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Acetylide-Bridged Organometallic Oligomers via the Photochemical Metathesis of Methyl−Iron(II) Complexes

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Abstract: The acetylido methyl iron(II) complexes, *cis/trans*-[Fe(dmpe)$_2$(C$\equiv$CR)(CH$_3$)] (**1**) and *trans*-[Fe(depe)$_2$(C$\equiv$CR)(CH$_3$)] (**2**) (dmpe = 1,2-dimethylphoshinoethane; depe = 1,2-diethylphosphinoethane), were synthesized by transmetalation from the corresponding alkyl halide complexes. Acetylido methyl iron(II) complexes were also formed by transmetalation from the chloride complexes, *trans*-[Fe(dmpe)$_2$(C$\equiv$CR)(Cl)] or *trans*-[Fe(depe)$_2$(C$\equiv$CR)(Cl)]. The structure of *trans*-[Fe(dmpe)$_2$(C$\equiv$CC$_6$H$_5$)(CH$_3$)] (**1a**) was determined by single-crystal X-ray diffraction. The methyl acetylido iron complexes, [Fe(dmpe)$_2$(C$\equiv$CR)(CH$_3$)] (**1**), are thermally stable in the presence of acetylenes; however, under UV irradiation, methane is lost with the formation of a metal bisacetylide. Photochemical metathesis of *cis*- or *trans*-[Fe(dmpe)$_2$(CH$_3$)(C$\equiv$CR)] (R = C$_6$H$_5$ (**1a**), 4-C$_6$H$_4$OCH$_3$ (**1b**)) with terminal acetylenes was used to selectively synthesize unsymmetrically substituted iron(II) bisacetylide complexes of the type *trans*-[Fe(dmpe)$_2$(C$\equiv$CR)(C$\equiv$CR′)] [R = Ph, R′ = Ph (**6a**), 4-CH$_3$OC$_6$H$_4$ (**6b**), ^{t}Bu (**6c**), Si(CH$_3$)$_3$ (**6d**), (CH$_2$)$_4$C$\equiv$CH (**6e**); R = 4-CH$_3$OC$_6$H$_4$, R′ = 4-CH$_3$OC$_6$H$_4$, (**6g**), ^{t}Bu (**6h**), (CH$_2$)$_4$C$\equiv$CH (**6i**), adamantyl (**6j**)]. The structure of the unsymmetrical iron(II) bisacetylide complex *trans*-[Fe(dmpe)$_2$(C$\equiv$CC$_6$H$_5$)(C$\equiv$CC$_6$H$_4$OCH$_3$)] (**6b**) was determined by single-crystal X-ray diffraction. The photochemical metathesis of the bis-acetylene, 1,7-octadiyne, with *trans*-[Fe(dmpe)$_2$(CH$_3$)(C$\equiv$CPh)] (**1a**), was utilized to synthesize the bridged binuclear species *trans,trans*-[(C$_6$H$_5$C$\equiv$C)Fe(dmpe)$_2$(μ-C$\equiv$C(CH$_2$)$_4$C$\equiv$C)Fe(dmpe)$_2$(C$\equiv$CC$_6$H$_5$)] (**11**). The trinuclear species *trans*,*trans*,*trans*-[(C$_6$H$_5$C$\equiv$C)Fe(dmpe)$_2$(μ-C$\equiv$C(CH$_2$)$_4$C$\equiv$C)Fe(dmpe)$_2$(μ-C$\equiv$C(CH$_2$)$_4$C$\equiv$C)Fe(dmpe)$_2$(C$\equiv$CC$_6$H$_5$)] (**12**) was synthesized by the photochemical reaction of Fe(dmpe)$_2$(C$\equiv$CPh)(C$\equiv$C(CH$_2$)$_4$C$\equiv$CH) (**6e**) with Fe(dmpe)$_2$(CH$_3$)$_2$. Extended irradiation of the bisacetylide complexes with phenylacetylene resulted in insertion of the terminal alkyne into one of the metal acetylide bonds to give acetylide butenyne complexes. The structure of the acetylide butenyne complex, *trans*-[Fe(dmpe)$_2$(C$\equiv$CC$_6$H$_4$OCH$_3$)(η^1-C(C$_6$H$_5$)=CH(C$\equiv$CC$_6$H$_4$OCH$_3$))] (**9a**) was determined by single-crystal X-ray diffraction.

Introduction

Oligomeric and polymeric rigid-rod metal acetylides have become an important target class of organometallic compounds. The metal acetylide fragment possesses a π bonding system that facilitates electronic communication between the conjugated organic ligand and the metal and the resulting bridged polynuclear organometallic compounds have applications in the fields of nonlinear optics,[1,2] liquid crystals,[3−6] and semiconducting materials.[6−9] There has been considerable recent interest in linking metals using conjugated polyacetylenic bridging units, to provide a mechanism for electronic communication between the metal centers.

The synthesis of acetylenic polymeric materials containing transition metals has mainly centered on the polycondensation reactions of bifunctional organic monomer units with bifunctional metal complexes. Typically, this approach has resulted in uncontrolled condensation often yielding high molecular weight polymeric material. The condensation reactions have generally relied either upon the coupling of acetylenic sites tethered to metal atoms[10] or on acetylenic substitution or coupling reactions at the metal centers.[11]

The demand for compounds with well-defined molecular weight requires careful stepwise syntheses, where each monomer unit is introduced in a controlled stepwise fashion to one terminus (or both termini) of a growing polymer. This in turn requires a suitable suite of synthetic methods for selectively forming the metal−acetylide bond.

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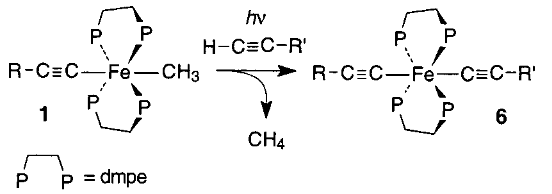
Scheme 1



The simple reaction of metal dihydride complexes, *cis*-[M(H)$_2$(dmpe)$_2$] (M = Fe, Ru) with mixtures of terminal alkynes has been explored as a route to unsymmetrical (and symmetrical) metal bisacetylide complexes.[12,13] The unsymmetrical reaction products can be purified from the product mixture by chromatography or fractional recrystallization; however, this approach is not atom efficient and selectivity for the mixed acetylenic substrates is generally poor. Furthermore, the synthetic method becomes impracticable when oligomeric or polymeric systems are required.[9]

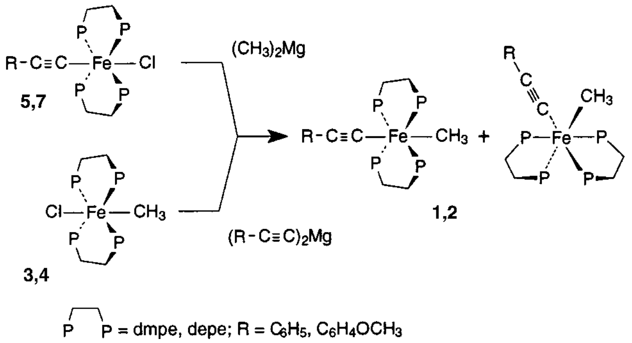
Unsymmetrically substituted ruthenium bisacetylide complexes have been synthesized by dehydrohalogenation of vinylidene ruthenium(II) complexes in the presence of a second terminal acetylene.[14] Unsymmetrical ruthenium bisacetylides have also been synthesized from acetylido ammonium ruthenium(II) complexes in the presence of a second terminal acetylene.[15]

In this paper we report the photochemical metathesis of acetylido alkyl iron(II) complexes in the presence of terminal acetylenes to form metal bisacetylides (Scheme 1). To our knowledge, the light-induced metathesis of metal alkyls to form metal acetylides has not previously been reported and represents a new approach to forming the metal−carbon bond. The photochemical metathesis reaction was exploited to selectively synthesize a number of unsymmetrically substituted iron(II) bisacetylide compounds.

Results and Discussion

Thermal metathesis reactions involving transition metal alkyl complexes have been reported previously and have involved substrates including boranes,[16] silanes and phosphines,[17] alcohols,[18,19] dihydrogen,[19,20] acids,[21,22] and terminal acetylenes.[20,21,23−28] There are various mechanisms for metal−alkyl metathesis reactions and there is evidence for reductive-elimination oxidative-addition or protonation-substitution or σ-bond metathesis mechanisms.[23,24,27,29,30] The metathesis reaction of rhodium(I) methyl complexes with alkynes has been reported[31] to form the corresponding rhodium acetylide complexes. A similar thermal metathesis reaction of uranium dialkyl complexes with acetylenes has also been reported[32] to give the corresponding uranylbisacetylide complexes.

Scheme 2



Acetylido Methyl Complexes of Iron. Acetylido methyl complexes [Fe(dmpe)$_2$(C$\equiv$CR)(CH$_3$)] (**1**) and [Fe(depe)$_2$(C$\equiv$CR)(CH$_3$)] (**2**) were synthesized by reaction of the corresponding chloro methyl complexes, [Fe(dmpe)$_2$(CH$_3$)(Cl)] (**3**) and [Fe(depe)$_2$(CH$_3$)(Cl)] (**4**), with magnesium bisacetylides. Alternatively, the acetylido methyl complexes could be synthesized by the reaction of chloro acetylido complexes [Fe(dmpe)$_2$(C$\equiv$CR)(Cl)] (**5**) or [Fe(depe)$_2$(C$\equiv$CR)(Cl)] (**6**) with dimethylmagnesium (Scheme 2). The rate of chloride substitution by the reaction of the methyl Grignard reagent with the acetylido chloro iron(II) complexes was slow (ca. 2 days) compared with the rate of chloride substitution by acetylido Grignard on the chloro methyl iron(II) complexes (ca. 10−45 min). The acetylido methyl complexes were obtained as stable, air-sensitive crystalline solids.

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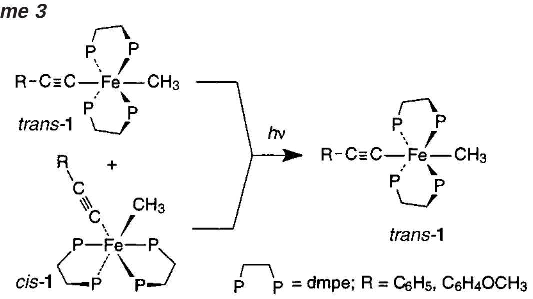
Scheme 3



When syntheses were performed at room temperature, the acetylido methyl complexes were obtained as mixtures of cis and trans isomers. The complex [Fe(dmpe)$_2$(C≡CPh)(CH$_3$)] (**1a**) could be obtained cleanly as the trans isomer if the synthesis was completed at low temperature (−78 °C). The cis and trans isomers of [Fe(dmpe)$_2$(C≡CPh)(CH$_3$)] do not interconvert readily at room temperature; however, at 100 °C, a toluene solution enriched in the trans isomer (trans:cis = 90:10) was obtained after 18 h. When a mixture of the cis and trans isomers was irradiated with UV light, the trans isomer formed exclusively within 10 min. These results suggest that the cis and trans isomers are kinetically relatively stable and that the isomerization of the cis isomer to the more stable trans isomer can be induced thermally or photochemically. The mechanism of isomerization probably involves the reversible loss of one end of a bidentate phosphine donor leading to an intermediate 5-coordinate species where there is less hindrance to structural reorganization (Scheme 3).

^{31}P{^{1}H} NMR of *trans*-[Fe(dmpe)$_2$(C≡CPh)(CH$_3$)] (**1a**) and *trans*-[Fe(depe)$_2$(C≡CPh)(CH$_3$)] (**2a**) shows singlets at δ 72.2 and 80.6 ppm, respectively. ^{31}P{^{1}H} NMR of *cis*-[Fe(dmpe)$_2$(C≡CPh)(CH$_3$)] (**1a**) exhibits four coupled 8-line multiplets at δ 55.3, 62.0, 71.0, and 75.0 ppm. The ^{1}H NMR of *trans*-[Fe(dmpe)$_2$(C≡CPh)(CH$_3$)] (**1a**) exhibits a distinct pentet for the iron bound CH$_3$ group at δ −1.79 ppm ($^3J_{\text{P-H}} = 7.3$ Hz) and the isomeric *cis*-[Fe(dmpe)$_2$(C≡CPh)(CH$_3$)] (**1a**) exhibits the methyl resonance as a multiplet (an apparent quartet) at δ −0.47 ppm. The corresponding methyl resonance for *trans*-[Fe(depe)$_2$(C≡CPh)(CH$_3$)] (**2a**) occurs at δ −1.60 ppm ($^3J_{\text{P-H}} = 6.6$ Hz). In ^{13}C NMR, the CH$_3$−Fe resonances of the trans isomers of **1** and **2** occur at approximately −20 ppm and exhibit a well-resolved ^{31}P coupling of 16−18 Hz. For the cis complexes, [Fe(dmpe)$_2$(C≡CPh)(CH$_3$)] (**1a**) and [Fe(dmpe)$_2$(C≡CC$_6$H$_4$OCH$_3$)(CH$_3$)] (**1b**), the CH$_3$−Fe resonances appear at δ −8.7 and −7.5 ppm, respectively.

Structural Characterization of *trans*-[Fe(dmpe)$_2$(C≡CC$_6$H$_5$)(CH$_3$)] (1a). The crystal structure of *trans*-[Fe(dmpe)$_2$(C≡CC$_6$H$_5$)(CH$_3$)] (**1a**) was determined by single-crystal X-ray diffraction from a suitable crystal grown by slow evaporation of toluene. An ORTEP[33] depiction of the structure of **1a** is provided in Figure 1, and selected bond lengths and angles are listed in Table 1.

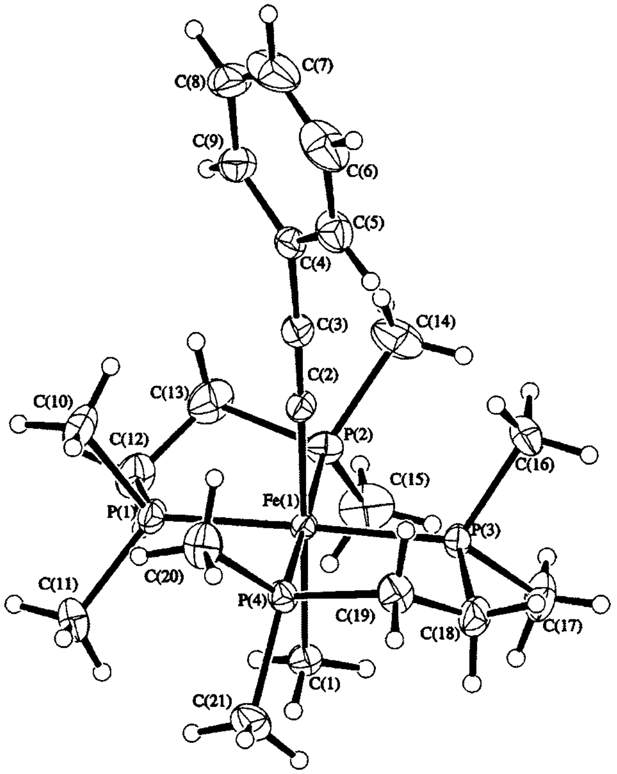


Figure 1. An ORTEP[33] depiction of *trans*-[Fe(dmpe)$_2$(C≡CC$_6$H$_5$)(CH$_3$)] (**1a**) with atom displacement ellipsoids shown at the 20% level.

Table 1. Selected Bond Lengths (Å) and Angles (deg) for *trans*-[Fe(dmpe)$_2$(C≡CC$_6$H$_5$)(CH$_3$)] (**1a**)

bond	length (Å)	bonds	angle (deg)
Fe(1)−C(1)	2.144(3)	C(1)−Fe(1)−C(2)	179.26(15)
Fe(1)−C(2)	1.923(3)	C(2)−Fe(1)−P(1)	90.65(10)
Fe(1)−P(1)	2.1965(9)	P(1)−Fe(1)−P(2)	86.47(4)
Fe(1)−P(3)	2.2083(9)	P(1)−Fe(1)−P(4)	93.61(4)
C(2)−C(3)	1.214(5)	P(1)−Fe(1)−P(3)	178.52(4)

Table 2. Comparison of Bond Lengths (Å) for *trans*-Acetylido Iron(II) Complexes

complex	M−P	M−C≡	C≡C	ref
trans-Fe(dmpe)$_2$-(C≡CPh)CH$_3$ (**1a**)	2.1965(9) 2.2035(10)	1.923(3)	1.214(5)	this work
trans-Fe(dmpe)$_2$-(C≡CPh)Cl (**5a**)	2.216(2) 2.216(2) 2.213(2) 2.217(2)	1.880(5)	1.216(8)	34
trans-Fe(dmpe)$_2$-(C≡CPh)$_2$ (**6a**)	2.191(3) 2.180(5)	1.925(6)	1.209(9)	35, 36

A comparison of the significant bond lengths in **1a** with other acetylido iron(II) complexes is given in Table 2. No significant changes in iron−phosphorus bond lengths were observed between **1a** and those in the related acetylido chloro iron(II) [Fe(dmpe)$_2$(C≡CPh)(Cl)] (**5a**)[34] and bisacetylido iron(II) [Fe(dmpe)$_2$(C≡CPh)$_2$] (**6a**)[35,36] complexes. The **1a** and **5a** triple bond lengths are the same (within error limits), suggesting that the chloride π interaction does not involve significant mixing with the acetylide π* orbitals. The relatively short metal−acetylide bond in **5a** presumably results from the trans influence of the chloride and reflects the weak σ donor capacity of the halide. The methyl ligand of **1a** acts only as a σ orbital donor to the iron center and therefore does not greatly influence the metal acetylide π-bond.

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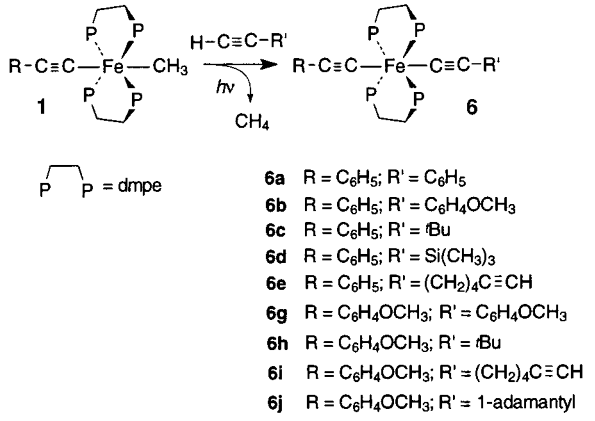
Scheme 4



6a R = C_6H_5; R' = C_6H_5
6b R = C_6H_5; R' = $C_6H_4OCH_3$
6c R = C_6H_5; R' = ^{t}Bu
6d R = C_6H_5; R' = $Si(CH_3)_3$
6e R = C_6H_5; R' = $(CH_2)_4C{\equiv}CH$
6g R = $C_6H_4OCH_3$; R' = $C_6H_4OCH_3$
6h R = $C_6H_4OCH_3$; R' = ^{t}Bu
6i R = $C_6H_4OCH_3$; R' = $(CH_2)_4C{\equiv}CH$
6j R = $C_6H_4OCH_3$; R' = 1-adamantyl

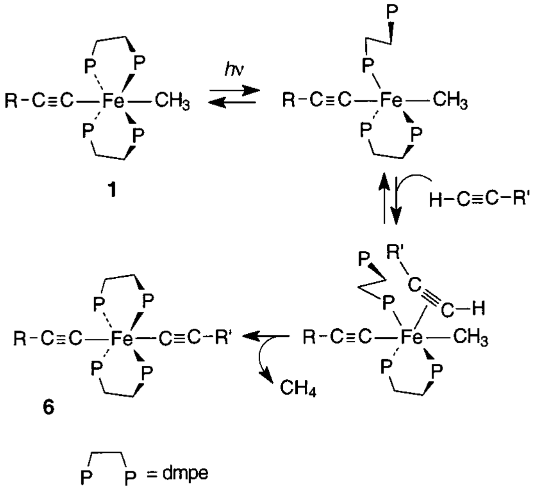
Metathesis Reactions of Acetylido Methyl Complexes. Heating a toluene solution of *trans*-[Fe(dmpe)$_2$(C$\equiv$CC$_6$H$_5$)(CH$_3$)] (**1a**) in the presence of an excess of a terminal acetylene produced no detectable reaction. However, UV irradiation of benzene or thf solutions of *trans*-[Fe(dmpe)$_2$(C$\equiv$CR)(CH$_3$)] (R = C$_6$H$_5$ (**1a**), 4-C$_6$H$_4$OCH$_3$ (**1b**)) in the presence of an excess of a terminal acetylene selectively afforded the bisacetylidoiron(II) complexes *trans*-[Fe(dmpe)$_2$(C$\equiv$CR)(C$\equiv$CR$'$)] [R = Ph, R$'$ = 4-C$_6$H$_4$OCH$_3$ (**6b**), ^{t}Bu (**6c**), Si(CH$_3$)$_3$ (**6d**), 7-octynyl (**6e**); R = 4-C$_6$H$_4$OCH$_3$, R$'$ = 4-C$_6$H$_4$OCH$_3$ (**6g**), ^{t}Bu (**6h**), 5-hexynyl (**6i**), adamantyl (**6j**)] (Scheme 4) with the elimination of methane.

The unsymmetrical iron(II) bisacetylides were isolated by removal of solvent and excess acetylene *in vacuo*. The complexes were soluble in most organic solvents and were purified by recrystallization from hexane or pentane at −78 °C. The unsymmetrical bisacetylidoiron(II) complexes, *trans*-[Fe(dmpe)$_2$(C$\equiv$CC$_6$H$_5$)(C$\equiv$CR$'$)] (R$'$ = ^{t}Bu (**6c**), Si(CH$_3$)$_3$ (**6d**), 5-hexynyl (**6e**)), were microanalytically pure as isolated. Desilylation of **6d** by treatment with potassium fluoride afforded *trans*-[Fe(dmpe)$_2$(C$\equiv$CC$_6$H$_5$)(C$\equiv$CH)] (**6f**).

During the irradiation of *cis*- and *trans*-[Fe(dmpe)$_2$(C$\equiv$CC$_6$H$_5$)(CH$_3$)] (**1a**) with terminal acetylenes, no intermediate complexes were detected by ^{31}P or ^{1}H NMR. Methane was detected in the reaction headspace by GC and this suggests a σ bond metathesis mechanism that is probably initiated by the photochemical loss of one end of the bidentate phosphine donor to open a free coordination site for the acetylene (Scheme 5).

The metathesis with aliphatic terminal acetylenes proceeded cleanly and relatively rapidly. Although the reactions proceed when stoichiometric amounts of the starting materials are used, in practice the reaction is significantly faster if the reacting acetylene is present in excess. With aromatic acetylenes, some photochemical decomposition of the acetylene occurred and this darkened the reaction solutions and prevented efficient irradiation as the reaction progressed. The photochemical reaction of [Fe(dmpe)$_2$(CH$_3$)(C$\equiv$CC$_6$H$_4$OCH$_3$)] (**1b**) with phenylacetylene resulted in the unsymmetrical bisacetylidoiron(II) complex *trans*-[Fe(dmpe)$_2$(C$\equiv$CC$_6$H$_5$)(C$\equiv$CC$_6$H$_4$OCH$_3$)] (**6b**) formed in sufficient quantities to be isolated before significant darkening of the reaction solution resulted. The complex was isolated and characterized structurally and spectroscopically.

Scheme 5



Scheme 6

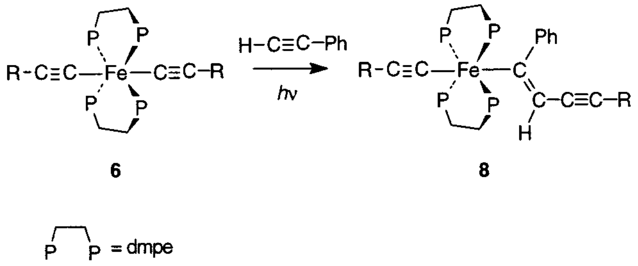


Table 3. Selected Bond Lengths (Å) and Angles (deg) for *trans*-[Fe(dmpe)$_2$(C$\equiv$CC$_6$H$_5$)(C$\equiv$CC$_6$H$_4$OCH$_3$)] (**6b**)

bond	length (Å)	bonds	angle (deg)
Fe(1)−P(1)	2.1924(16)	C(1)−Fe(1)−C(1)	180.00
Fe(1)−P(2)	2.2021(16)	P(1)−Fe(1)−P(1)	180.00
Fe(1)−C(1)	1.924(6)	P(1)−Fe(1)−P(2)	85.75(7)
C(1)−C(2)	1.198(7)	C(1)−Fe(1)−P(1)	92.32(16)
C(2)−C(3)	1.435(8)	Fe(1)−C(1)−C(2)	177.7(5)

A single crystal of *trans*-[Fe(dmpe)$_2$(C$\equiv$CC$_6$H$_5$)(C$\equiv$CC$_6$H$_4$OCH$_3$)] (**6b**) suitable for X-ray diffraction analysis was grown by slow evaporation from thf. An ORTEP depiction of the structure of **6b** is provided in Figure 2, and selected bond lengths and angles are listed in Table 3.

Comparison of the bond lengths with the corresponding symmetrical bisacetylidoiron(II) complexes *trans*-[Fe(dmpe)$_2$(C$\equiv$CC$_6$H$_5$)$_2$] (**6a**)[35] and *trans*-[Fe(dmpe)$_2$(C$\equiv$CC$_6$H$_4$OCH$_3$)$_2$] (**6g**)[37] with the unsymmetrical bisacetylidoiron(II) complex (**6b**) shows no major differences in the core bond lengths (Table 4).

Photochemical Reactions of Bisacetylide Complexes. Extended UV irradiation of the bisacetylide complexes in the presence of an excess of a terminal aromatic acetylene resulted in the insertion of the terminal alkyne into the metal acetylide bond to give a butenynyl complex of the type *trans*-[Fe(dmpe)$_2$(C$\equiv$CR)(C(Ph)$=$CH(C$\equiv$CR))] (**8**) (Scheme 6).

UV irradiation of the bisacetylide complexes with aromatic alkynes also resulted in exchange of acetylide ligands with the free alkyne. UV irradiation of the bisacetylide complex *trans*-[Fe(dmpe)$_2$(C$\equiv$CC$_6$H$_4$OCH$_3$)$_2$] (**6g**) with 20 equiv of phenylacetylene over 16 h resulted in a mixture of all three possible bisacetylide complexes, *trans*-[Fe(dmpe)$_2$(C$\equiv$CC$_6$H$_5$)(C$\equiv$CC$_6$H$_4$OCH$_3$)] (**6b**) (14%), *trans*-[Fe(dmpe)$_2$(C$\equiv$CPh)$_2$] (**6a**) (9%), and *trans*-[Fe(dmpe)$_2$(C$\equiv$CC$_6$H$_4$OCH$_3$)$_2$] (**6g**) (16%), and all four possible acetylide butenynyl complexes, *trans*-[Fe(dmpe)$_2$-

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(37) Pike, S. R. Ph.D. Thesis, 1997, The University of Sydney.

Table 4. Comparison of Bisacetylidoiron(II) Complex Bond Lengths (Å)

trans-bisacetylide complex	Fe–P	Fe–C≡	C≡C	≡C–C	ref
$[Fe(dmpe)_2(C\equiv CC_6H_5)(C\equiv CC_6H_4OCH_3)]$ (**6b**)	2.1924(16) 2.2021(16)	1.924(6)	1.198(7)	1.435(8)	this work
$[Fe(dmpe)_2(C\equiv CC_6H_5)_2]$ (**6a**)	2.191(3) 2.180(5)	1.925(6)	1.209(9)	1.438(9)	35
$[Fe(dmpe)_2(C\equiv CC_6H_4OCH_3)_2]$ (**6g**)	2.2055(9) 2.1999(9)	1.926(3)	1.207(4)	1.437(4)	37

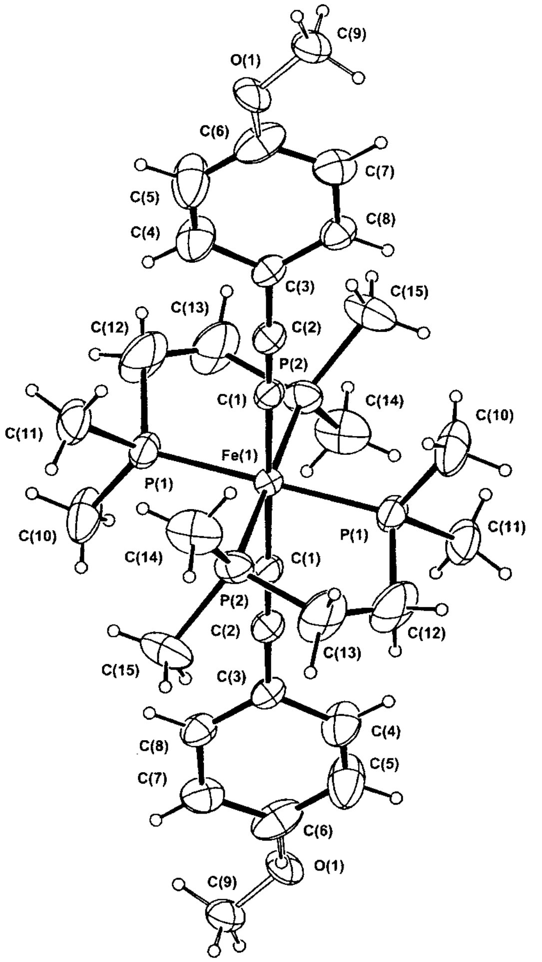

Figure 2. An ORTEP[33] depiction of *trans*-$[Fe(dmpe)_2(C\equiv CC_6H_5)(C\equiv CC_6H_4OCH_3)]$ (**6b**) with atom displacement ellipsoids shown at the 20% level. The molecule resides on a pseudo-crystallographic inversion center, and the crystal structure has axial ligand disorder about the inversion site, with the methoxy and C(6) hydrogen sites having refined occupancies of 0.5.

Scheme 7

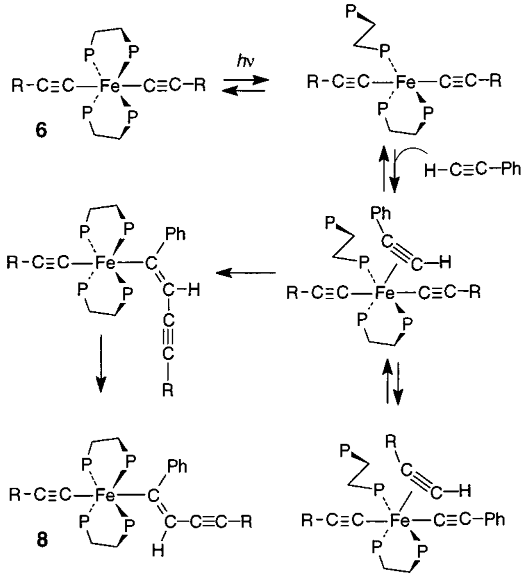

Table 5. Selected Bond Lengths (Å) and Angles (deg) for *trans*-$[Fe(dmpe)_2(C\equiv CC_6H_4OCH_3)(\eta^1\text{-}C(C_6H_5)=CH(C\equiv CC_6H_4OCH_3))]$ (**9a**)

bond	length (Å)	bond	angle (deg)
Fe(1)–C(18)	1.937(2)	C(18)–Fe(1)–C(4)	178.30(8)
Fe(1)–C(4)	2.067(2)	C(3)–C(4)–Fe(1)	126.00(16)
C(18)–C(19)	1.222(3)	C(19)–C(18)–Fe(1)	177.73(19)
Fe(1)–P(1)	2.2332(11)	C(2)–C(3)–C(4)	124.9(2)
C(1)–C(2)	1.203(3)	C(3)–C(4)–C(5)	110.08(18)

$(C\equiv CC_6H_4OCH_3)(\eta^1\text{-}C(C_6H_5)=CH(C\equiv CC_6H_4OCH_3))]$ (**9a**) (19%), *trans*-$[Fe(dmpe)_2(C\equiv CC_6H_5)(\eta^1\text{-}C(C_6H_5)=CH(C\equiv CC_6H_5))]$ (**9b**) (14%), *trans*-$[Fe(dmpe)_2(C\equiv CC_6H_4OCH_3)(\eta^1\text{-}C(C_6H_5)=CH(C\equiv CC_6H_5))]$ (**9c**) (8%), and *trans*-$[Fe(dmpe)_2(C\equiv CC_6H_5)(\eta^1\text{-}C(C_6H_5)=CH(C\equiv CC_6H_4OCH_3))]$ (**9d**) (8%). The complex *trans*-$[Fe(dmpe)_2(C\equiv CC_6H_4OCH_3)(\eta^1\text{-}C(C_6H_5)=CH(C\equiv CC_6H_4OCH_3))]$ (**9a**) was initially formed in the reaction mixture and isolated as an orange air-sensitive solid. Butenyne complexes are well-known as rearrangement products derived from iron bisacetylides.[38] An authentic sample of *trans*-$[Fe(dmpe)_2(C\equiv CC_6H_5)(\eta^1\text{-}C(C_6H_5)=CH(C\equiv CC_6H_5))]$ (**9b**) was synthesized independently by irradiation of phenylacetylene with *trans*-$[Fe(dmpe)_2(C\equiv CPh)_2]$ (**6a**). The insertion products **9c** and **9d** were characterized by ^{31}P NMR with singlet resonances at δ 65.9 and 65.8 ppm, respectively.

The photochemical insertion and exchange reactions can be rationalized by a reaction scheme analogous to Scheme 5 where photochemical loss of one end of the bidentate bisphosphine provides a free coordination site for binding a free acetylene prior to coupling or exchange (Scheme 7). The *Z/E* isomerization of the coordinated butenyne could be metal assisted; however, the photochemical isomerization of phenyl-substituted alkenes is well-known.

A single crystal of *trans*-$[Fe(dmpe)_2(C\equiv CC_6H_4OCH_3)(\eta^1\text{-}C(C_6H_5)=CH(C\equiv CC_6H_4OCH_3))]$ (**9a**) suitable for X-ray diffraction analysis was grown by slow evaporation from thf. An ORTEP[33] depiction of the **9a** crystal structure is provided in Figure 3, and selected bond lengths and angles are listed in Table 5.

The $^{31}P\{^1H\}$ NMR spectrum of *trans*-$[Fe(dmpe)_2(C\equiv CC_6H_4OCH_3)(\eta^1\text{-}C(C_6H_5)=CH(C\equiv CC_6H_4OCH_3))]$ (**9a**) exhibited a singlet resonance at δ 66.4 ppm, 2.7 ppm upfield of the corresponding bisacetylide complex (**6g**). The ^1H NMR spectrum of the complex exhibits a singlet resonance at 5.56 ppm due to the alkenyl proton and this shows no resolvable ^{31}P coupling. $^{13}C\{^1H\}$ NMR of the complex exhibited two pentets

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(38) Field, L. D.; George, A. V.; Purches, G. R.; Slip, I. H. M. *Organometallics* **1992**, *11,* 3019.

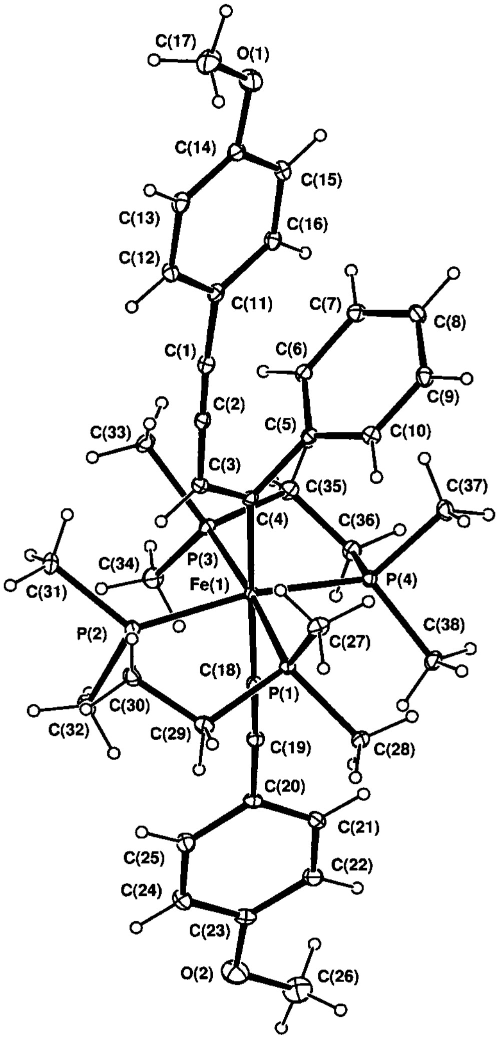
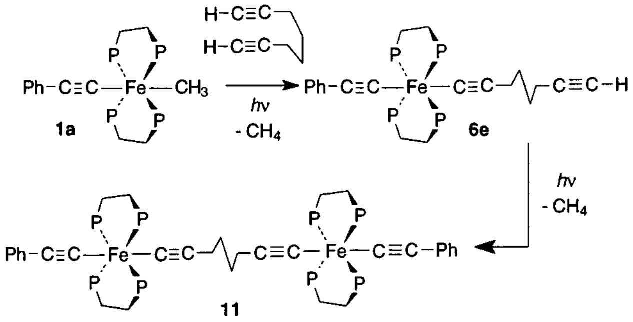


Figure 3. An ORTEP[33] depiction of *trans*-[Fe(dmpe)$_2$(C≡CC$_6$H$_4$OCH$_3$)(η^1-C(C$_6$H$_5$)=CH(C≡CC$_6$H$_4$OCH$_3$))] (**9a**) with atom displacement ellipsoids shown at the 20% level.

(at 206 ppm, $J = 18$ Hz and at 135 ppm, $J = 29$ Hz) which collapse to singlets upon ^{31}P decoupling and these corresponded to the two metal bound carbons of the alkenyl and acetylide ligands, respectively. The noncoordinated alkynyl carbons were observed at 88 and 93 ppm.

Reaction of *trans*-[Fe(depe)$_2$(CH$_3$)(C≡CPh)] (2a). In comparison to iron complexes containing dmpe ligands, complexes with bulkier bidentate phosphines are significantly more labile and exhibit a greater tendency to reversibly lose a phosphine.[39–41] UV irradiation of *trans*-[Fe(depe)$_2$(CH$_3$)(C≡CPh)] (**2a**) in the presence of 10 equiv of *tert*-butylacetylene rapidly afforded a mixture of three bisacetylidoiron(II) complexes, *trans*-[Fe(depe)$_2$(C≡CC$_6$H$_5$)$_2$] (**10a**), *trans*-[Fe(depe)$_2$(C≡CC$_6$H$_5$)(C≡C^{t}Bu)] (**10b**), and *trans*-[Fe(depe)$_2$(C≡C^{t}Bu)$_2$] (**10c**), in relative yields of approximately 3%, 61%, and 36%, respectively. No other phosphorus-containing species were observed and this reflects the lability of the phosphine donors which both promotes methyl group metathesis and also leads to alkyne scrambling. The three possible bisacetylidoiron(II) complexes, **10a**, **10b**, and **10c**, were observed by ^{31}P NMR as singlets at δ 77.1, 77.7, and 78.4 ppm, respectively. The symmetrical bisacetylide complexes were identified by comparison with authentic samples produced by an alternative synthetic route. The same mixture of iron bis-acetylides was formed when *trans*-[Fe(depe)$_2$(CH$_3$)(C≡CPh)] (**2a**) was heated at 65 °C with a benzene solution of *tert*-butylacetylene.

Scheme 8



Formation of Binuclear Complexes. The bridged dinuclear complex *trans,trans*-[C$_6$H$_5$C≡CFe(dmpe)$_2$(μ-C≡C(CH$_2$)$_4$C≡C)-Fe(dmpe)$_2$C≡CC$_6$H$_5$] (**11**) was formed by irradiation of thf or benzene solutions of [Fe(dmpe)$_2$(C≡CPh)(CH$_3$)] (**1a**) with 0.5 equiv of 1,7-octadiyne (Scheme 8).

The progress of the reaction was monitored clearly by ^{31}P NMR. The first addition of one terminus of the difunctional acetylene to [Fe(dmpe)$_2$(C≡CPh)(CH$_3$)] (**1a**) was characterized by the appearance of a singlet resonance at δ 72.2 ppm for the mixed bisacetylidoiron(II) monomer *trans*-[Fe(dmpe)$_2$(C≡CPh)(C≡C(CH$_2$)$_4$C≡CH)] (**6e**). The subsequent addition of *trans*-[Fe(dmpe)$_2$(C≡CPh)(CH$_3$)] (**1a**) to **6e** resulted in the formation of the binuclear complex **11** that was observed by ^{31}P NMR as a singlet at δ 68.03 ppm. The dinuclear complex was isolated as a microanalytically pure yellow powder with spectral properties entirely consistent with the formulation *trans,trans*-[C$_6$H$_5$C≡CFe(dmpe)$_2$(μ-C≡C(CH$_2$)$_4$C≡C)Fe(dmpe)$_2$-C≡CC$_6$H$_5$] (**11**).

Formation of a Trinuclear Complex. The trinuclear complex *trans,trans,trans*-[PhC≡CFe(dmpe)$_2$(μ-C≡C(CH$_2$)$_4$C≡C)-Fe(dmpe)$_2$(μ-C≡C(CH$_2$)$_4$C≡C)Fe(dmpe)$_2$C≡CPh] (**12**) was synthesized by extended irradiation of a thf solution of *trans*-[Fe(CH$_3$)$_2$(dmpe)$_2$] (**13**) with 2 equiv of *trans*-[C$_6$H$_5$C≡CFe-(dmpe)$_2$C≡C(CH$_2$)$_4$C≡CH] (**6e**) (Scheme 9). The reaction was followed by ^{31}P NMR in thf solution. The singlet resonances at δ 76.6 and 69.4 ppm due to *trans*-[Fe(dmpe)$_2$(CH$_3$)$_2$] (**13**) and *trans*-[C$_6$H$_5$C≡CFe(dmpe)$_2$C≡C(CH$_2$)$_4$C≡CH] (**6e**) disappeared slowly with the formation of two resonances at δ 69.8 and 72.8 ppm assigned to the intermediate dinuclear complex, *trans,trans*-[C$_6$H$_5$C≡CFe(dmpe)$_2$(μ-C≡C(CH$_2$)$_4$C≡C)-Fe(dmpe)$_2$CH$_3$)] (**14**). The resonances of **14** subsequently decreased as the resonances of the product (**12**) appeared at δ 69.1 and 69.9 ppm in a ratio of 2:1, respectively. The trinuclear complex was isolated as a microanalytically pure beige powder with spectral data entirely consistent with the formula *trans,trans,trans*-[PhC≡CFe(dmpe)$_2$(μ-C≡C(CH$_2$)$_4$C≡C)-Fe(dmpe)$_2$(μ-C≡C(CH$_2$)$_4$C≡C)Fe(dmpe)$_2$C≡CPh] (**12**).

The ^{13}C{^{1}H,^{31}P} NMR spectrum of **12** shows 6 acetylenic resonances at δ 110.4, 110.8, 111.7, 112.0, 115.4, and 141.2 ppm. All of the iron-bound carbons showed ^{31}P−^{13}C coupling when spectra were recorded without ^{31}P decoupling. The α and

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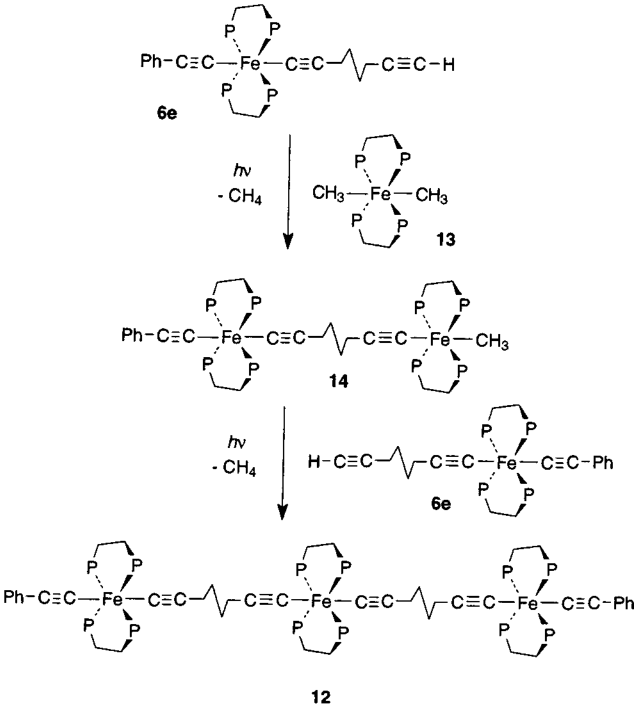
(39) Baker, M. V.; Field, L. D.; Hambley, T. W. *Inorg. Chem.* **1988**, *27*, 2872.
(40) Field, L. D.; Thomas, I. P. *Inorg. Chem.* **1996**, *35*, 2546.
(41) Field, L. D.; Thomas, I. P.; Turner, P.; Hambley, T. W. *Aust. J. Chem.* **2000**, *53*, 541.

Scheme 9



β carbon nuclei of the acetylide ligands experience a downfield chemical shift on coordination to the iron center similar to that of the symmetrical iron(II) bisacetylide complexes.

Mass Spectroscopy of Unsymmetrical Iron(II) Bisacetylide Complexes. Electrospray mass spectra of methanol solutions of unsymmetrical iron(II) bisacetylide complexes typically show strong molecular ions of the protonated cationic complexes. The spectra show fragmentation by sequential loss of the acetylenic ligands with retention of the dmpe ligands at the iron center. The dimeric complex (**11**) was observed in the mass spectrum as the protonated molecular cation at *m*/*z* 1019 amu and the diprotonated dication at *M*/*z* 510 amu. The trimeric complex (**12**) exhibited a protonated molecular ion at *M*/*z* 1479 and a diprotonated molecular dication at *M*/*z* 740 amu.

Conclusions

Methyl iron(II) complexes undergo photochemically induced σ bond metathesis with terminal alkynes to give iron acetylides. The mechanism of the reaction probably involves partial dissociation of one of the bidentate phosphine donors to give a free coordination site for metal−acetylene binding prior to metathesis.

The photochemical metathesis scheme provides a new method of forming the metal−acetylide bond in a clean and controlled fashion and was used to synthesize a range of unsymmetrically substituted iron bisacetylides. With appropriate bisacetylenes (or trisacetylenes) as substrates, this approach provides access to acetylide-bridged dinuclear, trinuclear, and more highly condensed organometallic oligomers.

Iron bisacetylides react slowly with aryl acetylenes under UV irradiation to give acetylido butenynyl products which arise from acetylene insertion into the metal alkyne bond.

Experimental Section

General. All syntheses and manipulations involving air-sensitive compounds were performed under a nitrogen atmosphere with a nitrogen-filled glovebox or by using Schlenk apparatus with double-ended needles and gastight syringes for transferring solvents and solutions.

All NMR spectra were recorded on a Bruker DRX 400 spectrometer fitted with a multinuclear probe tuned to 100.61, 400.13, and 162.00 MHz for ^{13}C, ^{1}H, and ^{31}P spectra, respectively. All NMR spectra were recorded at 300 K unless otherwise stated. Chemical shifts (δ) are reported in ppm. ^{13}C and ^{1}H NMR spectra were referenced to residual solvent resonances while ^{31}P NMR spectra were referenced to external, neat trimethyl phosphite taken to be 140.85 ppm at 300 K. Air-sensitive samples for NMR spectroscopy were prepared in a nitrogen-filled box and sealed with airtight septa or prepared with a resealable NMR tube fitted with a concentric Teflon valve. Infrared spectra were recorded on a Perkin-Elmer 1600 Series FTIR. Electrospray mass spectra of organometallic compounds were recorded on a Finnigan LCQ mass spectrometer by direct infusion of a methanol or thf solution of the complexes into the source. UV irradiation of metal complexes was achieved by using an Oriel 300-W high-pressure mercury vapor lamp with the incident beam directed through a water-filled jacket to filter infrared radiation.

All solvents used with air-sensitive compounds (benzene, toluene, hexane, pentane, thf, and ether) were either degassed with three to five freeze−pump−thaw cycles or distilled under nitrogen from sodium benzophenone ketyl.

Phenylacetylene, trimethylsilylacetylene, 1,7-octadiyne, and *tert*-butylacetylene were obtained from Aldrich and degassed prior to use. The bisphosphines dmpe and depe were obtained from Strem and used as supplied. A solution of dimethylmagnesium (0.5 M, thf) was synthesized following the reported procedure by Lühder *et al.*[42] *Trans*-$[Fe(dmpe)_2Cl_2]$ and *trans*-$[Fe(depe)_2Cl_2]$ were synthesized following literature methods.[43] Details of procedures for the synthesis of bis(phenylethynyl)magnesium, bis(4-methoxyphenylethynyl)magnesium, *trans*-$[Fe(dmpe)_2(CH_3)Cl]$ (**3**), and *trans*-$[Fe(depe)_2(CH_3)Cl]$ (**4**) are included in the Supporting Information.

$[Fe(dmpe)_2(CH_3)(C{\equiv}CC_6H_4OCH_3)]$ (1b) from *trans*-$[Fe(dmpe)_2Cl(C{\equiv}CC_6H_4OCH_3)]$ (5b). An excess of dimethylmagnesium (7.7 mL, *ca*. 1.4 M) in thf was added to a solution of *trans*-$[Fe(dmpe)_2Cl(C{\equiv}CC_6H_4OCH_3)]$ (**5b**) (830 mg, 1.60 mmol) in thf (10 mL). The color of the solution changed from orange to yellow over 2 days with the formation of the product. The solvent was removed and the crude product was extracted into hexane (2 × 100 mL). The product was recrystallized from hexane to afford a mixture of *trans*- and *cis*-$[Fe(dmpe)_2(CH_3)(C{\equiv}CC_6H_4OCH_3)]$ (**1b**) (770 mg, 95%) as a yellow crystalline solid. Mp 195 °C dec. The complexes were characterized spectroscopically as a mixture of cis and trans isomers (cis:trans $\approx$ 65:35). λ_{max}(thf; log ϵ) 352 (4.32), 252 (4.66).

***cis*-1b.** ^{31}P{^{1}H} NMR (benzene-d_6): δ 57.21 (ddd, $^{2}J_{P1P2} = 19$ Hz, $^{2}J_{P1P3} = 19$ Hz, $^{2}J_{P1P4} = 28$ Hz, 1P, **P1**), 63.93 (ddd, $^{2}J_{P2P3} = 40$ Hz, $^{2}J_{P2P4} = 38$ Hz, 1P, **P2**), 72.87 (ddd, $^{2}J_{P3P4} = 148$ Hz, 1P, **P3**), 76.76 (ddd, 1P, **P4**). ^{1}H{^{31}P} NMR (benzene-d_6): δ −0.47 (s, 3H, FeC**H**$_3$), 0.78 (s, 3H, PC**H**$_3$), 0.82 (s, 3H, PC**H**$_3$), 0.88 (s, 3H, PC**H**$_3$), 0.94 (s, 3H, PC**H**$_3$), 1.17 (s, 3H, PC**H**$_3$), 1.39 (s, 3H, PC**H**$_3$), 1.53 (s, 3H, PC**H**$_3$), 1.64 (s, 3H, PC**H**$_3$), 1.30−1.60 (m, 8H, PC**H**$_2$), 3.33 (s, 3H, OC**H**$_3$), 6.81 (m, 2H, Ar**H**), 7.24 (m, 2H, Ar**H**). ^{1}H NMR highfield (benzene-d_6): δ −0.47 (apparent quartet, splitting = 8.8 Hz, 3H, FeC**H**$_3$). ^{13}C{^{1}H,^{31}P} NMR (benzene-d_6): δ −7.5 (Fe-**C**H$_3$), 12.8 (P**C**H$_3$), 15.3 (P**C**H$_3$), 17.0 (P**C**H$_3$), 18.0 (P**C**H$_3$), 20.7 (2 × P**C**H$_3$), 21.2 (P**C**H$_3$), 21.8 (P**C**H$_3$), 28.3 (P**C**H$_2$), 29.8 (P**C**H$_2$), 31.0 (P**C**H$_2$), 34.9 (P**C**H$_2$), 56.4 (**C**H$_3$O), 113.0 (**C**≡C), 115.1 (Ar**C**H), 125.4 (Ar**C**), 132.3 (Ar**C**H), 141.9 (Fe-**C**), 156.9 (Ar**C**-O). *M*/*z* (%): 502 (92, M$^+$), 487 (27), 356 (17), 151 (100).

***trans*-1b.** υ_{max} (Nujol) 2037 cm^{-1} (υ_{cc}). ^{31}P{^{1}H} NMR (benzene-d_6): δ 74.1. ^{1}H{^{31}P} NMR (benzene-d_6): δ −1.81 (s, 3H, FeC**H**$_3$), 1.05 (s, 12H, PC**H**$_3$), 1.48 (s, 12H, PC**H**$_3$), 1.41 (m, 8H, PC**H**$_2$), 3.33

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[42] Lühder, K.; Nehls, D.; Madeja, K. *J. Prakt. Chem.* **1983**, 325, 1027.
[43] Chatt, J.; Hayter, R. G. *J. Chem. Soc.* **1961**, 5507−5511.

(s, 3H, OC**H**$_3$), 6.77 (m, 2H, Ar**H**), 7.44 (m, 2H, Ar**H**). ^{13}C{^{1}H,^{31}P} NMR (benzene-d_6): δ −19.1 (Fe**C**H$_3$), 13.5 (P**C**H$_3$), 17.2 (P**C**H$_3$), 32.1 (P**C**H$_2$), 56.4 (**C**H$_3$O), 114.8 (Ar**C**H), 114.9 (C≡**C**), 126.2 (Ar**C**-C), 131.72 (Ar**C**H), 139.8 (Fe**C**), 156.5 (Ar**C**). $C_{22}H_{42}FeOP_4$: Calculated: C 52.57, H 8.43. Found: C 52.9, H 8.7.

[Fe(dmpe)$_2$(CH$_3$)(C≡CC$_6$H$_5$)] (1a) from *trans*-[Fe(dmpe)$_2$(CH$_3$)-Cl] (3). A solution of di(phenylethynyl)magnesium (0.75 g, 3.3 mmol) in thf (50 mL) was added dropwise with stirring at room temperature to *trans*-[Fe(dmpe)$_2$(CH$_3$)Cl] (**3**) (2.45 g, 6.01 mmol) in thf (100 mL). The color of the solution changed from deep red to orange over 3 h. The solvent was removed *in vacuo* and the residue extracted into toluene (2 × 50 mL). The solvent was removed and the yellow solid was extracted into hot hexane (3 × 50 mL). Slow removal of solvent *in vacuo* led to the formation of a yellow powdery solid of 65.5% *cis*-**1a** and 34.5% *trans*-**1a** (2.20 g, 78%). The cis isomer was more soluble in toluene than the trans isomer and could be isolated by subsequent crystallization from toluene and filtration at −78 °C. The solvent was removed from the filtrate and the residue recrystallized from pentane to give *cis*-[Fe(dmpe)$_2$(CH$_3$)(C≡CC$_6$H$_5$)] (**1a**) as pale yellow needles.

***cis*-1a.** λ_{max}(thf; log ϵ): 370 (4.15), 260 (4.42), 254 (4.52), 248 (4.52), 216 (4.67). υ_{max} (benzene, NaCl cell) 2051 cm^{-1} (υ_{cc}). ^{31}P{^{1}H} NMR (benzene-d_6): δ 55.3 (ddd, $^2J_{P1P2}$ = 19 Hz, $^2J_{P1P3}$ = 19 Hz, $^2J_{P1P4}$ = 27 Hz, 1P, **P1**), 62.0 (ddd, $^2J_{P2P3}$ = 39 Hz, $^2J_{P2P4}$ = 36 Hz, 1P, **P2**), 71.0 (ddd, $^2J_{P3P4}$ = 145 Hz, 1P, **P3**), 75.0 (ddd, 1P, **P4**). ^{1}H{^{31}P} NMR (benzene-d_6): δ −0.51 (s, 3H, FeC**H**$_3$), 0.77 (s, 3H, PC**H**$_3$), 0.81 (s, 3H, PC**H**$_3$), 0.86 (s, 3H, PC**H**$_3$), 0.92 (s, 3H, PC**H**$_3$), 1.15 (s, 3H, PC**H**$_3$), 1.25−1.55 (m, 8H, PC**H**$_2$), 1.37 (s, 3H, PC**H**$_3$), 1.50 (s, 3H, PC**H**$_3$), 1.61 (s, 3H, PC**H**$_3$), 6.95, 7.17, 7.49 (m, 5H, Ar**H**). ^{13}C{^{1}H,^{31}P} NMR (thf-d_8): δ −8.73 (Fe**C**H$_3$), 11.7 (P**C**H$_3$), 13.3 (P**C**H$_3$), 14.6 (P**C**H$_3$), 17.4 (P**C**H$_3$), 20.0 (P**C**H$_3$), 20.1 (P**C**H$_3$), 20.5 (P**C**H$_3$), 21.3 (P**C**H$_3$), 28.1 (P**C**H$_2$), 29.6 (P**C**H$_2$), 34.5 (P**C**H$_2$), 34.6 (P**C**H$_2$), 113.5 (Ar**C**), 122.0 (Ar**C**H), 128.0 (Ar**C**H), 130.5 (Ar**C**H), 132.7 (FeC≡**C**), 147.6 (Fe**C**≡C). *M/z* (%): 472 (65, M$^+$), 356 (12), 167 (100), 151 (95).

***trans*-1a.** υ_{max} (benzene, NaCl cell) 2038 cm^{-1} (υ_{cc}). ^{31}P{^{1}H} NMR (benzene-d_6): δ 72.2. ^{1}H{^{31}P} NMR (benzene-d_6): δ −1.79 (p, $^3J_{PH}$ = 7.3 Hz, 3H, FeC**H**$_3$), 1.06 (s, 12H, PC**H**$_3$), 1.38 (m, 4H, PC**H**$_2$), 1.48 (s, 12H, PC**H**$_3$), 1.57 (m, 4H, PC**H**$_2$), 6.94 (m, 1H, Ar**H**), 7.16 (m, 2H, Ar**H**), 7.3 (m, 2H, Ar**H**). ^{13}C{^{1}H,^{31}P} NMR (thf-d_8): δ −20.0 (Fe**C**H$_3$), 13.5 (P**C**H$_3$), 17.8 (P**C**H$_3$), 31.2 (P**C**H$_2$), 115.7 (Ar**C**), 121.6 (Ar**C**H), 128.0 (Ar**C**H), 130.2 (Ar**C**H), 132.4 (FeC≡**C**), 145.4 (Fe**C**≡C). $C_{21}H_{40}FeP_4$ requires: C 53.37, H 8.54. Found: C 53.6, H 8.4.

[Fe(dmpe)$_2$(CH$_3$)(C≡CC$_6$H$_5$)] (1a) from *trans*-[Fe(dmpe)$_2$Cl-(C≡CC$_6$H$_5$)] (5a). An excess of dimethylmagnesium in thf (0.25 mL, *ca*. 0.9 M) was added to a thf solution (1.5 mL) of *trans*-[Fe(dmpe)$_2$Cl-(C≡CC$_6$H$_5$)] (**5a**) (15 mg, 29 μmol) and stirred for 3 days at room temperature. During this time, the color of the solution changed from orange to pale yellow. The solvent was removed and the residue extracted into benzene (2 × 1.0 mL) and the solvent removed. The yellow residue of *trans*-[Fe(dmpe)$_2$(CH$_3$)(C≡CC$_6$H$_5$)] (**1a**) possessed identical spectroscopic properties to that prepared previously.

Thermal Isomerization of *cis*-[Fe(dmpe)$_2$(CH$_3$)(C≡CC$_6$H$_5$)] (*cis*-1a) to *trans*-[Fe(dmpe)$_2$(CH$_3$)(C≡CC$_6$H$_5$)] (*trans*-1a). An NMR tube containing a benzene solution of 34.5% *trans*-**1a** and 65.5% *cis*-**1a** was heated at 90 °C for 18 h in darkness. The resulting solution was examined by ^{31}P NMR and found to contain 90% *trans*-**1a** isomer and 10% *cis*-**1a** isomer with no net loss of ^{31}P signal.

***trans*-[Fe(depe)$_2$(CH$_3$)(C≡CC$_6$H$_5$)] (2a).** A freshly prepared solution of di(phenylethynyl)magnesium in thf (3.50 mmol) was added dropwise to a solution of *trans*-[Fe(depe)$_2$Cl(CH$_3$)] (**4**) (1.50 g, 2.89 mmol) in thf at −78 °C. The deep red color of the solution faded as the solution was warmed to room temperature forming a yellow orange solution. The solvent was removed *in vacuo* and the yellow residue extracted into hexane (3 × 20 mL). The solvent was removed *in vacuo* and the residue dissolved in toluene and passed through a bed of neutral alumina at −78 °C under nitrogen. The solvent was slowly removed *in vacuo* to give *trans*-[Fe(depe)$_2$(CH$_3$)(C≡CC$_6$H$_5$)] (**2a**) as an orange crystalline solid (580 mg, 35%). Mp: 152−153 °C. υ_{max} (benzene, NaCl cell) 2031 cm^{-1} (υ_{cc}). ^{31}P{^{1}H} NMR (benzene-d_6): δ 80.6. ^{1}H{^{31}P} NMR (benzene-d_6): δ −1.60 (s, 3H, FeC**H**$_3$), 1.12 (t, 12H, CH$_2$C**H**$_3$), 1.27 (t, 12H, CH$_2$C**H**$_3$), 1.55−1.65 (m, 8H, PC**H**HC**H**HP, (C**H**)HCH$_3$)), 1.80−1.95 (m, 12H, 2 × (C**H**)HCH$_3$, PCH**H**CH**H**P), 2.64 (m, 4H, (C**H**)HCH$_3$), 7.01 (m, 1H, Ar**H**), 7.27 (m, 2H, Ar**H**), 7.44 (m, 2H, Ar**H**). ^{13}C{^{1}H,^{31}P} NMR (benzene-d_6): δ −20.4 (Fe**C**H$_3$), 10.7 (CH$_2$**C**H$_3$), 10.8 (CH$_2$**C**H$_3$), 19.9 (P**C**H$_2$CH$_2$), 22.1 (P**C**H$_2$CH$_3$), 23.0 (P**C**H$_2$CH$_3$), 118 (Ar**C**), 123 (Ar**C**H), 131 (2 × Ar**C**H), 133 (FeC≡**C**), 147 (Fe**C**≡C). *M/z* (%): 584 (4). $C_{29}H_{56}FeP_4$ requires C 59.56, H 9.66. Found: C 59.4, H 9.5.

Isomerization of *trans*/*cis*-[Fe(dmpe)$_2$(CH$_3$)(C≡CC$_6$H$_4$OCH$_3$)] (1b). An NMR tube containing *trans/cis*-[Fe(dmpe)$_2$(CH$_3$)(C≡CC$_6$H$_4$-OCH$_3$)] (**1b**) (cis:trans ≈ 65:35) in benzene-d_6 was irradiated with a mercury vapor lamp for 5 min. By ^{31}P NMR, all of the cis isomer was consumed with a corresponding increase in the amount of the trans isomer. There was no net loss of phosphine complex.

Reactions of Acetylido Methyl Iron(II) Complexes with Terminal Acetylenes: *trans*-[Fe(dmpe)$_2$(C≡CC$_6$H$_5$)(C≡CC$_6$H$_4$OCH$_3$)] (6b). A thf solution (0.5 mL) of *trans/cis*-[Fe(dmpe)$_2$(CH$_3$)(C≡CC$_6$H$_4$OCH$_3$)] (**1b**) (25 mg, 50 μmol) and phenylacetylene (10 μL, 91 μmol) was irradiated for 20 h until all starting material was consumed. The solvent was removed and the residue washed with methanol (2 × 0.5 mL) to give *trans*-[Fe(dmpe)$_2$(C≡CC$_6$H$_5$)(C≡CC$_6$H$_4$OCH$_3$)] (**6b**) as a solid yellow powder (24 mg, 83%). υ_{max} (KBr disk) 2041 cm^{-1} (υ_{cc}). ^{31}P{^{1}H} NMR (benzene-d_6): δ 69.1. ^{1}H{^{31}P} NMR (benzene-d_6): δ 1.64 (s, 12H, PC**H**$_3$), 1.65 (s, 12H, PC**H**$_3$), 1.75 (s, 8H, PC**H**$_2$), 3.57 (s, 3H, C**H**$_3$O), 7.03 (m, 2H, Ar**H**), 7.17 (m, 1H, Ar**H**), 7.39 (m, 2H, Ar**H**), 7.47 (m, 2H, Ar**H**), 7.58 (m, 2H, Ar**H**). ^{13}C{^{1}H,^{31}P} NMR (benzene-d_6): δ 16.8 (2 × P**C**H$_3$), 31.6 (P**C**H$_2$), 55.6 (**C**H$_3$O), 114.8 (Ar**C**H), 115.2 (**C**≡C), 116.2 (**C**≡C), 123.5 (Ar**C**H), 125.3 (C≡C**C**), 129.3 (Ar**C**H), 131.1 (Ar**C**H), 131.9 (Ar**C**H), 132.3 (C≡C**C**), 133.3 (Fe**C**), 139.1 (Fe**C**), 157.1 (Ar**C**OCH$_3$). *M/z* (%): 588 (M + 1, 100), 356 (68).

***trans*-[Fe(dmpe)$_2$(C≡CC$_6$H$_5$)(C≡C^{t}Bu)] (6c).** A benzene solution (10 mL) of *trans/cis*-[Fe(dmpe)$_2$(CH$_3$)(C≡CC$_6$H$_5$)] (**1a**) (120 mg, 0.25 mmol) and 8.5 equiv of *tert*-butylacetylene (260 μL, 2.12 mmol) was irradiated for 18 h until all starting material was consumed by ^{31}P NMR. The solvent was removed and the yellow powder extracted into pentane (4 × 5.0 mL) and filtered. The solvent was removed from the filtrate to give a pale yellow powdery solid that was recrystallized from ethanol (20 mL) to give *trans*-[Fe(dmpe)$_2$(C≡CC$_6$H$_5$)(C≡C^{t}Bu)] (**6c**) as a pale yellow crystalline solid (116 mg, 85%). Mp: 297 °C dec. υ_{max} (benzene, NaCl cell) 2046 cm^{-1} (υ_{cc}). ^{31}P{^{1}H} NMR (benzene-d_6): δ 68.9. ^{1}H{^{31}P} NMR (benzene-d_6): δ 1.25 (s, 9H, ^{t}Bu), 1.38 (s, 12H, PC**H**$_3$), 1.40 (s, 12H, PC**H**$_3$), 1.52 (bs, 8H, PC**H**$_2$), 6.92, 7.13, 7.30 (m, 5H, Ar**H**). ^{13}C{^{1}H,^{31}P} NMR (benzene-d_6): δ 16.7 (P**C**H$_3$), 17.0 (P**C**H$_3$), 31.5 (**C**(CH$_3$)$_3$, 31.6 (P**C**H$_2$), 34.3 (C(**C**H$_3$)$_3$, 109.1 (Fe−**C**≡C^{t}Bu), 115.9 (Ar**C**), 121.4 (Fe−C≡**C**^{t}Bu), 123.3 (Ar**C**H), 129.1 (Ar**C**H), 131.1 (Ar**C**H), 132.5 (Fe−C≡**C**Ph), 140.9 (Fe-**C**≡CPh). *M/z* (E.S.) (%): 539 (M + 1)$^+$ (76), 437 (100), 356 (85). $C_{26}H_{46}FeP_4$ requires C 57.97, H 8.62. Found: C 58.3, H 8.9.

***trans*-[Fe(dmpe)$_2$(C≡CC$_6$H$_5$)(C≡CSi(CH$_3$)$_3$)] (6d).** A solution of *trans/cis*-[Fe(dmpe)$_2$(CH$_3$)(C≡CC$_6$H$_5$)] (**1a**) (150 mg, 0.32 mmol) and 10 equiv of trimethylsilylacetylene (0.45 mL, 3.18 mmol) in thf (50 mL) was irradiated for 60 h until all starting material was consumed. The solvent was removed and the yellow solid was extracted into pentane and filtered and the solvent removed *in vacuo*. The yellow solid was recrystallized from hexane at −78 °C to give *trans*-[Fe(dmpe)$_2$(C≡CC$_6$H$_5$)(C≡CSi(CH$_3$)$_3$)] (**6d**) as a pale yellow powdery solid (115 mg, 65%). Mp: 297 °C dec. υ_{max} (benzene, NaCl cell) 2050 cm^{-1} ($\upsilon_{C\equiv C}$). ^{31}P{^{1}H} NMR (benzene-d_6): δ 67.4. ^{1}H{^{31}P} NMR (benzene-d_6): δ 0.26 (s, 9H, SiC**H**$_3$), 1.35 (s, 12H, PC**H**$_3$), 1.40 (s, 12H, PC**H**$_3$), 1.49 (m, 8H, PC**H**$_2$), 6.92, 7.12, 7.27 (m, 5H, Ar**H**). ^{13}C{^{1}H,^{31}P} NMR (benzene-d_6): δ 3.10 (Si**C**H$_3$), 16.5 (P**C**H$_3$), 16.8 (P**C**H$_3$), 31.4 (P**C**H$_2$), 116.0 (Fe−C≡**C**), 118.9

(Fe−C≡**C**), 123.5 (Ar**C**H), 129.0 (Ar**C**H), 131.1 (Ar**C**H), 132.2 (Ar**C**), 138.8 (Fe−**C**≡CPh), 165.6 (Fe−**C**≡CSi). *M/z* (%): 554 (M$^+$) (100), 453 (92), 356 (91). C$_{25}$H$_{46}$FeP$_4$Si requires C 54.14, H 8.37. Found: C 54.1, H 8.1.

***trans*-[Fe(dmpe)$_2$(C≡CC$_6$H$_5$)(C≡C(CH$_2$)$_4$C≡CH)] (6e).** A solution of *trans/cis*-[Fe(dmpe)$_2$(CH$_3$)(C≡CC$_6$H$_5$)] (**1a**) (300 mg, 0.64 mmol) and 12 equiv of 1,7-octadiyne (0.84 mL) in thf (50 mL) was irradiated for 80 h until all starting material was consumed. The solvent was removed and the yellow solid was recrystallized from hexane at −78 °C to give *trans*-[Fe(dmpe)$_2$(C≡CC$_6$H$_5$)(C≡C(CH$_2$)$_4$C≡CH)] (**6e**) as a pale yellow solid (346 mg, 97%). Mp: 154−155 °C. $\upsilon_{\max}$ (benzene, NaCl cell) 2047 ($\upsilon_{\mathrm{FeC\equiv C}}$), 2115 ($\upsilon_{\mathrm{C\equiv CH}}$), 3305 ($\upsilon_{\mathrm{\equiv C-H}}$) cm^{-1}. ^{31}P{^{1}H} NMR (benzene-*d*$_6$): δ 69.4. ^{1}H{^{31}P} NMR (benzene-*d*$_6$): δ 1.36 (s, 12H, PC**H**$_3$), 1.39 (s, 12H, PC**H**$_3$), 1.50 (m, 2H, C**H**$_2$), 1.52 (m, 8H, PC**H**$_2$), 1.60 (m, 2H, C**H**$_2$), 1.78 (t, $^3J_{\mathrm{HH}}$ = 2.7 Hz, 1H, C≡C**H**), 2.03 (dt, $^3J_{\mathrm{HH}}$ = 7.0 Hz, $^4J_{\mathrm{HH}}$ = 2.7 Hz, 2H, C**H**$_2$C≡CH), 2.27 (t, J_{HH} = 6.7 Hz, 2H, C**H**$_2$C≡CFe), 6.92, 7.13, 7.30 (m, 5H, Ar**H**). ^{13}C{^{1}H,^{31}P} NMR (thf-*d*$_8$): δ 16.3 (2 × P**C**H$_3$), 18.4 (**C**H$_2$), 22.3 (**C**H$_2$), 28.9 (**C**H$_2$), 31.4 (P**C**H$_2$), 31.5 (**C**H$_2$), 69.0 (C≡**C**H), 84.7 (**C**≡CH), 110.5 (Fe−C≡**C**CH$_2$), 112.3 (Fe-**C**≡CCH$_2$), 115.3 (Fe−C≡**C**Ph), 122.2 (Ar**C**H), 128.0 (Ar**C**H), 130.3 (Ar**C**H), 132.0 (Ar**C**), 140.7 (Fe-**C**≡CPh). *M/z* (E.S.) (%): 563 (M + 1)$^+$ (100), 457 (56), 356 (50). C$_{28}$H$_{46}$FeP$_4$ requires C 59.77, H 8.25. Found: C 59.9, H 8.3.

***trans*-[Fe(dmpe)$_2$(C≡CC$_6$H$_5$)(C≡CH)] (6f).** Two equivalents (10 mg) of potassium fluoride was added to a solution of *trans*-[Fe(dmpe)$_2$-(C≡CC$_6$H$_5$)(C≡CSi(CH$_3$)$_3$)] (**6d**) (45 mg, 81 μmol) in methanol (3.0 mL). The solution was refluxed for 1 h until the color of the reaction mixture was green. The solvent was removed and the green residue was extracted into hexane and filtered and the solvent removed *in vacuo*. The product was recrystallized from hexane at −78 °C to give *trans*-[Fe(dmpe)$_2$(C≡CH)(C≡CC$_6$H$_5$)] (**6f**) as a pale yellow powdery solid (24 mg, 62%). $\upsilon_{\max}$ (benzene, NaCl cell) 2050 (υ_{CC}), 3233 (υ_{CH}) cm^{-1}. ^{31}P{^{1}H} NMR (benzene-*d*$_6$): δ 68.9. ^{1}H{^{31}P} NMR (benzene-*d*$_6$): δ 1.38 (s, 12H, PC**H**$_3$), 1.44 (s, 12H, PC**H**$_3$), 1.47−1.57 (bs, 8H, PC**H**$_2$), 1.66 (p, $^4J_{\mathrm{PH}}$ = 3.1 Hz, Fe−C≡C−**H**), 6.93, 7.14, 7.30 (m, 5H, Ar**H**). ^{13}C{^{1}H,^{31}P} NMR (thf-*d*$_8$): δ 15.8 (P**C**H$_3$), 16.0 (P**C**H$_3$), 30.7 (P**C**H$_2$), 98.2 (**C**H), 98.3 (**C**H), 115.2 (C≡**C**Ph), 122.7 (Ar**C**H), 126.7 (Fe−**C**≡C), 130.3 (Ar**C**H), 131.5 (Ar**C**), 138.9 (Fe−**C**≡C). Selected ^{13}C{^{1}H} NMR (thf-*d*$_8$): δ 126.7 (p, $^2J_{\mathrm{PC}}$ = 25.9 Hz, Fe−**C**≡C), 138.9 (p, $^2J_{\mathrm{PC}}$ = 26.4 Hz, Fe−**C**≡C). *M/z* (E.S.) (%): 483 (M + 1)$^+$ (95), 457 (25), 381 (25), 356 (100).

***trans*-[Fe(dmpe)$_2$(C≡CC$_6$H$_4$OCH$_3$)(C≡C^{t}Bu)] (6h).** A toluene solution (0.5 mL) of *trans/cis*-[Fe(dmpe)$_2$ (CH$_3$)(C≡CC$_6$H$_4$OCH$_3$)] (**1b**) (34 mg, 68 μmol) and 12 equiv of *tert*-butylacetylene (100 μL) was irradiated for 4 h until all starting material was consumed. The solvent was removed to give *trans*-[Fe(dmpe)$_2$(C≡C^{t}Bu)(C≡CC$_6$H$_4$OCH$_3$)] (**6h**) as a yellow powdery solid (36 mg, 95%). The complex was characterized spectroscopically. $\upsilon_{\max}$ (thf, NaCl cell) 2051 cm^{-1} (υ_{cc}). ^{31}P{^{1}H} NMR (benzene-*d*$_6$): δ 68.9. ^{1}H{^{31}P} NMR (benzene-*d*$_6$): δ 1.28 (s, 9H, C(C**H**$_3$)$_3$), 1.43 (s, 12H, PC**H**$_3$), 1.46 (s, 12H, PC**H**$_3$), 1.58 (m, 8H, PC**H**$_2$), 3.35 (s, 3H, OC**H**$_3$), 6.8 (m, 2H, Ar**H**), 7.26 (m, 2H, Ar**H**). ^{13}C{^{1}H,^{31}P} NMR (benzene-*d*$_6$): δ 16.8 (P**C**H$_3$), 17.1 (P**C**H$_3$), 31.0 (**C**(CH$_3$)$_3$, 31.7 (P**C**H$_2$), 34.3 (C(**C**H$_3$)$_3$), 55.7 (O**C**H$_3$), 109.4 (Fe**C**≡C^{t}Bu), 114.8 (FeC≡**C**Ph), 114.9 (Ar**C**H), 121.4 (FeC≡**C**^{t}Bu), 125.7 (Ar**C**C≡C), 131.9 (Ar**C**H), 135.4 (Fe**C**≡CPh), 157.0 (Ar-**C**OCH$_3$). *M/z* (%): 569 (M + 1)$^+$.

***trans*-[Fe(dmpe)$_2$(C≡CC$_6$H$_4$OCH$_3$)(C≡C(CH$_2$)$_4$C≡CH)] (6i).** A solution of *trans/cis*-[Fe(dmpe)$_2$(CH$_3$)(C≡CC$_6$H$_4$OCH$_3$)] (**1b**) (32 mg, 64 μmol) and 12 equiv of 1,7-octadiyne (100 μL) in benzene-*d*$_6$ was irradiated for 4 h until all starting material was consumed. The solvent was removed and the residue washed with cold pentane (0.5 mL) to give *trans*-[Fe(dmpe)$_2$(C≡CC$_6$H$_4$OCH$_3$)(C≡C(CH$_2$)$_4$C≡CH)] (**6i**) as a yellow powdery solid (34 mg, 89%). The complex was characterized spectroscopically. $\upsilon_{\max}$ (KBr disk) 2049 cm^{-1} (υ_{cc}). ^{31}P{^{1}H} NMR (benzene-*d*$_6$): δ 69.5. ^{1}H{^{31}P} NMR (benzene-*d*$_6$): δ 1.39 (s, 12H, PC**H**$_3$), 1.42 (s, 12H, PC**H**$_3$), 1.49 (m, 2H, C**H**$_2$CH$_2$C≡CH), 1.55 (s, 8H, PC**H**$_2$), 1.59 (m, 2H, C**H**$_2$CH$_2$C≡CFe), 1.78 (t, $^3J_{\mathrm{HH}}$ = 2.7 Hz, 1H, C≡C**H**), 2.04 (m, 2H, C**H**$_2$C≡CH), 2.28 (m, 2H, C**H**$_2$C≡CFe), 3.32 (s, 3H, OC**H**$_3$), 6.76 (m, AA′XX′, 2H, Ar**H**), 7.22 (m, AA′XX′, 2H, Ar**H**). ^{13}C{^{1}H,^{31}P} NMR (benzene-*d*$_6$): δ 17.1 (2 × P**C**H$_3$), 19.2 (**C**H$_2$), 23.1 (**C**H$_2$), 29.3 (**C**H$_2$), 31.8 (P**C**H$_2$), 32.0 (**C**H$_2$), 55.7 (**C**H$_3$O), 69.3 (C≡**C**H), 85.6 (**C**≡CH), 110.8 (Fe**C**), 113.0 (FeC≡**C**), 114.8 (FeC≡**C**Ph), 114.9 (Ar**C**H), 125.7 (Ar**C**), 131.9 (Ar**C**H), 135.2 (Fe**C**), 157.0 (CH$_3$O**C**Ar). *M/z* (E.S.) (%) 593 (100) (M + 1)$^+$.

***trans*-[Fe(dmpe)$_2$(C≡CC$_6$H$_4$OCH$_3$)(C≡C-adamantyl)] (6j).** A solution of *trans/cis*-[Fe(dmpe)$_2$(CH$_3$)(C≡CC$_6$H$_4$OCH$_3$)] (**1b**) (15 mg, 30 μmol) and 12 equiv of 1-adamantylacetylene (57 mg) in toluene-*d*$_8$ was irradiated for 4 h until all starting material was consumed. The solvent was removed and the residue washed with methanol (0.5 mL) to give *trans*-[Fe(dmpe)$_2$(C≡CC$_6$H$_4$OCH$_3$)(C≡CC$_{10}$H$_{15}$)] (**6j**) as a yellow powdery solid (15 mg, 80%). The complex was characterized spectroscopically. $\upsilon_{\max}$ (KBr disk) 2050 cm^{-1} (υ_{cc}). ^{31}P{^{1}H} NMR (benzene-*d*$_6$): δ 68.8. ^{1}H{^{31}P} NMR (benzene-*d*$_6$): δ 1.44 (s, 12H, PC**H**$_3$), 1.47 (s, 12H, PC**H**$_3$), 1.58 (s, 8H, PC**H**$_2$), 1.67 (bs, 6H, adamantyl-C**H**$_2$), 1.86 (bs, 6H, adamantyl-C**H**$_2$), 1.91 (bs, 3H, adamantyl-C**H**), 3.32 (s, 3H, OC**H**$_3$), 6.77 (m, AA′XX′, 2H, Ar**H**), 7.24 (m, AA′XX′, 2H, Ar**H**). ^{13}C{^{1}H,^{31}P} NMR (benzene-*d*$_6$): δ 16.8 (P**C**H$_3$), 17.1 (P**C**H$_3$), 30.2 (adamantyl-**C**H), 31.8 (P**C**H$_2$), 33.1 (adamantyl-**C**), 38.2 (adamantyl-**C**H$_2$), 47.3 (adamantyl-**C**H$_2$), 55.7 (**C**H$_3$O), 109.8 (Fe**C**≡C-adamantyl), 114.7 (FeC≡**C**Ph), 114.9 (Ar**C**H), 122.7 (adamantyl-**C**≡C), 125.7 (Ar**C**), 131.9 (Ar**C**H), 135.5 (Fe**C**≡CPh), 160.0 (CH$_3$O**C**Ar). *M/z* (E.S.) (%): 647 (35) (M + 1)$^+$, 356 (100).

***trans,trans*-[C$_6$H$_5$C≡CFe(dmpe)$_2$(μ-C≡C(CH$_2$)$_4$C≡C)Fe-(dmpe)$_2$C≡CC$_6$H$_5$] (11).** A solution containing *trans/cis*-[Fe(dmpe)$_2$-(CH$_3$)(C≡CC$_6$H$_5$)] (**1a**) (94 mg, 199 μmol) and *trans*-[Fe(dmpe)$_2$-(C≡CC$_6$H$_5$)(C≡C(CH$_2$)$_4$C≡CH)] (**6e**) (112 mg, 199 μmol) in thf (10 mL) was irradiated for 100 h until all starting material was consumed. The solvent was removed and the yellow solid was recrystallized from benzene to give *trans,trans*-[C$_6$H$_5$C≡CFe(dmpe)$_2$(μ-C≡C(CH$_2$)$_4$C≡C)-Fe(dmpe)$_2$C≡CC$_6$H$_5$] (**11**) as a pale yellow powdery solid (199 mg, 98%). Mp: 340 °C dec. $\upsilon_{\max}$ (thf, NaCl cell) 2046 cm^{-1} ($\upsilon_{\mathrm{C\equiv C}}$). ^{31}P{^{1}H} NMR (thf-*d*$_8$): δ 68.03. ^{1}H{^{31}P} NMR (thf-*d*$_8$): δ 1.29−1.32 (m, 4H, C**H**$_2$CH$_2$C≡C), 1.48 (s, 24H, PC**H**$_3$), 1.50 (s, 24H, PC**H**$_3$), 1.73 (bs, 16H, PC**H**$_2$), 2.00 (t, $^3J_{\mathrm{HH}}$ = 6.0 Hz, 4H, C**H**$_2$C≡C), 6.73, 6.88, 6.93 (m, 10H, Ar**H**). ^{13}C{^{1}H,^{31}P} NMR (thf-*d*$_8$): δ 16.4 (P**C**H$_3$), 16.5 (P**C**H$_3$), 23.0 (**C**H$_2$), 31.5 (P**C**H$_2$), 32.5 (**C**H$_2$), 110.6 (Fe−C≡**C**CH$_2$), 111.6 (Fe-**C**≡CCH$_2$), 115.4 (Fe−C≡**C**Ph), 122.3 (Ar**C**H), 128.2 (ArCH), 130.5 (Ar**C**H), 132.2 (Ar**C**), 141.1 (Fe-**C**≡CPh). *M/z* (E.S.) (%): 1019 (M + 1)$^+$ (22), 457 (43), 356 (100). C$_{48}$H$_{82}$Fe$_2$P$_8$ requires C 56.57, H 8.12. Found: C 56.0, H 8.1.

Alternatively, a solution of *trans/cis*-[Fe(dmpe)$_2$(CH$_3$)(C≡CC$_6$H$_5$)] (**1a**) (30 mg, 0.064 mmol) and 0.5 equiv of 1,7-octadiyne (3.4 μL) in thf (0.5 mL) was irradiated for 60 h with monitoring by ^{31}P NMR until the reaction was complete. The solvent was removed from the mixture and the yellow solid was recrystallized from benzene to give *trans,trans*-[C$_6$H$_5$C≡CFe(dmpe)$_2$(μ-C≡C(CH$_2$)$_4$C≡C)Fe(dmpe)$_2$C≡CC$_6$H$_5$] (**11**) as a pale yellow powdery solid (31 mg, 95%) with identical spectroscopic properties to that prepared by the method above.

***trans,trans,trans*-[PhC≡CFe(dmpe)$_2$(μ-C≡C(CH$_2$)$_4$C≡C)Fe(dmpe)$_2$-(μ-C≡C(CH$_2$)$_4$C≡C)-Fe(dmpe)$_2$C≡CPh] (12).** A thf solution containing a mixture of *cis/trans*-[Fe(dmpe)$_2$(CH$_3$)$_2$] (20 mg, 52 μmol) and *trans*-[Fe(dmpe)$_2$(C≡CC$_6$H$_5$)(C≡C(CH$_2$)$_4$C≡CH)] (**6e**) (56 mg, 100 μmol) was irradiated for 40 h. The reaction was monitored by ^{31}P NMR until all of complex **6e** was consumed. The solvent was removed and the residue was washed with pentane (3 × 1 mL) then hexane (3 × 1 mL). The crude product was recrystallized from benzene/ethanol to give a beige powder of *trans,trans,trans*-[PhC≡CFe(dmpe)$_2$(μ-C≡C(CH$_2$)$_4$C≡C)Fe(dmpe)$_2$(μ-C≡C(CH$_2$)$_4$C≡C)Fe(dmpe)$_2$C≡CPh] (**12**) (61 mg, 79%). $\upsilon_{\max}$ (thf, NaCl cell) 2046 cm^{-1} (s, $\nu_{\mathrm{C\equiv C}}$), 2066 (w, $\nu_{\mathrm{C\equiv C}}$). ^{31}P{^{1}H} NMR (thf-*d*$_8$): δ 69.1 (s, 8P), 69.9 (s, 4P). ^{1}H{^{31}P} NMR (benzene-*d*$_6$): δ 1.41 (s, 24H, PC**H**$_3$), 1.42 (s, 24H, PC**H**$_3$), 1.47 (s, 24H, PC**H**$_3$), 1.55 (bs, 16H, PC**H**$_2$), 1.63 (bs, 8H, PC**H**$_2$), 2.35−

2.40 (m, 8H, C≡C−C**H**$_2$), 6.92 (m, 2H, Ar**H**), 7.12 (m, 4H, Ar**H**), 7.31 (m, 4H, Ar**H**), other CH$_2$ resonances masked by dmpe resonances. ^{13}C{^{1}H,^{31}P} NMR (thf-*d*$_8$): δ 16.4 (P**C**H$_3$), 16.5 (P**C**H$_3$), 16.6 (P**C**H$_3$), 22.9 (**C**H$_2$), 23.0 (**C**H$_2$), 31.5 (8 × P**C**H$_2$), 31.6 (4 × P**C**H$_2$), 32.5 (**C**H$_2$), 32.6 (**C**H$_2$), 110.4, 110.8 (2 × Fe−C≡**C**CH$_2$), 111.7, 112.0 (2 × Fe−**C**≡CCH$_2$) 115.4 (2 × Fe−C≡**C**−Ph), 122.3 (Ar**C**H), 128.1 (Ar**C**H), 130.5 (Ar**C**H), 132.2 (Ar**C**), 141.2 (2 × Fe−**C**≡C−Ph). *M/z* (E.S.) (%): 1479 (M + 1)$^+$ (18), 740 (M + 2)$^{2+}$ (12), 457 (90), 356 (100). C$_{68}$H$_{122}$Fe$_3$P$_{12}$ requires C 55.19, H 8.32. Found: C 55.8, H 8.1.

Acetylide Butenynyl Iron(II) Complexes: *trans*-[Fe(dmpe)$_2$(C≡CC$_6$H$_5$)(η^1-C(C$_6$H$_5$)═CH(C≡CC$_6$H$_5$))] (9b). A benzene solution of *trans*-[Fe(dmpe)$_2$(C≡CC$_6$H$_5$)$_2$] (**6a**) (24 mg, 43 μmol) and phenylacetylene (288 μL, 2.6 mmol, 60 equiv) was irradiated with a high-pressure mercury vapor lamp for 20 h. The reaction was followed by ^{31}P NMR until all starting material was consumed. The solution darkened from yellow to brown during the course of the irradiation. The solvent was removed and the residue extracted with ether (3 × 1.0 mL). The ether was removed *in vacuo* and the residue washed with pentane (3 × 1.0 mL). The residue was dissolved in benzene and filtered and the solvent removed to give *trans*-[Fe(dmpe)$_2$(C≡CC$_6$H$_5$)(η^1-C(C$_6$H$_5$)═CH(C≡CC$_6$H$_5$))] (**9b**) (10 mg, 35%) as an orange air-sensitive solid. The complex was characterized spectroscopically. $\nu_{\max}$ (KBr disk) 2042 ($\nu_{\mathrm{C\equiv C}}$), 2164 ($\nu_{\mathrm{C\equiv C}}$) cm^{-1}. ^{31}P{^{1}H} NMR (thf-*d*$_8$): δ 65.3 (s). ^{1}H{^{31}P} NMR (thf-*d*$_8$): δ 1.48 (s, 12H, PC**H**$_3$), 1.57 (s, 12H, PC**H**$_3$), 1.83 (m, 8H, PC**H**$_2$), 5.49 (s, 1H, C═C**H**), 6.64−7.07 (m, 15H, Ar**H**). ^{13}C{^{1}H,^{31}P} NMR (thf-*d*$_8$): δ 17.9 (P**C**H$_3$), 20.4 (P**C**H$_3$), 31.7 (P**C**H$_2$), 88.8 (**C**≡C), 94.9 (C≡**C**), 120.7 (Ar**C**), 121.1 (Ar**C**), 121.2 (═**C**H), 124.4 (Ar**C**H), 124.7 (Ar**C**H), 127.1 (Ar**C**H), 128.6 (Ar**C**H), 128.7 (Ar**C**H), 129.7 (Ar**C**H), 129.8, (Ar**C**H), 131.4 (Ar**C**H), 132.3 (Ar**C**H), 142.3 (Fe**C**), 164.8 (Ar**C**), 209.0 (Fe**C**). *M/z* (E.S.) (%): 661 (100) (M + 1)$^+$, 559 (27), 356 (27).

***trans*-[Fe(dmpe)$_2$(C≡CC$_6$H$_4$OCH$_3$)(η^1-C(C$_6$H$_5$)═CH(C≡CC$_6$H$_4$OCH$_3$))] (9a).** A benzene solution containing *trans*-[Fe(dmpe)$_2$(C≡CC$_6$H$_4$OCH$_3$)$_2$] (**6g**) (14 mg, 23 μmol) and phenylacetylene (150 μL, 1.4 mmol, 60 equiv) was irradiated with a high-pressure mercury vapor lamp for 16 h. The reaction was followed by ^{31}P NMR. The solution darkened from yellow to brown during the course of the irradiation. The solvent was removed and the residue was washed with ether (3 × 1.0 mL) then pentane (3 × 1.0 mL). The residue was dissolved in benzene and filtered and the solvent removed to give *trans*-[Fe(dmpe)$_2$(C≡CC$_6$H$_4$OCH$_3$)(η^1-C(C$_6$H$_5$)═CH(C≡CC$_6$H$_4$OCH$_3$))] (**9a**) as an orange air-sensitive solid (8 mg, 48%). $\nu_{\max}$ (KBr disk) 2050 ($\nu_{\mathrm{C\equiv C}}$), 2166 ($\nu_{\mathrm{C\equiv C}}$) cm^{-1}. ^{31}P{^{1}H} NMR (thf-*d*$_8$): δ 66.4 (s). ^{1}H{^{31}P} NMR (thf-*d*$_8$): δ 1.24 (s, 12H, PC**H**$_3$), 1.36 (s, 12H, PC**H**$_3$), 1.49−1.52 (m, 8H, PC**H**$_2$), 3.13 (s, 3H, C**H**$_3$O), 3.30 (s, 3H, C**H**$_3$O), 5.57 (s, C═C**H**), 6.51, 6.72, 6.82, 7.05, 7.07, 7.08−7.19 (m, 13H, Ar**H**). ^{13}C{^{1}H,^{31}P} NMR (thf-*d*$_8$): δ 19.4 (P**C**H$_3$), 21.9 (P**C**H$_3$), 33.2 (P**C**H$_2$), 56.6 (**C**H$_3$O), 56.7 (**C**H$_3$O), 88.3 (C≡**C**), 93.2 (**C**≡C), 115.3 (Ar**C**H), 115.6 (Ar**C**H), 119.5 (Fe−C≡**C**), 121.3 (═**C**H), 124.5 (Ar**C**H), 125.8 (Ar**C**), 128.7 (Ar**C**H), 131.4 (Ar**C**), 132.1 (Ar**C**H), 133.4 (Ar**C**H), 136.8 (Fe**C**═), 158.2 (Ar**C**O), 160.0 (Ar**C**O), 165.0 (Ar**C**), 205.8 (Fe**C**). *M/z* (E.S.) (%): 721 (100) (M + 1)$^+$, 356 (55).

Crystal Structure Determination for *trans*-[Fe(dmpe)$_2$(C≡CC$_6$H$_5$)(CH$_3$)] (1a), *trans*-[Fe(dmpe)$_2$(C≡CC$_6$H$_5$)(C≡CC$_6$H$_4$OCH$_3$)] (6b), and *trans*-[Fe(dmpe)$_2$(C≡CC$_6$H$_4$OCH$_3$)(η^1-C(C$_6$H$_5$)═CH(C≡CC$_6$H$_4$OCH$_3$))] (9a). Pertinent crystallographic details for **1a**, **6b**, and **9a** are listed in Table 6, and further detail is provided in the Supporting Information. Single-crystal X-ray diffraction data for **1a** and **9b** were collected with a Bruker SMART 1000 CCD diffractometer employing graphite monochromated Mo Kα generated from a sealed tube. The data integration and reduction were undertaken with SAINT and XPREP.[44] Data for **9a** were collected at 150(2) K using an Oxford Cryosystems Cryostream. Data for **6b** were obtained from a Rigaku AFC7R diffractometer employing graphite monochromated Cu Kα radiation from a rotating anode generator. The data processing and calculations for **6b** were undertaken with TEXSAN.[45] An empirical absorption correction determined with SADABS[46] was applied to the data obtained for **1a** and **9a**, and in the case of **9a** this was preceded by a Gaussian correction.[44] An empirical absorption correction based on azimuthal scans of three suitable reflections was applied to the data for **6b**. The data were corrected for Lorentz and polarization effects. The structures were solved by direct methods using the SIR97[47] (**1a** and **9a**) and SHELX86[48] (**6b**) computer programs, and refined with SHELXL-97[49] using the TEXSAN graphical user interface. ORTEP[33] depictions of the complex molecules with 20% atom displacement ellipsoids are provided in Figures 1−3. The non-hydrogen atoms were modeled with anisotropic displacement parameters and in general a riding atoms model was used for the hydrogen atoms. The H(3) hydrogen site in the structure of **9a** was located and modeled with an isotropic thermal parameter. The reflection intensity distribution for **6b** was ambiguous; however, the systematic absences clearly indicated the space group *P*21/*a*. Although the complex molecule **6b** does not have a center of symmetry, the molecule resides on a crystallographic inversion center in the centrosymmetric space group *P*21/*a*. Accordingly the structure has axial ligand disorder about the crystallographic inversion center, and the occupancies for the methoxy sites were refined and then fixed at 0.5. The residuals for the partial occupancy methoxy

Table 6. Crystallographic Data for *trans*-[Fe(dmpe)$_2$(C≡CC$_6$H$_5$)(CH$_3$)] (**1a**), *trans*-[Fe(dmpe)$_2$(C≡CC$_6$H$_5$)(C≡CC$_6$H$_4$OCH$_3$)] (**6b**), and *trans*-[Fe(dmpe)$_2$(C≡CC$_6$H$_4$OCH$_3$)(η^1-C(C$_6$H$_5$)═CH(C≡CC$_6$H$_4$OCH$_3$))] (**9a**)

compound	**1a**	**6b**	**9a**
empirical formula	C$_{21}$H$_{40}$FeP$_4$	C$_{29}$H$_{44}$FeOP$_4$	C$_{38}$H$_{52}$FeO$_2$P$_4$
formula weight	472.26	588.37	720.53
crystal system	monoclinic	monoclinic	triclinic
crystal habit	blade	cut prism	acicular
crystal color	orange	yellow	orange
space group	$P2_1/n$ (no. 14)	$P2_1/a$ (no. 14)	$P\bar{1}$ (no. 2)
Z value	4	2	2
a (Å)	9.1079(6)	9.108(2)	12.767(6)
b (Å)	8.9040(6)	18.090(3)	16.259(7)
c (Å)	30.985(2)	9.526(1)	9.811(4)
α (deg)			104.373(8)
β (deg)	95.7320(10)	94.42(1)	103.391(7)
γ (deg)			105.219(7)
V (Å$^{3)}$	2500.2(3)	1564.9(4)	1805.2(14)
T (°C)	21	21	−123
λ (Mo Kα, Å)	0.71073	1.54178 Å	0.71073
μ (Mo Kα, mm^{-1})	0.863	5.938	0.628
ρ_{calcd} (g cm^{-3})	1.255	1.249	1.326
GOF (all)	1.160	1.498	1.023
$R1(F)$,[d] $wR2(F^2)$[d]	0.0544, 0.1378[a]	0.0658, 0.1962[b]	0.0375, 0.0982[c]

[a] $w = 1/[\sigma^2(F_o^2) + (0.0488P)^2 + 2.6954P]$. [b] $w = 1/[\sigma^2(F_o^2) + (0.0700P)^2]$. [c] $w = 1/[\sigma^2(F_o^2) + (0.0476P)^2 + 0.7679$P] where $P = (F_o^2 + 2F_c^2)/3$. [d] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$ for $F_o > 2\sigma(F_o)$; $wR2 = (\sum w(F_o^2 - F_c^2)^2/\sum(wF_c^2)^2)^{1/2}$ for all reflections.

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model were significantly lower (1.2% lower for $R1(F)$ and 3.8% lower for $wR2(F^2)$) than a full occupancy methoxy model. Bond angle restraints were required for the methoxy residue of **6b**. An attempt to model the structure in the noncentrosymmetric space group $P2_1$ resulted in poor ligand geometry requiring restraints and rigid body refinement, presumably because of high levels of correlation and ligand disorder. The Flack[50] parameter for the $P2_1$ structure refined to 0.52(5), further supporting the decision to adopt the centrosymmetric structure as the best model. The methoxy residue site disorder persists in the $P2_1$ model.

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Supporting Information Available: X-ray crystallographic data files, in CIF format, for *trans*-[Fe(dmpe)$_2$(C≡CC$_6$H$_5$)(CH$_3$)] (**1a**), *trans*-[Fe(dmpe)$_2$(C≡CC$_6$H$_5$)(C≡CC$_6$H$_4$OCH$_3$)] (**6b**), and *trans*-[Fe(dmpe)$_2$(C≡CC$_6$H$_4$OCH$_3$)(η^1-C(C$_6$H$_5$)=CH(C≡C-C$_6$H$_4$OCH$_3$))] (**9a**); synthetic procedures and spectral data for bis(phenylethynyl)magnesium, bis(4-methoxyphenylethynyl)magnesium, *trans*-[Fe(dmpe)$_2$(CH$_3$)Cl] (**3**), and *trans*-[Fe(depe)$_2$(CH$_3$)Cl] (**4**) (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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