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Protonation and Rearrangement of Bis(acetylide) Complexes of Iron: Formation of Coordinated η^3-Butenynes

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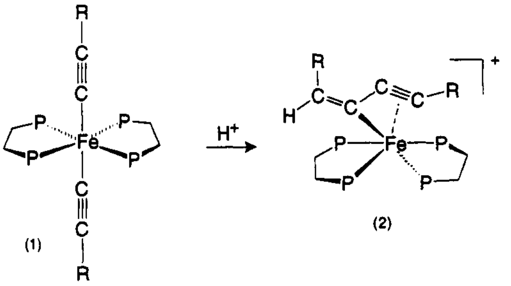
Bis(acetylide) complexes of iron(II) phosphines $Fe(DMPE)_2$ (DMPE = $(CH_3)_2PCH_2CH_2P(CH_3)_2$) rearrange in the presence of mild acids to give cationic complexes of general formula $[Fe(\eta^3\text{-}C(C{\equiv}CR){=}CHR)(DMPE)_2]^+$, containing an η^3-bound but-1-en-3-yn-2-yl ligand. A number of iron complexes with coordinated butenyne ligands have been fully characterized as their hexafluorophosphate salts, and their synthesis and properties are reported.

Introduction

Coordinated butenynes were first characterized crystallographically in the stable ruthenium complex $Ru(C(C{\equiv}CPh){=}CHPh)(O_2CCF_3)(CO)(PPh_3)_2$ in 1979,[1] and structures have been determined more recently for butenyne complexes of osmium,[2] iron,[3] tungsten,[4] and other complexes of ruthenium.[5-7] We have previously reported the formation of the complex $[Fe(\eta^3\text{-}C(C{\equiv}CPh){=}CHPh)(DMPE)_2]^+[PF_6]^-$ (DMPE = $(CH_3)_2PCH_2CH_2P(CH_3)_2$) as a product of the reaction of $FeCl_2(DMPE)_2$ with excess phenylacetylene under protic conditions in the presence of hexafluorophosphate.[8] During our investigations of the chemistry of acetylide and bis(acetylide) complexes of iron,[9] we have established that cationic complexes of general formula $[Fe(\eta^3\text{-}C(C{\equiv}CR){=}CHR)(DMPE)_2]^+$ (**2**) are readily formed from *trans*-$Fe(C{\equiv}CR)_2(DMPE)_2$ (**1**) complexes, by protonation and rearrangement (Scheme I).

Species containing substituted η^3-but-1-en-3-yne ligands have been suggested as key intermediates in alkyne dimerization/oligomerization processes, and there has been growing interest in the use of transition-metal complexes and clusters to mediate head-to-head and head-to-tail dimerization of 1-alkynes.[5,10] The substituted but-1-en-3-yn-2-yl ligand may coordinate in an η^1 fashion or an η^3 fashion,[11] depending on the requirements of the metal center, and it has been suggested that a change in coordination mode from η^3 to η^1 may be involved in the catalytic formation of C_4 units from terminal acetylenes.[10b]

Scheme I



The osmium complexes $Os(O_2CCF_3)_2(CO)(PPh_3)_2$, $OsH(O_2CCF_3)(CO)(PPh_3)_2$, and $Os(C(C{\equiv}CPh){=}CHPh)(O_2CCF_3)(CO)(PPh_3)_2$ serve as catalysts in the oligomerization of phenylacetylene to an uncharacterized hydrocarbon solid with a molecular weight in the range 800–1200,[7] while the cobalt and rhodium analogues show promise as selective dimerization agents.[10a,d,e] Thermal decomposition of the complexed C_4 unit results in formation of a 1,4-disubstituted buta-1,3-diyne in the case of a tris(trimethylphosphine)rhodium(I) chloride complex[10a] and cis-1,4-disubstituted butatriene in the case of $Ru(C(C{\equiv}CC(CH_3)_3){=}CHC(CH_3)_3)Cl(CO)(PPh_3)_2$.[10b] Titanocene species, generated in situ from $(\eta^5\text{-}C_5Me_5)_2TiCl_2$, are known to promote head-to-tail dimerization of terminal acetylenes under catalytic conditions.[12] There have been few mechanistic studies of transition-metal-mediated alkyne dimerization, although the kinetics of reductive elimination of an enyne from $Pt(PPh_3)_2(C(CH_2)CH_3)(C{\equiv}CC(CH_3)_3)$ has been investigated in detail by Stang and Kowalski.[13]

The formation of the complexes containing the but-1-en-3-yn-2-yl ligand has also been effected by direct reaction of a metal hydride with a 1,4-disubstituted but-1,3-diyne[7,10b] or with terminal acetylenes.[1,5] When bis(phenylethynyl)mercury is employed as a source of acetylide, mercury may be retained in the ligand as a substituent at the 1-position.[14]

In this paper, we report details of the chemistry, synthesis, and properties of a series of (η^3-butenyne)iron complexes.

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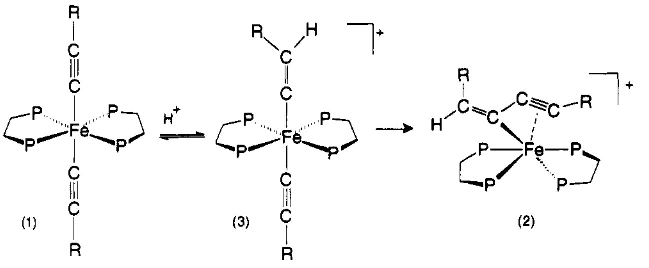
Scheme II



a $R = -CH_3$
b $R = -C(CH_3)_3$
c $R = -Ph$
d $R = -4-(HC\equiv C)C_6H_4$
e $R = -3,5-(HC\equiv C)_2C_6H_3$

Results and Discussion

Protonation and Rearrangement of Iron(II) Bis(acetylide) Complexes 1. In previous work,[9] we described the synthesis and structures of a number of bis(acetylide) complexes of iron(II), formed by reaction of terminal acetylenes with $FeH_2(DMPE)_2$ in alcohol solution. The iron bis(acetylide) complexes $Fe(C\equiv CR)_2(DMPE)_2$ (1) are reversibly protonated under mild conditions to form vinylidene complexes 3.

Protonation of any of the iron bis(acetylide) complexes 1, with trifluoroacetic acid (TFA) in tetrahydrofuran solvent, results in an immediate color change of the solution from yellow to green. The single ^{31}P resonance of the starting bis(acetylide) complexes (ca. δ 70 ppm) moves upfield by approximately 12 ppm on formation of the trans acetylide vinylidene complexes 3. Although we have not isolated the metal vinylidene species from the reaction mixture, electrophilic attack of metal acetylides at the carbon β to the metal center is one of the most important reactions of metal acetylides and protonation to form metal vinylidenes is well established.[15] Fast rotation around the bond between iron and the vinylidene carbon renders all four phosphorus atoms equivalent.[16] The vinylidene complexes 3 rearrange quantitatively over a period of several hours in solution, with coupling of the acetylenic and vinylic fragments, to yield deep red solutions containing $[Fe(\eta^3-C(C\equiv CR)=CHR)(DMPE)_2]^+$ (2; Scheme II).

The rearrangement and coupling is an intramolecular process. When $Fe(C\equiv CPh)_2(DMPE)_2$ (1c) was protonated and the rearrangement performed in the presence of a large excess of either *tert*-butylacetylene or 1,4-diethynylbenzene, no incorporation of the added ligand was observed. Similarly, when $Fe(C\equiv CC(CH_3)_3)_2(DMPE)_2$ (1b) was protonated and allowed to rearrange in the presence of excess phenylacetylene, no mixed coupling products were formed. The reaction probably involves a trans to cis isomerization of the vinylidene acetylide complex followed by coupling of the acetylide ligand to the α-carbon of the vinylidene fragment.

An authentic sample of the 1,4-diphenyl derivative 2c was obtained in an independent synthesis by treatment of $FeH_2(DMPE)_2$ with 1,4-diphenyl-1,3-butadiyne in alcohol solution.

Relative Rates of Rearrangement. The rate of protonation and rearrangement of $Fe(C\equiv CR)_2(DMPE)_2$ complexes depends markedly on the nature of the acetylene substituent, –R. In this multistep reaction, the transformation of the bis(acetylide) complex to one containing an η^3-butenyne ligand depends on a combination of factors which may include the ease of protonation and the rates of trans to cis isomerization and formation of the new carbon–carbon bond, as well as the capacity of the product complex to coordinate the η^3-butenyne ligand.

$Fe(C\equiv CCH_3)_2(DMPE)_2$ (1a) rearranged readily to $[Fe(\eta^3-C(C\equiv CCH_3)=CHCH_3)(DMPE)_2]^+$ (2a) in methanol solution at ambient temperatures without the addition of any other proton source. With the *tert*-butyl or aryl substituents, however, protonation to form the vinylidene intermediate required the addition of 1 drop of TFA to the solution. The aryl-substituted complexes rearranged over a period of a few hours, while the complex containing the *tert*-butyl substituent required approximately 24 h at room temperature before formation of the butenyne complex 2b was complete. For those substituted acetylides $Fe(C\equiv CR)_2(DMPE)_2$ (1) examined in this work, the ease of rearrangement followed the sequence

$$R = -CH_3 > -Ph > -4-(HC\equiv C)C_6H_4 > -3,5-(HC\equiv C)_2C_6H_3 \gg -C(CH_3)_3$$

Spectroscopic Characterization of $[Fe(\eta^3-C(C\equiv CR)=CHR)(DMPE)_2]^+$ (2). The butenyne complexes 2a–e are all highly colored red or brown solids with strong characteristic absorption bands in the range 410–470 nm in the visible region of the spectrum as well as in the regions 230–275 and 300–370 nm. No infrared absorption associated with the π-bound $C\equiv C$ triple bond was observed, although complexes containing an uncoordinated acetylene (2d,e) displayed weak bands near 2100 cm^{-1} associated with the $C\equiv C$—H triple bonds.

The ^{31}P NMR spectra of the butenyne complexes 2a–e exhibit four distinct phosphorus resonances, characteristic of an unsymmetrically substituted octahedral cis complex containing a MP_4 ligand set. Formally, each signal appears as a doublet of doublets of doublets (ddd) due to coupling with the three other phosphorus atoms. In all of the complexes, the two mutually trans phosphorus atoms exhibit a notably large coupling constant ($^2J_{PP} > 160$ Hz), while the value of $^2J_{PP}$ for the pairs of cis phosphorus atoms is generally in the range 20–50 Hz. The unambiguous assignment of the ^{13}C, ^{31}P, and ^1H spectra of $[Fe(\eta^3-C(C\equiv CCH_3)=CHCH_3)(DMPE)_2]^+$ (2a) was achieved using a combination of $^{31}P-^1H$, $^{13}C-^1H$ correlation spectroscopy and $^1H-^1H$ NOESY techniques. The phosphorus atom trans to the coordinated $C\equiv C$ moiety resonates to higher field than the other three phosphorus atoms. The ^1H NOESY spectrum indicates that the basic structure of 2a in solution corresponds to the X-ray crystal structure,[17] with the substituents of the coordinated butenyne directed away from the metal center and the vinylic hydrogen projecting toward the coordinated phosphines.

In the $^{13}C\{^1H\}$ NMR spectra of the complexes 2a–e, C2 of the coordinated η^3-but-1-en-3-yne ligand resonates between δ 155 and 165 ppm and the signal exhibits visible broadening due to coupling to ^{31}P. A chemical shift of δ 142 ppm has been observed for the bound vinylic carbon atom in the ruthenium complex $[Ru(\eta^3-RC_3CHR)(PhP(OEt)_2)_4][PF_6]$ (R = *p*-tolyl).[6a]

The ^{13}C resonances assigned to the "acetylenic" carbons (C3 and C4) of the coordinated η^3-but-1-en-3-yne ligand are shifted significantly compared to resonances for uncoordinated acetylenes, suggesting a deviation from typical sp hybridization. In the $^{13}C\{^1H\}$ NMR spectrum of 2c, C3 and C4 of the coordinated η^2-but-1-en-3-yn-2-yl ligand

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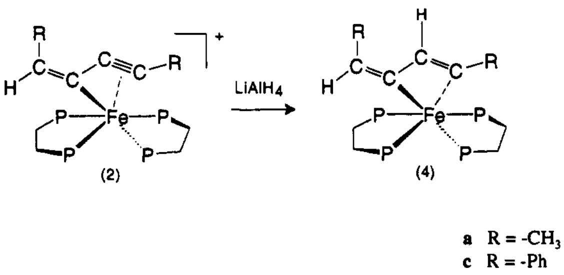
Scheme III



appear at δ 108.4 and 52.0 ppm, respectively, in contrast to the corresponding acetylenic carbons in unbound 1,4-diphenylbut-1-en-3-yne, which resonate at δ 89.8 and 92.3 ppm.[18] A single-crystal X-ray diffraction study on compound **2c**[3] reported a C2–C3–C4 bond angle of 149° and a C3–C4–Ph angle of 153°, and the C2–C3–C4 and C3–C4–CH_3 bond angles in **2a** are 147 and 149°, respectively,[17] consistent with η^3 binding of the ligand in both complexes. In contrast, in the structures of the complexes $Ru(C(C{\equiv}CPh){=}CHPh)(O_2CCF_3)(CO)(PPh_3)_2$[7] and $Ru(C(C{\equiv}CPh){=}C(Ph)HgCl)(CO)_2Cl(PMe_2Ph)_2$,[14] the corresponding angles are 173, 176° and 175, 176°, respectively, indicating a greater linearity of the butenyne fragment in these cases where the butenyne ligand is bound effectively in an η^1 fashion. As the mode of bonding moves from η^1 toward η^3 coordination, X-ray data show that there is also a lengthening of the C≡C triple bond and shortening of the C2–C3 bond in the coordinated butenyne.

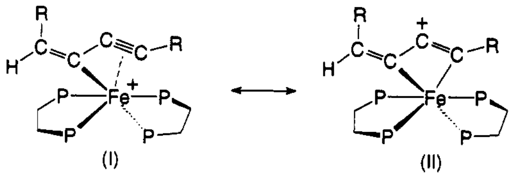
Reaction of $[Fe(\eta^3\text{-}C(C{\equiv}CR){=}CHR)(DMPE)_2]^+$ with Hydroxide and *tert*-Butoxide. When the phenyl-substituted butenyne complex **2c** is heated under reflux for 2 h in a tetrahydrofuran–ethanol solution saturated with potassium hydroxide or in a tetrahydrofuran solution saturated with potassium *tert*-butoxide, the iron bis(phenylacetylide) complex **1c** is reformed. The reaction probably proceeds by base abstraction of the proton from the 1,4-diphenylbut-1-en-3-yn-2-yl ligand with cleavage of the C2–C3 bond and cis to trans isomerization of the complex.

Nitrogen bases such as pyridine have no effect on a solution of the complex **2c** when stirred at room temperature. However, treatment of the complex **2c** with lithium phenylmethanethiolate, under similar conditions, resulted in the disappearance of the complexed phosphine resonances in the ^{31}P NMR spectrum and the appearance of a singlet associated with uncoordinated DMPE.

The conversion of iron bis(acetylides) to complexes with η^3-butenyne ligands under mildly acidic conditions and the reversal of this reaction with base suggest that the $Fe(DMPE)_2$ subunit may mediate in the synthesis and cleavage of carbon–carbon bonds.

Reaction of $[Fe(\eta^3\text{-}C(C{\equiv}CR){=}CHR)(DMPE)_2]^+$ with Lithium Aluminum Hydride. Treatment of the butenyne complexes **2a,c** with lithium aluminum hydride resulted in addition of hydride to C3 of the butenyne ligand with formation of 1,4-disubstituted but-1,3-diene-2,4-diyl iron complexes **4a,c** (Scheme III).

Attack of hydride at C3 of the butenyne ligand may be rationalized by considering canonical forms of the complex **2** where positive charge is concentrated at this position (structure II).



Formation of metallacyclobutenes such as **4a** and **4c** has been observed previously on addition of a second equivalent of acetylene to a metal acetylene complex,[19] by insertion of a methylene group into a π-bound acetylene,[20] or by the oxidative addition of cyclopropene to platinum(0) or iridium(I) complexes.[21] Although butenyne complexes may be intermediates in the formation of metallacyclobutene complexes, there are no previous reports of their formation from isolated samples of butenyne complexes.

The complex **4c** is stable for periods of several days in solution, but attempts to isolate it by removal of the solvent resulted only in decomposition. In the ^{13}C NMR spectrum of the ferracyclic complex **4c** the iron-bound carbons appear in the low-field region of the spectrum (δ 167 and 168 ppm) with strong coupling to phosphorus. A third resonance at δ 143 ppm displayed weak coupling to phosphorus and was assigned to the protonated carbon (C3) of the metallacyclic ring. The ^1H NMR spectrum of **4c** showed two resonances associated with the single protons attached to C1 and C3 at δ 6.2 and 8.0 ppm, respectively, with the resonance at δ 8.0 displaying weak coupling to phosphorus. In the ^1H NMR spectrum of the analogous complex with methyl substituents, **4a**, the resonance associated with the vinylic proton C1–H appears as a quartet at δ 4.8 ppm, while the proton attached to C3 resonates at δ 7.8 ppm and is broadened by coupling to the phosphorus atoms.

Conclusions

Bis(acetylide) complexes of iron are protonated under mildly acidic conditions at the β-carbon of the acetylide ligand. The vinylidene complexes so formed rearrange to stable cationic complexes containing 1,4-disubstituted but-1-en-3-yn-2-yl ligands bound to the metal in an η^3 fashion.

The butenyne complexes have moderate thermal stability under neutral and acidic conditions. In the presence of a base, however, proton abstraction and rearrangement to form *trans*-bis(acetylide)iron complexes occurs. In the presence of hydride or strong carbon nucleophiles, reaction to form a 1,3-butadiene-2,4-diyl complex occurs rapidly at room temperature.

Experimental Section

General Data. All reactions and manipulations were performed under nitrogen in a drybox or in a Schlenk apparatus. Tetrahydrofuran was distilled from benzophenone ketyl under nitrogen prior to use. Methanol and ethanol were dried by distillation from magnesium methoxide and magnesium ethoxide, respectively.[22] Trifluoroacetic acid (Merck) was distilled and potassium hexafluorophosphate (Merck) was recrystallized from aqueous sodium hydroxide prior to use. Phenylacetylene (Aldrich) and *tert*-butylacetylene (Aldrich) were used as received. *trans*-$Fe(C{\equiv}CR)_2(DMPE)_2$ complexes,[9] $FeH_2(DMPE)_2$,[23] and 1,4-di-

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ethynylbenzene[24] were prepared according to literature procedures. ^1H (400.1 MHz), ^{31}P (162.0 MHz), and ^{13}C (100.6 MHz) NMR spectra were recorded on a Bruker AMX-400 spectrometer, in the solvents indicated. ^1H and ^{13}C spectra were referenced to solvent residuals, and ^{31}P spectra were referenced to external neat trimethyl phosphite, taken to be δ 140.85 ppm. UV–visible spectra were recorded on a Hitachi 150-20 spectrometer with THF as the solvent. Infrared spectra were recorded using a Bio-Rad FTS 20/60 spectrometer with the sample pressed into a KBr disk. Microanalyses were performed by National Analytical Laboratories (NAL). All solvents were degassed by three to five freeze–pump–thaw cycles prior to use. Nitrogen (>99.5%) and propyne (>96.0%) were obtained from Commonwealth Industrial Gases (CIG) and used as received.

$[Fe(\eta^3\text{-}C(C\equiv CCH_3)=CHCH_3)(DMPE)_2]^+[PF_6]^-$ (2a). A solution of $FeH_2(DMPE)_2$ (20 mg, 56 μmol) in methanol (3 mL) was added to a methanol solution of propyne (2 mL, 0.22 M) with vigorous stirring. The color of the solution changed from yellow to orange after 1 h. Potassium hexafluorophosphate (10 mg, 56 μmol) was added to the solution, and the solvent was removed. The residue was recrystallized from ethanol to yield red needles of $[Fe(\eta^3\text{-}C(C\equiv CCH_3)=CHCH_3)(DMPE)_2]^+[PF_6]^-$ (**2a**; 26 mg, 80%): decomposed without melting >185 °C. Anal. Calcd for $FeC_{18}H_{39}P_5F_6$: C, 37.26; H, 6.78. Found: C, 36.8; H, 6.8. $^{31}P\{^1H\}$ NMR (methanol): δ 53.1 (ddd, $^2J_{P1P2}$ = 37 Hz, $^2J_{P1P3}$ = 21 Hz, $^2J_{P1P4}$ = 29 Hz, 1 P, *P1*), 58.7 (ddd, $^2J_{P2P3}$ = 34 Hz, $^2J_{P2P4}$ = 171 Hz, 1 P, *P2*), 62.1 (ddd, $^2J_{P3P4}$ = 47 Hz, 1 P, *P3*), 63.9 (ddd, 1 P, *P4*). $^1H\{^{31}P\}$ NMR (acetone-d_6): δ 0.69 (s, 3 H, CH_3), 0.84 (s, 3 H, CH_3), 1.41 (s, 3 H, CH_3), 1.46 (s, 3 H, CH_3), 1.62 (s, 3 H, CH_3), 1.87 (s, 3 H, CH_3), 2.04 (s, 3 H, CH_3), 2.29 (s, 3 H, CH_3), 1.8–2.4 (m, 8 H, CH_2), 2.37 (d, $^3J_{HH}$ = 6.4 Hz, 3 H, $C=CHCH_3$), 2.65 (s, 3 H, $C\equiv CCH_3$), 6.35 (q, $^3J_{HH}$ = 6.4 Hz, 1 H, $C=CHCH_3$). $^{13}C\{^1H,^{31}P\}$ (tetrahydrofuran-d_8): δ 10.0 (CH_3), 10.8 (CH_3), 12.3 ($C\equiv CCH_3$), 17.5 (CH_3), 19.0 (CH_3), 21.9 (CH_3), 21.9 (CH_3), 22.7 (CH_3), 23.0 (CH_3), 27.9 ($C=CHCH_3$), 28.9 (CH_2), 29.9 (CH_2), 34.4 (CH_2), 35.0 (CH_2), 106.1 ($C\equiv CCH_3$), 119.5 ($C\equiv CCH_3$), 128.8 ($C=CHCH_3$), 159.0 (FeC). λ_{max} (tetrahydrofuran, log ϵ): 238 (4.34), 336 (3.38), 466 nm (2.69). ν_{max} (KBr disk): 2980, 2912, 2841, 1423, 1303, 1284, 933, 894, 838, 727, 699, 557 cm^{-1}.

$[Fe(\eta^3\text{-}C(C\equiv CC(CH_3)_3)=CHC(CH_3)_3)(DMPE)_2]^+[PF_6]^-$ (2b). One drop of TFA (ca. 4 μmol) was added to a stirred solution of *trans*-$Fe(C\equiv CC(CH_3)_3)_2(DMPE)_2$ (**1b**; 20 mg, 39 μmol) in tetrahydrofuran (2 mL). Over a period of 4 days the color of the solution changed from green to orange to brown. Potassium hexafluorophosphate (10 mg, 56 μmol) was added, and the solvent was removed under vacuum. The residue was recrystallized from ethanol, to yield $[Fe(\eta^3\text{-}C(C\equiv CC(CH_3)_3)=CHC(CH_3)_3)(DMPE)_2]^+[PF_6]^-$ (**2b**; 26 mg, 98%) as a dark brown solid: decomposed without melting >220 °C. Anal. Calcd for $FeC_{24}H_{51}P_5F_6$: C, 43.39; H, 7.74. Found: C, 43.6; H, 7.4. $^{31}P\{^1H\}$ NMR (tetrahydrofuran-d_8): δ 51.3 (ddd, $^2J_{PP}$ = 19, 24, 38 Hz, 1 P), 53.2 (ddd, $^2J_{PP}$ = 36, 174 Hz, 1 P), 61.1 (ddd, $^2J_{PP}$ = 50 Hz, 1 P), 62.7 (ddd, 1 P). ^1H NMR (acetone-d_6): δ 0.81 (d, $^2J_{PH}$ = 8.8 Hz, 3 H, CH_3), 0.95 (d, $^2J_{PH}$ = 8.8 Hz, 3 H, CH_3), 1.42 (d, $^2J_{PH}$ = 7 Hz, 3 H, CH_3), 1.42 (s, 9 H, $C(CH_3)_3$), 1.52 (d, $^2J_{PH}$ = 7.6 Hz, 3 H, CH_3), 1.61 (s, 9 H, $C(CH_3)_3$), 1.62 (d, J_{PH} = 7.3 Hz, 3 H, CH_3), 1.88 (d, $^2J_{PH}$ = 7.6 Hz, 3 H, CH_3), 2.01 (d, $^2J_{PH}$ = 8.9 Hz, 3 H, CH_3), 2.44 (d, $^2J_{PH}$ = 7.6 Hz, 3 H, CH_3), 1.5–2.2 (m, 8 H, CH_2), 6.41 (s, 1 H, $C=CHBu^t$). $^{13}C\{^1H,^{31}P\}$ NMR (dichloromethane-d_2): δ 10.6 (CH_3), 10.7 (CH_3), 16.7 (CH_3), 20.0 (CH_3), 20.5 (CH_3), 21.0 (CH_3), 22.3 (CH_3), 28.1 (CH_3), 29.1 (CH_2), 29.7 (CH_2), 31.0 (3 C, $C(CH_3)_3$), 33.4 (3 C, $C(CH_3)_3$), 34.1 (CH_2), 34.4 (CH_2), 38.2 ($C(CH_3)_3$), 47.5 ($C(CH_3)_3$), 114.9 ($C\equiv CBu^t$), 142.1 ($C\equiv CBu^t$), 145.0 ($C=CHBu^t$), 163.7 (FeC). λ_{max} (tetrahydrofuran, log ϵ): 274 (4.49), 376 (3.78), 420 nm (3.96). ν_{max} (KBr disk): 3060, 2991, 2910, 1590, 1491, 1423, 1305, 1285, 931, 838, 697, 559 cm^{-1}.

$[Fe(\eta^3\text{-}C(C\equiv CPh)=CHPh)(DMPE)_2]^+[PF_6]^-$ (2c). One drop of TFA (ca. 4 μmol) was added to a stirred solution of *trans*-$Fe(C\equiv CPh)_2(DMPE)_2$ (**1c**; 20 mg, 35 μmol) in tetrahydrofuran (2 mL). The color of the solution immediately changed from yellow to green and, over a period of 24 h, finally to red. Potassium hexafluorophosphate (10 mg, 56 μmol) was added, and the solvent was removed under vacuum. The residue was recrystallized from ethanol to give $[Fe(\eta^3\text{-}C(C\equiv CPh)=CHPh)(DMPE)_2]^+[PF_6]^-$ (**2c**; 17 mg, 69%) as a dark red powdery solid: decomposed without melting >320 °C. Anal. Calcd for $FeC_{28}H_{43}P_5F_6$: C, 47.75; H, 6.15. Found: C, 47.5; H, 6.2. $^{31}P\{^1H\}$ NMR (acetone-d_6): δ 49.5 (ddd, $^2J_{PP}$ = 28, 31, 46 Hz, 1 P), 56.2 (ddd, $^2J_{PP}$ = 41, 185 Hz, 1 P), 62.8 (ddd, $^2J_{PP}$ = 21 Hz, 1 P), 63.1 (ddd, 1 P). ^1H NMR (acetone-d_6): δ 0.96 (d, $^2J_{PH}$ = 8.8 Hz, 3 H, CH_3), 1.08 (d, $^2J_{PH}$ = 8.8 Hz, 3 H, CH_3), 1.35 (m, 1 H, CH_2), 1.54 (d, $^2J_{PH}$ = 6.8 Hz, 3 H, CH_3), 1.55 (d, $^2J_{PH}$ = 6.8 Hz, 3 H, CH_3), 1.69 (d, $^2J_{PH}$ = 7.8 Hz, 3 H, CH_3), 1.70 (d, $^2J_{PH}$ = 7.8 Hz, 3 H, CH_3), 1.88 (d, $^2J_{PH}$ = 7.2 Hz, 3 H, CH_3), 1.7–2.3 (m, 8 H, CH_2), 2.23 (d, $^2J_{PH}$ = 8.8 Hz, 3 H, CH_3), 7.34 (m, 1 H, Ar *H*), 7.51 (m, 2 H, Ar *H*), 7.61 (s, 1 H, $C=CHPh$), 7.63 (m, 5 H, Ar *H*), 7.94 (m, 2 H, Ar*H*). $^{13}C\{^1H,^{31}P\}$ NMR (acetone-d_6): δ 10.2 (CH_3), 10.8 (CH_3), 16.9 (CH_3), 18.4 (CH_3), 20.6 (CH_3), 20.7 (2 C, CH_3), 21.5 (CH_3), 28.0 (CH_2), 29.4 (CH_2), 33.4 (CH_2), 34.2 (CH_2), 52.0 ($C\equiv CPh$), 108.4 ($C\equiv CPh$), 126.9 (2 C, Ar *C*H), 127.7 (Ar *C*H), 129.8 (Ar *C*H), 130.1 (2 C, Ar *C*H), 130.7 (2 C, Ar *C*H), 131.1 (2 C, Ar *C*H), 131.1 (Ar *C*), 134.0 ($C=CHPh$), 139.6 (Ar *C*), 155.8 (FeC). λ_{max} (tetrahydrofuran, log ϵ): 274 (3.40), 372 (3.95), 413 nm (3.00). ν_{max} (KBr disk): 3060, 2987, 2908, 1589, 1491, 1422, 1285, 932, 892, 838, 696, 558 cm^{-1}.

$[Fe(\eta^3\text{-}C(C\equiv CPh)=CHPh)(DMPE)_2]^+[PF_6]^-$ (**2c**) was formed in an independent synthesis by reaction of 1,4-diphenyl-1,3-butadiyne[25] with $FeH_2(DMPE)_2$ in methanol solution. The product obtained after addition of potassium hexafluorophosphate was identical in all respects to **2c** described above.

$[Fe(\eta^3\text{-}C(C\equiv CC_6H_4C\equiv CH)=CHC_6H_4C\equiv CH)(DMPE)_2]^+[PF_6]^-$ (2d). One drop of TFA (ca. 4 μmol) was added to a stirred solution of *trans*-$Fe(C\equiv CC_6H_4C\equiv CH)_2(DMPE)_2$ (**1d**; 20 mg, 33 μmol) in tetrahydrofuran (2 mL). Over a period of 4 h the color of the solution changed from yellow to green and finally to red. Potassium hexafluorophosphate (10 mg, 56 μmol) was added, and the solvent was removed under vacuum. The residue was recrystallized from ethanol, to afford $[Fe(\eta^3\text{-}C(C\equiv CC_6H_4C\equiv CH)=CHC_6H_4C\equiv CH)(DMPE)_2)]^+[PF_6]^-$ (**2d**; 19 mg, 77%) as a dark red powdery solid: decomposed without melting >180 °C. Anal. Calcd for $FeC_{32}H_{43}P_5F_6$: C, 51.08; H, 5.76. Found: C, 51.0; H, 5.5. $^{31}P\{^1H\}$ NMR (acetone-d_6): δ 48.9 (ddd, $^2J_{PP}$ = 23, 25, 41 Hz, 1 P), 56.0 (ddd, $^2J_{PP}$ = 36, 165 Hz, 1 P), 62.4 (ddd, $^2J_{PP}$ = 24 Hz, 1 P), 63.0 (ddd, 1 P). ^1H NMR (acetone-d_6): δ 0.95 (d, $^2J_{PH}$ = 8.3 Hz, 3 H, CH_3), 1.06 (d, $^2J_{PH}$ = 8.3 Hz, 3 H, CH_3), 1.55 (d, $^2J_{PH}$ = 8.3 Hz, 3 H, CH_3), 1.56 (d, $^2J_{PH}$ = 8.3 Hz, 3 H, CH_3), 1.70 (d, $^2J_{PH}$ = 7.2 Hz, 3 H, CH_3), 1.78 (d, $^2J_{PH}$ = 8.3 Hz, 3 H, CH_3), 1.90 (d, $^2J_{PH}$ = 7.2 Hz, 3 H, CH_3), 2.25 (d, $^2J_{PH}$ = 9.3 Hz, 3 H, CH_3), 1.8–2.4 (m, 8 H, CH_2), 3.83 (s, 1 H, $C\equiv CH$), 4.02 (s, 1 H, $C\equiv CH$), 7.62 (m, 2 H, Ar*H*), 7.65 (m, 2 H, Ar *H*), 7.67 (s, 1 H, $C=CHAr$), 7.73 (m, 2 H, Ar *H*), 7.95 (m, 2 H, Ar *H*). $^{13}C\{^1H,^{31}P\}$ NMR (acetone-d_6): δ 10.2 (CH_3), 10.9 (CH_3), 16.8 (CH_3), 18.3 (CH_3), 20.6 (2 C, CH_3), 21.2 (CH_3), 21.3 (CH_3), 27.9 (CH_2), 29.2 (CH_2), 33.4 (CH_2), 34.0 (CH_2), 54.4 ($C\equiv CAr$), 80.0 ($C\equiv CH$), 81.4 ($C\equiv CH$), 84.2 ($C\equiv CH$), 84.9 ($C\equiv CH$), 110.1 ($C\equiv CAr$), 121.2 (Ar *C*), 126.8 (2 C, Ar *C*H), 129.5 (Ar *C*), 131.2 (2C, Ar *C*H), 132.1 (Ar *C*), 133.7 (2 C, Ar *C*H), 134.0 (2 C, Ar *C*H), 133.2 ($C=CHAr$), 139.6 (Ar *C*), 158.9 (FeC). λ_{max} (tetrahydrofuran, log ϵ): 300 (4.30), 370 (3.81), 429 nm (3.73). ν_{max} (KBr disk): 3278, 2975, 2914, 2105, 1690, 1588, 1500, 1421, 1304, 932, 841, 559 cm^{-1}.

$[Fe(\eta^3\text{-}C(C\equiv C\text{-}3,5\text{-}(C\equiv CH)_2C_6H_3)=CH\text{-}3,5\text{-}(C\equiv CH)_2C_6H_3)(DMPE)_2]^+[PF_6]^-$ (2e). One drop of TFA (ca. 4 μmol) was added to a stirred solution of *trans*-$Fe(C\equiv C\text{-}3,5\text{-}(C\equiv CH)_2C_6H_3)_2(DMPE)_2$ (**1e**; 20 mg, 30 μmol) in tetrahydrofuran (2 mL). Over a period of 24 h the color of the solution changed from yellow to green and finally to red. Potassium hexafluorophosphate (10 mg, 56 μmol) was added, and the solvent was removed under vacuum. The residue was recrystallized from ethanol, to give $[Fe(\eta^3\text{-}C(C\equiv C\text{-}3,5\text{-}(C\equiv CH)_2C_6H_3)=CH\text{-}3,5\text{-}(C\equiv CH)_2C_6H_3)(DMPE)_2]^+[PF_6]^-$ (**2e**; 19 mg, 78%) as a dark red powdery solid: decomposed without melting >140 °C. $^{31}P\{^1H\}$ NMR (acetone-d_6): δ 48.5 (ddd, $^2J_{PP}$ = 28, 28, 36 Hz, 1 P), 55.3 (ddd, $^2J_{PP}$ = 45, 166 Hz, 1 P), 61.2 (ddd, $^2J_{PP}$ = 36 Hz, 1 P), 62.6 (ddd, 1 P). $^1H\{^{31}P\}$ NMR (acetone-d_6): δ 0.9 (s, 3 H, CH_3), 1.0 (s, 3 H, CH_3), 1.6 (s, 6 H, CH_3), 1.7 (s, 3 H, CH_3), 1.9 (s, 6 H, CH_3), 2.3 (s, 3 H, CH_3), 1.8–2.4 (m, 8 H, CH_2), 3.8 (s, 2 H, $C\equiv C{-}H$), 4.0 (s, 2 H, $C\equiv C{-}H$), 8.0 (m, 4 H, Ar *H*), 8.1 (s, 1 H, $C=CHAr$). $^{13}C\{^1H,^{31}P\}$

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(tetrahydrofuran-d_8): δ 2.7 (CH$_3$), 11.2 (CH$_3$), 12.2 (CH$_3$), 17.5 (CH$_3$), 19.4 (CH$_3$), 21.5 (2 C, CH$_3$), 22.1 (CH$_3$), 28.9 (CH$_2$), 30.2 (CH$_2$), 32.0 (CH$_2$), 35.0 (CH$_2$), 78.4 (2 C, C≡CH), 79.9 (2 C, C≡CH), 82.7 (2 C, C≡CH), 83.4 (2 C, C≡CH), 108.6 (C≡CAr), 119.6 (C≡CAr), 125.3 (Ar CH), 129.6 (Ar CH), 132.1 (Ar CH), 132.5 (Ar CH), 128.0–133.0 (6 C, Ar C), 138.0 (C=CHAr), 157.3 (FeC). λ_{max} (tetrahydrofuran): 232, 295, 435 nm. ν_{max} (KBr disk): 3291, 3984, 2920, 2113, 1681, 1580, 1425, 1205, 1134, 934, 839, 559 cm^{-1}.

Reaction of *cis*-$[Fe(\eta^3\text{-}C(C{\equiv}CC_6H_5){=}CHC_6H_5)(DMPE)_2]^+[PF_6]^-$ (2c) with Lithium Aluminum Hydride. Lithium aluminum hydride (ca. 2 mg) was added directly to a solution of $[Fe(\eta^3\text{-}C(C{\equiv}CPh){=}CHPh)(DMPE)_2]^+[PF_6]^-$ (3c; 19 mg, 26 mmol) in tetrahydrofuran-d_8 (0.5 mL). The color of the solution faded, and the solution was filtered and used directly for NMR studies. By ^{1}H and ^{31}P NMR spectroscopy the reaction is quantitative and complete, giving only one product, whose spectroscopic data are consistent with the formulation $[\overline{Fe{-}C({=}CHPh)CH{=}C}Ph(DMPE)_2]$ (4c). $^{31}P\{^1H\}$ NMR (tetrahydrofuran-d_8): δ 57.7 (ddd, $^2J_{PP}$ = 9, 17, 24 Hz, 1 P), 62.3 (ddd, $^2J_{PP}$ = 24, 33 Hz, 1 P), 68.9 (ddd, $^2J_{PP}$ = 151 Hz, 1 P), 73.7 (ddd, 1 P). ^{1}H NMR (tetrahydrofuran-d_8): δ 0.82 (d, $^2J_{PH}$ = 6.4 Hz, 3 H, CH_3), 1.24 (d, $^2J_{PH}$ = 4.9 Hz, 3 H, CH_3), 1.27 (d, $^2J_{PH}$ = 5.2 Hz, 3 H, CH_3), 1.45 (d, $^2J_{PH}$ = 6.5 Hz, 3 H, CH_3), 1.57 (d, $^2J_{PH}$ = 6.2 Hz, 3 H, CH_3), 1.61 (d, $^2J_{PH}$ = 8.0 Hz, 3 H, CH_3), 1.65 (d, $^2J_{PH}$ = 6.7 Hz, 3 H, CH_3), 1.4–2.1 (m, 8 H, CH_2), 1.70 (d, $^2J_{PH}$ = 8.3 Hz, 3 H, CH_3), 6.16 (s, 1 H, C=CHPh), 6.85 (m, 1 H, Ar H), 7.00 (m, 2 H, CH), 7.13 (m, 5 H, Ar H), 7.23 (m, 2 H, Ar H), 7.96 (m, 1 H, C=CH). $^{13}C\{^1H,^{31}P\}$ NMR (tetrahydrofuran-d_8): δ 17.6 (CH$_3$), 18.3 (CH$_3$), 21.7 (CH$_3$), 22.0 (CH$_3$), 22.1 (CH$_3$), 23.3 (2 C, CH$_3$), 23.4 (CH$_3$), 32.4 (CH$_2$), 32.9 (CH$_2$), 35.9 (CH$_2$), 36.4 (CH$_2$), 123.4 (Ar CH), 124.4 (Ar CH), 126.5 (=CHPh), 127.2 (2 C, Ar CH), 128.6 (2 C, Ar CH), 129.0 (2 C, Ar CH), 129.3 (2 C, Ar CH), 141.9 (=CH), 143.3 (Ar C), 159.3 (Ar C), 166.6 (FeC), 167.5 (FeC).

Reaction of *cis*-$[Fe(\eta^3\text{-}C(C{\equiv}CCH_3){=}CHCH_3)(DMPE)_2]^+[PF_6]^-$ (2a) with Lithium Aluminum Hydride. Lithium aluminum hydride (ca. 2 mg) was added directly to a solution of $[Fe(\eta^3\text{-}C(C{\equiv}CCH_3){=}CHCH_3)(DMPE)_2]^+[PF_6]^-$ (3a; 19 mg, 26 mmol) dissolved in tetrahydrofuran-d_8 (0.5 mL). The color of the solution faded, and the solution was filtered and used directly for NMR studies. By ^{1}H and ^{31}P NMR spectroscopy the reaction is quantitative, giving only one product whose spectroscopic data are consistent with the formulation $[\overline{Fe{-}C({=}CHCH_3)CH{=}C}CH_3(DMPE)_2]$ (4a). $^{31}P\{^1H\}$ NMR (tetrahydrofuran-d_8): δ 61.5–62.0 (m, 2 P), 72.6 (m, 1 P), 74.9 (m, 1 P). $^1H\{^{31}P\}$ NMR (tetrahydrofuran-d_8): δ 0.93 (s, 3 H, CH_3), 0.98 (s, 3 H, CH_3), 1.15 (s, 3 H, CH_3), 1.17 (d, 6 H, CH_3), 1.21 (s, 3 H, CH_3), 1.28 (s, 3 H, CH_3), 1.33 (s, 3 H, CH_3), 1.4–2.1 (m, 8 H, CH_2), 1.85 (d, $^3J_{HH}$ = 6.0 Hz, 3 H, C=CHCH_3), 1.91 (s, 3 H, CH_3), 4.82 (q, $^3J_{HH}$ = 6.0 Hz, 1 H, C=CHCH$_3$), 7.79 (s, 1 H, C=CH). $^{13}C\{^1H,^{31}P\}$ NMR (tetrahydrofuran-d_8): δ 14.9 (CH$_3$), 17.2 (CH$_3$), 18.1 (CH$_3$), 22.6 (CH$_3$), 22.9 (CH$_3$), 23.0 (CH$_3$), 23.5 (CH$_3$), 24.2 (CH$_3$), 24.2 (CH$_2$), 32.0 (CH$_2$), 32.7 (CH$_2$), 32.7 (CH$_3$), 36.5 (CH$_2$), 36.5 (CH$_3$), 115.7 (C=CHCH$_3$), 139.1 (CH=CCH$_3$), 153.2 (FeC), 161.3 (FeC).

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Ligand Substitution Processes on Carbonylmetal Derivatives. 2. Reaction of Tetracarbonylhydridoferrates with Phosphites[1]

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Ligand substitution processes on $KHFe(CO)_4$ (1) have been evidenced by reaction with various phosphites. The nature of the reaction products strongly depends on (i) the nature of the solvent, (ii) the Tolman cone angle of the phosphite, and (iii) the reaction conditions. In *protic* media (H_2O–THF), phosphites with small cone angles, such as $P(OMe)_3$, $P(OEt)_3$, and $P(OPh)_3$, react (2 equiv) with 1 at room temperature to give the corresponding complexes $H_2Fe(CO)_2[P(OR)_3]_2$ in >90% yield, whereas a phosphite with a larger cone angle ($P[O\text{-}o\text{-}C_6H_4Ph]_3$) reacts only at a higher temperature to afford the disubstituted $Fe(CO)_3[P\{O\text{-}o\text{-}C_6H_4Ph\}_3]_2$ derivative in 94% yield. When the reaction with phosphites having small cone angles is conducted with a 3-fold excess of phosphite at 65 °C, the trisubtituted derivatives $Fe(CO)_2[P(OR)_3]_3$ are formed in 75–96% yield. In *aprotic* medium (THF), 1 reacts with phosphites (2 equiv) at room temperature to yield the monosubstituted anionic hydrides $K^+[HFe(CO)_3\{P(OR)_3\}]^-$, which can be isolated in >90% yield. In refluxing THF the reaction of 1 with $P(OMe)_3$ (3 equiv) demonstrates the first synthesis of the hydridoferrate $K^+[HFe(CO)_2\{P(OMe)_3\}_2]^-$. Protonation of $K^+[HFe(CO)_3\{P(OR)_3\}]^-$ with trifluoroacetic acid in THF at −10 °C provides an excellent route for the high-yield synthesis of the monosubstituted dihydrides $H_2Fe(CO)_3[P(OR)_3]$. In situ reaction of the latter with another phosphane PZ_3 (Z = Ph, OPh) leads to the mixed dihydrides $H_2Fe(CO)_2[P(OR)_3][PZ_3]$ (R = Me, Et; Z = Ph, OPh), which are reported for the first time. Finally, reaction of $H_2Fe(CO)_2[P(OEt)_3]_2$ with KH under sonication allows the generation of the highly reduced derivative $K_2[Fe(CO)_2\{P(OEt)_3\}_2]$, the first disubstituted analogue of the Collman reagent.

Introduction

A large number of $Fe(CO)_{4-n}L_n$ (n = 1, 2) complexes have been synthesized directly by ligand substitution on iron pentacarbonyl.[2-4] In contrast, direct ligand substitutions on tetracarbonylhydridoferrates $M^+[HFe(CO)_4]^-$ have never been reported as a route to the substituted

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