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The reaction of iron acetylides with carbon dioxide

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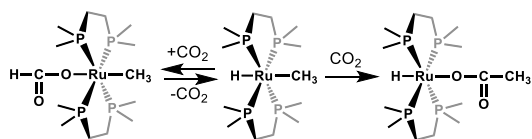
KEYWORDS. Carbon dioxide, CO₂ activation, metalalactone, metal acetylide, iron acetylide, metal hydride, iron hydride, metal formate, iron formate.

ABSTRACT: The acetylido iron hydride *trans*-[FeH(C≡CH)(depe)₂] reacts with an excess of CO₂ at ambient pressure and temperature to form a 5-membered metalalactone *cis*-[Fe(OC(=O)CHCH-κ²C,O)(depe)₂]. The reaction appears to proceed by electrophilic addition of CO₂ to the β-carbon of the coordinated acetylide and cyclization to form the metalalactone product. At low temperature, a second molecule of CO₂ is incorporated to give a carboxy-substituted metalalactone *cis*-[Fe(OC(=O)C(C(=O)OH)CH-κ²C,O)(depe)₂]. When the initial metal acetylido hydride is substituted at the β-acetylenic carbon, the addition of CO₂ results in a metalalactone where the substituent is in the position adjacent to the carbonyl in the metalalactone ring.

INTRODUCTION

The development of practical methods for sequestering and utilizing CO₂ is an important challenge for the sustainable management of this greenhouse gas.¹ CO₂ is an abundant feedstock that is a renewable 1-carbon synthon if synthetic pathways be established to useful commodity chemicals. Accordingly, there has been increasing interest in the use of transition metals to activate CO₂ and to promote reactivity toward organic substrates.²

In previous work, we have examined the reaction of CO₂ with iron and ruthenium hydrides and with iron and ruthenium alkyls.³ We noted that CO₂ readily inserted into the metal hydride and the metal alkyl bonds to give metal formates and metal carboxylates respectively. In the case of *trans*-[RuH(CH₃)(dmpe)₂] we observed the initial facile but reversible addition of CO₂ to the Ru-H bond to form the metal formate but over an extended period of time (or on heating) the thermodynamic product was that arising from insertion into the metal carbon-bond (Scheme 1).^{3c}



An inherent challenge to the industrial utilization of carbon dioxide as a chemical feedstock is the high thermodynamic stability of the molecule.⁴ Consequently, there has been a growing focus on the oxidative coupling of CO₂ with energetic substrates such as unsaturated hydrocarbons featuring C=C or C≡C bonds.²

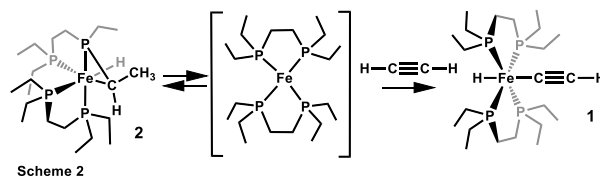
There has been considerable research⁵ targeting the coupling of carbon dioxide with alkenes such as ethylene, however, the investigation of the coupling of acetylenic substrates with CO₂ has been relatively less explored. Alkyne substrates offer the advantage that the C≡C functional group is generally less stable and more reactive than the C=C of alkenes, allowing for a more thermodynamically favorable coupling with the stable CO₂ molecule.⁶

Typically, the metal-mediated coupling of alkynes with carbon dioxide results in three broad reaction outcomes: (i) carboxylation;⁷ (ii) the formation of unsaturated metalalactones;⁸ or (iii) the formation of 2-pyrones.^{2, 7k, 9}

In this paper we describe the reaction of a series of hydrido iron acetylides with CO₂ with a view to exploring and understanding the mechanism for such reactivity.

RESULTS AND DISCUSSION

Trans-[FeH(C≡CH)(depe)₂] (**1**) (depe = 1,2-bis(diethylphosphino)ethane) was synthesized in near quantitative yield and in high purity by treatment of the cyclometalated complex [FeH{(CH₂CH(Et)PCH₂CH₂P(Et)₂-κ²C,P)}(depe)] (**2**) with acetylene (Scheme 2).



[FeH{(CH₃CH)(Et)PCH₂CH₂P(Et)₂-κ²C,P}(depe)] (**2**) is known to undergo reversible reductive elimination and oxidative addition via the coordinatively unsaturated, zero-valent species [Fe(depe)₂].¹⁰ This equilibrium means that the cyclometallated complex **2** effectively serves as a reservoir of [Fe(depe)₂] which can readily react with other substrates such as terminal acetylenes.

The acetylidohydride complex **1** was identified by the ¹H NMR signals at -17.68 and 1.12 ppm for the hydride and terminal acetylene protons respectively as well as the ³¹P NMR singlet at 92.5 ppm for the 4 equivalent P atoms and the ¹³C NMR signals at 97.5 and 132.2 ppm for the terminal acetylene carbon and iron-bound carbon respectively. Complex **1** is analogous to *trans*-[FeH(C≡CH)(dmpe)₂] (dmpe = 1,2-bis(dimethylphosphino)ethane) synthesized by treatment of [FeH(Np)(dmpe)₂] (Np = 2-naphthyl) with acetylene as reported by Ittel and Tolman.¹¹ The geometry of complex **1** was confirmed by X-ray crystallography (Figure 1, Table 1).

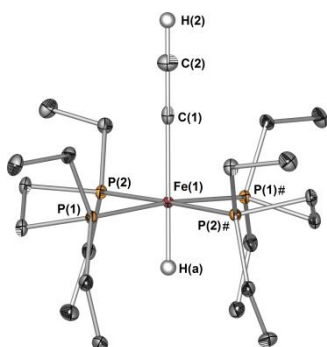


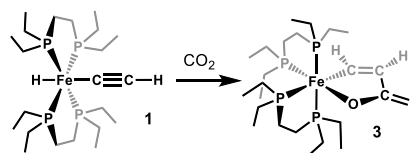
Figure 1. Solid state structure of *trans*-[FeH(C≡CH)(depe)₂] (**1**). Thermal ellipsoids are shown at the 50% probability level. Atoms denoted by a hash are generated through the symmetry operation -1/2-x, -1.5-y, z. Selected hydrogen atoms omitted for clarity.

Table 1. Selected average bond lengths and angles for *trans*-[FeH(C≡CH)(depe)₂] (**1**). Atoms denoted by hash are symmetry generated.

bond lengths / Å		bond angles / deg	
Fe(1)-C(1)	1.960(3)	P(1)-Fe(1)-P(2)#	93.771(17)
C(1)-C(2)	1.184(4)	P(1)-Fe(1)-P(2)	86.150(17)
Fe(1)-P(1)	2.1957(5)	P(1)-Fe(1)-C(1)	92.993(16)
Fe(1)-P(2)	2.1988(4)	P(2)-Fe(1)-C(1)	90.778(16)
Fe(1)-H	1.48(3)	Fe(1)-C(1)-C(2)	180

Treatment of *trans*-[FeH(C≡CH)(depe)₂] (**1**) with an excess of CO₂ at ambient pressure results in the exclusive formation of the unsaturated metalalactone *cis*-[Fe(OC(=O)CHCH-κ²C,O)(depe)₂] (**3**) in an isolated yield of 55% (Scheme 3).

The identity of the metalalactone **3** was established by NMR spectroscopy and growth of a crystal suitable for X-ray crystallography.



Scheme 3

The structure of **3** is given in Figure 2 and the key bond lengths and bond angles are given in Table 2. This structure represents the first example of an unsaturated iron-centered metalalactone.

The 4 mutually-coupled ³¹P NMR resonances at 66.1, 72.3, 76.2 and 83.0 ppm for metalalactone **3** are characteristic of an octahedral complex featuring 2 bidentate phosphine ligands and 2 non-identical ligands in the remaining *cis* disposed coordination sites. The phosphorus coupled ¹H NMR signals at 6.17 and 9.20 ppm collapse on ³¹P decoupling to doublets featuring an 8.2 Hz vicinal proton-proton coupling for the vinylic β and α protons respectively. The ¹³C NMR signals at 196.0, 182.2 and 136.1 ppm belong to the metal-bound carbon, the carbonyl carbon and the β-carbon respectively. These NMR features are consistent with those reported for related methyl propiolate¹² and metalalactone complexes.^{8a, 13}

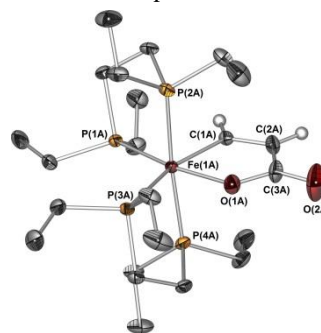


Figure 2. Solid state structure of *cis*-[Fe(OC(=O)CHCH-κ²C,O)(depe)₂] (**3**). Thermal ellipsoids are shown at the 50% probability level. Selected hydrogen atoms omitted for clarity.

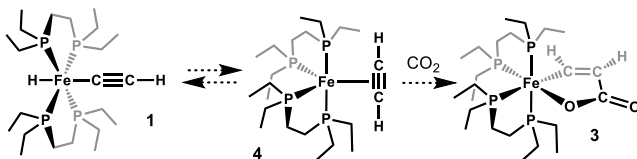
Table 2. Selected average bond lengths and angles for *cis*-[Fe(OC(=O)CHCH-κ²C,O)(depe)₂] (**3**).

bond lengths / Å		bond angles / deg	
Fe-C(1)	1.9755(19)	C(1)-Fe-O(1)	80.00(7)
Fe-O(1)	2.0254(14)	P(3)-Fe-O(1)	84.15(4)
C(3)-O(2)	1.240(3)	P(1)-Fe-P(3)	105.76(3)
O(1)-C(3)	1.304(2)	P(2)-Fe-P(4)	175.71(2)
C(1)-C(2)	1.335(3)	Fe-C(1)-C(2)	115.14(14)
Fe-P(1)	2.2029(7)	Fe-O(1)-C(3)	115.52(12)
Fe-P(2)	2.2194(7)	O(1)-C(3)-C(2)	113.92(17)
Fe-P(3)	2.2657(7)		
Fe-P(4)	2.2404(7)		

^a Average based upon corresponding bond parameters of the two molecular structures present in the asymmetric unit.

Typically, metalalactone formation proceeds through the electrocyclic coupling of a π-bound alkyne with carbon

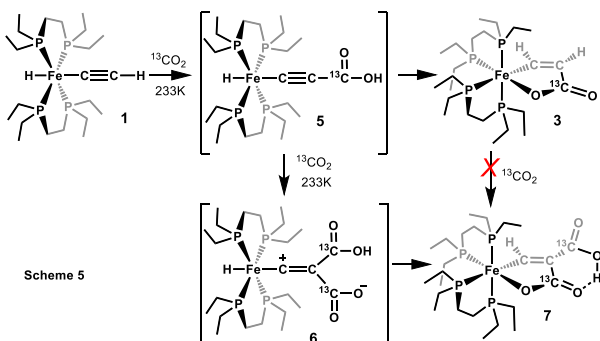
dioxide.^{6, 13c, i, 14} Accordingly, this could imply that the acetylide hydride complex *trans*-[FeH(C≡CH)(depe)₂] (**1**) exists in equilibrium with a π -CH≡CH isomer (**4**), which could subsequently undergo a nucleophilic cycloaddition with CO₂ (Scheme 4).



Scheme 4

We have not directly observed the π -CH≡CH isomer (**4**), however, an equilibrium between C-H activated acetylides and the η^2 -alkynes has been observed for [RhCl(η^2 -RC≡CH)(P^{*i*}Pr)₃]₂ (R = Ph, ^{*n*}Bu); however, the hydride and acetylide fragments in these complexes occupy mutually *cis* coordination sites.¹⁵

The addition of isotopically labelled ¹³CO₂ (3 atm) to a sample of *trans*-[FeH(C≡CH)(depe)₂] (**1**) at 233 K showed immediate reaction of CO₂ at the acetylenic carbon β to the metal to form an intermediate which we identify as the propiolic acid complex *trans*-[FeH(C≡C¹³C(=O)OH)(depe)₂] (**5**). After about 5 hours at 233 K, the intermediate **5** converted completely to a mixture of the unsaturated lactone product **3** as well as the doubly carboxylated product **7** (Scheme 5).



Scheme 5

It has not been possible to isolate complex **5**, however, the complex was spectroscopically characterized at 233 K. Complex **5** has a single ³¹P resonance at 83.7 ppm and this is consistent with the hydride and acetylide ligands occupying mutually *trans* positions in the coordination sphere. There is a ³¹P-coupled metal hydride resonance in the ¹H NMR spectrum at -8.16 ppm with a quintet splitting (²J_{PH} = 45.3 Hz). In addition, the resonance of the carboxylic acid proton appears at 18.37 ppm. The ¹³C-labelled carbon appears at 172.1 ppm in the ¹³C NMR spectrum.

The metalalactone **3** does not react with CO₂ under the reaction conditions, indicating that the carboxylated metalalactone **7** is not formed by direct carboxylation of metalalactone **3**. Moreover, if the reaction is conducted at 195 K, the carboxylated metalalactone **7** is formed exclusively after 24 hours. This suggests that **7** is formed from an intermediate (**6**) where 2 molecules of CO₂ add to the terminal carbon of the acetylide hydride complex (**1**), followed by cyclization to close the metalalactone ring. At

low temperatures, the conversion of intermediate **5** to metalalactone **3** is slowed down such that the second molecule of CO₂ is able to add to the β -carbon to form intermediate **6** quantitatively.

A crystal of the carboxylated metalacycle (**7**) suitable for X-ray crystallography was grown by slow evaporation of a THF-*d*₈ solution. The structure is given in Figure 3 and the key bond lengths and bond angles are given in Table 3. Similar to metalalactone **3**, complex **7** exhibits 4 mutually coupled ³¹P resonances at 64.1, 70.3, 78.7 and 82.5 ppm typical of an unsymmetrically substituted *cis* complex with bidentate phosphine ligands. The ¹H signals for the α -proton and the carboxylic acid proton are observed at 11.96 and 15.01 ppm respectively while ¹³C signals at 238.3, 183.2, 161.4 and 133.7 ppm were identified as corresponding to the α -carbon, carbonyl, carboxylic acid and β -carbon respectively. The ¹³C NMR spectrum of the carboxylated metalalactone **7** formed under ¹³C labelled ¹³CO₂, shows a ¹³C-¹³C coupling (7.9 Hz) between the carbonyl carbons verifying that both carbonyls derive from the labelled ¹³CO₂. In the ³¹P NMR spectrum, coupling is also observed between the labelled carbonyls and the phosphorus ligands.

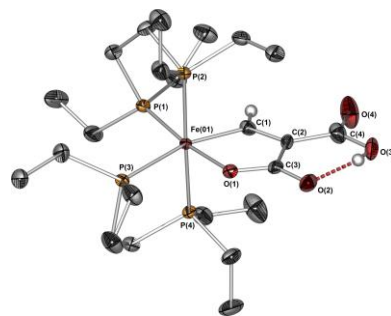
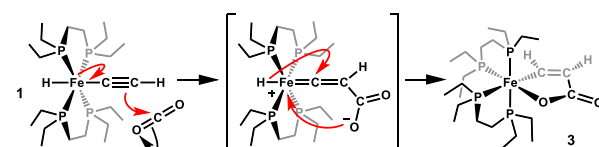


Figure 3. Solid state structure of λ -[Fe(O¹³C(=O)C(¹³C(=O)OH)CH- κ^2 C,O)(depe)₂] (**7**). Thermal ellipsoids are shown at the 50% probability level. Selected hydrogen atoms omitted for clarity. The dashed line between O(2)-H(4) denotes a hydrogen bond.

The insertion of CO₂ into the C-H bond of a σ -bound acetylide has not been previously reported, however, CO₂ is known to react with ethynyl Grignard reagents to generate carboxylated acetylenes as magnesium salts.¹⁶ Mechanistically, iron acetylides are well known to react with electrophiles at the β -acetylenic carbon, often via the formation of a vinylidene intermediate.¹⁷ Attack of the β -acetylenic carbon of the metal acetylide on the electrophilic carbon of CO₂ results in a vinylidene carboxylate and cyclization with migration of the metal-bound hydride would complete the formation of the metalalactone (**3**) (Scheme 6).^{17c}

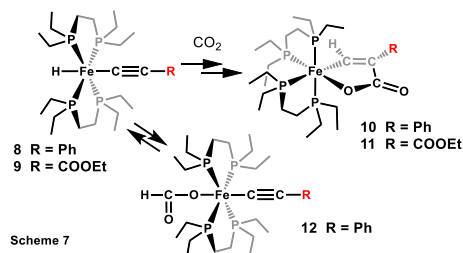


Scheme 6

Table 3. Selected bond lengths and angles λ -[Fe(O¹³C(=O)C(¹³C(=O)OH)CH- κ^2 C,O)(depe)₂] (**7**).

bond lengths / Å		bond angles / deg	
Fe-C(1)	1.928(3)	C(1)-Fe-O(1)	80.2(1)
Fe-O(1)	2.058(2)	P(3)-Fe-O(1)	87.66(6)
C(3)-O(2)	1.272(4)	P(1)-Fe-P(3)	97.38(3)
O(1)-C(3)	1.281(3)	P(2)-Fe-P(4)	178.01(3)
C(1)-C(2)	1.354(4)	C(1)-Fe-O(1)	95.5(1)
C(2)-C(3)	1.470(4)	Fe-O(1)-C(3)	114.5(2)
C(2)-C(4)	1.475(4)	Fe-C(1)-C(2)	115.9(2)
C(4)-O(3)	1.217(4)	C(1)-C(2)-C(3)	114.8(3)
C(4)-O(4)	1.388(4)	O(1)-C(3)-C(2)	114.5(3)
Fe-P(1)	2.2016(9)	C(3)-C(2)-C(4)	120.5(3)
Fe-P(2)	2.2526(9)	C(2)-C(4)-O(4)	116.1(3)
Fe-P(3)	2.2866(9)	C(1)-C(2)-C(4)-O(3)	178.3(3)
Fe-P(4)	2.2200(9)	O(4)-H(4)-O(2)	153.2(14)
O(4)-H(4)	1.756(7)		
O(4)-O(2)	2.534(3)		

If CO₂ reacts with analogues of the acetylidohydride complex *trans*-[FeH(C≡CH)(depe)₂] (**1**) which have been substituted at the β -acetylenic carbon, such as *trans*-[FeH(C≡CR)(depe)₂] (R = Ph, **8**; R = COOEt, **9**), then the product metalalactone is formed where the substituent is in the position adjacent to the lactone carbonyl [Fe(OC(=O)CRCH- κ^2 C,O)(depe)₂] (R = Ph, **10**; COOEt, **11**) (Scheme 7). This is consistent with the mechanism proposed in Scheme 6 where the metal acetylide reacts with CO₂ at the β -carbon followed by cyclisation to form the metalalactone.



Crystals of the phenyl-substituted metalalactone (**10**) suitable for crystallographic analysis were grown from a saturated diethyl ether solution (Figure 4, Table 4).

When the reaction between ¹³CO₂ and *trans*-[FeH(C≡CPh)(depe)₂] (**8**) was followed carefully by NMR spectroscopy at 298 K, a small amount of the labelled iron formate (**12-¹³C**) was formed (*ca.* 3% after 2 hours). It has not been possible to isolate the formate, however, its NMR signature is similar to other iron formates that have been reported.^{3a, 18}

The formyl proton appears as a ¹³C-coupled doublet at 7.81 ppm (*J*_{C-H} = 189.5 Hz) in the ¹H NMR spectrum and the formate carbon appears as a phosphorus-coupled pentet at 169.1 ppm (*J*_{C-P} = 2.3 Hz) in the ¹³C NMR spectrum.

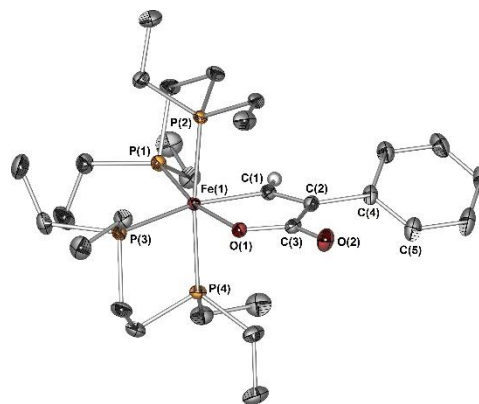


Figure 4. Solid state structure of λ -[Fe(OC(=O)C(Ph)CH- κ^2 C,O)(depe)₂] (**10**). Thermal ellipsoids are shown at the 50% probability level. Selected hydrogen atoms omitted for clarity.

Table 4. Selected bond lengths and angles λ -[Fe(OC(=O)C(Ph)CH- κ^2 C,O)(depe)₂] (**10**).

bond lengths / Å		bond angles / deg	
Fe-C(1)	1.945(2)	C(1)-Fe-O(1)	79.75(5)
Fe-O(1)	2.021(1)	P(3)-Fe-O(1)	84.82(3)
C(3)-O(2)	1.239(2)	P(1)-Fe-P(3)	105.69(2)
O(1)-C(3)	1.302(2)	P(2)-Fe-P(4)	173.36(2)
C(2)-C(3)	1.488(2)	P(1)-Fe(1)-C(1)	90.13(5)
C(1)-C(2)	1.354(2)	Fe(1)-C(1)-C(2)	117.1(1)
Fe-P(1)	2.2241(5)	Fe(1)-O(1)-C(3)	116.34(9)
Fe-P(2)	2.2416(6)	C(1)-C(2)-C(3)	113.1(1)
Fe-P(3)	2.2910(6)	O(1)-C(3)-C(2)	113.6(1)
Fe-P(4)	2.2535(6)	C(1)-C(2)-C(4)-C(5)	31.3(2)

The concentration of the formate complex (**12-¹³C**) remained approximately constant over the course of the reaction while the concentration of the phenyl-substituted metalalactone *cis*-[Fe(O¹³C(=O)C(Ph)CH- κ^2 C,O)(depe)₂] (**10-¹³C**) systematically increased over time. After 74 hours, the labeled metalalactone (**10-¹³C**) was the exclusive product. These observations suggest that CO₂ reacts with the hydrido iron acetylide **8** both to insert into the metal hydride bond and to also add to the β -carbon of the coordinated acetylide. While the reaction with the metal hydride gives rise to a metal formate, this reaction is reversible; whereas the addition of CO₂ to the β -acetylenic carbon results in cyclisation to the metalalactone in an irreversible reaction (Scheme 7). The reversible insertion of CO₂ into metal hydrides has been noted elsewhere.^{3a, c, 19} The acetylido metal formate is formed as a transient species in solution only when the acetylide hydride is present. Both the acetylide hydride starting material (**8**) and the metal formate (**12**) are eventually converted completely to the phenyl-substituted metalalactone (**10**).

Conclusions. The acetylide iron hydride *trans*-[FeH(C≡CH)(depe)₂] (**1**) reacts with an excess of CO₂ at ambient pressure and temperature to form a 5-membered metalalactone *cis*-[Fe(OC(=O)CHCH-κ²C,O)(depe)₂] (**3**). The reaction appears to proceed by electrophilic addition of CO₂ to the β-carbon of the acetylide, which is activated by coordination to the iron center. Subsequent cyclization with hydride migration results in the metalalactone product **3**. At low temperature, it is possible to add a second molecule of CO₂ to the β-carbon of the acetylide, resulting in a carboxy-substituted metalalactone *cis*-[Fe(OC(=O)C(C(=O)OH)CH-κ²C,O)(depe)₂] (**7**).

If the initial metal acetylide is substituted at the β-acetylenic carbon, then addition of CO₂ results in the product metalalactone where the substituent is in the position adjacent to the carbonyl in the metalalactone ring.

With the acetylide iron hydride *trans*-[FeH(C≡CPh)(depe)₂] (**8**), there was competition between insertion of CO₂ into the metal-hydride bond to give a metal formate and addition of CO₂ to the β-carbon of the coordinated acetylide. The insertion into the metal hydride is relatively rapid, but this process is reversible. In contrast, the addition of CO₂ to the coordinated acetylene is a slower process but the cyclization to the stable metalalactone is irreversible so eventually the metalalactone is the sole product.

EXPERIMENTAL SECTION

General procedures. All procedures involving air-sensitive compounds were carried out under dry argon using standard vacuum line, Schlenk or glove box techniques. Tetrahydrofuran was dried over and distilled from sodium benzophenone ketyl and stored over 3 Å molecular sieves (20% w/v). Hexane was dried over and distilled from sodium/benzophenone ketyl containing a small amount of tetraglyme (*ca.* 0.1% v/v) and stored over either a potassium mirror or over 3 Å molecular sieves (20% w/v). Pentane was dried and deoxygenated using an Innovative Technology Pure-Solv 400-4-MD solvent purification system and stored over 3 Å molecular sieves (20% w/v). 1,2-bis(diethylphosphino)ethane (depe) and phenylacetylene were obtained from Strem and used without further purification. Ethyl propiolate was obtained from Aldrich and distilled prior to use. *Trans*-[FeCl₂(depe)₂] was synthesised following the method of Chatt and Hayter.²⁰ KC₈ was synthesized by the literature method.²¹

Deuterated solvents were purchased from Cambridge Isotope Laboratories. THF-*d*₈ (D, 99.5%), C₆D₆ (D, 99.5%) were dried over sodium/benzophenone ketyl. Deuterated solvents for air sensitive NMR samples were vacuum distilled immediately prior to use.

Reagent gases and bulk compressed gases were used as supplied unless otherwise stated. Argon (>99.99%), was obtained from Air Liquide while acetylene (instrument grade: >99.6%) was obtained from Coregas. Isotopically labelled carbon dioxide (¹³CO₂) was obtained from Sigma

Aldrich and dried by vacuum distillation through an ethanol cold bath maintained at *ca.* -40 °C prior to use. Carbon dioxide (¹²CO₂) was obtained from Air Liquide and dried by passing it through a spiraled copper coil immersed in a cold bath maintained at *ca.* -40 °C prior to use.

¹H, ¹³C and ³¹P NMR spectra were acquired at 298 K on a Bruker Avance III 400 NMR spectrometer operating at 400, 100 and 162 MHz or a Bruker Avance III 600 NMR spectrometer operating at 600, 150 and 242 MHz. ¹H and ¹³C NMR spectra were referenced to solvent residuals²² while ³¹P NMR spectra were referenced in accordance to IUPAC guidelines using the unified scale.²³

Infrared spectra were obtained using a Nicolet Avatar 360 FT-IR or Nicolet iS10 FTR-IR spectrometer in the range of 4000 to 400 cm⁻¹. Single Crystal X-ray diffraction (SCXRD) was performed on a Bruker Nonius X8 Apex II CCD diffractometer (MoKα radiation, λ = 0.71073 Å, T = 100(2)K) by Dr. S. J. Dalgarno and Dr. R. D. McIntosh at Heriot-Watt University (complex **1**) or on a Bruker Kappa Apex II area detector diffractometer (MoKα radiation, λ = 0.71073 Å, T = 150(2)K) by Dr. M. Bhadbhade and Dr. P. Jurd at the Mark Wainwright Analytical Centre at the University of New South Wales (complexes **3**, **7**, **8**, and **10**). Microanalyses were conducted by the Campbell Microanalytical Laboratory at the University of Otago, NZ.

[FeH{(CH₃CH)(Et)PCH₂CH₂P(Et)₂-κ²C,P}(depe)] (**2**). The synthesis of [FeH{(CH₃CH)(Et)PCH₂CH₂P(Et)₂-κ²C,P}(depe)] (**2**) has been previously reported by Baker *et al.*¹⁰ However, in this work, the complex was prepared in synthetically useful quantities by reduction of *trans*-[FeCl₂(depe)₂] with potassium graphite. Under an atmosphere of argon, *trans*-[FeCl₂(depe)₂] (906 mg, 1.68 mmol) and potassium graphite (1.09 mg, 7.85 mmol, 4.7 eq.) were suspended in hexane (*ca.* 25 mL) and the mixture was sonicated for 20 min.

The flask was sealed and the mixture was stirred for 30 h, with sonication repeated after 16 h for 20 min. The reaction mixture was filtered and the residue was extracted with hexane (3 × 5 mL) to afford a brown orange solution containing [FeH{(CH₃CH)(Et)PCH₂CH₂P(Et)₂-κ²C,P}(depe)] (**2**) as a highly soluble yellow-brown oil. By ³¹P NMR, the reaction was complete and the product was clean (>95%) and the solution was titrated (see Supporting Information) and used directly without further purification (1.48 mmol, 83%). Selected spectroscopic data ¹H NMR (400 MHz, THF-*d*₈): δ -15.58 (ddt, ²J_{HP} = 63.0 Hz, ³J_{HP} = 39.1 Hz, ⁴J_{HP} = 24.3 Hz, 1H, FeH), -0.89 - -0.79 (m, 1H, FeCH(CH₃)). Selected ¹H{³¹P} NMR (400 MHz, THF-*d*₈): δ -15.58 (br s, 1H, FeH), -0.84 (qd, ³J_{HH} = 6.7 Hz, ³J_{HH} = 2.2 Hz, 1H, FeCH(CH₃)), 1.24 (d, ³J_{HH} = 6.7 Hz, 3H, FeCH(CH₃)) (lit.¹⁰ δ -15.587, -0.847, 1.237). ³¹P{¹H} NMR (162 MHz, THF-*d*₈): δ 50.8 (ddd, ²J_{PA-PC} = 54.7 Hz, ²J_{PA-PD} = 41.5 Hz, ²J_{PA-PB} = 11.1 Hz, P_A), 81.3 (ddd, ²J_{PB-PC} = 26.3 Hz, ²J_{PB-PD} = 19.4 Hz, ²J_{PB-PA} = 11.1 Hz, P_B), 87.2 (ddd, ²J_{PC-PA} = 54.7 Hz, ²J_{PC-PB} = 26.3 Hz, ²J_{PC-PD} = 10.8 Hz, P_C), 91.0 (ddd, ²J_{PD-PA} = 41.5 Hz, ²J_{PD-PB} = 19.4 Hz, ²J_{PD-PC} = 10.8 Hz, P_D) (lit.¹⁰ δ 50.93, 81.46, 87.42, 91.19). Selected ¹³C{¹H} NMR (100 MHz, THF-*d*₈): δ -21.2 - -20.8 (m, FeCH) (lit.¹⁰ δ -20.97).

Trans-[FeH(C≡CH)(depe)₂] (**1**). Under Ar, a standard solution of [FeH{(CH₃CH)(Et)PCH₂CH₂P(Et)₂-κ²C,P}(depe)] (**2**) in hexane (6.0 mL, 8.5 × 10⁻² M, 0.51 mmol) was diluted with hexane (*ca.* 25 mL) and degassed under reduced pressure. A flow of acetylene was introduced at ambient pressure for 2 min before the flask was sealed and allowed to stir for a further 20 min. The volatiles were removed under reduced pressure to yield *trans*-

[FeH(C≡CH)(depe)₂] (**1**) as an orange crystalline solid (245 mg, 0.505 mmol, 99%). Analysis calculated for C₂₂H₅₀FeP₄: C, 53.45; H, 10.19 (MW: 494.38) Found: C, 53.17; H, 10.32. Selected ¹H NMR (400 MHz, THF-*d*₈): δ -17.68 (p, ²J_{HP} = 44.1 Hz). ¹H{³¹P} NMR (400 MHz, THF-*d*₈): δ -17.68 (s, 1H, FeH), 1.00 (t, ³J_{HH} = 7.5 Hz, 12H, FeP(CH₂CH₃)(Et)), 1.12 (s, 1H, FeC≡CH), 1.14 (t, ³J_{HH} = 7.6 Hz, FeP(Et)(CH₂CH₃)), 1.40–1.50 (m, 4H, FeP(Et₂)CHHCHHP(Et₂)), 1.65–1.73 (m, 4H, FeP(Et₂)CHHCHHP(Et₂)), 1.88 (dq, ²J_{HH} = 14.8 Hz, ³J_{HH} = 7.4 Hz, 8H, FeP(Et)(CH₂CH₃)), 2.52 (dq, ²J_{HH} = 14.8 Hz, ³J_{HH} = 7.6 Hz, 8H, FeP(CH₂CH₃)(Et)). ³¹P{¹H} NMR (162 MHz, THF-*d*₈): δ 92.5 (s, 4P, FeP). ¹³C{¹H} NMR (101 MHz, THF-*d*₈): δ 8.3 (s, FeP(CH₂CH₃)(Et)), 8.5 (q, FeP(Et)(CH₂CH₃)), 22.5–22.7 (m, FeP(Et₂)C₂H₄P(Et)₂), 22.7–23.2 (m, FeP(Et₂)C₂H₄P(Et)₂), 23.6–23.8 (m, FeP(Et)(CH₂CH₃)), 97.5 (s, FeC≡CH), 132.2 (p, ²J_{CP} = 21.2 Hz, FeC≡CH) ppm. IR (Nujol): ν = 1798 m (ν_{sym}(Fe-H)), 1891 s (ν_{sym}(C≡C)) cm⁻¹.

Cis-[Fe(OC(=O)CHCH-κ²C,O)(depe)₂] (3**).** An excess of CO₂ was added to a degassed solution of *trans*-[FeH(C≡CH)(depe)₂] (**1**) (140.7 mg, 0.285 mmol) in THF (ca. 20 mL) for 5 min at ambient pressure with rapid stirring. The flask was sealed and the mixture left to stir for a further 2 h before the volatiles were removed under reduced pressure and the residue washed with cold pentane (o °C) (3 × 5 mL) to afford *cis*-[Fe(OC(=O)CHCH-κ²C,O)(depe)₂] (**1**) as a red orange crystalline solid (83.8 mg, 0.156 mmol, 55%). Analysis calculated for C₂₃H₅₀FeO₂P₄: C, 51.31; H, 9.36 (MW: 538.39) found: C, 50.86; H, 9.60. Selected ¹H NMR (400 MHz, THF-*d*₈): δ 6.14–6.20 (m, 1H, FeCH=CHC(=O)O), 9.20 (ddd, ³J_{HH} = 8.2 Hz, ³J_{HP} = 8.5 Hz, ³J_{HP} = 3.8 Hz, 1H, FeCH=CHC(=O)O). ¹H{³¹P} NMR (400 MHz, THF-*d*₈): δ 0.93 (t, ³J_{HH} = 7.6 Hz, 3H, P_D(CH₂CH₃)(Et)), 0.94 (t, ³J_{HH} = 7.6 Hz, 3H, P_C(CH₂CH₃)(Et)), 0.94–1.03 (m, 1H, P(Et)₂CHHCHHP(Et)₂(depe)), 0.99 (t, ³J_{HH} = 7.6 Hz, 3H, P_B(CH₂CH₃)(Et)), 1.10 (t, ³J_{HH} = 7.6 Hz, 6H, P_B(Et)(CH₂CH₃), P_D(Et)(CH₂CH₃)), 1.11 (t, ³J_{HH} = 7.5 Hz, 3H, P_C(Et)(CH₂CH₃)), 1.15 (t, ³J_{HH} = 7.6 Hz, 3H, P_A(CH₂CH₃)(Et)), 1.18–1.32 (m, 3H, P_D(CH₂CH₃)(Et), P(Et)₂CH₂CHHP(Et)₂(depe)), 1.23 (t, ³J_{HH} = 7.6 Hz, 3H, P_A(Et)(CH₂CH₃)), 1.30–2.10 (m, 19H, P_A(CHHCH₃)(Et), P_A(Et)(CH₂CH₃), P_B(CH₂CH₃)(Et), P_B(Et)(CH₂CH₃), P_C(CH₂CH₃)(Et), P_C(Et)(CH₂CH₃), P_D(Et)(CH₂CH₃), P(Et)₂CH₂CHHP(Et)₂(depe), P(Et)₂CHHCHHP(Et)₂(depe), (depe)P(Et)₂CH₂CH₂P(Et)₂, (depe)P(Et)₂CH₂CH₂P(Et)₂, 2.38 (dq, ²J_{HH} = 15.2 Hz, ³J_{HH} = 7.6 Hz, 1H, P_A(CHHCH₃)(Et)), 6.17 (d, ³J_{HH} = 8.2 Hz, 1H, FeCH=CHC(=O)O), 9.20 (d, ³J_{HH} = 8.2 Hz, 1H, FeCH=CHC(=O)O) ppm. ³¹P{¹H} NMR (162 MHz, THF-*d*₈): δ 66.1 (ddd, ²J_{PA-PB} = 33.7 Hz, ²J_{PA-PC} = 22.9 Hz, ²J_{PA-PD} = 9.5 Hz, P_A), 72.3 (ddd, ²J_{PB-PC} = 126.1 Hz, ²J_{PB-PA} = 33.7 Hz, ²J_{PB-PD} = 28.6 Hz, P_B), 76.2 (ddd, ²J_{PC-PB} = 126.1 Hz, ²J_{PC-PD} = 38.1 Hz, ²J_{PC-PA} = 22.9 Hz, P_C), 83.0 (ddd, ²J_{PD-PC} = 38.1 Hz, ²J_{PD-PB} = 28.6 Hz, ²J_{PD-PA} = 9.5 Hz, P_D) ppm. ¹³C{¹H} NMR (100 MHz, THF-*d*₈): δ 8.0 (d, ²J_{CP} = 5.0 Hz, P_C(CH₂CH₃)(Et)), 8.3 (d, ²J_{CP} = 5.6 Hz, P_C(Et)(CH₂CH₃)), 8.6 (d, ²J_{CP} = 5.4 Hz, P_B(CH₂CH₃)(Et)), 9.2 (d, ²J_{CP} = 6.8 Hz, P_A(CH₂CH₃)(Et)), 9.3 (d, ²J_{CP} = 5.7 Hz, P_D(CH₂CH₃)(Et)), 9.8–10.0 (m, P(CH₂)(Et)), 9.8 (d, ²J_{CP} = 6.7 Hz, P_B(Et)(CH₂CH₃), P_D(Et)(CH₂CH₃)), 9.9 (d, ²J_{CP} = 5.4 Hz, P_A(Et)(CH₂CH₃)), 13.7–14.0 (m, P_B(CH₂CH₃)(Et)), 18.1 (dd, ¹J_{CP} = 12.7 Hz, ¹J_{CP} = 1.7 Hz, P_A(CH₂CH₃)(Et)), 21.4 (dd, ¹J_{CP} = 16.4 Hz, ¹J_{CP} = 4.5 Hz, P(Et)(CH₂CH₃)), 22.1–22.8 (m, P_C(Et)(CH₂CH₃), (depe)P(Et)₂CH₂CH₂P(Et)₂, 23.3–23.9 (m, P(Et)(CH₂CH₃), P(Et)₂CH₂CH₂P(Et)₂(depe), (depe)P(Et)₂CH₂CH₂P(Et)₂, 24.8–25.5 (P(Et)₂CH₂CH₂P(Et)₂(depe), P_A(Et)(CH₂CH₃)(observed by solvent residual), 26.0–26.2 (m, P_D(CH₂CH₃)(Et)), 136.0–136.2 (m, FeCH=CHC(=O)O), 182.1–182.3 (m, FeOC(=O)), 195.4–196.6 (m, FeCH=CHC(=O)O) ppm. IR (Nujol): ν = 1582 vs (C=O) cm⁻¹.

Cis-[Fe(O¹³C(=O)C(¹³C(=O)OH)CH-κ²C,O)(depe)₂] (7-¹³C¹³C**)**
An excess of ¹³CO₂ (27.7 mg, 0.616 mmol, 32 eq.) was condensed into a frozen, degassed NMR sample of *trans*-

[FeH(C≡CH)(depe)₂] (**1**) (9.4 mg, 0.019 mmol) in THF-*d*₈ (ca. 0.6 mL) to give a substrate pressure of ca. 4 atm. The sample was placed into a cold acetone/dry-ice bath (-78 °C) for ca. 24 h before being allowed to gradually return to room temperature, resulting in quantitative formation of *cis*-[Fe(O¹³C(=O)C(¹³C(=O)OH)CH-κ²C,O)(depe)₂] (**7-¹³C¹³C**) as established by ³¹P{¹H} NMR spectroscopy. Analysis calculated for C₂₂¹³C₂H₅₀O₄P₄Fe: C, 49.67; H, 8.62 (MW: 582.40) Found: C, 49.32; H, 8.73. Selected ¹H NMR (400 MHz, THF-*d*₈): δ 11.92–12.00 (m, 1H, FeCH=C), 15.01 (d, ²J_{H-¹³C₂O} = 3.9 Hz, 1H, C(=O)OH). ¹H{³¹P} NMR (400 MHz, THF-*d*₈): δ 0.88 (t, ³J_{HH} = 7.5 Hz, 3H, P_C(CH₂CH₃)(Et)), 0.92 (t, ³J_{HH} = 7.5 Hz, 3H, P_B(CH₂CH₃)(Et)), 0.94–1.00 (m, 1H, (depe)P(Et)₂CHHCH₂P(Et)₂), 0.97 (t, ³J_{HH} = 7.5 Hz, 3H, P_D(CH₂CH₃)(Et)), 1.06 (t, ³J_{HH} = 7.5 Hz, 3H, P_C(Et)(CH₂CH₃)), 1.07–1.14 (m, 1H, (depe)P(Et)₂CH₂CHHP(Et)₂), 1.09 (t, ³J_{HH} = 7.5 Hz, 3H, P_B(Et)(CH₂CH₃)), 1.16 (t, ³J_{HH} = 7.5 Hz, 3H, P_D(Et)(CH₂CH₃)), 1.19 (t, ³J_{HH} = 7.5 Hz, 3H, P_A(CH₂CH₃)(Et)), 1.23–1.40 (m, 6H, P_C(CH₂CH₃)(Et), P_B(CHHCH₃)(Et), P(Et)₂CHHCH₂P(Et)₂(depe), P_D(CH₂CH₃)(Et)), 1.28 (t, ³J_{HH} = 7.5 Hz, 3H, P_A(Et)(CH₂CH₃)), 1.56–2.12 (14H, P_B(CHHCH₃)(Et), P_A(CHHCH₃)(Et), P_D(Et)(CHHCH₃), P_C(Et)(CH₂CH₃), P(Et)₂CHHCH₂P(Et)₂(depe), P_B(Et)(CH₂CH₃), P_A(Et)(CH₂CH₃), P(Et)₂CH₂CH₂P(Et)₂(depe), (depe)P(Et)₂CHHCH₂P(Et)₂, (depe)P(Et)₂CH₂CHHP(Et)₂, 2.16 (dq, ²J_{HH} = 15.0 Hz, ³J_{HH} = 7.5 Hz, 1H, P_D(Et)(CHHCH₃)), 2.28 (dq, ²J_{HH} = 15.0 Hz, ³J_{HH} = 7.5 Hz, 1H, P_A(CHHCH₃)(Et)), 11.97 (dd, ²J_{HC} = 10.5 Hz, ³J_{HC} = 5.5 Hz, 1H, FeCH=C), 15.01 (d, ²J_{H-¹³CO} = 3.9 Hz, 1H, C(=O)OH). ³¹P{¹H} NMR (162 MHz, THF-*d*₈): δ 64.1 (dddd, ²J_{PA-PB} = 36.0 Hz, ²J_{PA-PC} = 24.1 Hz, ²J_{PA-PD} = 12.4 Hz, ¹J_{P-¹³CO} = 12.0 Hz, P_A), 70.3 (ddd, ²J_{PB-PC} = 100.2 Hz, ²J_{PB-PA} = 36.0 Hz, ²J_{PB-PD} = 29.7 Hz, P_B), 78.7 (ddd, ²J_{PC-PB} = 100.2 Hz, ²J_{PC-PD} = 39.4 Hz, ²J_{PC-PA} = 24.1 Hz, P_C), 82.5 (ddd, ²J_{PD-PC} = 39.4 Hz, ²J_{PD-PB} = 29.7 Hz, ²J_{PD-PA} = 12.4 Hz, P_D). ¹³C{¹H} NMR (100 MHz, THF-*d*₈): δ 7.0 (d, ²J_{CP} = 5.8 Hz, P_C(CH₂CH₃)(Et)), 7.9 (d, ²J_{CP} = 4.5 Hz, P_B(CH₂CH₃)(Et)), 8.1–8.3 (m, P_C(Et)(CH₂CH₃), P_B(Et)(CH₂CH₃)), 8.9 (d, ²J_{CP} = 6.9 Hz, P_A(CH₂CH₃)(Et)), 9.3 (d, ²J_{CP} = 6.6 Hz, P_D(CH₂CH₃)(Et)), 9.4 (d, ²J_{CP} = 6.9 Hz, P_D(Et)(CH₂CH₃)), 9.5 (d, ¹J_{CP} = 19.7 Hz, P_C(CH₂CH₃)(Et)), 9.9 (d, ²J_{CP} = 5.8 Hz, P_A(Et)(CH₂CH₃)), 15.2 (dd, ¹J_{CP} = 22.1 Hz, ¹J_{CP} = 3.3 Hz, P_B(CH₂CH₃)(Et)), 18.1 (d, ¹J_{CP} = 13.2 Hz, P_A(CH₂CH₃)(Et)), 21.1 (dd, ¹J_{CP} = 17.5 Hz, ¹J_{CP} = 4.3 Hz, P_D(Et)(CH₂CH₃)), 21.7–22.3 (m, P_C(Et)(CH₂CH₃), P(Et)₂CH₂CH₂P(Et)₂(depe)), 23.0–23.3 (m, P_B(Et)(CH₂CH₃)), 23.6–24.1 (m, P_A(Et)(CH₂CH₃), P(Et)₂CH₂CH₂P(Et)₂(depe)), 24.7–25.5 (m, P_D(CH₂CH₃)(Et), (depe)P(Et)₂CH₂CH₂P(Et)₂, (depe)P(Et)₂CH₂CH₂P(Et)₂), 133.0–134.4 (m, FeCH=C), 161.4 (ddt, ²J_{CC} = 7.9 Hz, ¹J_{CP} = 2.5 Hz, ¹J_{CP} = 2.5 Hz, C(=O)OH), 183.2 (dd, ¹J_{CP} = 10.9 Hz, ²J_{CC} = 7.9 Hz, FeOC(=O)), 237.4–239.2 (m, FeCH=C). IR (Nujol): ν = 1492 s, 1656 s cm⁻¹.

Trans-[FeH(C≡CPh)(depe)₂] (8**)** Phenylacetylene (63.7 μL, 0.580 mmol, 0.9 eq.) was slowly added to a standard solution of [FeH{(CH₃CH)(Et)PCH₂CH₂P(Et)₂-κ²C,P}(depe)] (**2**) in hexane (35.0 mL, 0.0180 M, 0.629 mmol) under Ar resulting in the reaction mixture rapidly changing color from golden yellow to deep red. The mixture was allowed to stir for a further 1 h before the volatiles were removed under reduced pressure. The resulting yellow-red residue was washed with cold pentane (5 × 4 mL, ca. -40 °C) and the remaining yellow solid was extracted with pentane at room temperature (3 × ca. 10 mL). The solvent was slowly evaporated under reduced pressure to give *trans*-[FeH(C≡CPh)(depe)₂] (**8**) as a yellow microcrystalline solid (228 mg, 0.399 mmol, 69%). Analysis calculated for C₂₈H₅₄FeP₄: C, 58.95; H, 9.54 (MW: 570.48) Found: C, 58.96; H, 9.67. Selected ¹H NMR (400 MHz, C₆D₆): δ -16.89 (p, ²J_{HP} = 44.3 Hz, 1H, FeH). ¹H{³¹P} NMR (600 MHz, C₆D₆): δ -16.89 (s, 1H, FeH), 0.94 (t, ³J_{HH} = 7.6 Hz, 12H, FeP(CH₂CH₃)(Et)), 1.08 (dq, ²J_{HH} = 16.0 Hz, ³J_{HH} = 7.6 Hz, 4H, FeP(CHHCH₃)(Et)), 1.16 (t, ³J_{HH} = 7.7 Hz, 12H,

FeP(Et)(CH₂CH₃), 1.23–1.33 (m, 4H, FeP(Et)₂CHHCHHP(Et)₂), 1.56–1.66 (m, 4H, FeP(Et)₂CHHCHHP(Et)₂), 1.67 (dq, ²J_{HH} = 7.3 Hz, ³J_{HH} = 7.7 Hz, 4H, FeP(CHHCH₃)(Et)), 1.70 (dq, ²J_{HH} = 7.3 Hz, ³J_{HH} = 7.7 Hz, 4H, FeP(Et)(CHHCH₃)), 2.49 (dq, ²J_{HH} = 7.6 Hz, ³J_{HH} = 7.7 Hz, 4H, FeP(Et)(CHHCH₃)), 6.89–6.93 (app t, splitting = 7.6 Hz, 1H, *para*-ArH), 7.16–7.19 (1H, *ortho*-ArH) (obscured by solvent residual), 7.39–7.43 (app d, splitting = 76 Hz, 2H, *meta*-ArH). ³¹P{¹H} NMR (162 MHz, C₆D₆): δ 92.9 (s, 4P, FeP). ¹³C{¹H} NMR (100 MHz, C₆D₆): δ 8.7 (s, FeP(CH₂CH₃)(Et)), 9.0 (app p, splitting = 1.5 Hz, FeP(Et)(CH₂CH₃)), 23.1–23.7 (m, FeP(Et)(CH₂CH₃), FeP(Et)₂C₂H₄P(Et)₂), 24.1–24.3 (m, FeP(CH₂CH₃)(Et)), 117.3 (s, FeC≡CPh), 121.4 (s, *para*-ArCH), 127.4–127.9 (*ortho*-ArCH) (obscured by solvent residual), 130.0 (p, ²J_{CP} = 1.5 Hz, *meta*-ArCH), 132.1–132.2 (m, *ipso*-ArC), 145.5 (p, ²J_{CP} = 21.6 Hz, FeC≡CPh). IR (Nujol): ν = 1779 br w (ν_{sym}(Fe-H)), 2035 s (ν_{sym}(C≡CPh)) cm⁻¹. A single crystal suitable for X-ray crystallography was grown from a concentrated pentane solution of the complex at -25°C (see Supporting Information). The structure is disordered; the terminal ethyl groups were modelled over two major orientations in 60:40 occupancies.

Cis-[Fe(OC(=O)C(Ph)CH-κ²C,O)(depe)₂] (10) Carbon dioxide was added in excess to a degassed solution of *trans*-[FeH(C≡CPh)(depe)₂] (8) (222 mg, 0.389 mmol) in THF (ca. 40 mL) for 5 min at ambient pressure. The flask was sealed and left to stir for 64 h before the volatiles were removed under reduced pressure and the residue extracted with diethyl ether (3 × 20 mL). After filtering, the solvent was removed under reduced pressure and the residue was washed with hexane (3 × 5 mL) and dried under vacuum to afford *cis*-[Fe(OC(=O)C(Ph)CH-κ²C,O)(depe)₂] (9) as an orange microcrystalline solid (89.1 mg, 0.145 mmol, 37%). Analysis calculated for C₂₉H₅₄FeO₄P₄: C, 56.68; H, 8.86 (MW: 614.49) Found: C, 56.76; H, 8.78. Selected ¹H NMR (400 MHz, THF-*d*₈): δ 10.07 (dd, ²J_{HP} = 9.6 Hz, ³J_{HP} = 3.8 Hz, 1H, FeCH=C). ¹H{³¹P} NMR (400 MHz, THF-*d*₈): δ 0.84 (t, ³J_{HH} = 7.6 Hz, 3H, P_C(CH₂CH₃)(Et)), 0.93 (t, ³J_{HH} = 7.6 Hz, 3H, P_B(CH₂CH₃)(Et)), 0.98 (t, ³J_{HH} = 7.7 Hz, 3H, P_D(CH₂CH₃)(Et)), 0.99–1.09 (m 1H, (depe)P(Et)₂CH₂CHHP(Et)₂), 1.08 (t, ³J_{HH} = 7.6 Hz, 3H, P_C(Et)(CH₂CH₃)), 1.10 (t, ³J_{HH} = 7.6 Hz, 3H, P_B(Et)(CH₂CH₃)), 1.16 (t, ³J_{HH} = 7.7 Hz, 3H, P_D(Et)(CH₂CH₃)), 1.20 (t, ³J_{HH} = 7.6 Hz, 3H, P_A(CH₂CH₃)(Et)), 1.24–1.38 (m, 5H, P_C(CHHCH₃)(Et), P_D(CH₂CH₃)(Et), P_B(CHHCH₃)(Et), P(Et)₂CHHCH₃P(Et)₂(depe)), 1.27 (t, ³J_{HH} = 7.6 Hz, 3H, P_A(Et)(CH₂CH₃)), 1.44 (dq, ²J_{HH} = 15.1 Hz, ³J_{HH} = 7.6 Hz, 1H, P_C(CHHCH₃)(Et)), 1.58–1.96 (13H, P_A(CHHCH₃)(Et), P_B(CHHCH₃)(Et), P_D(Et)(CHHCH₃), P_C(Et)(CH₂CH₃), P(Et)₂CHHCH₃P(Et)₂(depe), P(Et)₂CH₂CHHP(Et)₂(depe), P_B(Et)(CH₂CH₃), (depe)P(Et)₂CH₂CH₂P(Et)₂, P_A(Et)(CH₂CH₃)), 2.05–2.14 (m, 2H, P(Et)₂CH₂CHHP(Et)₂(depe), (depe)P(Et)₂CH₂CHHP(Et)₂), 2.17 (dq, ²J_{HH} = 14.8 Hz, ³J_{HH} = 7.2 Hz, 1H, P_D(Et)(CHHCH₃)), 2.45 (dq, ²J_{HH} = 15.1 Hz, ³J_{HH} = 7.6 Hz, 1H, P_A(CHHCH₃)(Et)), 6.85 (app t, splitting = 7.5 Hz, 1H, *para*-ArH), 7.06 (app t, splitting = 7.5 Hz, 2H, *ortho*-ArH), 7.82 (app d, splitting = 7.5 Hz, 2H, *meta*-ArH), 10.07 (s, 1H, FeCH=C). ³¹P{¹H} NMR (162 MHz, THF-*d*₈): δ 65.6 (ddd, ²J_{PA-PB} = 34.0 Hz, ²J_{PA-PC} = 23.4 Hz, ²J_{PA-PD} = 8.1 Hz, P_A), 73.0 (ddd, ²J_{PB-PC} = 125.6 Hz, ²J_{PB-PA} = 34.0 Hz, ²J_{PB-PD} = 28.6 Hz, P_B), 77.5 (ddd, ²J_{PC-PB} = 125.6 Hz, ²J_{PC-PD} = 38.4 Hz, ²J_{PC-PA} = 23.4 Hz, P_C), 82.7 (ddd, ²J_{PD-PC} = 38.4 Hz, ²J_{PD-PB} = 28.6 Hz, ²J_{PD-PA} = 8.1 Hz, P_D). ¹³C{¹H} NMR (100 MHz, THF-*d*₈): δ 7.7 (d, ²J_{CP} = 4.9 Hz, P_C(CH₂CH₃)(Et)), 8.3 (d, ²J_{CP} = 5.7 Hz, P_C(Et)(CH₂CH₃)), 8.3 (d, ²J_{CP} = 3.6 Hz, P_B(Et)(CH₂CH₃)), 8.5 (d, ²J_{CP} = 5.0 Hz, P_B(CH₂CH₃)(Et)), 9.1 (d, ²J_{CP} = 7.0 Hz, P_A(CH₂CH₃)(Et)), 9.4 (d, ²J_{CP} = 5.8 Hz, P_D(CH₂CH₃)(Et)), 9.8 (d, ²J_{CP} = 6.9 Hz, P_D(Et)(CH₂CH₃)), 10.0 (d, ²J_{CP} = 5.4 Hz, P_A(Et)(CH₂CH₃)), 10.3 (d, ²J_{CP} = 19.6 Hz, P_C(CH₂CH₃)(Et)), 14.5 (dd, ¹J_{CP} = 20.7 Hz, ¹J_{CP} = 3.0 Hz, P_B(CH₂CH₃)(Et)), 17.8 (dd, ¹J_{CP} = 12.6 Hz, ³J_{CP} = 1.7 Hz, P_A(CH₂CH₃)(Et)), 21.1 (dd, ¹J_{CP} = 15.4 Hz,

²J_{CP} = 4.7 Hz, P_D(Et)(CH₂CH₃)), 22.2 (d, ¹J_{CP} = 17.3 Hz, P_C(Et)(CH₂CH₃)), 22.3–22.9 (m, P(Et)₂CH₂CH₂P(Et)₂(depe), P(Et)₂CH₂CH₂P(Et)₂(depe)), 23.3–23.5 (m, P_B(Et)(CH₂CH₃)), 23.7 (app t, splitting = 19.3 Hz, (depe)P(Et)₂CH₂CH₂P(Et)₂), 24.6 (d, ¹J_{CP} = 19.6 Hz, P_A(Et)(CH₂CH₃)), 24.7–25.5 (m, (depe)P(Et)₂CH₂CH₂P(Et)₂) (obscured by solvent residual), 25.9 (d, ¹J_{CP} = 19.6 Hz, P_D(CH₂CH₃)(Et)), 123.2 (s, *para*-ArC), 126.3 (s, *meta*-ArC), 127.3 (s, *ortho*-ArC), 142.5–142.6 (m, FeCH=C), 142.9–142.9 (m, *ipso*-ArC), 179.7 (dt, ³J_{CP} = 11.4 Hz, ³J_{CP} = 2.0 Hz, FeOC(=O)), 201.7–202.6 (m, FeCH=C). IR (Nujol): ν = 1581 s (ν_{sym}(C=O)) cm⁻¹.

Trans-[FeH(C≡CC(=O)OEt)(depe)₂] (9) Ethyl propiolate (74.0 μL, 0.730 mmol, 0.9 eq.) was added dropwise to a rapidly stirred standard solution of [FeH{(CH₃CH)(Et)PCH₂CH₂P(Et)₂-κ²C,P}(depe)] (2) in hexane (43.5 mL, 0.0180 M, 0.782 mmol) under Ar resulting in the golden solution turning a deep red. The reaction mixture was left to stir for a further 17 h before the solvent was removed under reduced pressure to afford a red oil containing a fine suspension. Scratching the residue and leaving it to stand for 4 d resulted in the precipitation of the product as an oily red solid (329 mg, 0.567 mmol, 78%). The product contained a minor amount of free depe ligand as an impurity. A standard solution of 9 in hexane was calibrated by taking an aliquot and integrating the ³¹P resonance against the resonance of a known amount of internal standard (triethyl phosphate). The standard solution was used without further purification in subsequent reactions. Selected ¹H NMR (400 MHz, THF-*d*₈): δ -15.96 (p, ²J_{HP} = 44.5 Hz, 1H, FeH). ¹H{³¹P} NMR (400 MHz, THF-*d*₈): δ -15.96 (s, 1H, FeH), 1.02 (t, ³J_{HH} = 7.5 Hz, 12H, FeP(CH₂CH₃)(Et)), 1.07 (t, ³J_{HH} = 7.1 Hz, 3H, C(=O)OCH₂CH₃), 1.17 (t, ³J_{HH} = 7.7 Hz, 12H, FeP(Et)(CH₂CH₃)), 1.25 (dq, ²J_{HH} = 15.6 Hz, ³J_{HH} = 7.9 Hz, 4H, FeP(CHHCH₃)(Et)), 1.45–1.54 (m, 4H, P(Et)₂CHHCHHP(Et)₂), 1.67–1.76 (m, 4H, P(Et)₂CHHCHHP(Et)₂), 1.73 (dq, ²J_{HH} = 15.1 Hz, ³J_{HH} = 7.6 Hz, 4H, FeP(Et)(CHHCH₃)), 1.89 (dq, ²J_{HH} = 14.8 Hz, ³J_{HH} = 7.4 Hz, 4H, FeP(CHHCH₃)(Et)), 2.35 (dq, ²J_{HH} = 15.4 Hz, ³J_{HH} = 7.8 Hz, 4H, FeP(Et)(CHHCH₃)), 3.83 (q, ³J_{HH} = 7.1 Hz, 2H, C(=O)OCH₂CH₃). ³¹P{¹H} NMR (162 MHz, THF-*d*₈): δ 91.9 (s, 4P, FeP). ¹³C{¹H} NMR (101 MHz, THF-*d*₈): δ 8.9 (s, FeP(CH₂CH₃)(Et)), 9.1 (app p, ²J_{CP} = 1.6 Hz, FeP(Et)(CH₂CH₃)), 15.0 (s, OCH₂CH₃), 23.6–24.1 (FeP(Et)₂CH₄P(Et)₂, FeP(Et)(CH₂CH₃)), 24.4–24.6 (m, FeP(CH₂CH₃)(Et)), 58.4 (s, OCH₂CH₃), 110.6 (s, FeC≡C), 150.8 (m, C(=O)OEt), 164.7 (p, ²J_{CP} = 20.6 Hz, FeC≡C). IR (Neat): ν = 1645 s (ν_{sym}(C=O)), 1778 br w (ν_{sym}(Fe-H)), 2005 s (ν_{sym}(C≡C)) cm⁻¹.

cis-[Fe(OC(=O)C(C(=O)OEt)CH-κ²C,O)(depe)₂] (11) A standard solution of *trans*-[FeH(C≡CC(=O)OEt)(depe)₂] (9) (9.35 mL, 0.0180 M, 0.168 mmol) was diluted with THF (30 mL) and degassed through three freeze-pump-thaw cycles. An excess of CO₂ was introduced at ambient pressure for 5 min and the reaction mixture stirred for 17 h. The volatiles were removed under reduced pressure and the yellow oily residue was washed with pentane (5 × 10 mL) then extracted with THF (2 × 10 mL) and filtered before the solvent was removed under reduced pressure. The resulting residue was washed with diethyl ether (4 × 10 mL) and the residue was dried *in vacuo* to afford *cis*-[Fe(OC(=O)C(C(=O)OEt)CH-κ²C,O)(depe)₂] (11) as an orange microcrystalline solid (21.4 mg, 35.1 μmol, 22%). Analysis calculated for C₂₆H₅₄FeO₄P₄: C, 51.16; H, 8.92 (MW: 610.45) Found: C, 51.12; H, 8.87. Selected ¹H NMR (400 MHz, THF-*d*₈): δ 11.40 (dd, ²J_{HP} = 10.1 Hz, ³J_{HP} = 4.2 Hz, 1H, FeCH=C). ¹H{³¹P} NMR (400 MHz, THF-*d*₈): δ 0.88 (t, ³J_{HH} = 7.6 Hz, 3H, P_C(CH₂CH₃)(Et)), 0.95 (t, ³J_{HH} = 7.6 Hz, 3H, P_B(CH₂CH₃)(Et)), 0.96 (t, ³J_{HH} = 7.6 Hz, 3H, P_D(CH₂CH₃)(Et)), 1.08 (t, ³J_{HH} = 7.6 Hz, 3H, P_C(Et)(CH₂CH₃)), 1.10 (t, ³J_{HH} = 7.6 Hz, 3H, P_B(Et)(CH₂CH₃)), 1.15 (t, ³J_{HH} = 7.6 Hz, 3H, P_D(Et)(CH₂CH₃)), 1.18 (t, ³J_{HH} = 7.1 Hz, 3H, C(=O)OCH₂CH₃), 1.18 (t, ³J_{HH} = 7.7 Hz, 3H, P_A(CH₂CH₃)(Et)), 1.23–2.14 (m, 23H, P_A(CHHCH₃)(Et), P_A(Et)(CH₂CH₃), P_B(CH₂CH₃)(Et),

$P_B(Et)(CH_2CH_3)$, $P_C(CH_2CH_3)(Et)$, $P_C(Et)(CH_2CH_3)$,
 $P_D(CH_2CH_3)(Et)$, $P_D(Et)(CH_2CH_3)$, $P(Et)_2CH_2CH_2P(Et)_2(depe)$,
 $(depe)P(Et)_2CH_2CH_2P(Et)_2$, 1.26 (t, $^3J_{HH} = 7.6$ Hz, 3H ,
 $P_A(Et)(CH_2CH_3)$), 2.41 (dq, $^3J_{HH} = 15.6$ Hz, $^3J_{HH} = 7.7$ Hz, 1H ,
 $P_A(CHHCH_3)(Et)$, 3.96–4.08 (m, 2H, $C(=O)OCH_2CH_3$), 11.40 (s, 1H ,
 $FeCH=C$). $^3P\{^1H\}$ NMR (161 MHz, THF- d_8): δ 64.2 (ddd,
 $^2J_{PA-PB} = 36.3$ Hz, $^2J_{PA-PC} = 24.7$ Hz, $^2J_{PA-PD} = 9.4$ Hz, P_A), 71.4 (ddd,
 $^2J_{PB-PC} = 114.9$ Hz, $^2J_{PB-PA} = 36.3$ Hz, $^2J_{PB-PD} = 28.1$ Hz, P_B), 78.0 (ddd,
 $^2J_{PC-PB} = 114.9$ Hz, $^2J_{PC-PD} = 37.6$ Hz, $^2J_{PC-PA} = 24.7$ Hz, P_C), 82.3 (ddd,
 $^2J_{PD-PC} = 37.6$ Hz, $^2J_{PD-PB} = 28.1$ Hz, $^2J_{PD-PA} = 9.4$ Hz, P_D). $^{13}C\{^1H\}$ NMR
(101 MHz, THF- d_8): δ 7.4 (d, $^2J_{CP} = 5.1$ Hz, $P_C(CH_2CH_3)(Et)$), 8.2–8.3
(m, $P_B(CH_2CH_3)(Et)$, $P_C(Et)(CH_2CH_3)$, $P_B(Et)(CH_2CH_3)$), 9.0 (d,
 $^2J_{CP} = 7.2$ Hz, $P_A(CH_2CH_3)(Et)$), 9.3 (d, $^2J_{CP} = 6.1$ Hz,
 $P_D(CH_2CH_3)(Et)$), 9.6 (d, $^2J_{CP} = 6.7$ Hz, $P_D(Et)(CH_2CH_3)$), 9.8 (dt,
 $^1J_{CP} = 20.1$ Hz, $^3J_{CP} = 1.5$ Hz, $P_C(CH_2CH_3)(Et)$), 10.0 (d, $^2J_{CP} = 5.4$ Hz,
 $P_A(Et)(CH_2CH_3)$), 14.6 (dd, $^1J_{CP} = 21.6$ Hz, $^3J_{CP} = 3.2$ Hz,
 $P_B(CH_2CH_3)(Et)$), 15.1 (s, $C(=O)OC_2C_3$), 17.7 (dd, $^1J_{CP} = 12.9$ Hz,
 $^3J_{CP} = 1.8$ Hz, $P_A(CH_2CH_3)(Et)$), 21.1 (ddd, $^1J_{CP} = 16.6$ Hz,
 $^3J_{CP} = 4.6$ Hz, $^3J_{CP} = 1.1$ Hz, $P_D(Et)(CH_2CH_3)$), 21.8–22.6 (m,
 $P_C(Et)(CH_2CH_3)$, $P(Et)_2CH_2CH_2P(Et)_2(depe)$,
 $(depe)P(Et)_2CH_2CH_2P(Et)_2$), 23.3–23.9 (m, $P_B(Et)(CH_2CH_3)$,
 $P_C(CH_2CH_3)(Et)$, $(depe)P(Et)_2CH_2CH_2P(Et)_2$), 24.4 (d,
 $^1J_{CP} = 12.3$ Hz, $P_A(Et)(CH_2CH_3)$), 24.7–25.5 (m, $P_D(CH_2CH_3)(Et)$,
 $P(Et)_2CH_2CH_2P(Et)_2$), 58.0 (s, $C(=O)OCH_2CH_3$), 137.5 (dd,
 $J_{CP} = 4.1$ Hz, $J_{CP} = 7.6$ Hz, $FeCH=C$), 162.9–163.0 (m, $C(=O)OEt$),
177.0 (dt, $^3J_{CP} = 11.3$ Hz, $^3J_{CP} = 1.8$ Hz, $FeOC(=O)$), 228.9–229.8 (m,
 $FeCH=C$). IR (Nujol): $\nu = 1599$ s ($FeOC(=O)$), 1694 s ($C(=O)OEt$)
 cm^{-1} .

ASSOCIATED CONTENT

Supporting Information

The supporting information is available free of charge via the Internet at <http://pubs.acs.org>.

Method for titrating a solution of $[FeH\{(CH_3CH)(Et)PCH_2CH_2P(Et)_2-\kappa^2C,P\}(depe)]$ (2). Crystallographic data for complexes *trans*- $[FeH(C\equiv CH)(depe)_2]$ (1), λ - $[Fe(OC(=O)CHCH-\kappa^2C,O)(depe)_2]$ (3), λ - $[Fe(O^3C(=O)C^13C(=O)OH)CH-\kappa^2C,O)(depe)_2]$ (7), *trans*- $[FeH(C\equiv CPh)(depe)_2]$ (8), λ - $[Fe(OC(=O)C(Ph)CH-\kappa^2C,O)(depe)_2]$ (10).

Accession Codes

CCDC 1969254-1969258 contain the crystallographic data for complexes *trans*- $[FeH(C\equiv CH)(depe)_2]$ (1), λ - $[Fe(OC(=O)CHCH-\kappa^2C,O)(depe)_2]$ (3), λ - $[Fe(O^3C(=O)C^13C(=O)OH)CH-\kappa^2C,O)(depe)_2]$ (7), λ - $[Fe(OC(=O)C(Ph)CH-\kappa^2C,O)(depe)_2]$ (10), and *trans*- $[FeH(C\equiv CPh)(depe)_2]$ (8). The data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif or by emailing data_request@ccdc.cam.ac.uk or by contacting the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: +44 1223 336033.

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