aviv, I.; Gross, Z. *Chem. Commun.* **2007**, 1987–1999.
(4) (a) Simkhovich, L.; Gross, Z. *Tetrahedron Lett.* **2001**, *42*, 8089–8092. (b) Zdilla, M. J.; Abu-Omar, M. M. *J. Am. Chem. Soc.* **2006**, *128*, 16971–16979.
(5) (a) Liu, H.-Y.; Yam, F.; Xie, Y.-T.; Li, X.-Y.; Chang, C.-K. *J. Am. Chem. Soc.* **2009**, *131*, 12890–12891. (b) Liu, H.-Y.; Mahmood, M. H. R.; Qiu, S.-X.; Chang, C.-K. *Coord. Chem. Rev.* **2013**, *257*, 1306–1333. (c) Liu, H.-Y.; Lai, T.-S.; Yeung, L.-L.; Chang, C.-K. *Org. Lett.* **2003**, *5*, 617–620.
(6) (a) Zhang, R.; Newcomb, M. *Acc. Chem. Res.* **2008**, *41*, 468–477. (b) Harischandra, D. N.; Lowery, G.; Zhang, R.; Newcomb, M. *Org. Lett.* **2009**, *11*, 2089–2092. (c) Biswas, A. N.; Das, P.; Agarwala, A.; Bandyopadhyay, D.; Bandyopadhyay, P. *J. Mol. Catal. A: Chem.* **2010**, *326*, 94–98. (d) Kumari, P.; Nagpal, R.; Chauhan, S. M. S. *Catal. Commun.* **2012**, *29*, 15–20. (e) Pariyar, A.; Bose, S.; Biswas, A. N.; Das, P.; Bandyopadhyay, P. *Catal. Commun.* **2013**, *32*, 23–27. (f) Zhang, R.; Vanover, E.; Chen, T. H.; Thompson, H. *Appl. Catal. A: Gen.* **2013**, *464–465*, 95–100.
(7) (a) Gross, Z.; Simkhovich, L.; Galili, N. *Chem. Commun.* **1999**, 599–600. (b) Simkhovich, L.; Mahammed, A.; Goldberg, I.; Gross, Z. *Chem.–Eur. J.* **2001**, *7*, 1041–1055. (c) Aviv, I.; Gross, Z. *Synlett* **2006**, *6*, 951–953. (d) Aviv, I.; Gross, Z. *Chem. Commun.* **2006**, 4477–4479. (e) Aviv, I.; Gross, Z. *Chem.–Eur. J.* **2008**, *14*, 3995–4005. (f) Liang, L.; Lv, H.-B.; Yu, Y.; Wang, P.; Zhang, J.-L. *Dalton Trans.* **2012**, *41*, 1457–1460.
(8) Nakano, K.; Kobayahi, T.; Ohkawara, T.; Imoto, H.; Nozaki, K. *J. Am. Chem. Soc.* **2013**, *135*, 8456–8459.

DOI: 10.1021/acs.organomet.5b00069
Organometallics 2015, 34, 2791–2795

(9) Kuwano, T.; Kurahashi, T.; Matsubara, S. *Chem. Lett.* **2013**, *42*, 1241−1243.
(10) (a) Wittig, G.; Geissler, G. *Justus Liebigs Ann. Chem.* **1953**, *580*, 44−57. (b) Maryanoff, B. E.; Reitz, A. B. *Chem. Rev.* **1989**, *89*, 863−927. (c) Padwa, A.; Hornbuckle, S. F. *Chem. Rev.* **1991**, *91*, 263−309. (d) Cristau, H.-J. *Chem. Rev.* **1994**, *94*, 1299−1313. (e) Shen, Y.-C. *Acc. Chem. Res.* **1998**, *31*, 584−592. (f) Sun, X.-L.; Tang, Y. *Acc. Chem. Res.* **2008**, *41*, 937−948. (g) Wang, P.; Liu, C.-R.; Sun, X.-L.; Chen, S.-S.; Li, J.-F.; Xie, Z.-W.; Tang, Y. *Chem. Commun.* **2012**, 290−292.
(11) (a) Zhang, X.-Y.; Chen, P. *Chem.−Eur. J.* **2003**, *9*, 1852−1859. (b) Lee, M. Y.; Chen, Y.; Zhang, X. P. *Organometallics* **2003**, *22*, 4905−4909. (c) Das, R. K.; Saha, B.; Rahaman, S. M. W.; Bera, J. K. *Chem.−Eur. J.* **2010**, *16*, 14459−14468. (d) Strand, D.; Rein, T. *J. Organomet. Chem.* **2010**, *695*, 2220−2224. (e) Lebel, H.; Davi, M.; Roy, M. N.; Zeghida, W.; Charette, A. B. *Synthesis* **2011**, *14*, 2275−2280.
(12) (a) Mirafzal, G. A.; Cheng, G.-L.; Woo, L. K. *J. Am. Chem. Soc.* **2002**, *124*, 176−177. (b) Chen, Y.; Huang, L.-Y.; Zhang, X. P. *Org. Lett.* **2003**, *5*, 2493−2496. (c) Cheng, G.-L.; Mirafzal, G. A.; Woo, L. K. *Organometallics* **2003**, *22*, 1468−1474. (d) Chen, Y.; Huang, L.-Y.; Ranade, M. A.; Zhang, X. P. *J. Org. Chem.* **2003**, *68*, 3714−3717. (e) Sun, W.; Kühn, F. E. *Tetrahedron Lett.* **2004**, *45*, 7415−7418. (f) Chinnusamy, T.; Rodionov, V.; Kühn, F. E.; Reiser, O. *Adv. Synth. Catal.* **2012**, *354*, 1827−1831. (g) Gharaati, S.; Moghadam, M.; Tangestaninejad, S.; Mirkhani, V.; Mirkhani, V.; Mohammadpoor-Baltork, I. *J. Organomet. Chem.* **2012**, *720*, 26−29.
(13) (a) Paolesse, R.; Pandey, R. K.; Forsyth, T. P.; Jaquinod, L.; Gerzevske, K. R.; Nurco, D. J.; Senge, M. O.; Licoccia, S.; Boschi, T.; Smith, K. M. *J. Am. Chem. Soc.* **1996**, *118*, 3869−3882. (b) Steene, E.; Wondimagegn, T.; Ghosh, A. *J. Phys. Chem. B* **2001**, *105*, 11406−11413. Erratum: Steene, E.; Wondimagegn, T.; Ghosh, A. *J. Phys. Chem. B* **2002**, *106*, 5312. (c) Cai, S.; Licoccia, S.; D'Ottavi, C.; Paolesse, R.; Nardis, S.; Bulach, V.; Zimmer, B.; Shokhireva, T. K.; Walker, F. A. *Inorg. Chim. Acta* **2002**, *339*, 171−178. (d) Pomarico, G.; Vecchi, A.; Mandoj, F.; Bortolini, O.; Cicero, D. O.; Galloni, P.; Paolesse, R. *Chem. Commun.* **2014**, *50*, 4076−4078.
(14) (a) Lu, X.-Y.; Fang, H.; Ni, Z.-J. *J. Organomet. Chem.* **1989**, *373*, 77−84. (b) Herrman, W. A.; Wang, M. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 1641−1643. (c) Santos, A. M.; Romão, C. C.; Kühn, F. E. *J. Am. Chem. Soc.* **2003**, *125*, 2414−2415. (d) Cao, P.; Li, C.-Y.; Kang, Y.-B.; Xie, Z.-W.; Sun, X.-L.; Tang, Y. *J. Org. Chem.* **2007**, *72*, 6628−6630. (e) Li, C.-Y.; Wang, X.-B.; Sun, X.-L.; Tang, Y.; Zheng, J.-C.; Xu, Z.-H.; Zhou, Y.-G.; Dai, L.-X. *J. Am. Chem. Soc.* **2007**, *129*, 1494−1495. (f) Sha, Q.; Wei, Y.-Y. *ChemCatChem* **2014**, *6*, 131−134.
(15) Fujimura, O.; Honma, T. *Tetrahedron Lett.* **1998**, *39*, 625−626.
(16) (a) Albright, T. A.; Freeman, W. J.; Schweizer, E. E. *J. Org. Chem.* **1976**, *41*, 2716−2720. (b) Bestmann, H. J.; Soliman, F. M.; Geibel, K. *J. Organomet. Chem.* **1980**, *192*, 177−182.
(17) Pedro, F. M.; Santos, A. M.; Baratta, W.; Kühn, F. E. *Organometallics* **2007**, *26*, 302−309.
(18) ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.28 (t, 3H, $-CH_3$), 4.21 (q, 2H, $-CH_2CH_3$), 7.46−7.69 (m, 15H, −phenyl), 7.77 (d, 1H, $-N{=}CH$). ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.49, 138.14, 133.55, 132.56, 128.77, 127.65, 59.77, 14.43. ^{31}P NMR (162 MHz, $CDCl_3$): δ 22.89.
(19) Carey, F. A.; Sundberg, R. J. *Advanced Organic Chemistry, Part B: Reactions and Synthesis*, 4th ed.; Kluwer Academic/Plenum Publishers: New York, 2001; pp 112−113.

DOI: 10.1021/acs.organomet.5b00069
Organometallics 2015, 34, 2791−2795