ORGANOMETALLICS

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Piano-Stool Iron Complexes as Precatalysts for *gem*-Specific Dimerization of Terminal Alkynes

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Cite This: https://dx.doi.org/10.1021/acs.organomet.0c00271 Read Online

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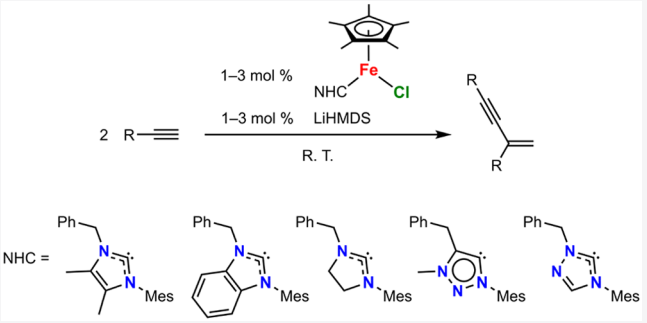
ABSTRACT: A series of piano-stool Fe−NHC complexes have been prepared and characterized. The NHC ligands used herein possess a benzyl and a mesityl wingtip groups and have different electronic structures within the NHC rings. The catalytic activities of these Fe complexes have been examined for the homodimerization of terminal alkynes.



INTRODUCTION

The catalytic dimerization of terminal alkynes is an effective synthetic route for conjugated enynes, owing to its unity atom economy and the availability of various alkyne precursors.[1−5] The main challenge is to control the regio- and stereoselectivity. The homodimerization of a terminal alkyne may yield up to three isomeric enyne products,[1−3] whereas the cross-dimerization of two different terminal alkynes may result in an even more complicated mixture of products.[1−3] Moreover, the formations of cumulenes, higher oligomers, and polymers may further complicate the reaction outcome.[1−3] A large number of catalysts, mostly precious-metal catalysts and f-block elements, have been extensively investigated.[1−3,6−22] Meanwhile, there have been increasing research endeavors toward the development of sustainable and environmentally benign alternatives to noble-metal catalysts for alkyne dimerization.[23−40] Such an effort is evidenced by the rapid development of iron-based catalysts. For example, a few iron-hydride complexes of P,N,P-pincer ligands have proven effective toward the *Z*-selective dimerization of arylacetylenes at room temperature without any additive.[34−36] The iron complex of a cyclic (alkyl)aminocarbene ligand has been reported as an *E*-selective catalyst toward the dimerization of arylacetylenes in the presence of a large excess of KO^{t}Bu at high temperatures.[37] The cation-dependent *E*/*Z* selectivity has been demonstrated in the dimerization of arylacetylenes catalyzed by the iron(II) complex of an N,N,N-tridentate ligand.[38]

N-heterocyclic carbenes (NHCs) are widely used ligands in coordination chemistry and homogeneous catalysis due to their strong σ-donating and weak π-accepting nature along with their easily accessible and tunable structures.[41−56] Our group has been interested in the chemistry of iron−NHC complexes toward organic transformations, especially when ligand-based reactivity is involved.[39,40,57−61] We have developed a piano-stool iron catalyst featuring Cp* and picolyl−NHC ligands toward the geminal specific dimerization of terminal alkynes (**I** in Chart 1).[39] Both aryl and aliphatic alkynes are compatible, and a broad range of functional groups can be tolerated, including NH and OH groups. Experimental and computational studies show that the bulky mesityl group on the NHC ligand is crucial for both the alkyne C−H activation and geminal specificity and that the pyridine group of the ligand retards the catalytic activity by coordinating to the metal center to generate stable off-cycle 18e species. These results have led to rational catalyst designs, replacing the picolyl wingtip group of the NHC ligand with noncoordinating substituents of various sizes. Among the series of complexes examined, [FeClCp*(IMesBn)] (where IMesBn is the NHC with mesityl and benzyl wingtip groups) shows the highest catalytic performance (**II** in Chart 1).[40] With the optimal wingtip groups determined, we set out to compare the catalytic activity of piano-stool iron complexes of NHCs bearing the optimal wingtip groups and various electronic properties. Herein we report the syntheses, characterizations, and catalytic activities of a new series of [FeClCp*(NHC)] complexes **1**−**5**, where the NHC ligands are 4,5-dimethylimidazolylidene (**L1**), benzimidazolylidene (**L2**), 4,5-dihydro-imidazolylidene (**L3**),

Received: April 21, 2020

https://dx.doi.org/10.1021/acs.organomet.0c00271
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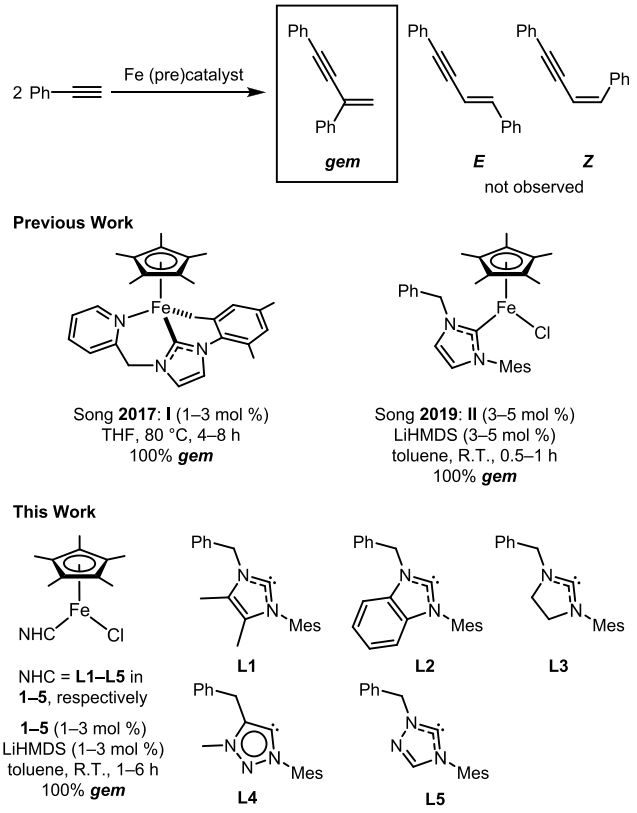
Chart 1. Piano-Stool Fe-NHC Precatalysts toward the Dimerization of Terminal Alkynes

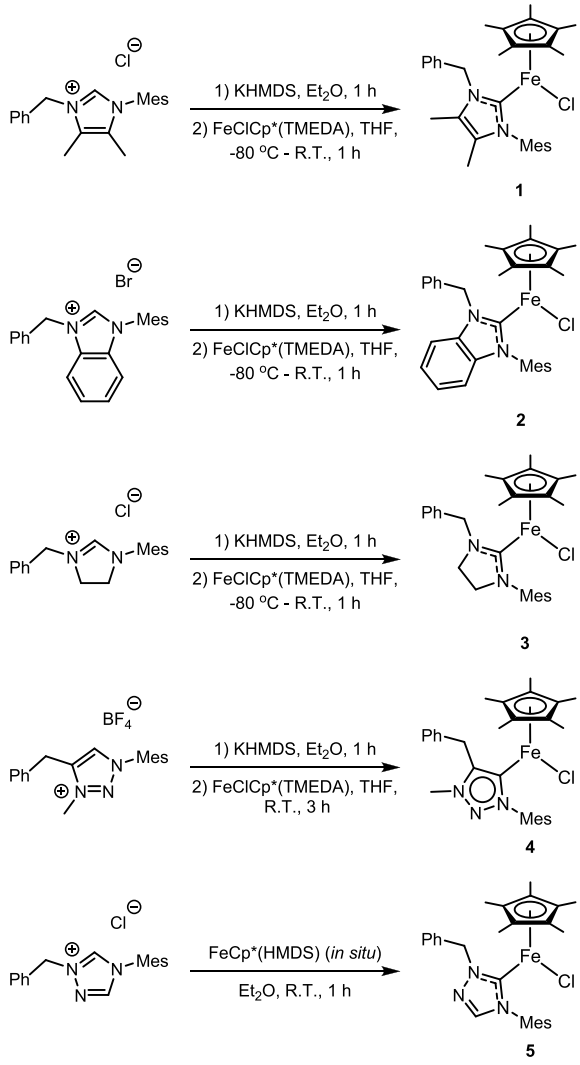


1,2,3-triazolylidene (**L4**), and 1,2,4-triazolylidene (**L5**), respectively (Chart 1).

RESULTS AND DISCUSSION

Syntheses and Characterizations of Precatalysts. Complexes **1**−**4** were synthesized from the reaction of [FeClCp*(TMEDA)][62] with the *in situ* generated carbene ligands **L1**−**L4**, respectively, and isolated in 70−83% yields (Scheme 1). Complex **5** was prepared from the reaction of [H**L5**]Cl with the *in situ* generated [FeCp*(HMDS)][63] (HMDS = hexamethyldisilazide). The ^{1}H NMR spectra of **1**−**5** in C_6D_6 at room temperature show broadened and paramagnetically shifted resonances spanning the range of −95 to +146 ppm. One of the methyl groups in **2**, **4**, and **5** could not be observed in the ^{1}H NMR spectra, presumably due to the close interaction with the iron center (i.e., one of the *o*-methyl groups of the mesityl group). The solution magnetic moments of **1**−**5** at room temperature (measured by the Evans method)[64] were determined to be 3.4−3.7 μ_B, consistent with intermediate-spin Fe(II) centers (S = 1).[40,65] The solid-state structures of **1**−**5** feature the two-legged piano-stool geometry (Figure 1). To the best of our knowledge, complex **5** represents the first crystallographically characterized 1,2,4-triazolylidene complex of iron. The Fe−$C_{carbene}$ bond lengths in **1** (1.981(5) and 1.982(5) Å) (Table 1) are comparable to that found in **II** (1.980(4) Å).[40] The Fe−$C_{carbene}$ bond length in **5** (1.962(2) Å) is statistically similar to those in **1** and **II**. The Fe−$C_{carbene}$ bond length in **3** (1.942(2) Å) is shorter than those in **1** and **II**, while the Fe−$C_{carbene}$ bond length in **4** (2.033(7) Å) is longer. The Fe−Cp*$_{cent}$ distances in complexes **1**−**5** are within the range of 1.784(1)−1.896(4) Å, similar to those of the related piano-stool complexes with intermediate-spin ferrous centers.[40,65] The quality of the crystallographic data for **2** (1.954(8) and 1.923(9) Å) makes it difficult to make a meaningful comparison. The Fe−Cp*$_{cent}$ distance and Fe−Cl bond length in **4** are also longer than those in **1**−**3** and **5**, respectively. Consequently, **4** is much more unstable in comparison to **1**−**3** and **5**. For example, **1**−**3** and **5** slowly decompose into [$FeCl_2(NHC)_2$] and $FeCp^*_2$ in both solution and the solid state at room temperature but can be stored at −35 °C for months without significant decomposition, similar to complex **II**; in contrast, **4** slowly decomposes even at −35 °C in both solution and the solid state.

Scheme 1. Syntheses of Complexes 1−5



Catalytic Dimerization of Phenylacetylene. On the basis of the established catalytic conditions used for the piano-stool iron−NHC complex **II** (Chart 1), the iron complexes **1**−**5** were evaluated toward the catalytic dimerization of phenylacetylene using a 3 mol % loading of the [**Fe**] precatalyst and LiHMDS in toluene at room temperature. Complex **1** featuring the 4,5-dimethylimidazolidene ligand gives an 81% conversion of phenylacetylene to the geminal dimer within 3 h (Table 2, entry 1). Complex **2** with the benzimidazolylidene ligand gives a 97% conversion in 1 h and full conversion within 3 h (Table 2, entry 2). Complex **3** with the 4,5-dihydroimidazolidene ligand gives an 89% conversion in 1 h (i.e., slightly less active than complex **2**) and full

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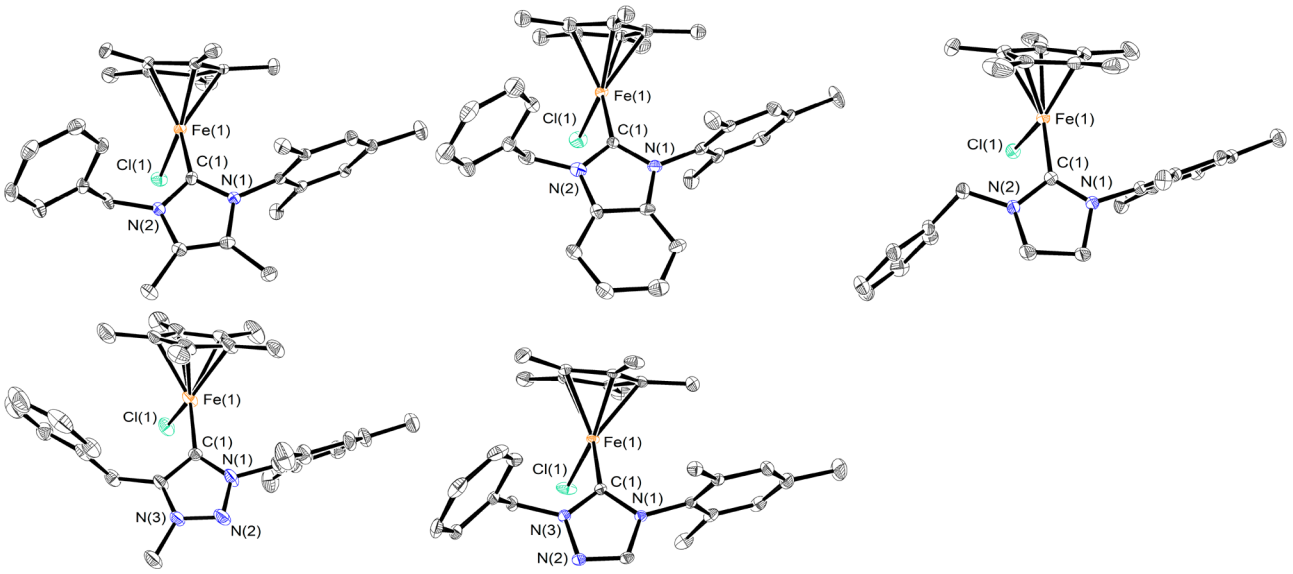

Figure 1. X-ray structures of **1** (top left), **2** (top middle), **3** (top right), **4** (bottom left), and **5** (bottom right). The thermal ellipsoids are shown at 30% probability. Hydrogen atoms are omitted, and only one component of the disordered portions is shown for clarity.

Table 1. Bond Lengths (Å) and Angles (deg) for 1−5

	1[a]	2[a]	3	4	5
Fe−$C_{carbene}$	1.981(5)	1.954(8)	1.942(2)	2.033(7)	1.962(2)
	1.982(5)	1.923(9)			
Fe−Cl	2.252(2)	2.249(3), 2.21(3)[b]	2.2518(7)	2.290(2)	2.234(1)
	2.250(2)	2.256(3), 2.21(2)[b]			
$C_{carbene}$−Fe−Cl	92.1(1)	90.9(2)	94.17(5)	99.2(2)	91.19(7)
	92.1(2)	91.2(3)			
Fe−Cp^*_{cent}	1.803(3)	1.843(4), 1.819(4)[b]	1.788(1)	1.896(4)	1.784(1)
	1.832(7), 1.787(7)[b]	1.785(4)			

[a]Two crystallographically independent molecules are found in the asymmetric unit. [b]Disordered component.

conversion within 3 h (Table 2, entry 3). Complex **4** possessing a 1,2,3-triazolylidene ligand displays reactivity (Table 2, entry 5) similar to that of complex **2**. Complex **5**, possessing a 1,2,4-triazolylidene ligand, shows poor reactivity, giving only 30% conversion in 3 h (Table 2, entry 4); the NMR yield of the enyne product is even lower, which is not yet fully understood. We also examined the robustness of catalysts **1**−**4** by lowering the catalyst loadings. With a 1 mol % loading of [**Fe**] precatalyst and LiHMDS, only **2** gives full conversion in 6 h (Table 2, entries 6−9). No other product was observed in the ^{1}H NMR spectra in all cases. In comparison, the previously reported complex **II** (Chart 1)[40] gives full conversion at a 3 mol % catalyst loading within 0.5 h at room temperature and poor conversions at a 1 mol % catalyst loading due to catalyst decomposition.

Catalytic Dimerization of Terminal Alkynes. Having identified complex **2** as the most active and robust precatalyst among **1**−**5**, next we explored the substrate scope using **2**. Phenylacetylene and *p*-Me-, *p*-F-, *p*-NMe_2-, and *m*-NH_2-substituted phenylacetylenes can be fully converted into the corresponding geminal enyne products within 3 h at room temperature (Table 3, entries 1−5). The dimerization of *p*-NH_2-substituted phenylacetylene is slightly slower and lower yielding (Table 3, entry 6). Ferrocenylacetylene can also be fully converted into the corresponding geminal enyne product in 3 h with a good yield under the standard conditions (Table 3, entry 7). The dimerization of 1-hexyne retains the high yield and geminal specificity (Table 3, entry 8), although the reaction is slightly slower than the dimerization of phenylacetylene. The functionalized aliphatic alkynes *N*-methyl-*N*-propargylbenzylamine and 5-chloro-1-pentyne can also be fully converted in 3 h under the standard conditions (Table 3, entries 9 and 10). With *N*,*N*-dimethylpropargylamine and 3,3-diethoxypropyne substrates, the reactions could only give moderate conversions and low yields (Table 3, entries 11 and 12). The unprotected propargyl alcohol shows no conversion (Table 3, entry 13).

CONCLUSION

A series of piano-stool [FeClCp*(NHC)] complexes **1**−**5** were prepared and characterized. The NHC ligands **L1**−**L5** have the same wingtip groups (mesityl and benzyl) but differ from one another electronically within the five-membered NHC rings. The thermal stabilities of **1**−**3** and **5** are similar to that of **II**, whereas **4** is the least stable: i.e., it decomposes even at −35 °C in both the solid state and in solution. The catalytic activities of **1**−**5** toward the homodimerization of terminal alkynes have been examined in the presence of an equimolar amount of LiHMDS. With a 3 mol % catalyst loading at room temperature, complexes **1**−**5** can give the corresponding *gem*-1,3-enynes exclusively with poor to excellent yields. Among the five new complexes reported herein, complex **2** with a benzimidazolylidene ligand shows the highest catalytic activity and robustness under ambient conditions at low catalyst

https://dx.doi.org/10.1021/acs.organomet.0c00271
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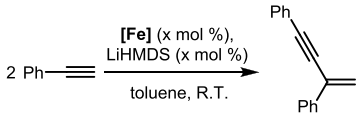
Table 2. Catalytic Activities of Complexes 1−5 toward the *gem*-Specific Dimerization of Phenylacetylene[a]



entry	[Fe]	x (mol %)	t (h)	conversn (%)	yield (%)
1	**1**	3	1	37	22
			3	81	64
2	**2**	3	1	97	96
			3	>99	98
3	**3**	3	1	89	86
			3	>99	98
4	**4**	3	1	>99	90
			3	>99	98
5	**5**	3	1	20	6
			3	30	8
6	**1**	1	6	46	36
7	**2**	1	6	>99	98
8	**3**	1	6	67	28
9	**4**	1	6	49	30

[a]General conditions: phenylacetylene (0.2 mmol), mesitylene (28 μL, 0.2 mmol, internal standard), precatalyst solution in toluene (0.5 mL, 1.2×10^{-2} M, 6 μmol, 3 mol %), LiHMDS solution in toluene (0.5 mL, 1.2×10^{-2} M, 6 μmol, 3 mol %), room temperature. The conversions (of phenylacetylene) and yields (of the geminal product) are based on the ^{1}H NMR integrations using mesitylene as the internal standard.

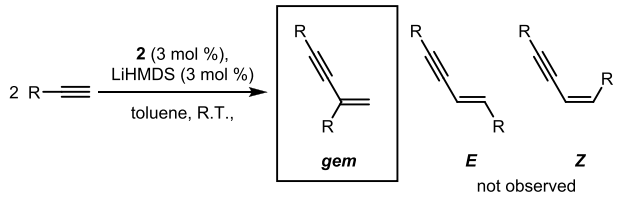
loadings. In addition, complex **2** is compatible with both alkylacetylenes and arylacetylenes bearing various functional groups, maintaining its *gem* specificity. Such an overall catalytic performance places complex **2** among the best *gem*-selective catalysts to date.[3,9,11,13,23,67−70]

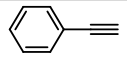
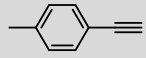
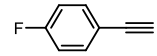
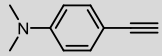
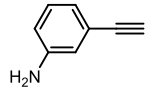
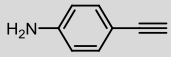
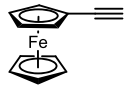
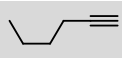
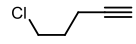
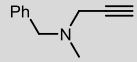
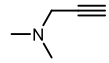
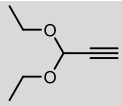
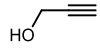
Among all the NHC ligands in the series of Fe complexes compared herein, **L2** is the least electron donating one. Such an electronic property of **L2** may contribute to the best thermal stability of the corresponding complex **2** because the relatively weak trans influence of **L2** makes the Cp* in complex **2** less labile in comparison to those in the other complexes. With such a ligand effect in mind, the use of a weaker donor, such as simple tertiary phosphines, in lieu of NHCs might result in more robust catalysts. However, monodentate ligands with weaker donors (including simple phosphines) are usually quite labile when they are bound to open-shell iron centers, which would likely cause more instability in the complexes. To improve the stability of the two-legged piano-stool iron (pre)catalysts, tethering the NHC and Cp* ligands together is likely an effective strategy, taking advantage of the chelate effect. Such an effort is underway in our laboratory.

EXPERIMENTAL SECTION

All reactions were carried out in a dinitrogen-filled glovebox or using the standard Schlenk techniques under dinitrogen. Glassware was dried in a 180 °C oven overnight. Diethyl ether, hexanes, pentane, and toluene solvents were dried by refluxing and distilling over sodium under dinitrogen. THF solvent was dried by refluxing and distilling over sodium benzophenone ketyl under dinitrogen. C_6D_6, and $CDCl_3$ were degassed through three consecutive freeze−pump−thaw cycles. All solvents were stored over 3 Å molecular sieves prior to use. Unless otherwise noted, all NMR spectra were recorded on an Agilent DD2 600 MHz spectrometer at 25 °C. Chemical shifts are referenced to the

Table 3. Substrate Scope[a]



Entry	Substrate	t (h)	Conv. (%)	Yield (%)
1		3	>99	98
2		3	>99	90
3		3	>99	88
4		3	>99	90
5		3	>99	80
6		3 6	92 >99	62 76
7		3	>99	90
8		3 6	87 >99	82 98
9		3	>99	92
10		3	>99	82
11		3	51	30
12		3	46	26
13		3	0	0

[a]General conditions: phenylacetylene (0.2 mmol), mesitylene (28 μL, 0.2 mmol, internal standard), toluene solution of **2** (0.5 mL, 1.2×10^{-2} M, 6 μmol, 3 mol %), LiHMDS solution in toluene (0.5 mL, 1.2×10^{-2} M, 6 μmol, 3 mol %), room temperature. The conversions (of the alkyne starting materials) and yields (of the geminal products) are based on the ^{1}H NMR integrations using mesitylene as the internal standard.

solvent signals. Solution magnetic moments were measured at 25 °C using the method originally described by Evans with stock and experimental solutions containing a known amount of a cyclohexane standard.[64] Elemental analyses were carried out at the ANALEST at the University of Toronto. Due to the poor thermal stability of complexes **1**−**5**, we were unable to obtain satisfactory elemental analysis results. The best elemental analysis results obtained so far are provided below. Unless otherwise noted, all chemicals were purchased from commercial sources and used as received.

Syntheses of 1−3. To a solid mixture of the ligand precursor (0.5 mmol) and KHMDS (99.7 mg, 0.5 mmol) was added 5 mL of diethyl ether. The reaction mixture was stirred for 1 h and then filtered through Celite. The filtrate was cooled to −80 °C and then slowly added into a cold (−80 °C) stirred suspension of FeClCp*-

https://dx.doi.org/10.1021/acs.organomet.0c00271
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(TMEDA)[62] (171.4 mg, 0.5 mmol) in 2 mL of THF. The resulting mixture was warmed to room temperature slowly with stirring over 1 h. All volatiles were removed under vacuum. The residue was dissolved in diethyl ether (5 mL) and filtered through Celite. The filtrate was concentrated under reduced pressure to ∼2 mL and cooled to −35 °C to yield a crystalline solid of product. The supernatant was decanted off, and the crystals were washed with cold diethyl ether (1 mL) and pentane (3 × 1 mL) and dried under vacuum. X-ray-quality crystals were obtained by cooling a concentrated diethyl ether solution at −35 °C. The preparation protocols of precursors of **L1**, **L2**, **L4**, and **L5** are detailed in the Supporting Information, while the precursor of **L3** was prepared using a literature procedure.[66]

Complex ***1***. By the general procedure using [H**L1**]Cl (170.5 mg, 0.5 mmol), **1** was obtained as a yellow crystalline solid (202.3 mg, 76%). ^{1}H NMR (600 MHz, C_6D_6): δ 114.90 (15H), 46.01 (3H), 27.94 (3H), 22.71 (3H), −1.81 (1H), −2.74 (2H), −8.28 (3H), −12.56 (2H), −17.58 (2H), −26.67 (2H). One of the methyl groups (3H) was not observed in the range of +200 to −200 ppm. μ_{eff} (Evans): 3.5 μ_B. Anal. Calcd for $C_{31}H_{39}N_2FeCl$: C, 70.13; H, 7.40; N, 5.28. Found: C, 69.49; H, 6.90; N, 5.31.

Complex ***2***. By the general procedure using [H**L2**]Br (203.7 mg, 0.5 mmol), **2** was obtained as red-orange crystals (229.6 mg, 83%). ^{1}H NMR (600 MHz, C_6D_6): δ 34.06 (3H), 33.17 (15H), 23.18 (1H), 15.50 (d, J = 6.8 Hz, 1H), 14.52 (1H), 14.19 (d, J = 6.8 Hz, 1H), 3.91 (1H), 1.21 (d, J = 6.9 Hz, 2H), 0.38 (t, J = 6.8 Hz, 1H), −4.76 (s, 1H, 3H), −7.30 (1H), −8.64 (2H), −10.46 (1H), −21.00 (3H), −88.35 (1H). μ_{eff} (Evans): 3.7 μ_B. Anal. Calcd for $C_{33}H_{37}N_2FeCl$: C, 71.68; H, 6.74; N, 5.07. Found: C, 71.16; H, 6.98; N, 4.95.

Complex ***3***. By the general procedure using [H**L3**]Cl (157.5 mg, 0.5 mmol), **3** was obtained as yellow crystals (182.0 mg, 72%). ^{1}H NMR (600 MHz, C_6D_6): δ 41.30 (3H), 34.90 (15H), 24.72 (1H), 18.03 (1H), 9.03 (1H), 7.02 (2H), 5.29 (2H), 4.07 (1H), −4.88 (3H), −6.30 (1H), −7.84 (1H), −10.10 (1H), −21.02 (3H), −44.89 (1H), −95.15 (1H). μ_{eff} (Evans): 3.4 μ_B. Anal. Calcd for $C_{29}H_{37}N_2FeCl$: C, 68.98; H, 7.39; N, 5.55. Found: C, 68.91; H, 7.23; N, 5.10.

Synthesis of 4. To a solid mixture of [H**L4**][BF_4] (189.6 mg, 0.5 mmol) and KHMDS (99.7 mg, 0.5 mmol) was added 5 mL of diethyl ether. The reaction mixture was stirred for 1 h and then filtered through Celite. The filtrate was added to a suspension of FeClCp*(TMEDA) (171.4 mg, 0.50 mmol) in 2 mL of THF. The resulting mixture was stirred for 3 h at room temperature. All volatiles were removed under vacuum. The residue was dissolved in diethyl ether (5 mL) and filtered through Celite. The filtrate was concentrated under reduced pressure to ∼2 mL and cooled to −35 °C to yield an orange crystalline solid of **4**. The supernatant was decanted off, and the crystals were washed with cold diethyl ether (1 mL) and pentane (3 × 1 mL) and dried under vacuum (180.3 mg, 70%). X-ray-quality crystals were obtained by cooling a concentrated diethyl ether solution at −35 °C. ^{1}H NMR (600 MHz, C_6D_6): δ 146.36 (15H), 10.18 (3H), 2.08 (1H), 1.97 (2H), −4.27 (2H), −5.47 (2H), −8.33 (3H), −12.67 (2H). One of the methyl groups (3H) was not observed in the range of +200 to −200 ppm. μ_{eff} (Evans): 3.4 μ_B. Anal. Calcd for $C_{29}H_{36}N_3FeCl$: C, 67.25; H, 7.01; N, 8.11. Found: C, 66.23; H, 7.08; N, 7.98.

Synthesis of 5. To a stirred suspension of FeClCp*(TMEDA) (171.4 mg, 0.50 mmol) in 2 mL of THF was added KHMDS (99.7 mg, 0.5 mmol) in 2 mL of THF. The mixture was stirred for 1 h and slowly added to a suspension of [H**L5**]Cl in 2 mL of THF. The mixture was stirred for 1 h at room temperature. All volatiles were removed under vacuum. The residue was dissolved in diethyl ether (5 mL) and filtered through Celite. The filtrate was concentrated under reduced pressure to ∼2 mL and cooled to −35 °C to yield a yellow solid of **5**. The supernatant was decanted off, and the crystals were washed with cold diethyl ether (1 mL) and pentane (3 × 1 mL) and dried under vacuum (164.7 mg, 65%). X-ray-quality crystals were obtained by cooling a concentrated diethyl ether solution at −35 °C. ^{1}H NMR (600 MHz, C_6D_6): δ 41.42 (15H), 37.86 (1H), 33.89 (2H), 3.83 (d, J = 7.6 Hz, 2H), 3.46 (t, J = 7.1 Hz, 1H), −0.92 (2H), −5.12 (3H), −8.68 (2H), −19.89 (3H). One of the methyl groups (3H) was not observed in the range of +200 to −200 ppm. μ_{eff} (Evans): 3.7 μ_B. Anal. Calcd for $C_{28}H_{34}N_3FeCl$: C, 66.74; H, 6.80; N, 8.34. Found: C, 65.16; H, 6.26; N, 8.49.

General Procedure for the Catalytic Dimerization of Alkynes. A 2-dram vial was charged with LiHMDS solution in toluene (0.5 mL, 1.2×10^{-2} M, 6 μmol, 3 mol %), mesitylene (28 μL, 0.2 mmol, internal standard), alkyne substrate (0.2 mmol), and the Fe-catalyst solution in toluene (0.5 mL, 1.2×10^{-2} M, 6 μmol, 3 mol %) in that sequence. The reaction mixture was stirred for the indicated time. An NMR sample was prepared using 0.1 mL of the reaction mixture in 0.4 mL of $CDCl_3$ and filtered. The conversion and yield of the reaction were calculated on the basis of the integrations of the ^{1}H NMR signals of the starting material and product, respectively, relative to that of the internal standard (600 MHz, 16 scans, 25 s relaxation delay, 90° pulse).

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.organomet.0c00271.

Experimental procedures, selected crystallographic data tables, and NMR spectra (PDF)

Accession Codes

CCDC 1998142−1998147 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, UK; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

We thank the Natural Sciences and Engineering Research Council (NSERC) of Canada for funding. Q.L. thanks the Ontario government for an Ontario Graduate Scholarship. K.R. thanks the NSERC of Canada for an Undergraduate Summer Research Award. JLJS thanks the Mexican National Council for

Science and Technology (CONACyt) for a graduate fellowship. We also acknowledge the Canadian Foundation for Innovation Project #19119 and the Ontario Research Fund for funding the CSICOMP NMR laboratory at the University of Toronto, enabling the purchase of several new spectrometers.

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