5920 *Organometallics* **1998,** *17,* 5920−5923

Synthesis of $\mathrm{Fe{-}C{\equiv}C{-}M}$ Complexes through Condensation of $\mathrm{Fe{-}C{\equiv}C{-}H}$ with $\mathrm{M{-}H}$ or $\mathrm{M{-}NMe_2}$

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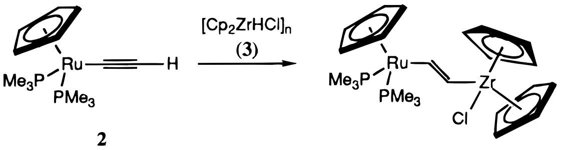
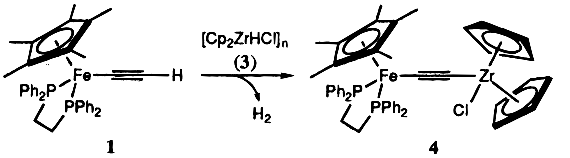
Summary: The iron acetylide Cp(dppe)FeC≡CH (Cp* = η^5-C_5Me_5, dppe = $Ph_2PCH_2CH_2PPh_2$) reacted with $[Cp_2Zr(H)Cl]_n$ (Schwartz's reagent, Cp = η^5-C_5H_5) to produce the C≡C-bridged complex Cp*(dppe)Fe-C≡CZrClCp$_2$ in nearly quantitative yield instead of the expected CH=CH-bridged hydrozirconation product. The bulky ligand set around iron is postulated to prevent the addition of hydride at the carbon α to the metal center. Reaction of Cp*(dppe)FeC≡CH with (dimethylamino)-trimethyltin gave the condensed product Cp*(dppe)Fe-C≡CSnMe$_3$ in nearly quantitative yield.*

We have reported experimental and theoretical investigations of a series of half-sandwich butadienediyl-bridged diiron complexes.[1] In search of an efficient way to prepare $[Cp^*(dppe)Fe]_2(\mu\text{-}CH{=}CHCH{=}CH)$[2] (Cp* = η^5-C_5Me_5, dppe = $Ph_2PCH_2CH_2PPh_2$) and longer bridge analogues, we attempted the hydrometalation of Cp*(dppe)FeC≡CH (**1**)[3] with the intention of coupling the Cp*(dppe)FeCH=CHML$_n$ products. Organic terminal acetylenes readily undergo hydrozirconization,[4] hydroalumination,[5] and hydroboration[6] reactions. In addition, $Cp(PMe_3)_2RuC{\equiv}CH$ (**2**, Cp = η^5-C_5H_5) was reported by Bullock and co-workers to react with $[Cp_2Zr(H)Cl]_n$ (**3**) to give $Cp(PMe_3)_2RuCH{=}CHZrClCp_2$ (eq 1).[7] However, we uniformly failed to obtain the desired addition products such as $Cp^*(dppe)FeCH{=}CHZrClCp_2$. Instead we herein report these reactions as efficient ways to prepare C_2-bridged heterodinuclear complexes.



(1)

Treatment of the yellow benzene-d_6 solution of iron acetylide **1** with Schwartz's reagent, $[Cp_2Zr(H)Cl]_n$ (**3**), at room temperature gave rise to a dark red solution in about 10 min. The reaction progress was monitored by ^{1}H NMR, and the starting material **1** was consumed in 6 h. NMR showed an almost quantitative conversion of **1** to a new compound showing a single peak (1.52 ppm) in the Cp* region and no olefinic signals. A preparative-scale reaction afforded the new compound in 98% yield. The IR spectrum displayed a strong asymmetric carbon−carbon triple-bond absorption at 1843 cm^{-1}. When mixed with wet benzene, the dark red benzene solution turned yellow-orange instantly, and ^{1}H NMR showed that iron acetylide **1** was formed. On the basis of the spectroscopic data and the hydrolysis reaction, we assigned the structure of the new compound as $Cp^*(dppe)FeC{\equiv}CZrClCp_2$ (**4**, eq 2), one of relatively few complexes with a C_2-bridge connecting an electron-deficient early transition metal to an electron-rich late transition metal. Similar condensed products were apparently also produced upon mixing **1** with diisobutylaluminum hydride (DIBAL-H)[8] or catecholborane (HBcat),[9] although these reactions were not as clean. Hydrolysis of both products also led smoothly to **1**.



(2)

These hydrogen-elimination transformations are apparently unprecedented in the reactions of terminal alkynes with Schwartz's reagent or catecholborane. In the hydroalumination of terminal alkynes, 1-alkynylaluminum compounds are observed only as minor products (<10%).[10] A related reaction is the higher temper-

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[1] Etzenhouser, B. A.; Cavanaugh, M. D.; Spurgeon, H. N.; Sponsler, M. B. *J. Am Chem. Soc.* **1994**, *116*, 2221−2222. Etzenhouser, B. A.; Chen, Q.; Sponsler, M. B. *Organometallics* **1994**, *13*, 4176−4178. Sponsler, M. B. *Organometallics* **1995**, *14*, 1921−1927.

[2] This complex has been prepared by a different route (Gu, X. Ph.D. Dissertation, Syracuse University, 1997) and was desired for comparison to work by Lapinte and co-workers (see ref 3).

[3] Le Narvor, N.; Toupet, L.; Lapinte, C. *J. Am. Chem. Soc.* **1995**, *117*, 7129−7138.

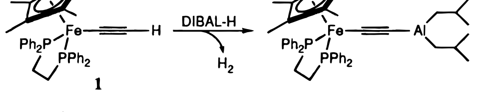
[4] Temple, J. S.; Schwartz, J. *J. Am. Chem. Soc.* **1980**, *102*, 7381−7382.

[5] Eisch, J. J. In *Comprehensive Organic Synthesis*; Trost, B. M., Fleming, I., Eds.; Pergamon: Oxford, 1992; Vol. 8, p 733.

[6] Brown, H. C.; Gupta, S. K. *J. Am. Chem. Soc.* **1972**, *94*, 4370−4371. Suseela, Y.; Periasamy, M. *J. Organomet. Chem.* **1993**, *450*, 47−52.

[7] Lemke, F. R.; Szalda, D. J.; Bullock, R. M. *J. Am. Chem. Soc.* **1991**, *113*, 8466−8477.

[8]



To a solution of **1** (20 mg, 0.033 mmol) in benzene (2 mL) was added 50 μL of 1 M diisobutylaluminum hydride (0.050 mmol) in hexane. Bubbles evolved upon mixing. The solution was stirred at room temperature overnight, then evaporated under vacuum, and the residue was washed with two portions of pentane (1 mL each). The product (20 mg) was obtained as a brown solid in 64% yield (corrected for purity, estimated at 80% by NMR integration). ^{1}H NMR (C_6D_6): δ 7.76 (t, J = 8 Hz, 4H, Ph), 7.40 (t, J = 8 Hz, 4H, Ph), 6.90−7.25 (m, 12H, Ph), 2.24 (nonet, J = 7 Hz, 2H, *i*Bu), 2.82 (m, 2H, PCH$_2$), 2.15 (m, 2H, PCH$_2$), 1.39 (s, 15H, Cp*), 0.74 (d, J = 7 Hz, 12H, *i*Bu), 0.24 (d, J = 7 Hz, 4H, *i*Bu). ^{31}P NMR: δ 100.7. IR (KBr, cm^{-1}): 3040w, 2939m, 1961m, 1614s, 1463m, 1429s, 1252s. MS(EI): 613 ($M^+ -$ Al(*i*Bu)$_2$), 640 ($M^+ -$ 2*i*Bu), 654 ($M^+ -$ *i*Bu − *i*Pr), 668 ($M^+ -$ 2*i*Pr).

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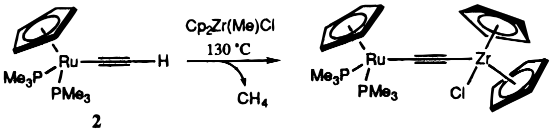
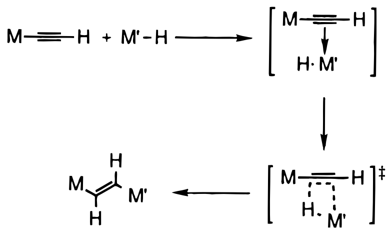
ature alumination of terminal alkynes with trialkylaluminum reagents, in which alkanes are extruded.[11] Similar reactions are also known for alkyl zirconium complexes, such as the methane elimination shown in eq 3.[7]



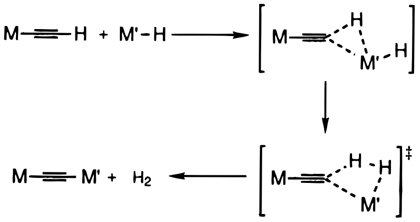
(3)

The observed reactions may be viewed formally as acid−base reactions, similar to the formation of metal acetylides from the reaction of terminal alkynes and NaH or KH. However, unusually facile deprotonation does not appear to be a reasonable explanation for the observed reactivity. Compound **1** is not expected to be a particularly acidic alkyne, given the electron-rich character of the iron center. The most striking difference between **1** and **2**, whose reactions with **3** show completely different chemoselectivity (eqs 1 and 2), is the degree of steric congestion near the metal center. We therefore propose that the facile condensation of **1** with various hydrides is attributable primarily to steric congestion around the iron center, which effectively blocks delivery of the hydride to the α-carbon of the iron acetylide. Lapinte's extensive studies on complexes of Cp*(dppe)Fe offer strong evidence for large steric effects, such as the remarkable persistence observed for various 16-,[12] 17-,[13] and 19-electron[14] complexes. Also indicative of unusual steric effects is the result that Cp*(dppe)FeC≡CMe[15] was found to be unreactive to **3** even at 70 °C, while other internal alkynes such as $Cp(PMe_3)_2RuC{\equiv}CMe$,[7] $(\eta^5\text{-}C_5H_4Me)_2ClZrC{\equiv}CMe$,[16] and *t*-BuC≡CMe[17] are reported to undergo smooth hydrozirconation at ambient temperature.[18]

Scheme 1



Scheme 2



A standard hydrometallation mechanism,[19] illustrated in Scheme 1, requires that the hydride reagent come significantly closer to the iron center than is necessary for the observed condensation, illustrated in Scheme 2. If the α-carbon is sterically inaccessible, the electrophilic hydride instead may react with the less electronically favorable but more accessible C−H bond. The three-center, two-electron intermediate and four-center transition state in Scheme 2 are offered as a possible mechanism.

Molecular mechanics calculations offer further support for steric hinderance as a primary cause of the differing reactivity. Comparison of space-filling representations of **1** and **2** (Figure 1) reveals a marked difference in the accessibility of the α-carbon. In addition, the steric repulsion energies that accompany complexation of either the C≡C bond or the C−H bond to the Zr of **3** (i.e., the intermediates of Schemes 1 and 2) were evaluated. For **1**, complexation at the C≡C bond was found to cost 15 kcal/mol more than complexation at the C−H bond. However, for **2** the difference was only 1 kcal/mol.

Bullock and co-workers also reported a reaction between **2** and (dimethylamino)trimethyltin (Me_2NSnMe_3), cleanly producing $Cp(PMe_3)_2RuC{\equiv}CSnMe_3$.[7] We found that this transformation also works well for **1**. The reaction between **1** and Me_2NSnMe_3 (eq 4) was finished in ca. 30 min at room temperature. The red-brown crystalline complex Cp*(dppe)FeC≡CSnMe₃ (**5**) was obtained in almost quantitative yield (98%). A strong IR absorption at 1949 cm^{-1} resulting from the asymmetric C≡C stretch in complex **5** was comparable to 1919 cm^{-1} for $Cp(PMe_3)_2RuC{\equiv}CSnMe_3$. Hydrolysis

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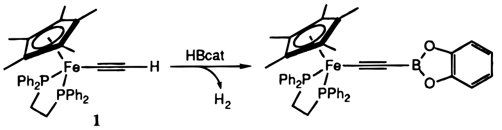
(9)



1

To a solution of **1** (20 mg, 0.033 mmol) in benzene (2 mL) was added 50 μL of 1 M catecholborane (0.050 mmol) in THF at ambient temperature. The solution was stirred for 30 min, then evaporated under vacuum, and the residue was washed with two portions of pentane (1 mL each). The product (18 mg) was obtained as a brown solid in 53% yield (corrected for purity, estimated at 70% by NMR integration). ^{1}H NMR (C_6D_6): δ 8.10 (t, *J* = 8 Hz, 4H, Ph), 6.80−7.60 (m, 20H, Ph), 2.60 (m, 2H, PCH_2), 2.25 (m, 2H, PCH_2), 1.45 (s, 15H, Cp*). ^{31}P NMR: δ 101.5. IR (KBr, cm^{-1}): 3058m, 2957s, 2923s, 2863m, 1994s, 1615s, 1480s, 1227s, 1049s, 732m. MS(EI): 732 (M^+).

[10] See, for example: Negishi, E.; Takahashi, T.; Baba, S. *Org. Synth.* **1988**, *66*, 60−66. When an amine complex of a dialkylaluminum hydride is used, however, the amine-complexed 1-alkynyl aluminum compound becomes the major product: Binger, P. *Angew. Chem., Int. Ed. Engl.* **1963**, *2*, 686.

[11] Mole, T.; Surtees, J. R. *Aust. J. Chem.* **1964**, *17*, 1229−1235.

[12] Hamon, P.; Toupet, L.; Rabaâ, H.; Saillard, J.-Y.; Hamon, J.-R.; Lapinte, C. *Organometallics* **1996**, *15*, 10−12.

[13] Roger, C.; Hamon, P.; Toupet, L.; Rabaâ, H.; Saillard, J.-Y.; Hamon, J.-R.; Lapinte, C. *Organometallics* **1991**, *10*, 1045−1054. See also ref 14.

[14] Hamon, P.; Hamon, J.-R.; Lapinte, C. *J. Chem. Soc., Chem. Commun.* **1992**, 1602−1603.

[15] Cp*(dppe)FeC≡CMe was made by methylation (methyl triflate, 78% yield) of iron acetylide **1** and subsequent deprotonation (KO*t*-Bu, 98% yield), following the general procedure of Selegue: Adams, R. D.; Davison, A.; Selegue, J. P. *J. Am. Chem. Soc.* **1979**, *101*, 7232−7238. ^{1}H NMR (C_6D_6): δ 8.06 (t, *J* = 8 Hz, 4H), 7.40−7.10 (m, 16H), 2.65 (m, 2H), 2.14 (s, 3H), 1.84 (m, 2H), 1.55 (s, 15H). ^{13}C NMR (0.05 M Cr(acac)₃): δ 141−129 (m, Ph), 138.8 (t, $^2J_{PC}$ = 43 Hz, FeC, tentative assignment due to overlap with Ph), 110.3 (s, ≡*C*Me), 87.3 (s, Cp*), 31.3 (t, $^1J_{PC}$ = 21 Hz, PCH_2), 10.8 (s, Cp*), 8.9 (s, ≡C*Me*). ^{31}P NMR: δ 101.3.

[16] Erker, G.; Frömberg, W.; Angermund, K.; Schlund, R.; Krüger, C. *J. Chem. Soc., Chem. Commun.* **1986**, 372−374.

[17] Hart, D. W.; Blackburn, T. F.; Schwartz, J. *J. Am. Chem. Soc.* **1975**, *97*, 679−680.

[18] We cannot rule out the possibility that electronic effects might also play a role in determining the mode of reactivity, but note that **1** and **2** are reasonably comparable in terms of electron-richness of the metal centers. In addition, the fact that clean hydrozirconation is observed for both $Cp(PMe_3)_2RuC{\equiv}CMe$ and $(\eta^5\text{-}C_5H_4Me)_2ClZrC{\equiv}CMe$ indicates that this reaction is not very sensitive to electron density.

[19] Yamamoto, A. *Organotransition Metal Chemistry*; Wiley: New York, **1986**; pp 260−262.

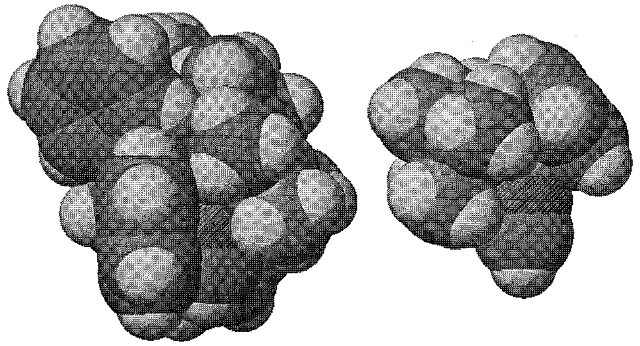
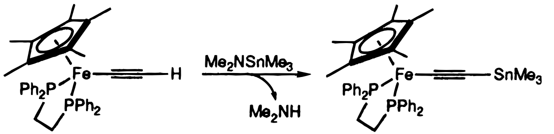


Figure 1. Space-filling representations of molecular mechanics-optimized structures of **1** (left) and **2** (right). The α-carbons of the acetylide ligands are shaded. In each case, the perspective that allowed the least obstructed view of the α-carbon was selected.

of **5** in wet benzene cleanly formed **1**. Solid samples of **5** were stable in the open air, while solution samples decomposed slowly (2 days) to **1**.



1 **5** (4)

Complexes with C_2 ligands σ-bonded to two metal atoms are not common.[20] Such complexes have been prepared by several methods, including substitution reactions of metal halide compounds with deprotonated metal acetylide complexes (transmetalation),[21] deprotonation of cationic μ-η^1-η^2-acetylide complexes,[22] alkyne metathesis of metal acetylide complexes,[18] and condensation reactions like the ones in eqs 3 and 4. Formation of C_2-bridged complexes such as **2** from the reaction of terminal metal acetylide complexes with electrophilic hydrides adds another method to the synthetic list, although the reaction will probably be limited to highly hindered acetylides. Since the functional groups $ZrClCp_2$, $Al(iBu)_2$, Bcat, and $SnMe_3$ are often employed in coupling reactions,[23] the new complexes might be useful as building blocks for the preparation of substituted iron acetylides or conjugated dinuclear complexes.

In summary, acetylide **1** reacts anomalously with Schwartz's reagent **3** and other electrophilic hydrides to form C_2-bridged heterodinuclear complexes. The unusual and complete chemoselectivity is most reasonably attributed to the steric protection of the α-carbon of the iron acetylide ligand provided by the Cp* and dppe ligands.

Experimental Section

All reactions were performed under nitrogen using standard Schlenk techniques or with an inert atmosphere drybox. Solvents were distilled under nitrogen from a drying agent (THF: sodium/benzophenone; benzene, pentane: calcium hydride). All reagents were obtained from common commercial sources unless otherwise stated and were used as received. Compound **1** was prepared from $FeCl_2$ in four steps according to the literature method.[3] Benzene-d_6 was vacuum-transferred from calcium hydride, degassed by the freeze−pump−thaw method, and stored over 4 Å molecular sieves. All NMR spectra were recorded in benzene-d_6 on a 300 MHz (Bruker-300 or General Electric QE-300) spectrometer. All chemical shifts are referenced to TMS by using known shifts of residual proton (7.15 ppm) or carbon (128.39 ppm) signals in benzene-d_6 or to external 85% aqueous phosphoric acid (^{31}P NMR). Chromium(III) acetylacetonate was used as a relaxation agent for ^{13}C NMR. Electron impact mass spectra were obtained from the MS facilities at University of Illinois, Urbana−Champaign. IR spectra were recorded in KBr disks on an Perkin Elmer 1660 series IR spectrometer. Elemental analyses were performed by E & R Microanalysis Co., Corona, NY.

Cp*(dppe)FeC≡CZrClCp$_2$ (4). To a stirred solution of **1** (40 mg, 0.066 mmol) in benzene (2 mL) was added solid $[Cp_2ZrHCl]_n$ (**3**, 26 mg, 0.1 mmol) at ambient temperature. Over 10 min the solution color turned from yellow-brown to dark red. After 6 h, excess **3** was removed by filtration through a Celite pad, and solvent was evaporated under vacuum. Washing the product with pentane (2 × 1 mL) and drying under vacuum afforded 56 mg of **4** in 98% yield. ^1H NMR: δ 7.98 (t, $J = 8$ Hz, 4H, Ph), 7.38 (t, $J = 8$ Hz, 4H, Ph), 7.21 (m, 4H, Ph), 7.05 (m, 8H, Ph), 6.03 (s, 10H, Cp), 2.79 (m, 2H, PCH_2), 2.01 (m, 2H, PCH_2), 1.52 (s, 15H, Cp*). ^{13}C NMR (0.06 M Cr(acac)$_3$): δ 207.1 (s, ZrC), 192.2 (t, $^2J_{PC} = 40$ Hz, FeC), 139.8−128.9 (m, Ph), 111.9 (s, Cp), 89.3 (s, Cp*), 31.4 (t, $^2J_{PC} = 21$ Hz, PCH_2), 10.8 (s, Cp*). ^{31}P NMR: δ 102.2. IR (KBr, cm^{-1}): 3052w, 2901m, 1843vs, 1471m, 1428m, 1084m, 1013m, 719s, 741m, 691s, 670m, 527s, 484m. MS(EI): 868 (M^+). Isotope pattern (% calcd, % found): 866(6.0, 6.4), 867(4.5, 4.3), 868-(100, 100), 869(76.7, 76.4), 870(91.7, 91.6), 871(49.1, 49.0), 872-(57.8, 57.8), 873(27.3, 27.0), 874(22.7, 22.7), 875(10.1, 10.1), 876(4.3, 4.4), 877(1.4, 1.2). Anal. Calcd for $C_{48}H_{49}ClFeP_2Zr$: C, 66.24; H, 5.67. Found: C, 66.18; H, 5.89.

Complex **4** was also cleanly formed when the reaction was performed under the conditions employed by Bullock and coworkers for the reaction between **2** and **3** (use of THF as solvent, warming slowly from −78 °C to room temperature).

Cp*(dppe)FeC≡CSnMe$_3$ (5). To a solution of **1** (50 mg, 0.082 mmol) in benzene (2 mL) was added 21 μL of neat (dimethylamino)trimethyltin (0.122 mmol). The solution was stirred for 30 min and then evaporated under vacuum. The residue was washed with two portions of pentane (1 mL each). Complex **5** (63 mg, 0.080 mmol) was obtained in 98% yield. ^1H NMR: δ 8.13 (t, $J = 8$ Hz, 4H, Ph), 7.25 (m, 12H, Ph), 7.03 (m, 4H, Ph), 2.86 (m, 2H, PCH_2), 1.85 (m, 2H, PCH_2), 1.52 (s, 15H, Cp*), 0.22 (s, with $^{117,119}Sn$ satellites, $^2J_{SnH} = 25, 29$ Hz, 9H, $SnMe_3$). ^{13}C NMR (0.05 M Cr(acac)$_3$): δ 165.2 (t, $^2J_{PC} = 36$ Hz, FeC), 140.4−129.2 (m, Ph), 117.8 (s, SnC), 87.8 (s, Cp*), 31.4 (t, $^1J_{PC} = 23$ Hz, PCH_2), 10.7 (s, Cp*), −7.0 (s, $SnMe_3$). ^{31}P NMR: δ 101.5. IR (KBr, cm^{-1}): 3054w, 2918s, 2847w, 1949vs, 1554m, 1425s, 1179w, 1082m, 740m, 688s, 662m, 527s, 489m. Anal. Calcd for $C_{41}H_{48}FeP_2Sn$: C, 63.36; H, 6.22. Found: C, 63.65; H, 6.35.

Computational Methods. Molecular mechanics calculations were performed by using CAChe, version 4.02 (Oxford Molecular, Ltd.). The augmented MM2 parameter set was used. The C≡C and C−H complexes from Schemes 1 and 2, respectively (either **1**−**3** or **2**−**3**), were geometry optimized in orientations consistent with the subsequent reactions. In each case, several starting structures were employed in order to find the best relative orientation of the two components. Steric repulsion energies due to complexation were calculated by subtraction of the total energies of optimized components from the total energy of the optimized complex (eq 5). To prevent inclusion of binding energy, the components were taken as **1**

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[20] Koutsantonis, G. A.; Selegue, J. P. *J. Am. Chem. Soc.* **1991**, *113*, 2316−2317, and references therein.

[21] Cross, R. J.; Davidson, M. F. *J. Chem. Soc., Dalton Trans.* **1986**, 411−414. Ogawa, H.; Onitsuka, K.; Joh, T.; Takahashi, S.; Yamamoto, Y.; Yamazaki, H. *Organometallics* **1988**, *7*, 2257−2260. Weng, W.; Bartik, T.; Brady, M.; Bartik, B.; Ramsden, J. A.; Arif, A. M.; Gladysz, J. A. *J. Am. Chem. Soc.* **1995**, *117*, 11922−11931.

[22] Akita, M.; Terada, M.; Oyama, S.; Mor-oda, Y. *Organometallics* **1990**, *9*, 816−825.

[23] Heck, R. F. *Palladium Reagents in Organic Synthesis*; Academic Press: New York, 1985; Chapter 6.

(or **2**) and a model complex without steric repulsions (with the cyclopentadienyl and phosphine ligands on **1** or **2** replaced by a single chloride ligand). The total energy of the sterically modified **1** or **2** appeared as a positive term in the steric repulsion energy in order to compensate for the appearance of this molecule in the first component.

$$\text{Steric repulsion energy } (\mathbf{1}\cdots\mathbf{3}) = E(\mathbf{1}\cdots\mathbf{3}) - E(\mathbf{1}) - E(\text{ClFeC}{\equiv}\text{CH}\cdots\mathbf{3}) + E(\text{ClFeC}{\equiv}\text{CH}) \quad (5)$$

The steric repulsion energies calculated in this way do include significant and unwanted van der Waals attractions between components (unwanted because such attractions are roughly compensated by solvation in the solution-phase reaction). By reporting only the difference of two steric repulsion energies (for C≡C and C−H coordination), the effect of these attractions is minimized, assuming them to be similar in the two coordination modes.

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