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Synthesis and Study of the Thermal Rearrangement of $(CO)_4Fe[P(R)(H)(C\equiv CR')]Co_2(CO)_6$ Complexes (R = N(*i*-Pr)$_2$, NMe$_2$, or Me, R′ = Ph; R = N(*i*-Pr)$_2$, R′ = *t*-Bu)

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The synthesis and thermal rearrangement of $(CO)_4Fe[P(R)(H)(C\equiv CR')]Co_2(CO)_6$ complexes are described (R = N(i-Pr)$_2$, NMe$_2$, or Me, R′ = Ph; R = N(i-Pr)$_2$, R′ = t-Bu). Contrary to the case previously described where R = t-Bu and R′ = Ph, no formation of complexed phosphaallene $RP(C{=}CHR')$ is observed. The reactions lead to low yields of $FeCo_2(CO)_9(\mu_3\text{-}\eta^2\text{-}CCHR')$ (R′ = Ph, t-Bu) and $FeCo_2(CO)_9(\mu_3\text{-}PR)$ (R = Me, NMe$_2$, N(i-Pr)$_2$) clusters, with $FeCo_2(CO)_7(\mu\text{-}PRH)(\mu_3\text{-}\eta^2\text{-}C\equiv CR')$ complexes as the main product of the reaction. When R = Me and R′ = Ph, the formation of $Fe_2(CO)_6[\mu\text{-}P(Me)C{=}C(Ph)C(O)C(Ph){=}CP(Me)]$ is also observed. During the synthesis of $(CO)_4Fe[P(NMe_2)(H)(C\equiv CPh)]$, the compound $[PPh_4][((CO)_4Fe)_3P_2(C\equiv CPh)_2(NMe)_2]$ was isolated. It reacts with $Co_2(CO)_8$ to generate a cluster containing an alkenylphosphinidene in which the carbon–carbon triple bond is π-bonded to a $Co_2(CO)_6$ entity, viz. $FeCo_2(CO)_9(\mu_3\text{-}PC\equiv CPh)Co_2(CO)_6$. A second product isolated contains an alkynylphosphido ligand and is formulated as $FeCo(CO)_7[\mu\text{-}P(NMe_2)(C\equiv CPh)]$.

In a recent publication,[1] we have shown that a possible synthesis of complexed phosphacumulenes starts with $(CO)_4Fe[P(t\text{-}Bu)(H)(C\equiv CPh)]Co_2(CO)_6$ and involves the thermally induced migration of the hydrogen from phosphorus to the unsaturated β-carbon. Actually, the expected $FeCo_2(CO)_9[\mu_3\text{-}\eta^2\text{-}t\text{-}BuP(C{=}CHPh)]$ was obtained in low yield (3%), while $FeCo_2(CO)_9[\mu_3\text{-}P(t\text{-}Bu)]$ was the main product of the reaction.

With the aim of improving the yield of the phosphacumulene complex, we have studied the influence of the nature of R and R′ groups in the $(CO)_4Fe[P(R)(H)(C\equiv CR')]Co_2(CO)_6$ compounds on their thermal rearrangement reactions. The R and R′ groups have been chosen to present various degrees of electronic and steric properties, but their choice was limited by the availability of the starting $P(R)(Cl)(C\equiv CR')$ phosphines. In this paper, we report that in no case has the formation of complexes containing the phosphaalkenylidene ligand been detected. However, we have observed interesting rearrangements leading among others to polynuclear complexes containing alkynylphosphinidene or alkynylphosphido ligands. To our knowledge, these are the first examples of these types of ligands. Further, the formation of vinylidene and acetylide ligands was observed in these reactions.

Results and Discussion

To synthesize the $(CO)_4Fe[P(R)(H)(C\equiv CR')]Co_2(CO)_6$ complexes, we have retained the strategy used for the preparation of $(CO)_4Fe[P(t\text{-}Bu)(H)(C\equiv CPh)]Co_2(CO)_6$,[1] i.e. the formation of $(CO)_4Fe[P(R)(H)(C\equiv CR')]$ upon reaction of $[PPh_4][HFe(CO)_4]$ with the phosphines $P(R)(Cl)(C\equiv CR')$, followed by complexation of the alkynyl triple bond upon reaction with $Co_2(CO)_8$.

Synthesis of the Phosphines $P(R)(Cl)(C\equiv CR')$. One method for the synthesis of the alkynylphosphines[2] is to react the dichlorophosphine with 1 equiv of lithium acetylide. The reaction is generally complex and affords a mixture of $P(R)Cl_{2-x}(C\equiv CR')_x$ compounds (x = 1 or 2). Table I summarizes the observed proportions determined by ^{31}P NMR spectroscopy of the two phosphines formed before purification.

Table I. Observed Proportions of the $RPCl(C\equiv CR')$ and $RP(C\equiv CR')_2$ Phosphines[a] Formed during the Reaction of $RPCl_2$ with $R'C\equiv CLi$

R	R′	RPCl(CCR′)	RP(CCR′)$_2$
N-i-Pr$_2$	Ph	36	64
N-i-Pr$_2$	t-Bu	95	5
NMe$_2$	Ph	31	69
Me	Ph	51	49
CH(SiMe$_3$)$_2$	Ph	19	81

[a] % calculated for consummed $RPCl_2$.

The occurrence of the $PR(C\equiv CR')_2$ phosphines that polymerize during distillation makes it difficult to purify the $P(R)(Cl)(C\equiv CR')$ phosphines.

So, we have chosen a different route avoiding the formation of the dialkynylphosphines. This method[3] benefits from the lability of the $P(NMe_2)$ bond and is summarized by the following equations

$$PRCl(NMe_2) + LiC\equiv CR' \rightarrow PR(NMe_2)(C\equiv CR') + LiCl \quad (1)$$

$$PR(NMe_2)(C\equiv CR') + PCl_3 \rightarrow PClR(C\equiv CR') + PCl_2NMe_2 \quad (2)$$

with R = Me or NMe$_2$.

This method has allowed us to prepare the phosphines $P(NMe_2)(Cl)(C\equiv CPh)$ and $P(Me)(Cl)(C\equiv CPh)$ in 40 and 54% yields, respectively.

Synthesis of $Fe(CO)_4P(R)(CCR')(H)$ Complexes. For the synthesis of these complexes, we have used $[PPh_4][HFe(CO)_4]$ which reacts with chlorophosphines to give complexed secondary phosphines[4] in one step (eq 3).

$$P(R)(Cl)(C\equiv CR') + [PPh_4][HFe(CO)_4] \rightarrow (CO)_4Fe[P(R)(H)(C\equiv CR')] \quad (3)$$

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[1] Mathieu, R.; Caminade, A.-M.; Majoral, J.-P.; Daran, J.-C. *J. Am. Chem. Soc.* **1986**, *108*, 8007.

[2] Maier, L. In *Organic Phosphorus Compounds*; Kosolapoff, G. M., Maier, L., Eds.; Wiley-Interscience: New York, London, Sydney, Toronto, 1972; Vol. 1, p 1.

[3] Bozolyubov, G. M.; Petrov, A. A. *Zh. Obshch. Khim.* **1967**, *37*, 229.

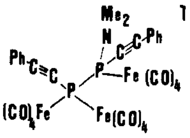

Figure 1. Proposed structure for complex 1.

The reaction works well when R = N(i-Pr)$_2$ and R′ = Ph or t-Bu and when R = Me and R′ = Ph, and the iron complexes are isolated in 80–95% yield as liquids which have been identified from their spectroscopic properties by comparison with those of $(CO)_4Fe[P(t\text{-}Bu)(H)(C{\equiv}CPh)]$.[1]

When R = NMe$_2$ and R′ = Ph, we have faced some difficulties due to the instability of the iron complex. Indeed, the major product of the reaction is an anionic complex, 1, isolated as a liquid, whose nature has been deduced from spectroscopic data. Its infrared spectrum gives evidence of the presence of a free alkynyl group, with an absorption band at 2168 cm^{-1}, and the spectrum in the ν(CO) stretching region closely resembles that of $[(PR\text{–}PRH)[Fe(CO)_4]_3]^-$ complexes obtained upon reacting RPCl$_2$ phosphines with an excess of $[HFe(CO)_4]^-$.[4] The phosphorus NMR spectrum shows two doublets centered at 112 and 2 ppm with a coupling constant of 389 Hz. Furthermore, the proton-coupled ^{31}P NMR spectrum indicates that the phosphorus resonating at 112 ppm is bonded to an NMe$_2$ group. The proton NMR spectrum confirms the presence of the NMe$_2$ and PPh$_4$ groups and of the phenyl of the alkynyl fragments in the 1:1:2 ratio.

Considering these observations, we propose for 1 the structure shown in Figure 1 which is in agreement with the spectroscopic data. The mechanism for the formation of 1 is not clear as it implies formally the elimination of NMe$_2$H between two $(CO)_4FeP(NMe_2)(H)(C{\equiv}CPh)$ molecules and the elimination of molecular hydrogen, one atom of hydrogen being provided by $[HFe(CO)_4]^-$. Confirmation of the instability of the neutral iron complex comes from the observation that if it is isolated by extraction, it slowly changes in solution to an intractable mixture (20 peaks observed in the ^{1}H NMR in the NMe$_2$ region of resonance!).

To overcome the difficulties in isolating pure $(CO)_4FeP(NMe_2)(H)(C{\equiv}CPh)$, we have prepared the iron cobalt complex by quickly adding Co$_2$(CO)$_8$ to the reaction mixture (vide infra).

Synthesis of $(CO)_4Fe[P(R)(H)(C{\equiv}CR')]Co_2(CO)_6$ Complexes. (a) Case Where R = N(i-Pr)$_2$ and R′ = Ph or t-Bu and R = Me and R′ = Ph. Addition of 1 equiv of Co$_2$(CO)$_8$ to the iron complexes leads to immediate CO evolution at room temperature. The isolated products of the reaction are oils that were purified by column chromatography. Spectroscopic data are quite similar to those of $(CO)_4Fe[P(t\text{-}Bu)(H)(C{\equiv}CPh)]Co_2(CO)_6$[1] and support the same structure in which the Co$_2$(CO)$_6$ group is complexed to the triple bond.

(b) Case Where R = NMe$_2$ and R′ = Ph. As mentioned above, Co$_2$(CO)$_8$ was added in a stoichiometric quantity to the reaction mixture of the synthesis of $(CO)_4Fe[P(NMe_2)(H)C{\equiv}CPh]$. Hexane extraction and chromatography separated four products.

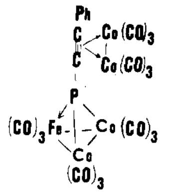

Figure 2. Proposed structure for complex 2.

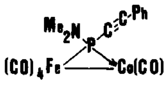

Figure 3. Proposed structure for complex 3.

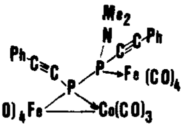

Figure 4. Proposed structure for complex 5.

The first product 2, isolated as brown crystals, exhibits a mass spectrum showing a molecular ion with m/z 844 and the successive loss of 15 CO. This and analytical data are consistent with the formulation $FeCo_4(CO)_{15}P(C{\equiv}CPh)$. Proton NMR indicated the presence of phenyl and no other hydrocarbon groups, and no signal was observed in the ^{31}P NMR certainly due to the broadening of the resonance by the cobalt nucleus.

Infrared spectroscopy shows absorption of terminal carbonyl groups only in the ν(CO) stretching region, and part of the spectrum closely resembles that of a Co$_2$(CO)$_6$ fragment bonded to a carbon–carbon triple bond.[5] All these observations suggest for 2 the structure shown in Figure 2. It consists of a FeCo$_2$(CO)$_9$ cluster stabilized by an alkynylphosphinidene ligand. Furthermore, the carbon–carbon triple bond is π-bonded to a Co$_2$(CO)$_6$ unit. This constitutes the first example of an alkynylphosphinidene stabilized by complexation.

The second complex isolated 3 is a red liquid for which infrared spectroscopy indicates the presence of a free alkynyl bond and terminal carbonyl groups. The presence of one NMe$_2$ and one phenyl group in a 1:1 ratio is deduced from proton NMR spectroscopy. Moreover, in the ^{31}P NMR spectrum a broad signal is observed at 196 ppm. Mass spectrometry is consistent with the $FeCo(CO)_7P(NMe_2)(C{\equiv}CPh)$ formulation. We propose for this compound the structure shown in Figure 3 in which a $P(NMe_2)(C{\equiv}CPh)$ phosphido ligand bridges a $(CO)_4Fe\text{–}Co(CO)_3$ unit, a structure found for the analogous $(CO)_7FeCo(PMe_2)$ complex.[6]

The third complex 4, isolated as brown crystals, is the expected $(CO)_4Fe[P(NMe_2)(H)(C{\equiv}CPh)]Co_2(CO)_6$ obtained in 10% yield. The spectroscopic data are in perfect agreement with the formulation.

For the last compound 5, isolated as a brown liquid, mass spectrometry indicates a mass of 787 and the successive loss of 11 carbonyl groups consistent with the $Fe_2Co(CO)_{11}P_2(NMe_2)(C{\equiv}CPh)_2$ formulation.

In the infrared spectrum, evidence of a free alkynyl group and of terminal carbonyl ligands is obtained. Furthermore, the proton NMR spectrum confirms the presence of the NMe$_2$ and phenyl groups in a 1:2 ratio. The $^{31}P\{^1H\}$ NMR spectrum consists of two doublets (J_{PP} = 194 Hz) centered at 110 and 140 ppm, the latter being broad. ^{31}P NMR spectra indicate that the phosphorus resonating at 110 ppm is bonded to the NMe$_2$ group.

All these spectroscopic data suggest for 5 a structure derived from the structure of 1. It is shown in Figure 4. This structure results from the substitution in 1 of [Fe-

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[4] Mathieu, R.; Caminade, A.-M.; Majoral, J.-P.; Attali, S.; Sanchez, M. *Organometallics* **1986**, *5*, 1914.

[5] Dickson, R. S.; Fraser, P. J. *Adv. Organomet. Chem.* **1974**, *12*, 323.

[6] Keller, E.; Vahrenkamp, H. *Chem. Ber.* **1977**, *110*, 430.

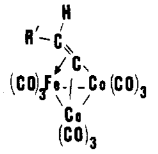

Figure 5. Structure of complexes **6a** (R = Ph) and **6b** (R = *t*-Bu).

$(CO)_4]^-$ by the isoelectronic $Co(CO)_4$ group and from the formation of an Fe–Co bond due to the loss of a molecule of CO.

This structure is consistent with the small variation of $\delta(^{31}P)$ of the $P(NMe_2)(C{\equiv}CPh)$ group between **1** and **5** and with the shift of the $P(C{\equiv}CPh)$ group toward a lower field due to the formation of the metal–metal bond.[7]

To summarize, compounds **2**, **3**, and **5** appear to result from the reaction of **1** with $Co_2(CO)_8$, while the formation of **2** and **3** implies phosphorus–phosphorus bond breaking in **1**.

Study of the Thermolysis of the $(CO)_4Fe[P(R)(H)(C{\equiv}CR')]Co_2(CO)_6$ Complexes. Thermolysis was generally carried out in boiling hexane except in the case where R = Me and R' = Ph where it was necessary to operate in boiling toluene to observe significant change.

The reactions usually lead to a complex mixture of compounds that were separated by chromatography. When R is a dialkylamino group, three types of complexes have been isolated. They have in common a $FeCo_2$ metallic core stabilized by bridging ligands coming from the phosphine, but in no case was formation of a phosphallenyl group detected.

The first type of complex isolated formulates as $FeCo_2(CO)_9(\mu_3\text{-}\eta^2\text{-}C{=}CHR)$ (**6a**, R = Ph; **6b**, R = *t*-Bu) (Figure 5). These complexes have been obtained recently by a more direct way,[8] and our spectroscopic data are in good agreement with theirs. They have been obtained in low yield in the cases where *R* = NMe_2 and R' = Ph and R = $N(i\text{-}Pr)_2$ and R' = *t*-Bu or in trace amounts (R = $N(i\text{-}Pr)_2$, R' = Ph).

The second type of complex obtained is stabilized by a phosphinidene ligand (PR), formulated as $FeCo_2(CO)_9(\mu_3\text{-}PR)$ (**7a**, R = $N(i\text{-}Pr)_2$; **7b**, R = NMe_2). These are the major products isolated subsequent to chromatography. They have been further identified by comparison of their spectroscopic data with published values.[9]

The last family of compounds **8** has been obtained in low yield. These complexes decompose during column chromatography, but infrared spectra of the reaction solution before treatment shows that they are actually the major complexes formed during thermolysis. Their infrared spectra show only the terminal carbonyl group absorption while proton NMR gives evidence for the presence of the R and R' groups and of a P–H entity.

In the case where R = $N(i\text{-}Pr)_2$ and R' = Ph, it was possible to obtain the $^{31}P\{^1H\}$ NMR spectrum showing a broad resonance (30 ppm at half-height) centered at 229 ppm, evidence for the presence of a phosphido bridging ligand. Mass spectra are consistent with the $FeCo_2(CO)_7P(R)(H)(CCR')$ formulation. From these data, two possible structures can be proposed. They are shown in Figure 6. The broadness of the ^{31}P NMR spectrum suggests that form A is the more likely.

To summarize, it appears that in such thermal rearrangement reactions of $(CO)_4Fe[P(NR_2)(H)(C{\equiv}CR')]$-

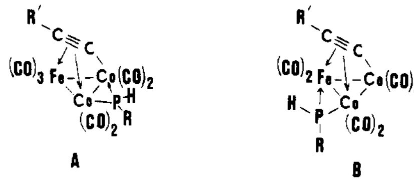

Figure 6. The two possible structures for complexes **8** (R = $N(i\text{-}Pr)_2$, NMe_2; R' = Ph).

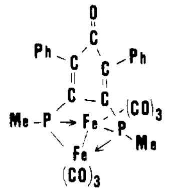

Figure 7. Proposed structure for complex **9**.

$Co_2(CO)_6$ complexes, the products afforded result from the usual reactivity of $R_2P(C{\equiv}CR')$ phosphines toward cluster compounds, i.e., the breaking of the *P*-alkynyl bond[10] generating acetylide and phosphido ligands.

In the case of $(CO)_4Fe[P(Me)(H)(C{\equiv}CPh)]Co_2(CO)_6$, it was necessary to work at the boiling temperature of toluene to observe significant reaction. Extensive decomposition occurred, and the yield of the isolated complexes was very low. Three complexes were isolated by chromatography: **6a** in trace amount, $FeCo_2(CO)_9(\mu_3\text{-}PMe)$ (**11**) in 10% yield, and a third complex, **9**, as a pink oil. The infrared spectrum of **9** in the $\nu(CO)$ stretching region is typical of $Fe_2(CO)_6(\mu\text{-}X)_2$ systems,[12] but an adsorption of medium intensity is also observed at 1709 cm^{-1}. The ^1H NMR spectrum show the presence of phenyl groups and of a pseudotriplet characteristic of $X_nAA'X'_n$ spin systems in the PMe region. The two groups are in a 1:1 ratio. In the $^{31}P\{^1H\}$ NMR spectrum, a singlet is observed at 107 ppm.

The molecular ion is detected by mass spectrometry at *m/z* 602 with successive loss of six CO groups, compatible with the $Fe_2(CO)_6[P(Me)(CCPh)]_2CO$ formulation. Other fragments are observed, corresponding to the $Fe_2P_2C_5OPh_2$, $Fe_2P_2C_5OPh$, and $Fe_2P_2Me_2C_5OPh$ ions. The 1709 cm^{-1} peak in the IR spectrum shows that the seventh CO in the formulation corresponds to a ketonic group. Unfortunately, the quantity of isolated **9** was not sufficient to have a conclusive ^{13}C NMR spectrum (only phenyl resonances at 131.3, 128.8, and 128.2 ppm were clearly detectable).

From all these spectroscopic data, we suggest for **9** the structure shown in Figure 7. It consists of a $Fe_2(CO)_6$ unit bridged by a diphosphido ligand, P(Me)CC(Ph)C(O)C(Ph)CP(Me) resulting from the coupling of two $MeP(C{\equiv}CPh)$ units and one CO group.

Iron–alkyne chemistry gives several examples of coupling of alkynes with carbon monoxide,[13] but this seems to be the first case where the alkyne used is functionalized by a phosphorus entity.

To conclude, this study shows that our strategy for the synthesis of complexes containing phosphacumulene ligands is not general since the different phosphine complexes exhibit a diversified but interesting thermal behavior. Nevertheless, the expected migration of hydrogen from the phosphorus to the β-carbon of the alkynyl group is ob-

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[7] Carty, A. J. *Adv. Chem. Ser.* **1982**, *No. 196*, 163.

[8] Albiez, T.; Bernhardt, W.; von Schnering, C.; Roland, E.; Bantel, H.; Vahrenkamp, H. *Chem. Ber.* **1987**, *120*, 141.

[9] Honrath, V.; Vahrenkamp, H. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1984**, *39B*, 559.

[10] Carty, A. J. *Pure Appl. Chem.* **1982**, *54*, 113.

[11] Müller, M.; Vahrenkamp, H. *Chem. Ber.* **1983**, *116*, 2311.

[12] Arabi, M. S.; Mathieu, R.; Poilblanc, R. *J. Organomet. Chem.* **1979**, *177*, 199.

[13] Hübel, W. In *Organic Synthesis via Metal Carbonyls*; Wender, I., Pino, P., Eds.; Wiley: New York, 1968; Vol. 1, p 273.

served in all cases (except when R = Me), but the predominant reactions imply the cleavage of the phosphorus–alkynyl ligand P–C bond. Unexpected rearrangements leading to novel examples of alkynylphosphinidene or phosphido ligands have also been noted.

Experimental Section

All the reactions were performed in a dry argon atmosphere. Dry and oxygen-free solvents were used at all times. ^{1}H NMR spectra were recorded on a Bruker WH90 spectrometer and ^{31}P NMR spectra on a Bruker AC80 machine. Infrared spectra were obtained on a Perkin-Elmer 225 spectrometer in hexane or dichloromethane solutions. Mass spectra were obtained on a Varian MAT 311A. Microanalysis were performed in our laboratory. [PPh$_4$][HFe(CO)$_4$] was synthesized by published procedure.[14]

Synthesis of P(R)(Cl)(C≡CR′) Phosphines. (a) Case Where R = N(*i*-Pr)$_2$ and R′ = Ph or *t*-Bu. The R′C≡CLi compound, prepared by the reaction of BuLi with R′C≡CH at −78 °C in diethyl ether (40 mL), was added at −78 °C to an equimolecular solution of [N(*i*-Pr)$_2$]PCl$_2$ in diethyl ether (30 mL). The solution then was stirred for 2 h at room temperature. After filtration, the resulting solution was fractionally distilled, giving the following.

(i) [(*i*-Pr)$_2$N]P(Cl)(C≡CPh): a yellow liquid; bp 126 °C (0.1 mmHg); 31% yield; ^{1}H NMR δ 1.27 (d, J_{HH} = 7 Hz, 6 H, CH$_3$), 1.35 (d, J_{HH} = 7 Hz, 6 H, CH$_3$), 3.9 (br, 2 H, CH), 7.4 (m, 5 H, C$_6$H$_5$); ^{31}P NMR δ 90 (t, J_{PH} = 11 Hz); IR ν(C≡C) 2168 cm^{-1}.

Anal. Calcd for C$_{14}$H$_{19}$ClNP: C, 62.80; H, 7.10; N, 5.23. Found: C, 62.65; H, 6.85; N, 5.02.

(ii) (*i*-Pr$_2$N)P(Cl)(C≡C-*t*-Bu): a colorless liquid; bp 64 °C (0.08 mmHg); 35% yield; ^{1}H NMR δ 1.05 (d, J_{HH} = 7 Hz, 6 H, CH$_3$), 1.07 (s, 9 H, *t*-Bu), 1.18 (d, J_{HH} = 7 Hz, 6 H, CH$_3$), 3.9 (br, 2 H, CH); ^{31}P NMR δ 91; IR ν(C≡C) 2150 cm^{-1}.

Anal. Calcd for C$_{12}$H$_{23}$ClNP: C, 58.18; H, 9.29; N, 5.65. Found: C, 57.92; H, 9.18; N, 5.59.

(b) Case Where R = NMe$_2$ and R′ = Ph. To a suspension of PhC≡CLi (91 mmol) in 45 mL of diethyl ether at −50 °C was slowly added a solution of PCl(NMe$_2$)$_2$ (91 mmol) in 90 mL of diethyl ether. The resulting mixture was stirred for 1 h at room temperature. The solution was filtered and cooled to −30 °C, and to this solution was slowly added 82 mmol of PCl$_3$ in 20 mL of diethyl ether. The mixture was stirred for 5 h at room temperature and then fractionally distilled under reduced pressure, giving 7 g of (Me$_2$N)P(Cl)(C≡CPh) as a yellow liquid: bp 80 °C (0.1 mmHg); ^{1}H NMR (C$_6$D$_6$) δ 2.58 (d, J_{PH} = 13 Hz, 6 H, CH$_3$), 7.1 (m, 5 H, C$_6$H$_5$); ^{31}P{^{1}H} NMR δ 103; IR ν(C≡C) 2165 cm^{-1}.

Anal. Calcd for C$_{10}$H$_{11}$ClNP: C, 56.73; H, 5.20; N, 6.61. Found: C, 56.89; H, 5.12; N, 6.50.

(c) Case Where R = Me and R′ = Ph. A solution of P(NMe$_2$)$_3$ (7 mL, 36.5 mmol) in 10 mL of diethyl ether was added at −10 °C to a solution of P(Me)Cl$_2$ (3.4 mL, 36.5 mmol) in 35 mL of diethyl ether. This mixture then was stirred for 3 h at room temperature, and ^{31}P NMR spectroscopy showed that is consisted in a 1:1 mixture of (Me)P(Cl)(NMe$_2$) and PCl(NMe$_2$)$_2$. This solution was slowly added to a suspension of PhC≡CLi (73 mmol) in 35 mL of diethyl ether cooled to −50 °C. After being stirred for 2 h at room temperature, the solution was filtered and 6.1 mL of PCl$_3$ (70 mmol) in 25 mL of diethyl ether was added at −30 °C. The mixture was stirred for 3 h at room temperature and then fractionnally distilled under vacuo giving 3.6 g of MePCl(C≡CPh) (54% yield) and 3 g of P(NMe$_2$)Cl(C≡CPh). (Me)P(Cl)(C≡CPh): yellow liquid; bp 77 °C (0.3 mmHg); ^{1}H NMR δ 1.31 (d, J_{PH} = 7 Hz, 3 H, CH$_3$), 7.3 (m, 5 H, C$_6$H$_5$); ^{31}P{^{1}H} NMR δ 59; IR ν(C≡C) 2160 cm^{-1}.

Anal. Calcd for C$_9$H$_8$ClP: C, 59.18; H, 4.38. Found: C, 59.12; H, 4.09.

Synthesis of (CO)$_4$Fe[P(R)(H)(C≡CR′)] Complexes. (a) General Procedure for R = N(*i*-Pr)$_2$ and R′ = Ph or *t*-Bu and R = Me and R′ = Ph. To a solution of 4 mmol of the chlorophosphine in 15 mL of dichloromethane was added a solution of [PPh$_4$][HFe(CO)$_4$] (2.03 g, 4 mmol) in 15 mL of dichloromethane. The mixture was stirred for 2 h at room temperature and then evaporated to dryness. The residue was extracted with 4 × 10 mL of diethyl ether, and the extracts were evaporated to dryness under vacuo, leaving (CO$_4$)Fe[P(R)(H)(C≡CR′)] complexes as oils.

(CO)$_4$Fe[P(N(*i*-Pr)$_2$)H(C≡CPh)]: brown liquid; 88% yield; *m/z* 401; IR (CH$_2$Cl$_2$ solution) 2170 (w) (ν (C≡C)), 2050 (m), 1973 (m), 1940 (s) (ν(CO)) cm^{-1}; ^{1}H NMR (CD$_2$Cl$_2$) δ 1.23 (d, J_{HH} = 7 Hz, 6 H, CH$_3$), 1.41 (d, J_{HH} = 7 Hz, 6 H, CH$_3$), 3.80 (d, sept, J_{PH} = 15 Hz, J_{HH} = 7 Hz, 2 H, CH), 7.4 (m, 5 H, C$_6$H$_5$), 7.61 (d, J_{PH} = 438 Hz, 1 H, PH); ^{31}P NMR δ 24 (dt, $^1J_{PH}$ = 438 Hz, $^3J_{PH}$ = 15 Hz).

Anal. Calcd for C$_{18}$H$_{20}$NO$_4$PFe: C, 53.86; H, 4.98; N, 3.49. Found: C, 53.43; H, 4.92; N, 3.12.

(CO)$_4$Fe[P(N(*i*-Pr)$_2$)H(C≡C-*t*-Bu)]: yellow liquid; 35% yield; *m/z* 381; IR (hexane solution) 2160 (w) (ν(C≡C)), 2054 (m), 1980 (m), 1950 (s) (ν(CO)) cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 1.16 (d, J_{HH} = 7 Hz, 6 H, CH$_3$), 1.23 (s, 9 H, C(CH$_3$)$_3$), 1.32 (d, J_{HH} = 7 Hz, 6 H, CH$_3$), 3.88 (d, sept, J_{PH} = 15 Hz, J_{HH} = 7 Hz, 2 H, CH), 7.33 (d, J_{PH} = 433 Hz, 1 H, PH); ^{31}P NMR δ 24 (dt, $^1J_{PH}$ = 433 Hz, $^3J_{PH}$ = 15 Hz).

Anal. Calcd for C$_{16}$H$_{24}$NO$_4$PFe: C, 50.39; H, 6.29; N, 3.67. Found: C, 50.00; H, 6.44; N, 3.42.

(CO)$_4$Fe[P(Me)H(C≡CPh)]: brown liquid; 78% yield; *m/z* 316; IR (CH$_2$Cl$_2$) 2169 (w) (ν(C≡C)), 2053 (m), 1982 (m), 1949 (s) (ν(CO)) cm^{-1}; ^{31}P NMR δ −17 (dq, $^1J_{PH}$ = 397 Hz, $^2J_{PH}$ = 9 Hz).

Anal. Calcd for C$_{13}$H$_9$O$_4$PFe: C, 49.36; H, 2.84. Found: C, 49.12; H, 2.65.

(b) Case of P(NMe$_2$)(Cl)(C≡CPh). To a solution of the phosphine (0.42 g, 2 mmol) in 10 mL of dichloromethane was added a solution of [PPh$_4$][HFe(CO)$_4$] (1.02 g, 2 mmol) in 8 mL of dichloromethane. The mixture was stirred for 10 min at room temperature, and infrared spectroscopy gave evidence of the formation of (CO)$_4$Fe[P(NMe$_2$)(H)(C≡CPh)] (2166 (w) (ν(C≡C)), 2062 (m), 1980 (m), 1943 (s) (ν(CO)) cm^{-1}), but the complex was not isolated and the mixture was reacted with Co$_2$(CO)$_8$ (vide infra).

When the mixture was left for 2 h at room temperature, infrared spectroscopy showed the disappearance of the iron complex and formation of 1. The solution was evaporated to dryness, and extraction of the residue with diethyl ether and evaporation of ether gave 1 as a red liquid (0.3 g, 37% yield): IR (CH$_2$Cl$_2$) 2165 (w) (ν(C≡C)), 2051 (w), 2040 (m), 2015 (s), 1933 (br) (vs) (ν(CO)) cm^{-1}; ^{31}P NMR δ 112 (d, sept, J_{PP} = 389 Hz, J_{PH} = 10 Hz), 22 (s), 2 (d, J_{PP} = 389 Hz); ^{1}H NMR δ 3.12 (br, d, J_{PH} = 10.9 Hz, 6 H, N(CH$_3$)$_2$), 7.50 (m, 10 H, C$_6$H$_5$), 7.91, 8.01 (m, 20 H, P(C$_6$H$_5$)$_4$).

Anal. Calcd for C$_{54}$H$_{36}$Fe$_3$NO$_{12}$P$_3$: C, 56.29; H, 3.12; N, 1.22. Found: C, 56.72; H, 3.62; N, 1.10.

Synthesis of (CO)$_4$Fe[P(R)(H)(C≡CR′)]Co$_2$(CO)$_6$ Complexes. (a) General Procedure of Synthesis. To a solution of (CO)$_4$Fe[P(R)(H)(C≡CR′)] (ca. 3 mmol) in 15 mL of CH$_2$Cl$_2$ (or to the reaction mixture from the synthesis of (CO)$_4$Fe[P(NMe$_2$)(H)(C≡CPh)]) was added Co$_2$(CO)$_8$ (1.03 g, 3 mmol) dissolved in 15 mL of hexane. The mixture was stirred at room temperature for 15–20 min until CO evolution ceased. It was then evaporated to dryness under vacuo, and the residue was extracted with 3 × 15 mL of hexane. Evaporation of hexane gave brown liquids that were purified by chromatography on Florisil with hexane as eluent.

(CO)$_4$Fe[P(N(*i*-Pr)$_2$)(H)(C≡CPh)]Co$_2$(CO)$_6$: a brown liquid; 65% yield; *m/z* 687; IR (hexane) 2095 (m), 2060 (s), 2050 (m), 2035 (s), 2015 (m), 1980 (m), 1945 (s), 1937 (sh), 1933 (sh) cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 1.29 (d, J_{HH} = 7 Hz, 6 H, CH$_3$), 1.32 (d, J_{HH} = 7 Hz, 6 H, CH$_3$), 3.79 (d, sept, J_{PH} = 15 Hz, J_{HH} = 7 Hz, 2 H, CH), 7.4 (m, 5 H, C$_6$H$_5$), 7.89 (d, J_{PH} = 403 Hz, PH); ^{31}P NMR (CDCl$_3$) δ 74 (dt, $^1J_{PH}$ = 403 Hz, $^3J_{PH}$ = 15 Hz).

Anal. Calcd for C$_{24}$H$_{20}$NO$_{10}$PCo$_2$Fe: C, 41.92; H, 2.91; N, 2.03. Found: C, 41.52; H, 3.21; N, 2.24.

(CO)$_4$Fe[P(N(*i*-Pr)$_2$)(H)(C≡C-*t*-Bu)]Co$_2$(CO)$_6$: a brown liquid; 95% yield; *m/z* 667; IR (hexane) 2092 (m), 2072 (s), 2054 (m), 2032 (s), 2022 (m), 1971 (m), 1947 (s) cm^{-1}; ^{1}H NMR δ 1.05 (d, J_{HH} = 7 Hz, 6 H, CH$_3$), 1.13 (d, J_{HH} = 7 Hz, 6 H, CH$_3$), 3.54 (d, sept, J_{PH} = 15 Hz, J_{HH} = 7 Hz, 2 H, CH), 1.31 (s, 9 H, C(CH$_3$)$_3$), 7.42 (d, J_{PH} = 400 Hz); ^{31}P NMR δ 79 (dt, $^1J_{PH}$ = 400 Hz, $^3J_{PH}$ = 15 Hz).

Anal. Calcd for C$_{22}$H$_{24}$NO$_{10}$PCo$_2$Fe: C, 39.58; H, 3.59; N, 2.09. Found: C, 39.13; H, 3.32; N, 1.96.

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[14] Mitsubo, T.; Watanabe, Y.; Nakanishi, H.; Morishima, I.; Imubushi, T.; Takegami, Y. *J. Chem. Soc., Dalton Trans.* **1978**, 1298.

$(CO)_4Fe[P(Me)(H)(CCPh)]Co_2(CO)_6$: a red-brown liquid; 60% yield; *m/z* 602; IR (hexane) 2100 (m), 2073 (s), 2056 (m), 2037 (s), 2020 (m), 1987 (m), 1951 (s) cm^{-1}.

Anal. Calcd for $C_{19}H_9O_{10}PCo_2Fe$: C, 37.87; H, 1.49. Found: C, 37.93; H, 1.73.

(b) Case of the Reaction of $(CO)_4Fe[P(NMe_2)(H)C{\equiv}CPh]$ with $Co_2(CO)_8$. Chromatography on Florisil with hexane as eluent separated four fractions.

$FeCo_4(CO)_{15}P(C{\equiv}CPh)$ (**2**): brown crystals; *m/z* 424; IR (hexane) 2105 (w), 2083 (m), 2071 (s), 2051 (s), 2035 (s), 2029 (sh), 2010 (sh), 2001 (w), 1982 (w) cm^{-1}. ^1H NMR δ 7.4 (m, C_6H_5).

Anal. Calcd for $C_{23}H_5O_{15}PCo_4Fe$: C, 32.70; H, 0.59. Found: C, 32.33; H, 1.2.

$FeCo(CO)_7[P(NMe_2)(C{\equiv}CPh)]$ (**3**): red liquid; *m/z* 487; IR (hexane) 2164 cm^{-1} (w) ($\nu(C{\equiv}C)$), 2089 (m), 2082 (m), 2028 (vs), 2017 (s), 2007 (s), 1989 (m), 1979 (m) cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.90 (d, J_{PH} = 14 Hz, 6 H, CH_3), 7.4 (m, 5 H, C_6H_5); ^{31}P NMR δ 196.

Anal. Calcd for $C_{17}H_{11}O_7NPCoFe$: C, 41.89; H, 2.26; N, 2.87. Found: C, 41.65; H, 2.13; N, 2.96.

$(CO)_4Fe[P(NMe_2)(H)(C{\equiv}CPh)]Co_2(CO)_6$ (**4**): red-brown crystals; 10% yield; *m/z* 631; IR (hexane) 2092 (m), 2058 (s), 2049 (m), 2037 (m), 2030 (m), 2012 (w), 1980 (m), 1945 (s) cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.97 (d, J_{PH} = 11 Hz, 6 H, CH_3), 7.4 (m, 5 H, C_6H_5), 7.68 (d, J_{PH} = 421 Hz, 1 H, PH); ^{31}P NMR δ 113 (d, sept, $^1J_{PH}$ = 421 Hz, $^3J_{PH}$ = 11 Hz).

Anal. Calcd for $C_{20}H_{12}O_{10}NPCo_2Fe$: C, 38.07; H, 1.92; N, 2.22. Found: C, 38.01; H, 1.75; N, 2.05.

$Fe_2Co(CO)_{11}P_2(NMe_2)(C{\equiv}CPh)_2$ (**5**): brown crystals; *m/z* 787; IR (hexane) 2172 (w) ($\nu(C{\equiv}C)$), 2091 (m), 2056 (s), 2035 (s), 2023 (sh), 2018 (s), 1990 (m), 1975 (m), 1956 (m) ($\nu(CO)$) cm^{-1}; ^1H NMR δ 3.22 (dd, J_{PH} = 12 Hz, J_{PH} = 4.7 Hz, 6 H, CH_3), 7.4 (m, 10 H, C_6H_5); ^{31}P NMR δ 110 (d, sept, $^1J_{PP}$ = 194 Hz, J_{PH} = 12 Hz), 140 (d, J_{PP} = 194 Hz).

Anal. Calcd for $C_{29}H_{16}O_{11}NP_2CoFe_2$: C, 44.22; H, 2.03; N, 1.78. Found: C, 44.01; H, 2.12; N, 1.93.

Thermolysis of $(CO)_4Fe[P(R)(H)(C{\equiv}CR')]Co_2(CO)_6$ Complexes. Except in the case where R = Me and R′ = Ph, thermolysis was conducted in boiling hexane. For R = Me, it was carried out in boiling toluene. The course of the reaction was monitored by IR spectroscopy and stopped when only traces of starting material were detected. The reaction was over in 1 h except when R = NMe_2 and R′ = Ph where 6 h were needed. At the end of the reaction the solution was evaporated to dryness and the mixture of products was separated by chromatography on Florisil, elution being performed with hexane/toluene with increasing amount of toluene.

(a) Case Where R = $N(\textit{i}\text{-}Pr)_2$ and R′ = Ph. Three fractions were separated and identified.

$FeCo_2(CO)_9(\mu_3\text{-}\eta^2\text{-}CCHPh)$ (**6a**): trace amounts identified by its IR spectrum in the $\nu(CO)$ stretching region (vide infra).

$FeCo_2(CO)_9[\mu_3\text{-}P(N(\textit{i}\text{-}Pr)_2)]$ (**7a**): violet crystals; 4% yield; *m/z* 557; IR (hexane) 2088 (w), 2040 (m), 2030 (s), 2025 (sh), 1995 (w), 1981 (w), 1965 (w) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.45 (d, J_{HH} = 7 Hz, 12 H, CH_3), 4.06 (d, sept, J_{PH} = 16 Hz, J_{HH} = 7 Hz, 2 H, CH).

Anal. Calcd for $C_{15}H_{14}O_9NPCo_2Fe$: C, 32.30; H, 2.51; N, 2.51. Found: C, 31.92; H, 2.73; N, 2.28.

$FeCo_2(CO)_7[P(N(\textit{i}\text{-}Pr)_2)(H)(C{\equiv}CPh)]$ (**8a**): a maroon liquid; 4% yield; *m/z* 603; IR (hexane) 2060 (m), 2024 (s), 2018 (s), 1990 (m), 1970 (w) cm^{-1}. ^1H NMR ($CDCl_3$) δ 1.37 (d, J_{HH} = 7 Hz, 12 H, CH_3), 3.60 (d, sept, J_{PH} = 14 Hz, J_{HH} = 7 Hz, 2 H, CH), 7.4 (m, 5 H, C_6H_5), 8.24 (d, J_{PH} = 345 Hz, 1 H, PH); ^{31}P NMR δ 229.

Anal. Calcd for $C_{21}H_{20}O_7NPCo_2Fe$: C, 41.79; H, 3.31; N, 2.32. Found: C, 40.98; H, 3.12; N, 2.14.

(b) Case Where R = $N(\textit{i}\text{-}Pr)_2$ and R′ = *t*-Bu. Three fractions were isolated. $FeCo_2(CO)_9(\mu_3\text{-}\eta^2\text{-}CCH(\textit{t}\text{-}Bu))$ (**6b**): brown crystals; 3% yield; *m/z* 508; IR (hexane) 2096 (m), 2049 (s), 2040 (s), 2033 (s), 2013 (m), 1979 (m) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.83 (s, 9 H, $C(CH_3)_3$), 5.82 (s, 1 H, CH).

$FeCo_2(CO)_9[\mu_3\text{-}PN(\textit{i}\text{-}Pr)_2]$ (**7a**): 4% yield.

$FeCo_2(CO)_7[\mu\text{-}P(N(\textit{i}\text{-}Pr)_2)H][\mu_3\text{-}\eta^2\text{-}C{\equiv}C(t\text{-}Bu)]$ (**8b**): a maroon liquid; 7% yield; *m/z* 583; IR (hexane) 2057 (m), 2019 (s), 2012 (s), 1976 (m), 1967 (w) cm^{-1}; ^1H NMR δ 1.32 (d, J_{HH} = 7 Hz, 12 H, CH_3), 1.62 (s, 9 H, $C(CH_3)_3$), 8.14 (d, J_{PH} = 344 Hz, 1 H, PH).

Anal. Calcd for $C_{19}H_{24}O_7NPCo_2Fe$: C, 39.11; H, 4.12; N, 2.40. Found: C, 39.32; H, 4.60; N, 2.72.

(c) Case Where R = NMe_2 and R′ = Ph. Two products have been isolated by chromatography, but the main product of the reaction, as evidenced by infrared spectroscopy of the reaction mixture, is $FeCo_2(CO)_7(\mu\text{-}P(NMe_2)H)(\mu_3\text{-}\eta^2\text{-}C{\equiv}CPh)$, which decomposed during chromatography ($\nu(CO)$ 2064, 2024, 2019, 1989, 1968 cm^{-1}). The products isolated were the following.

$FeCo_2(CO)_9(\mu_3\text{-}\eta^2\text{-}CCHPh)$ (**6a**): 3% yield; *m/z* 528; IR (hexane) 2098 (m), 2053 (s), 2044 (s), 2037 (s), 2015 (m), 1989 (m), 1983 (w) cm^{-1}; ^1H NMR ($CDCl_3$) δ 6.88 (s, 1 H, CH), 7.35 (m, 5 H, C_6H_5).

$FeCo_2(CO)_9[\mu_3\text{-}P(NMe_2)]$: purple crystals; 11% yield; *m/z* 501; IR (hexane) 2091 (w), 2044 (m), 2035 (s), 1985 (w), 1969 (w) cm^{-1}.

Anal. Calcd for $C_{11}H_6O_9NPCo_2Fe$: C, 26.34; H, 1.19; N, 2.79. Found: C, 26.16; H, 1.10; N, 2.62.

(d) Case Where R = Me and R′ = Ph. Chromatography of the reaction mixture gave evidence of the formation of six products, three of which were in sufficient quantity to be identified.

$FeCo_2(CO)_9(\mu_3\text{-}\eta^2\text{-}CCHPh)$ (**6a**): a trace amount.

$FeCo_2(CO)_9(\mu_3\text{-}PMe)$ (**7c**): purple crystals; 2% yield; IR (hexane) 2095 (w), 2050 (s), 2040 (s), 2032 (m), 1985 (w), 1971 (w) cm^{-1}.

$Fe_2(CO)_6[(PMe)_2(CCPh)_2CO]$ (**9**): a pink liquid; 10% yield: *m/z* 602; IR (hexane) 2058 (m), 2024 (s), 1993 (m), 1985 (m), 1972 (w), 1709 (w) cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.09 (t, J_{PH} = 7 Hz, CH_3), 7.39 (m, 5 H, C_6H_5); $^{31}P\{^1H\}$ NMR δ 107.

Anal. Calcd for $C_{25}H_{16}O_7P_2Fe_2$: C, 49.83; H, 2.66. Found: C, 49.95; H, 2.83.

Registry No. **1**, 115796-69-5; **2**, 115796-61-7; **3**, 115796-62-8; **4**, 115796-63-9; **5**, 115826-44-3; **6a**, 101934-92-3; **6b**, 101934-93-4; **7a**, 115796-64-0; **7b**, 115796-67-3; **7c**, 87160-19-8; **8a**, 115796-65-1; **8b**, 115796-66-2; **9**, 115796-68-4; PhC≡CH, 536-74-3; *t*-BuC≡CH, 917-92-0; $[N(\textit{i}\text{-}Pr)_2]PCl_2$, 921-26-6; $[(\textit{i}\text{-}Pr)_2N]P(Cl)(C{\equiv}CPh)$, 115757-09-0; $(\textit{i}\text{-}Pr_2N)P(Cl)(C{\equiv}\textit{t}\text{-}Bu)$, 115757-10-3; PhC≡CLi, 4440-01-1; $PCl(NMe_2)_2$, 3348-44-5; PCl_3, 7719-12-2; $(Me_2N)P(Cl)(C{\equiv}CPh)$, 115757-11-4; $P(NMe_2)_3$, 1608-26-0; $P(Me)Cl_2$, 676-83-5; $(Me)P(Cl)(NMe_2)$, 4073-29-4; $MePCl(C{\equiv}CPh)$, 13891-83-3; $[PPh_4][HFe(CO)_4]$, 103616-27-9; $(CO)_4Fe[P(NMe_2)(H)(C{\equiv}CPh)]$, 115796-55-9; $(CO)_4Fe[P(N(\textit{i}\text{-}Pr)_2)H(C{\equiv}CPh)]$, 115796-56-0; $(CO)_4Fe[P(N(\textit{i}\text{-}Pr)_2)H(C{\equiv}C\textit{t}\text{-}Bu)]$, 115796-57-1; $(CO)_4Fe[P(Me)H(C{\equiv}CPh)]$, 115796-58-2; $Co_2(CO)_8$, 15226-74-1; $(CO)_4Fe[P(N(\textit{i}\text{-}Pr)_2)(H)(C{\equiv}CPh)]Co_2(CO)_6$, 115796-59-3; $(CO)_4Fe[P(N(\textit{i}\text{-}Pr)_2)(H)(C{\equiv}C\textit{t}\text{-}Bu)]Co_2(CO)_6$, 115826-43-2; $(CO)_4Fe[P(Me)(H)(C{\equiv}CPh)]Co_2(CO)_6$, 115796-60-6.