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Highly β(Z)-Selective Hydrosilylation of Terminal Alkynes Catalyzed by Thiolate-Bridged Dirhodium Complexes

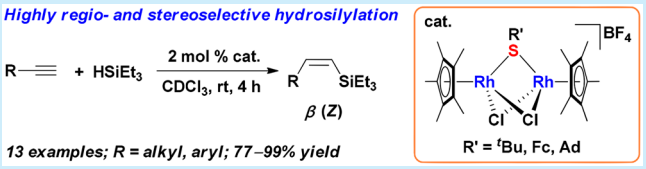
Xiangyu Zhao,[†] Dawei Yang,*[,†] Yahui Zhang,[†] Baomin Wang,[†] and Jingping Qu[†,‡]

[†]State Key Laboratory of Fine Chemicals, Dalian University of Technology, Dalian 116024, People's Republic of China

[‡]Key Laboratory for Advanced Materials, East China University of Science and Technology, Shanghai 200237, People's Republic of China

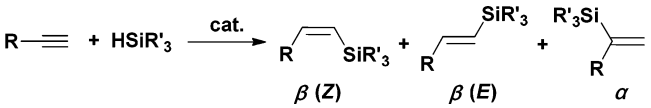
Supporting Information

ABSTRACT: A series of novel monothiolate-bridged dirhodium complexes, $[Cp^*Rh(\mu\text{-}SR)(\mu\text{-}Cl)_2RhCp^*][BF_4]$ {$Cp^* = \eta^5\text{-}C_5Me_5$, R = tertiary butyl (^{t}Bu), **1a**; R = ferrocenyl (Fc), **1b**; R = adamantyl (Ad), **1c**} were designed and successfully synthesized, which can smoothly facilitate highly regioselective and stereoselective hydrosilylation of terminal alkynes to afford β(Z) vinylsilanes with good functional group compatibility. Furthermore, the hydride bridged dirhodium complex $[Cp^*Rh(\mu\text{-}S^tBu)(\mu\text{-}Cl)(\mu\text{-}H)RhCp^*][BF_4]$ (**5**) as a potential intermediate was obtained by the reaction of **1a** with excess $HSiEt_3$.



Vinylsilanes are a versatile category of building blocks for the synthesis of various functional organic compounds and polymeric organsilicon materials.[1] The hydrosilylation of alkynes promoted by transition-metal complexes is one of the most straightforward and effective approaches to access such compounds.[2] However, using this synthetic method with terminal alkynes commonly generates three regioselective and stereoselective isomers, namely, β(Z), β(E), and α vinylsilanes, as shown in Scheme 1. Except for this key issue, some other

Scheme 1. Catalytic Hydrosilylation of Terminal Alkynes



side reactions such as alkyne hydrogenation[3] make product distribution more complicated. Therefore, the precise control of regioselective and stereoselective synthesis of only one desired isomer with high activity is still challenging.

Over past decades, several late-transition-metal complexes have been reported for effective alkyne hydrosilylation with high selectivity, such as classic noble Ru,[4] Rh,[5] Ir,[6] and Pt[7] catalysts. Recently, because of increasing concerns of sustainable development, Earth-abundant base-metal catalysts, such as iron and cobalt, were investigated for alkyne hydrosilylation.[8,9] Particularly, recent explosively growing Co complexes were proven to be effective for facilitating alkyne hydrosilylation to selectively produce β(Z),[10] β(E),[11] and α[12] vinylsilanes. In both β vinylsilanes, highly selective synthesis for thermodynamically unstable β(Z) vinylsilanes is regarded as a more challenging task,[4a,b,e−n,6b−d,7e,10] because β(Z) product is usually prone to isomerize to the stable β(E) isomer.[5c,6a,b,10a]

In recent decades, highly selective organic transformations promoted by bimetallic complexes have attracted considerable attention for the distinctive cooperative effect between two metallic centers,[13] which are also common in the catalytic cycles mediated by metalloenzymes in biology.[14] For instance, carboxylate-bridged dirhodium complexes were well-developed as excellent catalysts for highly site-selective and stereoselective functionalization of nonactivated C−H bonds.[15] Compared with extensive development in mononuclear metal catalysts for hydrosilylation of terminal alkynes, the rational design of bimetallic catalysts toward the catalytic precise synthesis of β(Z) vinylsilanes is still rare.

Our group focuses on the construction of novel thiolate-bridged bimetallic or multimetallic complexes for inert small molecule activation and catalytic transformation,[16] especially biomimetic nitrogen fixation using the diiron scaffold.[17] To further develop richer functions of catalytic conversion, we also extended to other transition metals in Group VIII, such as Ru, Ni, and Co.[18] Herein, we design and synthesize a series of monothiolate-bridged dirhodium complexes, which can smoothly facilitate *Z*-selective anti-Markovnikov hydrosilylation of terminal alkynes with tertiary silanes.

Initially, to provide stable reaction framework and enough interaction space for catalytic transformation of organic substrates, we constructed a series of monothiolate-bridged dirhodium complexes $[Cp^*Rh(\mu\text{-}SR)(\mu\text{-}Cl)_2RhCp^*][BF_4]$ (R = ^{t}Bu, **1a**; R = Fc, **1b**; R = Ad, **1c**). As illustrated in Scheme 2, treatment of precursor $[Cp^*Rh(\mu\text{-}Cl)_3RhCp^*][BF_4]$[19] with 1 equiv of sodium thiolate with large sterically hindered substituents, such as ^{t}Bu, Fc, and Ad, from −78 °C to room temperature gave the corresponding desired complexes **1a−1c** in good yields. These complexes were fully characterized by ^{1}H NMR, ^{13}C NMR, ESI-HRMS, and elemental analysis, as well as single-crystal X-ray diffraction (XRD) analysis.

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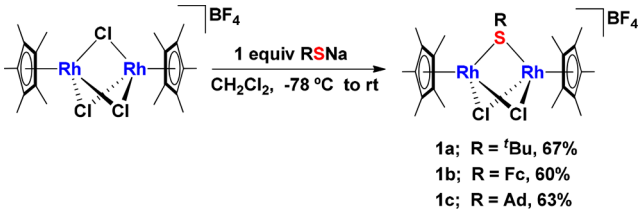
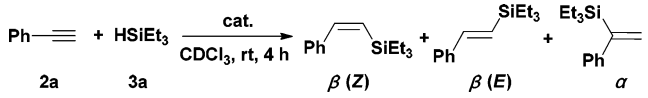
Scheme 2. Synthesis of Dirhodium Complexes



Only one proton signal at ~1.65 ppm and two carbon signals at ~10 and 97 ppm suggest that complexes **1a−1c** are all in a symmetric arrangement in the solution state. Furthermore, ESI-HRMS and elemental analysis data provide strong evidence for the determination of their molecular composition. The above spectroscopic data are in good agreement with their solid-state structures. As shown in Figure 1, the crystal structures of **1a−1c** reveal that the two Rh centers are linked by two chloride groups and one thiolate ligand in trigonal bipyramid geometry. The Rh1−Rh2 distances of **1a−1c** are 3.2417(3), 3.2026(4), and 3.2225(4) Å, which are obviously longer than those observed in other reported thiolate-bridged dirhodium complexes.[20] The two Cp* ligands in **1a−1c** are almost parallel, with dihedral angles of 15.33(10)°, 9.74(17)°, and 18.96(15)°. This minor discrepancy is attributed to different steric hindrance effect of substituents in the bridging thiolate ligands. These monothiolate-bridged dirhodium complexes represent a novel family with only one {Rh−S−Rh} active fragment, which are obviously different from conventional dithiolate or trithiolate-bridged cyclopentadienyl dirhodium complexes.[21]

Next, to examine the catalytic activity of monothiolate-bridged dirhodium complexes **1a−1c**, the hydrosilylation of terminal alkynes was investigated as a model reaction, and the experimental results are summarized in Table 1. Initially, to obtain deep insight into the influence of bimetallic cooperative effect on catalytic activity and reaction selectivity, some representative monorhodium and dirhodium complexes were also chosen as catalysts. In the presence of 4 mol % monorhodium complexes as catalysts, the reactions of phenylacetylene (**2a**) with $HSiEt_3$ (**3a**) at room temperature exhibited poor catalytic activity and irregular product distributions (Table 1, entries 1−3). When using 2 mol % dirhodium complex $[(cod)Rh(\mu\text{-}Cl)]_2$[5a,22] (cod = 1,5-cyclooctadiene), lower activity and poorer selectivity were observed (Table 1, entry 4). Interestingly, when employing Cp* to substitute cod as the auxiliary ligand, the activity was remarkably improved; however, the selectivity

Table 1. Catalytic Activity of Rhodium Complexes[a]



entry	catalyst	yield[b] (%)	$\beta(Z)/\beta(E)/\alpha$[b]
1	$(PPh_3)_3RhCl$[c]	41	6:93:1
2	$[Cp^*Rh(MeCN)_3][PF_6]_2$[c]	22	89:9:2
3	$[(cod)_2Rh][PF_6]/2PPh_3$[c]	11	17:83:0
4	$[(cod)Rh(\mu\text{-}Cl)]_2$	2	19:70:11
5	$[Cp^*Rh(\mu\text{-}Cl)Cl]_2$	99	50:50:0
6	**1a**	99	98:1:1
7	**1b**	99	98:1:1
8	**1c**	98	94:5:1

[a]Reaction conditions: phenylacetylene (0.5 mmol), $HSiEt_3$ (0.6 mmol, 1.2 equiv), catalyst (0.01 mmol, 2 mol %), $CDCl_3$ (0.6 mL), rt, for 4 h. [b]Yields and selectivity are calculated, based on mellithene as an internal standard, via ^1H NMR. [c]Catalyst concentration = 4 mol %.

still was not very good, with two main products $\beta(Z)/\beta(E)$ formed at a ratio of 1:1 (Table 1, entry 5). To our delight, complexes **1a−1c** were proven to be efficient catalysts for hydrosilylation of terminal alkynes without any additives under the same conditions. With these dinuclear systems, $\beta(Z)$ vinylsilanes were all selectively obtained in excellent yields (Table 1, entries 6−8), which indicates the steric effect of substituent in thiolate ligands has only a small influence on product selectivity. In addition, solvent effect was also not observed in this catalytic system, except for MeCN (see the Supporting Information (Table S1, entries 3−7)). It is especially noteworthy that there was no obvious isomerization of $\beta(Z)$ when the reaction time was prolonged to 24 h, which indicates that the thiolate-bridged dirhodium complexes can efficiently hinder the isomerization (Table S1, entries 8−10).

In addition, we chose **1a** as the catalyst and investigated reactions of phenylacetylene and a series of silanes for activity and regioselectivity (see Table 2). When utilizing tertiary silanes such as $HSiEt_3$ or $HSiPh_3$ (Table 2, entries 1 and 2), excellent yields and selectivity were observed. When the substituent of tertiary silanes was replaced by an electron-withdrawing alkoxyl such as OMe or OEt, the yields were significantly decreased; however, $\beta(Z)$ vinylsilanes were still obtained as the main products. Interestingly, when secondary silane H_2SiPh_2 (Table 2, entry 5) was adopted, the main product was $\beta(E)$ vinylsilane. However, there is no hydrosilylation product observed using $H_2Si^tBu_2$.

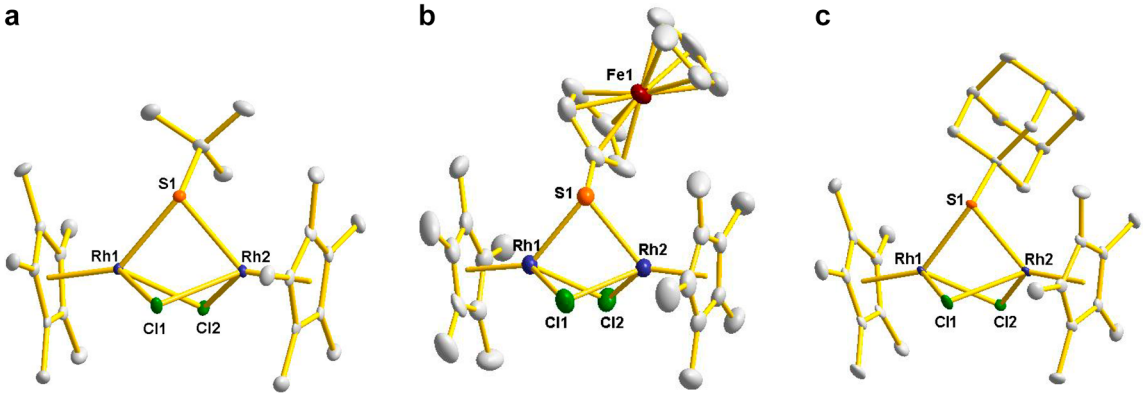


Figure 1. ORTEP (ellipsoids at 50% probability) diagrams of complexes **1a** (left), **1b** (middle), **1c** (right). All hydrogen atoms and counterion BF_4^- are omitted for the sake of clarity.

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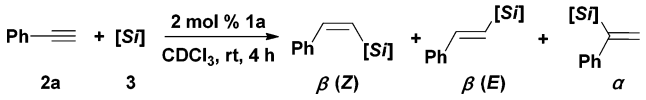
Table 2. Hydrosilylation of Phenylacetylene with Different Silanes Catalyzed by Complex 1a[a]

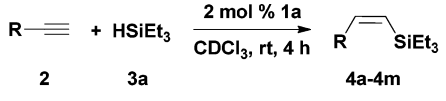


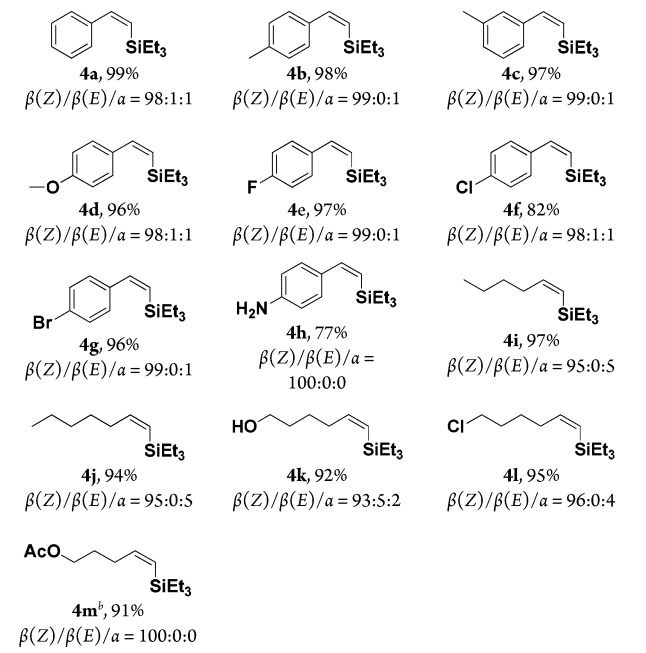
entry	[Si]	conversion[b] (%)	yield[b] (%)	$\beta(Z)/\beta(E)/\alpha$[b]
1	$HSiEt_3$ (**3a**)	100	99	98:1:1
2	$HSiPh_3$ (**3b**)	100	99	99:0:1
3	$HSi(OMe)_3$ (**3c**)	94	68	85:15:0
4	$HSi(OEt)_3$ (**3d**)	86	69	98:2:0
5	H_2SiPh_2 (**3e**)	100	54	1:94:5

[a]Reaction conditions: phenylacetylene (0.5 mmol), silane (0.6 mmol, 1.2 equiv), **1a** (0.01 mmol, 2 mol %), $CDCl_3$ (0.6 mL), rt, for 4 h. [b]The conversion of phenylacetylene, the yields of vinylsilanes containing $\beta(Z)$, $\beta(E)$, α and the selectivity were calculated, based on using mellithene as an internal standard, via ^1H NMR.

With the optimal reaction conditions in hand, we next investigated the substrate scope of the hydrosilylation reaction using complex **1a** (2 mol %) as the catalyst and $HSiEt_3$ as the silane source. As shown in Scheme 3, complex **1a** was proven

Scheme 3. Hydrosilylation of Terminal Alkynes Catalyzed by Complex 1a[a]



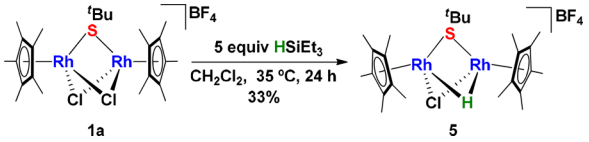


[a]General reaction conditions: Terminal alkynes (0.5 mmol), $HSiEt_3$ (0.6 mmol, 1.2 equiv), **1a** (0.01 mmol, 2 mol %), $CDCl_3$ (0.6 mL), rt, for 4 h; yield and selectivity isomers were determined, based on mellithene as an internal standard, via ^1H NMR. [b]1,1,2,2-tetrachloroethane was used as an internal standard.

to be effective in the selective formation of $\beta(Z)$ vinylsilanes from aryl- or alkyl-substituted terminal alkynes in high yields. Whether terminal alkynes were modified by electron-withdrawing or electron-donating groups such as alkoxyl, halogen, amine, hydroxyl, ester, and $\beta(Z)$ vinylsilanes were always selectively obtained in high yields. These results indicate this dirhodium catalytic system exhibits good functional group tolerance under mild conditions. Furthermore, we also explored the hydrosilylation of internal alkynes under similar conditions. Taking diphenylacetylene as an example, the conversion and yield are obviously reduced in contrast with terminal alkynes. In addition, the selectivity is also poor, with a $\beta(Z)/\beta(E)/\alpha$ ratio of 40:58:2.

To shed light on the possible mechanism, the stoichiometric reactions of **1a** with phenylacetylene and $HSiEt_3$ were performed. No expected ligand exchange reaction between complex **1a** and phenylacetylene was observed, which may be attributed to poor coordination capacity of neutral alkyne, compared to negative bridged ligands in **1a**. This result is absolutely distinct from the reactivity of thiolate-bridged diiron complexes toward alkynes.[23] To our delight, treatment of **1a** with excess $HSiEt_3$ in CH_2Cl_2 at 35 °C for 24 h afforded a rare monothiolate-bridged dirhodium hydride complex $[Cp^*Rh(\mu\text{-}S^tBu)(\mu\text{-}Cl)(\mu\text{-}H)RhCp^*][BF_4]$ (**5**) in 33% yield (see Scheme 4).

Scheme 4. Reaction of Complex 1a with $HSiEt_3$



Notably, thiolate-bridged diiron,[17] dicobalt,[24] and nickel–iron[25] complexes cannot activate tertiary silane $HSiEt_3$ under similar conditions. The ^1H NMR spectrum of **5** exhibits a characteristic resonance for the bridging hydride as a triplet at δ = −10.48 ppm with $^1J_{Rh,H}$ = 24 Hz in the high-field region, which is similar to those found in the previously reported dirhodium hydride bridged complexes.[21d,26] In addition, the ESI-HRMS data provides further experimental evidence for the existence of a hydride subunit.

As expected, the molecular structure of complex **5** shown in Figure 2 was fully consistent with the structure predicted

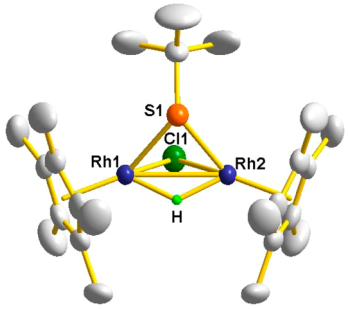


Figure 2. ORTEP (ellipsoids at 50% probability) diagram of complex **5**. All hydrogen atoms and BF_4^- are omitted for the sake of clarity, except for the bridging hydride.

by the above spectroscopic data. Because of the formation of three-center two-electron bond between two Rh centers and a bridging hydride, the Rh1–Rh2 distance (2.7280(9) Å) of **5** is significantly shortened, compared with that of **1a** (3.2417(3) Å). In contrast with **1a**, another obvious structural feature is the change of dihedral angle between the two Cp* ligands from 15.33(10)° to 49.00(24)°. Importantly, complex **5** also shows good catalytic activity toward selectively furnishing $\beta(Z)$ vinylsilanes (86% yield, $\beta(Z)/\beta(E)/\alpha$ ratio = 87:9:4) although

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the selectivity is not better than those of complexes **1a**−**1c** under the same conditions.

Furthermore, we also conducted deuterium-labeling experiments using PhC≡CD or $DSiEt_3$ under similar conditions. Hydrosilylation of PhC≡CD with $HSiEt_3$ in the presence of **1a** as the catalyst exhibits excellent selectivity with a $\beta(Z)/\beta(E)/\alpha$ ratio of 97:2:1. The ^1H and ^2H NMR spectra of d-$\beta(Z)$-**4a** clearly confirmed that the deuterium atom is almost intact on the C atom bearing the silyl group. Moreover, the deuteriosilylation of phenylacetylene with $DSiEt_3$ also displays high $\beta(Z)$-selectivity and the deuterium atom is located at the C atom linked to the phenyl group. The above results suggest that this hydrosilylation of terminal alkynes promoted by dirhodium complexes proceeds through a *trans*-addition of silane to the C≡C bond.

Based on the above experimental results and some classic mechanistic proposals for hydrosilylation of alkyne such as the Chalk−Harrod mechanism,[2a] we proposed a potential pathway for $\beta(Z)$-selective hydrosilylation of terminal alkyne catalyzed by thiolate-bridged dirhodium complexes. First, heterolytic splitting of the silane mediated by dirhodium centers and terminal alkynes gave an intermediate hydride-bridged complex **5** and active species $[R_3Si{-}CH{=}C{-}R']^+$. Then, nucleophilic attack of the bridging hydride over $[R_3Si{-}CH{=}C{-}R']^+$ facilely gives $\beta(Z)$ vinylsilanes, which is similar to the recently reported mononuclear Rh system.[3a] In this process, the cooperative effect of dirhodium centers and steric effect of two Cp* ligands are essential to access the high regioselectivity and stereoselectivity of hydrosilylation of terminal alkynes, and a similar strategy was also adopted in the thiolate-bridged diruthenium systems.[27]

In summary, based on the steric and electronic effects of thiolate and Cp* ligands, a class of novel monothiolate-bridged dirhodium complexes were precisely designed and successfully constructed. By the cooperative effect between the two Rh centers, highly regioselective and stereoselective hydrosilylation of terminal alkynes to afford $\beta(Z)$-vinylsilanes was achieved in high yields and isomerization from $\beta(Z)$ to $\beta(E)$ isomer was efficiently suppressed. Moreover, this bimetallic catalytic system exhibits good functional group compatibility and broad substrate scope. Unexpectedly, the hydride bridged dirhodium complex **5** as an intermediate species was successfully synthesized, which is essential to reveal the actual reaction pathway. Further mechanistic investigations for this catalytic transformation and other catalytic applications are in progress.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.8b02267.

Experimental details and spectroscopic data (PDF)

Accession Codes

CCDC 1581607−1581609, 1584588 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, U.K.; fax: +44 1223 336033.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: yangdw@dlut.edu.cn.

ORCID

Dawei Yang: 0000-0002-7646-3891
Baomin Wang: 0000-0001-9058-4983
Jingping Qu: 0000-0002-7576-0798

Notes

The authors declare no competing financial interest.

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■ REFERENCES

(1) (a) Langkopf, E.; Schinzer, D. *Chem. Rev.* **1995**, *95*, 1375−1408. (b) Ojima, I.; Li, Z.; Zhu, J. *The Chemistry of Organic Silicon Compounds*; Rappoport, Z., Apeloig, Y., Eds.; Wiley: New York, 1998; pp 1687−1792. (c) Curtis-Long, M. J.; Aye, Y. *Chem. - Eur. J.* **2009**, *15*, 5402−5416. (d) Szudkowska-Frątczak, J.; Hreczycho, G.; Pawluć, P. *Org. Chem. Front.* **2015**, *2*, 730−738.

(2) (a) *Hydrosilylation: A Comprehensive Review on Recent Advances*; Marciniec, B., Ed.; Springer: Berlin, 2009. (b) Lim, D. S. W.; Anderson, E. A. *Synthesis* **2012**, *44*, 983−1010.

(3) (a) Iglesias, M.; Sanz Miguel, P. J.; Polo, V.; Fernández-Alvarez, F. J.; Pérez-Torrente, J. J.; Oro, L. A. *Chem. - Eur. J.* **2013**, *19*, 17559−17566. (b) Navarro, M.; Smith, C. A.; Albrecht, M. *Inorg. Chem.* **2017**, *56*, 11688−11701.

(4) For examples, see: (a) Esteruelas, M. A.; Herrero, J.; Oro, L. A. *Organometallics* **1993**, *12*, 2377−2379. (b) Na, Y.; Chang, S. *Org. Lett.* **2000**, *2*, 1887−1889. (c) Trost, B. M.; Ball, Z. T. *J. Am. Chem. Soc.* **2001**, *123*, 12726−12727. (d) Kawanami, Y.; Sonoda, Y.; Mori, T.; Yamamoto, K. *Org. Lett.* **2002**, *4*, 2825−2827. (e) Martín, M.; Sola, E.; Lahoz, F. J.; Oro, L. A. *Organometallics* **2002**, *21*, 4027−4029. (f) Aricó, C. S.; Cox, L. R. *Org. Biomol. Chem.* **2004**, *2*, 2558−2562. (g) Nagao, M.; Asano, K.; Umeda, K.; Katayama, H.; Ozawa, F. *J. Org. Chem.* **2005**, *70*, 10511−10514. (h) Menozzi, C.; Dalko, P. I.; Cossy, J. *J. Org. Chem.* **2005**, *70*, 10717−10719. (i) Trost, B. M.; Ball, Z. T. *J. Am. Chem. Soc.* **2005**, *127*, 17644−17655. (j) Hayashi, A.; Yoshitomi, T.; Umeda, K.; Okazaki, M.; Ozawa, F. *Organometallics* **2008**, *27*, 2321−2327. (k) Ding, S.; Song, L.-J.; Chung, L. W.; Zhang, X.; Sun, J.; Wu, Y.-D. *J. Am. Chem. Soc.* **2013**, *135*, 13835−13842. (l) Gao, R.; Pahls, D. R.; Cundari, T. R.; Yi, C. S. *Organometallics* **2014**, *33*, 6937−6944. (m) Ding, S.; Song, L.-J.; Wang, Y.; Zhang, X.; Chung, L. W.; Wu, Y.-D.; Sun, J. *Angew. Chem., Int. Ed.* **2015**, *54*, 5632−5635. (n) Mutoh, Y.; Mohara, Y.; Saito, S. *Org. Lett.* **2017**, *19*, 5204−5207.

(5) For examples, see: (a) Takeuchi, R.; Tanouchi, N. *J. Chem. Soc., Perkin Trans. 1* **1994**, 2909−2913. (b) Takeuchi, R.; Nitta, S.; Watanabe, D. *J. Org. Chem.* **1995**, *60*, 3045−3051. (c) Faller, J. W.; D'Alliessi, D. G. *Organometallics* **2002**, *21*, 1743−1746. (d) Mori, A.; Takahisa, E.; Yamamura, Y.; Kato, T.; Mudalige, A. P.; Kajiro, H.; Hirabayashi, K.; Nishihara, Y.; Hiyama, T. *Organometallics* **2004**, *23*, 1755−1765. (e) Sato, A.; Kinoshita, H.; Shinokubo, H.; Oshima, K. *Org. Lett.* **2004**, *6*, 2217−2220. (f) Jiménez, M. V.; Pérez-Torrente, J. J.; Bartolomé, M. I.; Gierz, V.; Lahoz, F. J.; Oro, L. A. *Organometallics* **2008**, *27*, 224−234. (g) Huckaba, A. J.; Hollis, T. K.; Howell, T. O.; Valle, H. U.; Wu, Y. *Organometallics* **2013**, *32*, 63−69. (h) Morales-Cerón, J. P.; Lara, P.; López-Serrano, J.; Santos, L. L.; Salazar, V.; Álvarez, E.; Suárez, A. *Organometallics* **2017**, *36*, 2460−2469.

(6) For examples, see: (a) Tanke, R. S.; Crabtree, R. H. *J. Am. Chem. Soc.* **1990**, *112*, 7984−7989. (b) Sridevi, V. S.; Fan, W. Y.; Leong, W. K. *Organometallics* **2007**, *26*, 1157−1160. (c) Iglesias, M.; Pérez-Nicolás, M.; Sanz Miguel, P. J.; Polo, V.; Fernández-Alvarez, F. J.; Pérez-Torrente, J. J.; Oro, L. A. *Chem. Commun.* **2012**, *48*, 9480−9482. (d) Pérez-Torrente, J. J.; Nguyen, D. H.; Jiménez, M. V.;

DOI: 10.1021/acs.orglett.8b02267
Org. Lett. XXXX, XXX, XXX−XXX

Modrego, F. J.; Puerta-Oteo, R.; Gómez-Bautista, D.; Iglesias, M.; Oro, L. A. *Organometallics* **2016**, *35*, 2410−2422.
(7) For examples, see: (a) Aneetha, H.; Wu, W.; Verkade, J. G. *Organometallics* **2005**, *24*, 2590−2596. (b) Berthon-Gelloz, G.; Schumers, J.-M.; De Bo, G.; Markó, I. E. *J. Org. Chem.* **2008**, *73*, 4190−4197. (c) Silbestri, G. F.; Flores, J. C.; de Jesús, E. *Organometallics* **2012**, *31*, 3355−3360. (d) Ortega-Moreno, L.; Peloso, R.; Maya, C.; Suárez, A.; Carmona, E. *Chem. Commun.* **2015**, *51*, 17008−17011. (e) Dierick, S.; Vercruysse, E.; Berthon-Gelloz, G.; Markó, I. E. *Chem. - Eur. J.* **2015**, *21*, 17073−17078. (f) Żak, P.; Bołt, M.; Kubicki, M.; Pietraszuk, C. *Dalton Trans.* **2018**, *47*, 1903−1910.
(8) (a) Bart, S. C.; Lobkovsky, E.; Chirik, P. J. *J. Am. Chem. Soc.* **2004**, *126*, 13794−13807. (b) Belger, C.; Plietker, B. *Chem. Commun.* **2012**, *48*, 5419−5421. (c) Greenhalgh, M. D.; Frank, D. J.; Thomas, S. P. *Adv. Synth. Catal.* **2014**, *356*, 584−590. (d) Challinor, A. J.; Calin, M.; Nichol, G. S.; Carter, N. B.; Thomas, S. P. *Adv. Synth. Catal.* **2016**, *358*, 2404−2409.
(9) (a) Isobe, M.; Nishizawa, R.; Nishikawa, T.; Yoza, K. *Tetrahedron Lett.* **1999**, *40*, 6927−6932. (b) Yong, L.; Kirleis, K.; Butenschön, H. *Adv. Synth. Catal.* **2006**, *348*, 833−836. (c) Konno, T.; Taku, K.; Yamada, S.; Moriyasu, K.; Ishihara, T. *Org. Biomol. Chem.* **2009**, *7*, 1167−1170. (d) Huang, K.-H.; Isobe, M. *Eur. J. Org. Chem.* **2014**, *2014*, 4733−4740. (e) Rivera-Hernández, A.; Fallon, B. J.; Ventre, S.; Simon, C.; Tremblay, M.-H.; Gontard, G.; Derat, E.; Amatore, M.; Aubert, C.; Petit, M. *Org. Lett.* **2016**, *18*, 4242−4245. (f) Sun, J.; Deng, L. *ACS Catal.* **2016**, *6*, 290−300.
(10) (a) Teo, W. J.; Wang, C.; Tan, Y. W.; Ge, S. *Angew. Chem., Int. Ed.* **2017**, *56*, 4328−4332. (b) Du, X.; Hou, W.; Zhang, Y.; Huang, Z. *Org. Chem. Front.* **2017**, *4*, 1517−1521.
(11) (a) Mo, Z.; Xiao, J.; Gao, Y.; Deng, L. *J. Am. Chem. Soc.* **2014**, *136*, 17414−17417. (b) Docherty, J. H.; Peng, J.; Dominey, A. P.; Thomas, S. P. *Nat. Chem.* **2017**, *9*, 595−600. (c) Wu, C.; Teo, W. J.; Ge, S. *ACS Catal.* **2018**, *8*, 5896−5900.
(12) (a) Guo, J.; Lu, Z. *Angew. Chem., Int. Ed.* **2016**, *55*, 10835−10838. (b) Zuo, Z.; Yang, J.; Huang, Z. *Angew. Chem., Int. Ed.* **2016**, *55*, 10839−10843.
(13) (a) Hetterscheid, D. G. H.; Chikkali, S. H.; de Bruin, B.; Reek, J. N. H. *ChemCatChem* **2013**, *5*, 2785−2793. (b) Buchwalter, P.; Rosé, J.; Braunstein, P. *Chem. Rev.* **2015**, *115*, 28−126. (c) *Homo- and Heterobimetallic Complexes in Catalysis: Cooperative Catalysis*, Kalck, P., Ed.; Springer: Berlin, 2016.
(14) Fontecilla-Camps, J. C.; Amara, P.; Cavazza, C.; Nicolet, Y.; Volbeda, A. *Nature* **2009**, *460*, 814−822.
(15) (a) Paudyal, M. P.; Adebesin, A. M.; Burt, S. R.; Ess, D. H.; Ma, Z.; Kürti, L.; Falck, J. R. *Science* **2016**, *353*, 1144−1147. (b) Liao, K.; Negretti, S.; Musaev, D. G.; Bacsa, J.; Davies, H. M. L. *Nature* **2016**, *533*, 230−234. (c) Liao, K.; Pickel, T. C.; Boyarskikh, V.; Bacsa, J.; Musaev, D. G.; Davies, H. M. L. *Nature* **2017**, *551*, 609−613.
(16) (a) Chen, Y.; Zhou, Y.; Qu, J. *Organometallics* **2008**, *27*, 666−671. (b) Tao, Y.; Wang, B.; Wang, B.; Qu, L.; Qu, J. *Org. Lett.* **2010**, *12*, 2726−2729. (c) Tao, Y.; Wang, B.; Zhao, J.; Song, Y.; Qu, L.; Qu, J. *J. Org. Chem.* **2012**, *77*, 2942−2946.
(17) (a) Chen, Y.; Zhou, Y.; Chen, P.; Tao, Y.; Li, Y.; Qu, J. *J. Am. Chem. Soc.* **2008**, *130*, 15250−15251. (b) Li, Y.; Li, Y.; Wang, B.; Luo, Y.; Yang, D.; Tong, P.; Zhao, J.; Luo, L.; Zhou, Y.; Chen, S.; Cheng, F.; Qu, J. *Nat. Chem.* **2013**, *5*, 320−326.
(18) (a) Yang, D.; Li, Y.; Wang, B.; Zhao, X.; Su, L.; Chen, S.; Tong, P.; Luo, Y.; Qu, J. *Inorg. Chem.* **2015**, *54*, 10243−10249. (b) Sun, P.; Yang, D.; Li, Y.; Zhang, Y.; Su, L.; Wang, B.; Qu, J. *Organometallics* **2016**, *35*, 751−757. (c) Zhang, Y.; Tong, P.; Yang, D.; Li, J.; Wang, B.; Qu, J. *Chem. Commun.* **2017**, *53*, 9854−9857.
(19) Rybinskaya, M. I.; Kudinov, A. R.; Kaganovich, V. S. *J. Organomet. Chem.* **1983**, *246*, 279−285.
(20) Meng, X.; Wang, F.; Jin, G.-X. *Coord. Chem. Rev.* **2010**, *254*, 1260−1272.
(21) (a) Connelly, N. G.; Johnson, G. A. *J. Chem. Soc., Dalton Trans.* **1978**, 1375−1379. (b) Tang, Z.; Nomura, Y.; Ishii, Y.; Mizobe, Y.; Hidai, M. *Organometallics* **1997**, *16*, 151−154. (c) Tang, Z.; Nomura, Y.; Ishii, Y.; Mizobe, Y.; Hidai, M. *Inorg. Chim. Acta* **1998**, *267*, 73−79. (d) Iwasa, T.; Shimada, H.; Takami, A.; Matsuzaka, H.; Ishii, Y.; Hidai, M. *Inorg. Chem.* **1999**, *38*, 2851−2859. (e) Ishii, Y.; Ogio, K.; Nishio, M.; Retbøll, M.; Kuwata, S.; Matsuzaka, H.; Hidai, M. *J. Organomet. Chem.* **2000**, *599*, 221−231.
(22) Takeuchi, R.; Tanouchi, N. *J. Chem. Soc., Chem. Commun.* **1993**, 1319−1320.
(23) Chen, Y.; Liu, L.; Peng, Y.; Chen, P.; Luo, Y.; Qu, J. *J. Am. Chem. Soc.* **2011**, *133*, 1147−1149.
(24) Tong, P.; Xie, W.; Yang, D.; Wang, B.; Ji, X.; Li, J.; Qu, J. *Dalton Trans.* **2016**, *45*, 18559−18565.
(25) Yang, D.; Li, Y.; Su, L.; Wang, B.; Qu, J. *Eur. J. Inorg. Chem.* **2015**, *2015*, 2965−2973.
(26) (a) McBee, J. L.; Escalada, J.; Tilley, T. D. *J. Am. Chem. Soc.* **2009**, *131*, 12703−12713. (b) Kumar, A.; Beattie, N. A.; Pike, S. D.; Macgregor, S. A.; Weller, A. S. *Angew. Chem., Int. Ed.* **2016**, *55*, 6651−6656.
(27) (a) Matsuzaka, H.; Takagi, Y.; Ishii, Y.; Nishio, M.; Hidai, M. *Organometallics* **1995**, *14*, 2153−2155. (b) Qu, J.; Masui, D.; Ishii, Y.; Hidai, M. *Chem. Lett.* **1998**, *27*, 1003−1004.

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