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Schiff Base Cobalt(II) Complex-Catalyzed Highly Markovnikov-Selective Hydrosilylation of Alkynes

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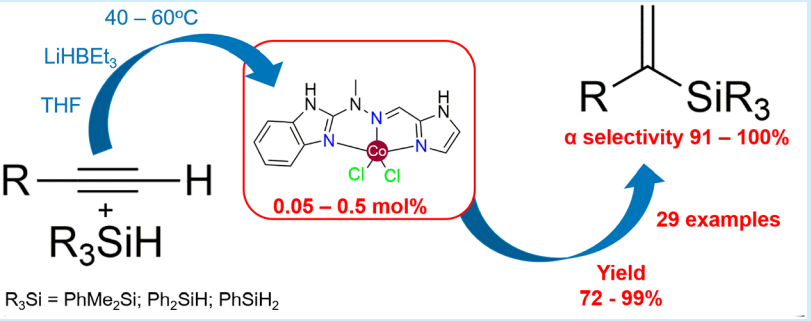

ABSTRACT: A bench-stable cobalt(II) complex, with 3N-donor socket-type benzimidazole-imine-2*H*-imidazole ligand is reported as a precatalyst for regioselective hydrosilylation of terminal alkynes. Both aromatic and aliphatic alkynes could be effectively hydrosilylated with primary, secondary, and tertiary silane to give α-vinylsilanes in high yields with excellent Markovnikov selectivity and extensive functional-group tolerance. Catalyst loading varies within 0.5−0.05 mol %, which is one of the most efficient reported so far in the literature on cobalt-catalyzed alkyne hydrosilylation.

Organosilicon compounds are particularly interesting and powerful tools in organic chemistry. Vinylsilanes, which belong to this group, are applied in the syntheses of natural products,[1] cross coupling reactions,[2] and stereocontrolled reactions,[3] especially in hydrogenation processes.[4] Among all the synthetic pathways for obtaining vinylsilanes, the noble metal-catalyzed hydrosilylation of alkynes and 1,3-dienes has been generally accepted as the most effective route.[5−10] One of the main problems in hydrosilylation of internal and terminal alkynes is the control of regio- and stereoselectivity. Development of newer and more sophisticated catalysts, in terms of structure, that would help to solve this problem has been the challenge for a number of research groups.[11]

From the environmental and economic point of view, compounds based on earth abundant metals are more desirable as catalysts than those based on noble metals. On the other hand, in the era of molecular-heavy and complex ligands, it is essential to develop a rational and sustainable coordination environment. New, simple ligands must be designed to compete with multistep synthesized ones in terms of activity, chemo- regio-, and stereoselectivity. Complexes of first row transition metals, such as Fe or Co, have been proven to be efficient and selective in the reaction of hydrosilylation of alkynes,[12−23] providing β-(*E*/*Z*)-vinylsilanes or α-vinylsilanes. Although these catalysts show high catalytic activity, obtaining α-vinylsilanes as a result of hydrosilylation of alkynes is still challenging and rarely reported, and is usually achieved with cobalt(II) precatalysts.[24−30]

For this purpose, as illustrated in Scheme 1, Huang's and Lu's research groups have developed efficient systems based on pyridine-bis(oxazoline) (PyBox)[24] or iminopyridine-oxazoline (IPO)[25] 3N tridentate pincer ligands, whereas Yang's[26] and Jin's[27] groups have proposed structurally simpler (amine)-pyridine-imine ligands. Regiocontrol in Markovnikov hydrosilylation of terminal alkynes can be also achieved using $Co(OAc)_2{\cdot}4H_2O$/2,2′-bipyridine catalytic system.[28] To the best of our knowledge, all these catalytic systems are active in reactions of terminal alkynes involving primary and secondary silanes.

Recently we have synthesized a series of new cobalt(II) chloride precatalysts coordinated to structurally similar hydrazone Schiff base ligands, easily obtained in a two-step synthetic protocol.[31] These complexes are air- and moisture-stable, and are operationally simple and easy to handle on the laboratory bench. The synthesized cobalt(II) complexes have been evaluated for their ability to act as olefin hydrosilylation

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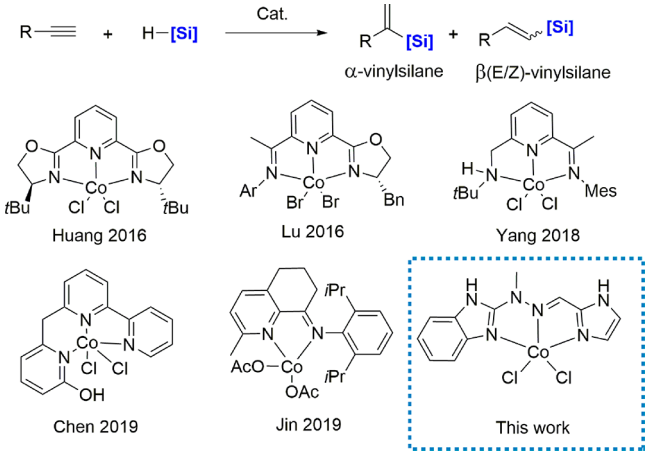
Scheme 1. Cobalt(II) Based Precatalysts for α-Selective Alkyne Hydrosilylation



catalysts in the presence of alkali metal trialkylborohydrides. The cobalt(II) chloride complex containing benzimidazole-imine-2*H*-imidazole ligand (complex **1**, Scheme 1) has been selected as the most efficient in terms of hydrosilylation activity and selectivity toward β-addition. Successful use of complex **1** as a catalyst for hydrosilylation of olefins prompted us to investigate its catalytic activity in the reaction with alkynes. Herein we describe highly selective hydrosilylation of internal and terminal alkynes with primary, secondary, and tertiary silanes in the presence of Schiff base cobalt(II) complex.

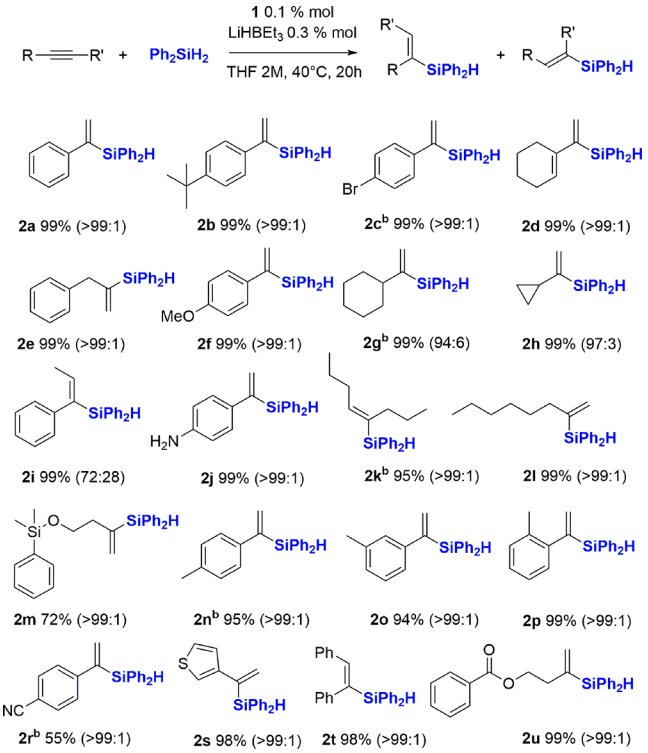
For the optimization reaction (Table 1), phenylacetylene and diphenylsilane were chosen as model substrates. To minimize the amount of wastes, the reaction setup was based on an equimolar ratio of alkyne to silane. The initial reaction was carried out in the presence of 3 mol % of precatalyst **1** with 9 mol % of sodium triethylborohydride in toluene as an activator. The concentration of silane was set to 2 M in THF at the temperature of boiling solvent (Table 1, entry 1). High conversion of diphenylsilane and regioselectivity toward α-addition were observed. To satisfy our aims we also investigated the reaction with $LiHBEt_3$ in THF as an activator. Fortunately, the use of the alternative reducing agent led to increased selectivity toward Markovnikov product, while maintaining high conversion of diphenylsilane (Table 1, entry 2). Experiments with toluene and dioxane as solvents (Table 1, entry 3–4) were successful, but resulted in yielding a mixture of 95% of α-vinylsilane and 5% of β-vinylsilane. Encouraged by these results we tried to lower the concentrations of cobalt precatalyst and borohydride activator. In our investigation, the catalyst loading was lowered from 3 mol % to 0.1 mol %, preserving its activity and selectivity (Table 1, entry 7). Reaction of phenylacetylene with diphenylsilane was completed in 1h at 40 °C. Further decreases in the catalyst loading (0.05 mol % of **1** and 0.15 mol % $LiHBEt_3$) resulted in a slightly lower diphenylsilane conversion (85%), even at elevated temperatures. Having optimized the conditions for hydrosilylation of phenylacetylene with diphenylsilane, the reaction scope was explored by using a variety of terminal and internal alkynes. In addition, the influence of functional groups, i.e., electron-donating and electron-withdrawing substituents to phenyl ring, was investigated. In most experiments, the yields of the reaction products were quantitative, and selectivities toward α-addition products exceeded 99% (Scheme 2).

Table 1. Optimization Protocol for Hydrosilylation of Phenylacetylene with Diphenylsilane[a]

entry	solvent	temp. [°C]	cat. **1** loading [mol %]	Ph_2SiH_2 conversion[b] [%]	selectivity[b] (α:β)
1[d]	THF	70	3	>99	95:5
2	THF	70	3	>99	99:1
3	toluene	70	1	>99	95:5
4	dioxane	70	1	>99	95:5
5	THF	40	1	>99	99:1
6[e]	THF	40	1	52	87:13
7	THF	40	0.5	>99	98:2
8[c]	THF	40	0.1	>99	99:1
9[c]	THF	RT	0.1	85	95:5
10	THF	60	0.05	85	99:1

[a]Conditions: Ph_2SiH_2 (0.5 mmol), phenylacetylene (0.5 mmol), precatalyst (0.05–3 mol %), $LiHBEt_3$ (0.15–9 mol %), 20h, solvent 0.25 mL, unless stated otherwise. [b]Calculated by GC with decane as internal standard. [c]1 h. [d]Reaction with $NaHBEt_3$ (9 mol %). [e]Reaction with *t*-BuONa (2 mol %).

Scheme 2. Range of Alkynes in Hydrosilylation with Diphenylsilane[a]



[a]Conditions: alkyne (1 mmol), diphenylsilane (1 mmol), complex **1** (0.1 mol %), $LiHBEt_3$ (0.3 mol %). Ratio of α to β-addition products determined using GC. Isolation yields. [b]Reaction performed at 60 °C with 0.5% mol **1** and 1.5% mol $LiHBEt_3$.

The reactions with alkynes effectively occurred in the presence 0.1 mol % catalyst **1** and 0.3 mol % $LiHBEt_3$ concentration at 40 °C but required a relatively long time (20 h). Phenylacetylene reacted with diphenylsilane to give the corresponding α-vinylsilane with 99% isolated yield (**2a**). To check the impact of different substituents, the reactions

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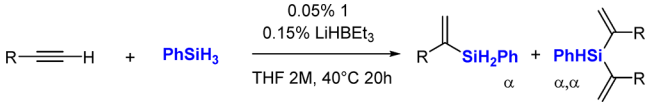
involving para-substituted phenylacetylene were performed. 4-*tert*-Butylphenylacetylene, 4-ethynylanisole, and 4-ethynylaniline reacted with 99:1 selectivity (α/β-vinylsilane), with a 99% isolated yield (**2b**, **2f**, **2j**).

Halide substituents such as 4-bromophenylacetylene underwent the reaction with excellent yield, employing increased catalyst loading (**2c**). Cycloaliphatic alkynes, ethynylcyclohexane, cyclohexenyleacetylene, and cyclopropylacetylene, were also smoothly hydrosilylated according to our protocol (**2d**, **2g**, **2h**). However, despite excellent conversions of cycloaliphatic alkynes, trace amounts of β-addition products were observed (3−6%). Aliphatic alkynes, 3-phenylprop-1-yne and oct-1-yne, were transformed easily to the corresponding α-vinylsilanes, and no β-addition products were observed (**2e**, **2l**). Symmetrical internal alkynes, 4-octyne and diphenylacetylene, underwent hydrosilylation with total conversion of diphenylsilane (**2k**, **2t**), giving selectively the corresponding (*E*)-silylalkenes. Interestingly, the reaction with 1-phenylprop-1-yne resulted in a mixture of α and β-addition products (in favor of α), presumably due to a low steric hindrance of a methyl group (**2i**). Heteroaromatic thiophene moiety was tolerated, and the reaction proceeded smoothly to yield single α-vinylsilane isomer (**2s**). It is worth noting that the reactive groups such as nitrile and ester were compatible with the hydrosilylation conditions (**2r**, **2u**). We also examined the impact of a methyl group substituted to phenyl ring. In contrast to 4-ethynyltoluene, which required elevated temperature and increased catalyst loading (**2n**), 2-ethynyltoluene and 3-ethynyltoluene were transformed easily (**2o**, **2p**) to the corresponding α-vinylsilanes. Masked alcohol, (but-3-yn-1-yloxy)dimethyl(phenyl)silane, appeared to be less reactive and gave the corresponding product with 72% yield (**2m**).

To highlight the utility of this procedure for the synthesis of α-vinylsilane, we conducted the synthesis on a gram-scale under the optimized conditions. The hydrosilylation of phenylacetylene (4 mmol) with Ph_2SiH_2 (4 mmol) in the presence of 0.1 mol % **1** and 0.3 mol % $LiHBEt_3$ afforded 1.12 g of diphenyl(1-phenylvinyl)silane (**2a**) in 98% isolated yield with 99:1 α/β selectivity.

Our next aim was to investigate the reactivity of primary silane in the reaction with terminal alkynes. The reaction of phenylacetylene with phenylsilane catalyzed by **1** activated with $LiHBEt_3$ under standard conditions (0.1 mol % of **1**, 0.3 mol % of $LiHBEt_3$, 40 °C, 20 h) results in a mixture of Markovnikov addition product, phenyl(1-phenylvinyl)silane, and a product of subsequent hydrosilylation of the latter, phenyldi(1-phenylvinyl)silane. During optimization of the reaction conditions (SI), we found that the lowering of catalyst **1** loading to 0.05 mol % resulted in the total conversion of substrates and did not substantially affect hydrosilylation selectivity. Further lowering of the catalyst **1** loading to 0.005 mol % resulted in a decrease in phenylsilane conversion; however, the catalyst still remained very active (TOF as high as 8000 h^{-1}). In all cases only Markovnikov addition products were detected, and no trace amounts of β-addition products were observed. In the optimized conditions (0.05 mol % of **1**, 0.15 mol % of $LiHBEt_3$, 40 °C, 20 h), the substrate scope of the Markovnikov-selective hydrosilylation was investigated with a range of electronically different terminal alkynes (Table 2). Aromatic and aliphatic alkynes underwent successful hydrosilylation with phenylsilane in excellent yields and regioselectivity; however, small amounts of double addition products (α,α-divinylsilanes) were observed. Phenylacetylene derivatives with electron-donating groups such as methoxy, amine, and methyl reacted smoothly (99% yields), whereas the presence of electron-withdrawing 4-bromo-substituent decreased the reaction yield (38%). Cyclopropylacetylene and 3-phenyl-prop-1-yne also underwent successful hydrosilylation in good yields. In all cases, exclusive formation of α-addition products was observed and no β-vinylsilanes were detected.

Table 2. Scope of Alkynes in Hydrosilylation with Phenylsilane[a]



entry	R	yield [%] (isolated)	selectivity $\alpha:\beta$	selectivity $\alpha:\alpha,\alpha$
1	Ph (**3a**)	99 (98)	>99:1	79:21
2	4-*t*-BuC_6H_4	99	>99:1	100:0
3	4-BrC_6H_4	38	>99:1	97:3
4	4-MeOC_6H_4	99	>99:1	>99:1
5	4-$NH_2C_6H_4$	99	>99:1	>99:1
6	4-MeC_6H_4	99	>99:1	97:3
7	3-MeC_6H_4 (**3g**)	99 (94)	>99:1	91:9
8	2-MeC_6H_4 (**3h**)	99 (99)	>99:1	91:9
9	Cyclopropyl	99	>99:1	91:9
10	$PhCH_2$	93	>99:1	97:3

[a]Conditions: alkyne (1 mmol), phenylsilane (1 mmol), **1** (0.05 mol %), $LiHBEt_3$ (0.15 mol %), 40 °C, 20 h. Product ratio and reaction yield determined by GC.

Complex **1** was found to successfully catalyze hydrosilylation of alkynes with tertiary silane−dimethylphenylsilane. To the best of our knowledge, Markovnikov hydrosilylation of terminal alkynes with tertiary silanes is very scarce using cobalt catalysis. A single example of regioselective hydrosilylation of phenylacetylene with $PhMe_2SiH$ (84% yield, $\alpha:\beta$ = 88:12) has been reported recently.[25] In our experiments, dimethylphenylsilane underwent quantitative reactions with terminal alkynes; however, the reaction required higher concentration of the catalyst (0.5 mol %) and elevated temperature (60 °C) in comparison with the protocol developed for primary and secondary silanes. Applying the optimized conditions, we examined the impact of alkyne structure on silane conversion and hydrosilylation selectivity (Scheme 3). Phenylacetylene was hydrosilylated easily by dimethylphenylsilane with 91% selectivity toward α-addition product (**4a**). The presence of alkyl substituents at the phenyl ring led to increased selectivity toward α-addition, irrespective of their position (**4b**, **4f−h**). Bromo, amino and methoxy groups were tolerated, however, hydrosilylation of 4-bromophenylacetylene and 4-aminophenylacetylene (**4c** and **4e**) proceeded with lower yields (75−79%) than the other compounds. Cyclopropylacetylene underwent hydrosilylation with excellent yield and selectivity (**4i**), but 3-phenylprop-1-yne was not reactive in the reaction with dimethylphenylsilane.

Our protocol seems to be the first effective cobalt complex-catalyzed Markovnikov-selective hydrosilylation of aromatic and cycloaliphatic alkynes with $PhMe_2SiH$. Unfortunately, increasing the reaction temperature and the precatalyst loading did not afford positive results for the reaction of other tertiary silanes such as triphenylsilane, triethoxysilane, or triethylsilane with terminal alkynes, which implies that it is the inherent

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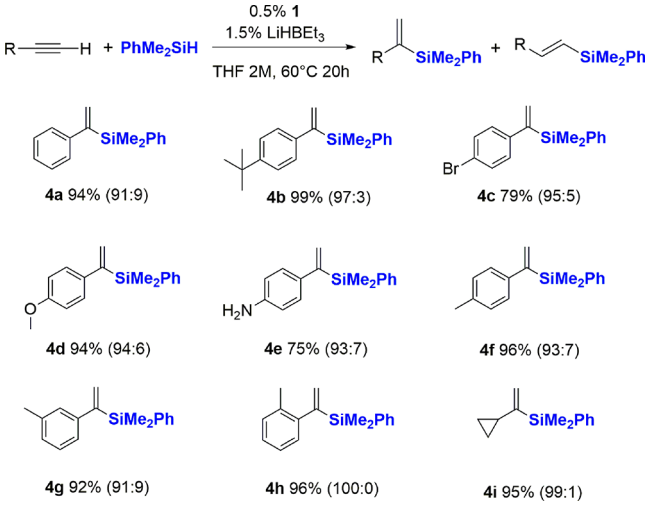
Scheme 3. Range of Alkynes in Hydrosilylation with Dimethylphenylsilane[a]

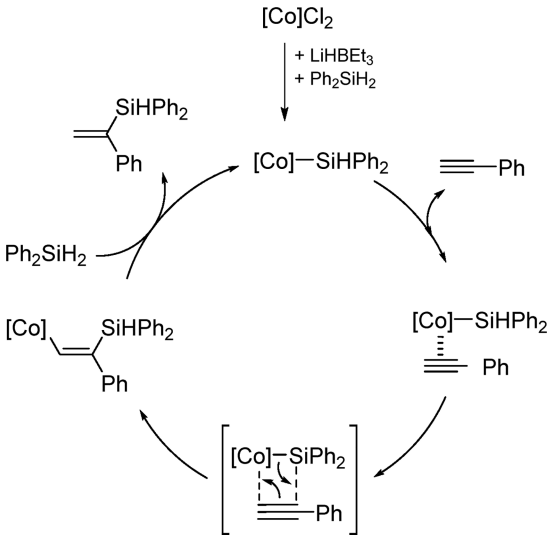


[a]Conditions: alkyne (1 mmol), dimethylphenylsilane (1 mmol), **1** (0.5 mol %), $LiHBEt_3$ (1.5 mol %), THF, 60 °C, 20 h. Isolated yields. Regioselectivity α:β-(*E*) determined by ^{1}H NMR.

nature of the catalyst to be insufficiently active for this group of compounds.

To understand the nature of silane addition to alkyne, NMR studies with deuterium labeled phenylacetylene were performed. Reaction of D_1-phenylacetylene and diphenylsilane afforded *syn*-addition product, and no *anti*-addition products were observed (SI). On the basis of deuterium labeling experiments and the previously reported data,[30] we propose the following simplified mechanism for cobalt-catalyzed α-selective alkyne hydrosilylation (Scheme 4). Cobalt(II) precatalyst reacts with borohydride and silane to form in situ cobalt(I)-silyl intermediate. Following this, migratory insertion of alkyne into Co−Si bond takes place to produce vinylcobalt species, which can undergo reaction with silane to afford α-vinylsilane and regenerate the catalytically active cobalt-silyl intermediate. Alternatively, Co(0) pathway of Markovnikov-selective hydrosilylation, recently proposed for 3N pincer−cobalt complex on the basis of DFT calculations, can be considered.[32]

Scheme 4. Proposed Mechanism for Cobalt-Catalyzed α-Selective Alkyne Hydrosilylation



In conclusion, a pentacoordinated cobalt(II) chloride complex with benzimidazole/2*H*-imidazole-based ligand, activated by lithium triethylborohydride, has been found to act as a good catalyst for regioselective hydrosilylation of alkynes by primary, secondary, and tertiary silanes. Mild reaction conditions, low catalyst loading, functional group tolerance (amine, halide, ester, nitrile, etc.), and extremely high selectivity toward α-hydrosilylation products are unique features of the developed methodology. We believe that the possibility of using tertiary silane makes it more universal than the previously reported catalytic systems based on cobalt complexes with 3N-donor ligands.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.orglett.0c03721.

Experimental details, characterization data, and copies of ^{1}H NMR, ^{13}C NMR, and IR spectra (PDF)

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Notes

The authors declare no competing financial interest.

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■ REFERENCES

(1) Langkopf, E.; Schinzer, D. *Chem. Rev.* **1995**, *95* (5), 1375−1408.
(2) Szudkowska-Frątczak, J.; Hreczycho, G.; Pawluć, P. *Org. Chem. Front.* **2015**, *2* (6), 730−738.
(3) Fleming, I.; Barbero, A.; Walter, D. *Chem. Rev.* **1997**, *97* (6), 2063−2192.
(4) Lautens, M.; Zhang, C. H.; Goh, B. J.; Crudden, C. M.; Johnson, M. J. A. *J. Org. Chem.* **1994**, *59* (21), 6208−6222.

(5) Marciniec, B.; Maciejewski, H.; Pietraszuk, C.; Pawluć, P. *Hydrosilylation: A Comprehensive Review on Recent Advances*; Springer, 2009.
(6) Trost, B. M.; Ball, Z. T. *Synthesis* **2005**, *6*, 853−887.
(7) Sun, J.; Deng, L. *ACS Catal.* **2016**, *6* (1), 290−300.
(8) Zaranek, M.; Marciniec, B.; Pawluć, P. *Org. Chem. Front.* **2016**, *3* (10), 1337−1344.
(9) Greenhalgh, M. D.; Jones, A. S.; Thomas, S. P. *ChemCatChem* **2015**, *7* (2), 190−222.
(10) Chen, J.; Guo, J.; Lu, Z. *Chin. J. Chem.* **2018**, *36* (11), 1075−1109.
(11) Wen, H.; Liu, G.; Huang, Z. *Coord. Chem. Rev.* **2019**, *386*, 138−153.
(12) Mo, Z.; Xiao, J.; Gao, Y.; Deng, L. *J. Am. Chem. Soc.* **2014**, *136* (50), 17414−17417.
(13) Bart, S. C.; Lobkovsky, E.; Chirik, P. J. *J. Am. Chem. Soc.* **2004**, *126* (42), 13794−13807.
(14) Wu, C.; Teo, W. J.; Ge, S. *ACS Catal.* **2018**, *8* (7), 5896−5900.
(15) Teo, W. J.; Wang, C.; Tan, Y. W.; Ge, S. *Angew. Chem., Int. Ed.* **2017**, *56* (15), 4328−4332.
(16) Docherty, J. H.; Peng, J.; Dominey, A. P.; Thomas, S. P. *Nat. Chem.* **2017**, *9* (6), 595−600.
(17) Du, X.; Hou, W.; Zhang, Y.; Huang, Z. *Org. Chem. Front.* **2017**, *4* (8), 1517−1521.
(18) Hu, M.-Y.; He, P.; Qiao, T.-Z.; Sun, W.; Li, W.-T.; Lian, J.; Li, J.-H.; Zhu, S.-F. *J. Am. Chem. Soc.* **2020**, *142* (39), 16894−16902.
(19) Cheng, Z.; Xing, S.; Guo, J.; Cheng, B.; Hu, L.-F.; Zhang, X.-H.; Lu, Z. *Chin. J. Chem.* **2019**, *37*, 457−461.
(20) Guo, J.; Wang, H.; Xing, S.; Hong, X.; Lu, Z. *Chem.* **2019**, *5*, 881−895.
(21) Cheng, Z.; Guo, J.; Lu, Z. *Chem. Commun.* **2020**, *56*, 2229−2239.
(22) Guo, J.; Shen, X.; Lu, Z. *Angew. Chem., Int. Ed.* **2017**, *56*, 615−618.
(23) Wen, H.; Liu, G.; Huang, Z. *Coord. Chem. Rev.* **2019**, *386*, 138−153.
(24) Zuo, Z.; Yang, J.; Huang, Z. *Angew. Chem., Int. Ed.* **2016**, *55* (21), 10839−10843.
(25) Guo, J.; Lu, Z. *Angew. Chem., Int. Ed.* **2016**, *55* (36), 10835−10838.
(26) Zhang, S.; Ibrahim, J. J.; Yang, Y. *Org. Lett.* **2018**, *20* (19), 6265−6269.
(27) Zong, Z.; Yu, Q.; Sun, N.; Hu, B.; Shen, Z.; Hu, X.; Jin, L. *Org. Lett.* **2019**, *21*, 5767−5772.
(28) Wu, G.; Chakraborty, U.; Jacobi von Wangelin, A. J. *Chem. Commun.* **2018**, *54*, 12322−12325.
(29) Kong, D.; Hu, B.; Yang, M.; Chen, D.; Xia, H. *Organometallics* **2019**, *38* (21), 4341−4350.
(30) Kong, D.; Hu, B.; Chen, D. *Chem. - Asian J.* **2019**, *14*, 2694−2703.
(31) Bocian, A.; Skrodzki, M.; Kubicki, M.; Gorczyński, A.; Pawluć, P.; Patroniak, V. *Appl. Catal., A* **2020**, *602*, 117665.
(32) Ma, Y.; Han, Z. *J. Org. Chem.* **2018**, *83* (23), 14646−14657.

https://dx.doi.org/10.1021/acs.orglett.0c03721
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