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Heterometallic Derivatives of [$Fe_2Cp_2(\mu$-PCy)(μ-CO)$(CO)_2$]: Rational Synthesis of Polynuclear Complexes from Neutral Precursors Having Pyramidal−Phosphinidene Bridges

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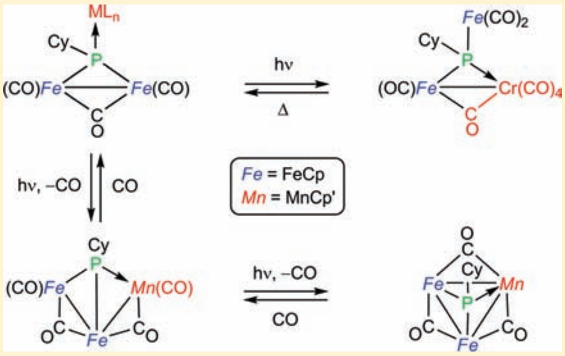
S *Supporting Information*



ABSTRACT: The title complex (Cp = η^5-C_5H_5) reacted with the labile carbonyl complexes [$M(CO)_5$(THF)] (M = Cr, Mo, W) and [$MnCp'(CO)_2$(THF)] (Cp' = η^5-C_5H_4Me) to give phosphinidene-bridged trimetallic compounds of formula [$Fe_2MCp_2(\mu_3$-PCy)(μ-CO)$(CO)_7$] (Cr−P = 2.479(1) Å) and [$Fe_2MnCp_2Cp'(\mu_3$-PCy)(μ-CO)$(CO)_4$], respectively, after formation of a new M−P bond in each case, and related heterometallic complexes [$Fe_2MClCp_2(\mu_3$-PCy)(μ-CO)$(CO)_2$] (M = Cu, Au; Au−P = 2.262(1) Å) were cleanly formed upon reaction with CuCl or the labile tetrahydrothiophene (THT) complex [AuCl(THT)]. The reaction with [$Fe_2(CO)_9$] proceeded analogously to give the triiron derivative [$Fe_3Cp_2(\mu_3$-PCy)(μ-CO)$(CO)_6$] in high yield (new Fe−P bond =2.318(1) Å), along with a small amount of the pentanuclear compound [{$Fe(CO)_3$}{(μ_3-PCy)$Fe_2Cp_2(\mu$-CO)$(CO)_2$}$_2$], the latter displaying a central $Fe(CO)_3P_2$ core with a distorted bipyramidal geometry (P−Fe−P = 164.2(1)°). In contrast, the reaction with [$Co_2(CO)_8$] resulted in a full disproportionation process to give the salt [{$Co(CO)_3$}{(μ_3-PCy)$Fe_2Cp_2(\mu$-CO)$(CO)_2$}$_2$][$Co(CO)_4$], having a pentanuclear Fe_4Co cation comparable to the above Fe_5 complex (P−Co−P = 165.3(2)°). The attempted photochemical decarbonylation of the above trinuclear complexes gave results strongly dependent on the added metal fragment. Thus, the irradiation with visible or visible−UV light of the new Fe_3 and Fe_2Cr species caused no decarbonylation but a tautomerization of the metal framework to give the corresponding isomers [$Fe_2MCp_2(\mu_3$-PCy)(μ-CO)$(CO)_n$] now exhibiting a dangling $FeCp(CO)_2$ moiety (M = Cr, $n = 7$, Cr−Fe = 2.7370(3) Å; M = Fe, $n = 6$, new Fe−Fe bond = 2.6092(9) Å) as a result of the cleavage of the Fe−Fe bond in the precursor and subsequent formation of a new M−Fe bond. These processes are reversible, since the new isomers gave back the starting complexes under low (Cr) or moderate (Fe) thermal activation. In contrast, the manganese−diiron complex [$Fe_2MnCp_2Cp'(\mu_3$-PCy)(μ-CO)$(CO)_4$] could be decarbonylated stepwise, to give first the tetracarbonyl complex [$Fe_2MnCp_2Cp'(\mu_3$-PCy)$(\mu$-CO$)_2(CO)_2$] and then the tricarbonyl cluster [$Fe_2MnCp_2Cp'(\mu_3$-PCy)$(\mu$-CO$)_3$], the latter having a closed triangular metal core (Fe−Fe = 2.568(7) Å; Mn−Fe = 2.684(8) and 2.66(1) Å).

INTRODUCTION

The study of phosphinidene (PR) complexes has been a very prolific area of research within the organometallic chemistry over the past three decades.[1] This highly versatile ligand can act both as a two-electron or as a four-electron donor coordinated to one (A−C in Chart 1), two (D−F in Chart 1), three (G in Chart 1), and up to four metal atoms (H in Chart 1).

In the compounds of types G and H, the M−P bonds can be described as essentially single, and the phosphinidene moiety can be regarded as a robust ligand that prevents the fragmentation of the metal core, although some reactions involving those bonds can take place.[1n,2] The first example of these compounds was the triiron cluster [$Fe_3(\mu_3$-$PC_6F_5)_2(CO)_9$], reported in 1971,[3] and several synthetic strategies to build up phosphinidene-bridged polynuclear species have been developed since then. The most usual procedure relies on the thermal or photochemical reaction of metal carbonyls, such as the trinuclear ones [$M_3(CO)_{12}$] (M = Fe, Ru, Os), with primary phosphines (PRH_2) to afford clusters bearing μ_3-PR and μ_4-PR ligands resulting from progressive decarbonylation and P−H bond cleavage steps.[1n,4] This method can be adapted to yield heterometallic clusters, e.g., by reacting PRH_2 or PRH-bridged complexes with metal carbonyls.[5] Another strategy involves the reaction of neutral or anionic metal carbonyl complexes with dihalophosphines (PRX_2), usually requiring further steps to give a phosphinidene-bridged cluster.[1n,6] Again, this synthetic approach can be adapted to yield heterometallic clusters, for instance, by reacting dihalophosphine or halophosphide-bridged complexes with metal carbonyls, e.g., [$Fe_2MnCp(\mu_3$-PR)$(\mu$-CO$)_2(CO)_6$] from [$MnCp(CO)_2(PCl_2R)$] and [$Fe_2(CO)_9$].[7] A third approach to prepare PR-bridged clusters involves the cleavage of P−C bonds in clusters bearing

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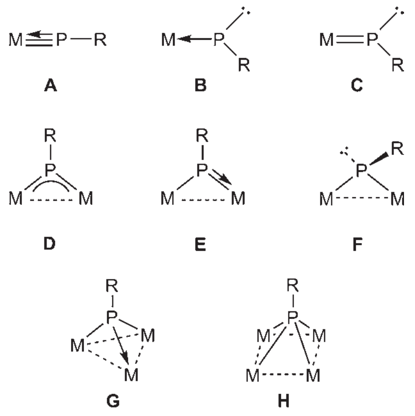
Chart 1



an appropriate phosphine, diphosphine, or phosphide-bridged ligands,[1n] e.g., $[Os_3(CO)_{11}(\mu_3\text{-}PR)(\mu_3\text{-}C_6H_4)]$ from the thermolysis of triosmium clusters of the type $[Os_3(CO)_{11}(PRPh_2)]$.[8]

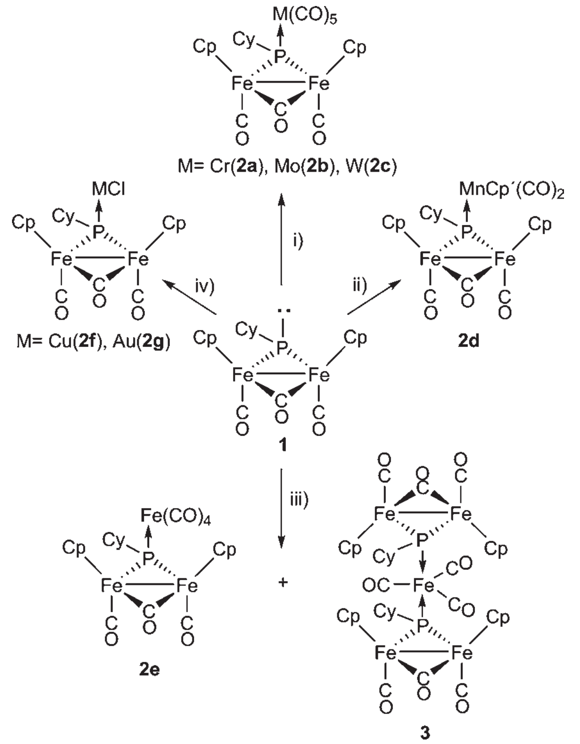
A fourth and rational approach that might be envisaged to prepare PR-bridged polynuclear complexes would be the reaction of binuclear PR-bridged substrates (D−F in Chart 1) with suitable metal complexes, but this has been little explored in the past. Carty et al.[9a] and Scheer et al.[9b] have recently reported the preparation of clusters starting from complexes of type D, and we have also described the addition of different metal fragments to several dimolybdenum complexes of type E as a synthetic route to heterometallic derivatives having phosphinidene bridges.[10] Complexes having pyramidal (or bent) phosphinidene bridges (type F in Chart 1) still remain less explored in this respect. In fact, we can only quote a few examples involving the reaction of anionic phosphinidene complexes (generated in situ through deprotonation of suitable μ-PRH precursors) with group 11 and 12 metal halides or halocomplexes.[11] Recently, we developed efficient synthetic procedures to prepare diiron compounds of the type $[Fe_2Cp_2(\mu\text{-}PR)(\mu\text{-}CO)(CO)_2]$ (R = Cy, Ph, 2,4,6-$C_6H_2Me_3$, 2,4,6-$C_6H_2{}^tBu_3$) containing pyramidal-phosphinidene ligands.[12] These neutral complexes have been shown to be nucleophilic enough to add to different organic molecules, then leading to the formation of novel organophosphorus ligands.[12−14] Thus, they seemed to be suitable substrates for the rational building up of heterometallic derivatives and clusters through their reactions with suitable carbonyl complexes and further decarbonylation steps.

In this paper, we report that the cyclohexylphosphinidene complex $[Fe_2Cp_2(\mu\text{-}PCy)(\mu\text{-}CO)(CO)_2]$ (**1**) indeed reacts easily with different metal complexes of the groups 6, 7, 8, 9, and 11 to give heterometallic derivatives bearing μ_3-PR ligands, resulting from the expected formation of a new M−P bond (Scheme 1). The products so obtained were afterward photolyzed with visible−UV light, this inducing either a tautomerization of the metal framework or decarbonylation, depending on the nature of M, with the latter process being accompanied by the formation of new Fe−M bonds to finally yield a triangular metal core.

RESULTS AND DISCUSSION

Reactions of the Phosphinidene Complex 1 with Metal Compounds of Groups 6−9 and 11. Compound **1** reacts at room temperature with the labile tetrahydrofuran adducts $[M(CO)_5(THF)]$ (M = Cr, Mo, W)[15] and $[MnCp'(CO)_2(THF)]$ (Cp′ = η^5-C_5H_4Me),[16] to give the corresponding

Scheme 1[a]



[a] (i) $[M(CO)_5(THF)]$. (ii) $[MnCp'(CO)_2(THF)]$. (iii) $[Fe_2(CO)_9]$. (iv) CuCl or $[AuCl(THT)]$.

trimetallic compounds $[Fe_2MCp_2(\mu_3\text{-}PCy)(\mu\text{-}CO)(CO)_7]$ (M = Cr (**2a**), Mo (**2b**), W (**2c**)) and $[Fe_2MnCp_2Cp'(\mu_3\text{-}PCy)(\mu\text{-}CO)(CO)_4]$ (**2d**; Scheme 1), with this reactivity pattern being analogous to that of phosphines with the same metal fragments.[17] In contrast, **1** failed to displace efficiently the THF ligand from the adduct $[ReCp(CO)_2(THF)]$, and no rhenium analogue of **2d** could be thus obtained, even through direct photolysis of **1** and $[ReCp(CO)_3]$ in toluene solutions.

Compound **1** also reacts with $[Fe_2(CO)_9]$, a well-known precursor of the $[Fe(CO)_4]$ fragment, to give the expected triiron derivative $[Fe_3Cp_3(\mu_3\text{-}PCy)(\mu\text{-}CO)(CO)_6]$ (**2e**), along with small amounts of the pentanuclear species $[\{Fe(CO)_3\}\{(\mu_3\text{-}PCy)Fe_2Cp_2(\mu\text{-}CO)(CO)_2\}_2]$ (**3**), a side product of uncertain origin (see below). The reaction of **1** with the cobalt dimer $[Co_2(CO)_8]$ also yielded a related pentanuclear complex, but now as the major product. We have been able to characterize this compound as the salt $[\{Co(CO)_3\}\{(\mu_3\text{-}PCy)Fe_2Cp_2(\mu\text{-}CO)(CO)_2\}_2][Co(CO)_4]$ (**4**, Chart 2). This product obviously follows from a disproportionation reaction reminiscent of those reported in the literature for the reactions of phosphines with $[Co_2(CO)_8]$ to give salts of the type $[Co(CO)_3(PR_3)_2]$-$[Co(CO)_4]$.[18] Finally, the phosphinidene complex **1** expectedly adds group 11 metal halide fragments easily. For instance, the reactions with CuCl or the tetrahydrothiophene complex $[AuCl(THT)]$ give quantitatively the corresponding derivatives $[Fe_2MClCp_2(\mu_3\text{-}PCy)(\mu\text{-}CO)(CO)_2]$ (M = Cu (**2f**), Au (**2g**); Scheme 1).

Structural Characterization of Compounds 2. The structures of **2a**, **2e**, and **2g** were confirmed through single crystal X-ray diffraction studies (Figure 1 and Table 1). All of these structures are similar and display two CpFe(CO) fragments bridged by CO and PCy ligands, with the latter being also bound to the third metal fragment. This causes little perturbation of the Fe_2 core present in the parent phosphinidene complex.[12] The main structural difference in these compounds arises from the third metal fragment to which the PCy ligand is attached. In the case of **2a**, a $Cr(CO)_5$ moiety is bound to the P atom, completing an almost regular octahedron around the Cr atom. The Cr—P distance of 2.479(1) Å, however, is significantly longer (by 0.1—0.2 Å) than those measured for related PR_3 derivatives of the type $[Cr(CO)_5(PR_3)]$.[19] A similar situation is observed in **2e**, this bearing a $Fe(CO)_4$ moiety axially bound by the P atom that then completes a trigonal bipyramidal (TBP) environment around Fe. In that case, the Fe—P distance of 2.318(1) Å is ca. 0.07 Å longer than those measured in mononuclear phosphine complexes of the type $[Fe(CO)_4L]$.[20] Finally, the PCy ligand in **2g** is linearly bound to a Au—Cl moiety (P—Au—Cl = 177.3(1)°), but now the P—Au length is comparable to those measured in conventional gold phosphine complexes (ca. 2.24 Å).[20c,21] The observed lengthening of the M—P distances in **2a** and **2e** might be attributed to the steric pressure introduced in the molecule by the presence of relatively bulky $M(CO)_n$ fragments, and this is also reflected in a modest lengthening of the Fe—P lengths in the Fe_2 core (Table 1) and in the puckering of the central Fe_2CP rhombus of these molecules as we increase the size of the third metal fragment, with the angles defined by the Fe_2P and Fe_2C planes being ca. 163° (**2g**), 157° (**2e**), and 155°(**2a**).

The IR spectra of these compounds in the C—O stretching region can be described as derived from a superimposition of the bands originated by relatively independent oscillators of the type $Fe_2(\mu\text{-}CO)(CO)_2$ and either $[M(CO)_5L]$, $[MnCp'(CO)_2L]$, or $[Fe(CO)_4L]$ fragments, respectively.[22] The bands corresponding to the latter fragments in compound **2** are usually ca. 30 cm^{-1}

Chart 2

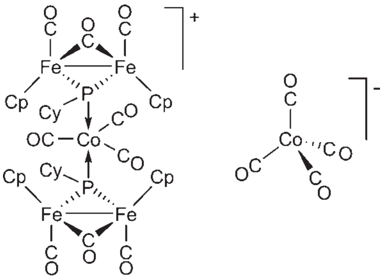


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Table 1. Selected Bond Lengths (Å) for Compounds 2a, 2e and 2g

bond	2a	2e	2g
Fe1—Fe2	2.6135(5)	2.6260(4)	2.6131(7)
Fe1—P	2.288(1)	2.255(1)	2.223(1)
Fe2—P	2.284(1)	2.271(1)	2.218(1)
M—P	2.479(1)	2.318(1)	2.262(1)
Fe1—C1	1.759(3)	1.757(2)	1.759(4)
Fe1—C3	1.933(2)	1.930(2)	1.928(4)
Fe2—C2	1.755(3)	1.765(2)	1.754(4)
Fe2—C3	1.926(3)	1.933(2)	1.950(4)

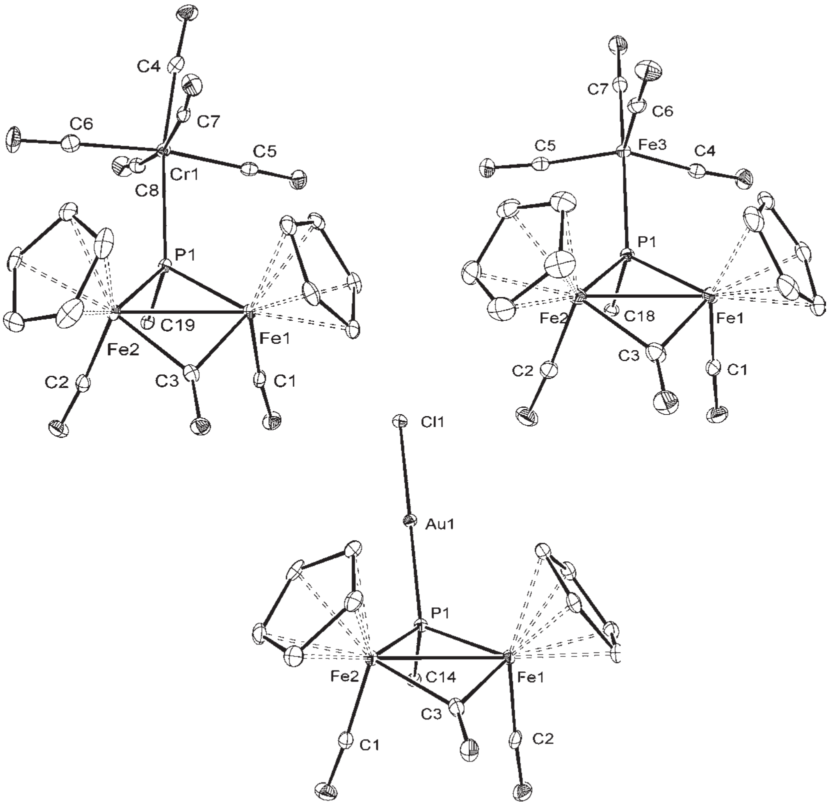


Figure 1. ORTEP diagrams for compounds **2a** (top left), **2e** (top right), and **2g** (bottom), with H atoms and Cy groups (except the C^1 atoms) omitted for clarity. Only one of the two independent molecules is shown for either **2a** or **2e**.

Table 2. Selected IR, and $^{31}P\{^1H\}$ NMR Data for New Compounds

compound	ν(CO)[a]	δ_P[b]
$[Fe_2Cp_2(\mu\text{-PCy})(\mu\text{-CO})(CO)_2]$ (**1**)[c]	1977 (vs), 1940 (w), 1773 (m)	531.6
$[CrFe_2Cp_2(\mu_3\text{-PCy})(\mu\text{-CO})(CO)_7]$ (**2a**)	2043 (m), 1989 (s), 1962 (m), 1927 (sh, s), 1911 (vs), 1791 (m)	434.5
$[Fe_2MoCp_2(\mu_3\text{-PCy})(\mu\text{-CO})(CO)_7]$ (**2b**)	2057 (m), 1989 (s), 1967 (w), 1933 (sh, s), 1922 (vs), 1792 (m)	404.0[d]
$[Fe_2WCp_2(\mu_3\text{-PCy})(\mu\text{-CO})(CO)_7]$ (**2c**)	2056 (m), 1990 (s), 1963 (m), 1924 (sh, s), 1913 (vs), 1792 (m)	363.1,[e] J_{PW} = 193
$[Fe_2MnCp_2Cp'(\mu_3\text{-PCy})(\mu\text{-CO})(CO)_4]$ (**2d**)	1978 (vs), 1950 (w), 1904 (m), 1841 (m), 1773 (m)	503.2[d]
$[Fe_3Cp_2(\mu_3\text{-PCy})(\mu\text{-CO})(CO)_6]$ (**2e**)	2028 (m), 1991 (vs), 1964 (w), 1952 (w), 1914 (s), 1793 (m)	421.5
$[CuFe_2ClCp_2(\mu_3\text{-PCy})(\mu\text{-CO})(CO)_2]$ (**2f**)	1988 (vs), 1960 (w), 1792 (m)	353.5
$[AuFe_2ClCp_2(\mu_3\text{-PCy})(\mu\text{-CO})(CO)_2]$ (**2g**)	2001 (vs), 1971 (w), 1808 (m)	329.3
$[\{Fe(CO)_3\}\{(\mu_3\text{-PCy})Fe_2Cp_2(\mu\text{-CO})(CO)_2\}_2]$ (**3**)	1984 (vs), 1954 (w), 1839 (m), 1783 (m)	467.6[f]
$[\{Co(CO)_3\}\{\mu_3\text{-PCy})Fe_2Cp_2(\mu\text{-CO})(CO)_2\}_2]$-$[Co(CO)_4]$ (**4**)	2021 (w), 2003 (vs), 1979 (w), 1951 (m), 1888 (s), 1810 (m)	376.5[e]
$[CrFe_2Cp_2(\mu_3\text{-PCy})(\mu\text{-CO})(CO)_7]$ (**5a**)	2037 (w), 2027 (w), 2009 (vs), 1971 (s), 1937 (vs), 1910 (s), 1781 (m)	301.1[g] (*syn*), 304.3[g] (*anti*)
$[Fe_3Cp_2(\mu_3\text{-PCy})(\mu\text{-CO})(CO)_6]$ (**5e**)	2034 (vs), 2003 (s), 1985 (s), 1941 (s), 1762 (m)	283.7
$[Fe_2MnCp_2Cp'(\mu_3\text{-PCy})(\mu\text{-CO})_2(CO)_2]$ (**6**)	1969 (w), 1934 (sh, s), 1922 (s), 1890 (m), 1788 (vs), 1738 (w)	537.8−598.2[h]
$[Fe_2MnCp_2Cp'(\mu_3\text{-PCy})(\mu\text{-CO})_3]$ (**7**)	1785 (vs), 1729 (m)	558.4

[a] Recorded in dichloromethane solution, with C−O stretching bands (ν(CO)) in cm^{-1}. [b] Recorded in CD_2Cl_2 solutions at 290 K and 162.00 MHz unless otherwise stated; δ in ppm relative to external 85% aqueous H_3PO_4; *J* in Hertz. [c] Data taken from ref 12c. [d] In toluene-d_8 solution. [e] In acetone-d_6 solution. [f] In C_6D_6 solution. [g] Recorded at 213 K. [h] Recorded at 213 K; six resonances were present at 537.8, 540.4, 587.7, 590.3, 592.8, and 598.2 ppm, corresponding to different isomers of the complex (see text).

less energetic than those of the reference mononuclear PR_3 complexes, and this denotes that the PCy ligand in **1** effectively behaves as a stronger donor than conventional phosphine ligands. In compounds **2f** and **2g**, the third metal fragment bears no carbonyl ligands, and therefore the IR spectra of these products are completely analogous to that of the parent compound **1** but with the bands shifted to higher frequencies, as an anticipated result of the binding of the acidic MCl moiety to phosphorus. Compounds **2a**−**g** display ^{31}P NMR resonances in the range 325−505 ppm, expectedly more shielded than that of the parent phosphinidene **1** (Table 2), and with a strong influence of the third metal atom, with this yielding the anticipated orderings Cr > Mo > W and Cu > Au.[23] Other spectroscopic features of these compounds are unremarkable.

Synthesis and Structural Characterization of Compound 3. Even if formally derived by replacing the axial carbonyl in the $Fe(CO)_4$ fragment of **2e** with a second molecule of the phosphinidene **1**, independent experiments revealed that this reaction actually does not take place even in refluxing toluene or under photochemical activation. Although at present we cannot give a satisfactory explanation for the formation of **3**, we note that the synthesis of related bis(phosphine) complexes of the type $[Fe(CO)_3(PR_3)_2]$ generally requires quite forcing conditions when starting from $[Fe(CO)_5]$ or $[Fe(CO)_4(PR_3)]$ precursors.[24]

The structure of **3** in the solid state (Figure 2 and Table 3) is built from two molecules of **1** axially bound to a trigonal $Fe(CO)_3$ moiety, thus completing a TBP environment around the central Fe atom. The bond lengths and angles within each $[Fe_2Cp_2(\mu\text{-PCy})(\mu\text{-CO})(CO)_2]$ fragment are comparable to those measured for $[Fe_2Cp_2(\mu\text{-PPh})(\mu\text{-CO})(CO)_2]$.[12a,c] The two $Fe_2(\mu$-PCy) subunits in **3** are arranged in an eclipsed disposition, as opposed to the more common staggered conformations typically found for $[Fe(CO)_3(PR_3)_2]$ complexes.[24] The steric congestion around the central Fe atom caused by this arrangement is partly relieved by a distortion of the $Fe_2(\mu$-PCy) subunits away from the ideal axial positions (P1−Fe−P2 = 164.2(1)°), with a concomitant widening of the angle between the closest CO ligands (C−Fe−C =139.3(2)°). However, this asymmetric distribution is balanced in the crystal lattice by the packing of the molecules of **3** in pairs held by strong intermolecular $\pi\cdots\pi$ stacking interactions,[25] with the closest inter-ring distances of ca. 3.30 Å (Figure 2) being slightly shorter than the interlaminar spacing in graphite (ca. 3.35 Å).

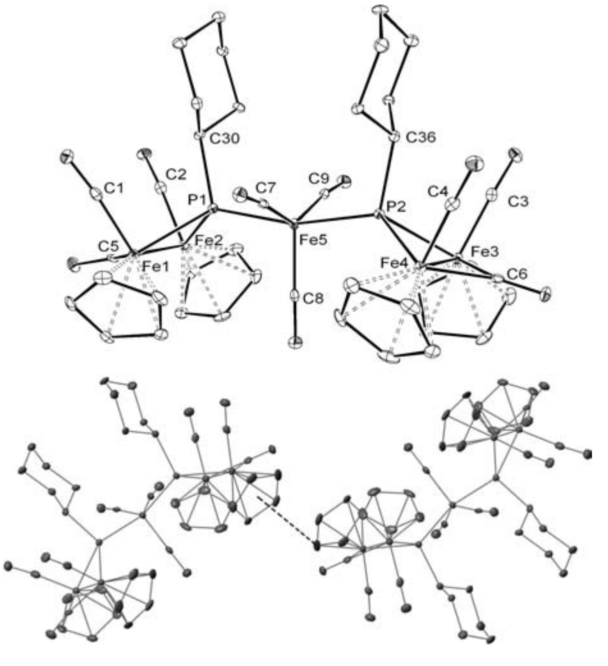
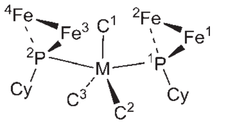


Figure 2. ORTEP diagram for compound **3** with H atoms omitted for clarity (top) and view of the π−π interactions between Cp rings in the crystal lattice of this complex (bottom).

Table 3. Selected Bond Lengths (Å) and Angles (deg)[a] for Compound 3 and the Cation in Compound 4

parameter	**3** (M = Fe)	**4** (M = Co)
Fe1−Fe2	2.6057(8)	2.6151(9)
Fe3−Fe4	2.6116(8)	2.6156(9)
Fe1−P1	2.274(1)	2.254(1)
Fe2−P1	2.275(1)	2.250(1)
Fe3−P2	2.266(1)	2.257(1)
Fe4−P2	2.271(1)	2.252(1)
M−P1	2.259(1)	2.320(1)
M−P2	2.267(1)	2.310(1)
P1−M−P2	164.2(1)	165.3(2)
C1−M−C2	111.3(1)	111.3(2)
C1−M−C3	109.4(2)	108.4(2)
C2−M−C3	139.3(2)	140.4(2)

[a] According to the labeling shown in the figure here:



The IR spectrum of **3** can be once again described as a superimposition of the bands originated by relatively independent $Fe_2(\mu\text{-}CO)(CO)_2$ and trigonal $Fe(CO)_3$ oscillators.[22] The band at 1839 cm^{-1} can be thus assigned to the asymmetric C−O stretch of the trigonal $Fe(CO)_3$ moiety, with a frequency substantially lower than those measured for related phosphine complexes of the type $[Fe(CO)_3(PR_3)_2]$ (ca. 1900 cm^{-1}), this being again indicative of the strong electron-donor power of the PCy ligand of **1**.

Structural Characterization of Compound 4. The structure of **4** in the solid state displays a conventional tetrahedral $[Co(CO)_4]^-$ anion and a pentanuclear Fe_4Co cation comparable to the iron complex **3** if we just replace Fe with Co in the trigonal $M(CO)_3$ fragment (Figure 3 and Table 3). Again, the phosphinidene groups display an eclipsed conformation around the central metal atom, and the steric congestion introduced by this arrangement is partially relieved by the bending of the P1−Co−P2 axis (165.3(2)°) and the opening of the angle between the closest carbonyls (C−Co−C = 140.4(2)°). Yet the Co−P distances in the cation of **4** (ca. 2.32 Å) are ca. 0.08 Å longer than those in related PR_3 complexes such as $[Co(CO)_3(PPh_3)_2]^+$,[26] suggesting the persistence of significant steric pressure in the cation. As observed for **3**, the asymmetric structure of the pentanuclear molecules is balanced in the crystal lattice by the grouping of the cations in centrosymmetric pairs, now displaying double, although possibly weaker $\pi\cdots\pi$ stacking interactions between neighboring Cp ligands (the Cp rings are not strictly parallel to each other—see Figure 3—minimum C···C separation ca. 3.30 Å).

The $^{31}P\{^1H\}$ NMR spectrum of **4** exhibits a single resonance at 376.5 ppm, almost 100 ppm more shielded than that of the iron complex **3**, probably due to the positive charge of the cobalt complex. Again, its IR spectrum can be described as a superimposition of the bands originated from relatively independent oscillators in the molecule, and the bands at 2021 (w) and 1951 (m) cm^{-1} can be thus attributed to the C−O stretches of the central $Co(CO)_3$ fragment and are some 40−50 cm^{-1} less energetic than those of $[Co(CO)_3(PR_3)_2]^+$ cations,[27] this being once more illustrative of the strong donor ability of the PCy ligand in **1**.

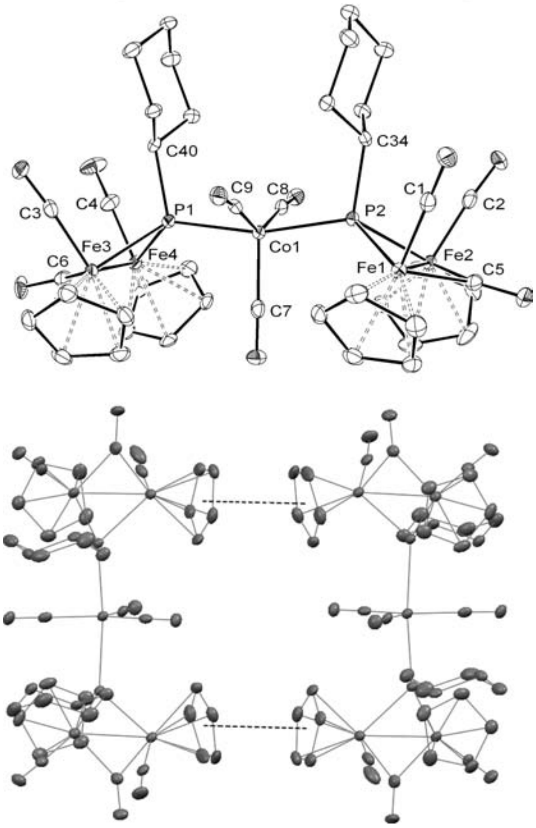
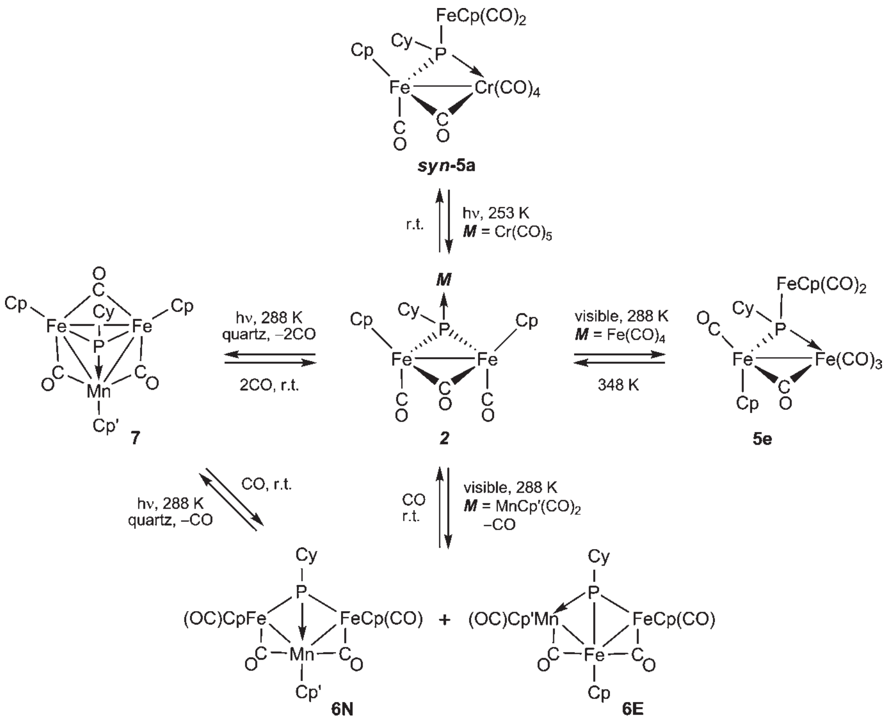


Figure 3. ORTEP diagram for the cation of compound **4** with H atoms omitted for clarity (top) and a view of the $\pi\cdots\pi$ interactions between Cp rings in the crystal lattice of this compound (bottom).

Photochemical Tautomerization of Compounds 2a and 2e. Although compounds **2a**−**e** were thermally stable in refluxing toluene (no changes being appreciated in ca. 2 h), some changes could be induced photochemically, but only for the manganese compound could we induce the release of CO ligands in a controlled way (Scheme 2). The irradiation of **2a** with visible−UV light in a Pyrex Schlenk flask at 253 K rapidly induces its complete isomerization to give $[CrFe_2Cp_2(\mu_3\text{-}PCy)(\mu\text{-}CO)(CO)_7]$ (**5a**), a tautomer displaying a Cr−Fe bond. Decarbonylation of **2a** is surely induced when carrying out the photolytic experiment in a quartz Schlenk tube, but then a complex mixture of products is formed that we could not isolate nor properly characterize. Compound **5a** is only stable at temperatures below 253 K, and it rearranges back to **2a** in ca. 15 min at 293 K. We also performed analogous photolytic experiments with the molybdenum and tungsten compounds. In those cases, no reaction was observed when using Pyrex glassware. When a quartz flask was used for the photolysis, then the IR spectra of the corresponding solutions revealed the presence of new C−O stretching bands comparable to those of compound **5a**. However, the half-life of these isomers was so short (even at low temperatures) that we could not isolate nor characterize these new species. The irradiation of the triiron complex **2e** with visible light induces a tautomerization similar to that of the chromium complex, thus giving $[Fe_3Cp_2(\mu_3\text{-}PCy)(\mu\text{-}CO)(CO)_6]$ (**5e**) in high yield. This complex, however, is more stable than its chromium analogue

Scheme 2



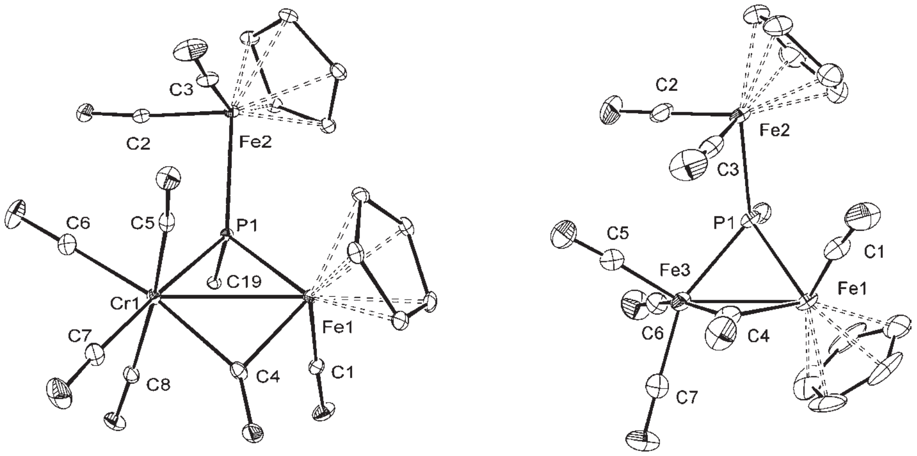


Figure 4. ORTEP diagram for compounds **5a** (left) and **5e** (right) with H atoms and Cy groups (except C^1 atom) omitted for clarity.

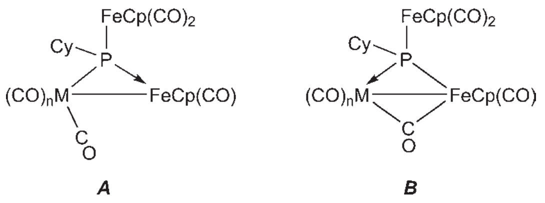
and only gives back **2e** under heating, with the transformation in toluene solution being completed in ca. 30 min at 348 K. Besides, if the photolysis of **2e** is carried out using visible−UV light, then a complex mixture of compounds (including some **5e**) was formed, as shown by the $^{31}P\{^1H\}$ NMR spectrum of the reaction mixture, but we could not isolate nor characterize any of the new species present there.

The gross structural features of **5a** and **5e** in the crystal are similar to each other in that both of them display metal−metal bonded FeCp(CO) and $M(CO)_n$ moieties bridged by a carbonyl (closer to M) and a μ_3-PCy ligand further bound to a FeCp(CO)$_2$ fragment (Figure 4 and Table 4). They differ, however, in the positioning of the latter fragment with respect to the Cp ligand of the FeCp(CO) moiety, this being of the *syn* type for **5a** and *anti* for **5e**, and in the puckering of the central MFePC rhombus, much more pronounced for the triiron complex (angles between MFeP and MFeC planes ca. 159° and 125°, respectively). The P−FeCp(CO)$_2$ lengths of ca. 2.33 Å are comparable to the values measured in the trimetallaphosphonium cation $[\{FeCp(CO)_2\}_3(\mu_3\text{-PH})]^+$ (ca. 2.33 Å)[28] and certainly longer than the values of ca. 2.13−2.21 Å for different complexes of the type $[Fe_2Cp_2(\mu\text{-CO})_2(CO)(L)]$ having classical two-electron donor phosphines and phosphites (L)[29] and hence dative P→Fe bonds. Thus, we can assume that the μ_3-PCy ligand in compound **5** provides the FeCp(CO)$_2$ fragment with one electron, as required by the effective atomic number (EAN) formalism. This leaves the μ_3-PCy ligand as a three-electron donor to the M−Fe center, thus resembling the donor ability of a

Table 4. Selected Bond Lengths (Å) and Angles (deg) for Compounds 5a and 5e.

parameter	**5a** (M = Cr)	**5e** (M = Fe)
Fe1−M	2.7370(3)	2.6092(9)
Fe1−P	2.2739(4)	2.253(1)
Fe2−P	2.3351(4)	2.322(1)
M−P	2.3859(4)	2.277(1)
Fe1−C1	1.750(2)	1.741(5)
Fe1−C4	2.012(2)	2.002(5)
M−C4	2.024(2)	1.916(5)
M−Cn (av.)	1.886(2)	1.765(5)
Fe1−P−Fe2	124.3(1)	122.4(1)
M−P−Fe2	127.1(1)	121.2(1)
C1−Fe1−M	100.7(1)	116.0(2)
C1−Fe1−P	91.6(1)	91.1(2)
C1−Fe1−C4	86.0(1)	84.5(2)
C1−Fe1−P−Fe2	135.1(1)	6.3(2)

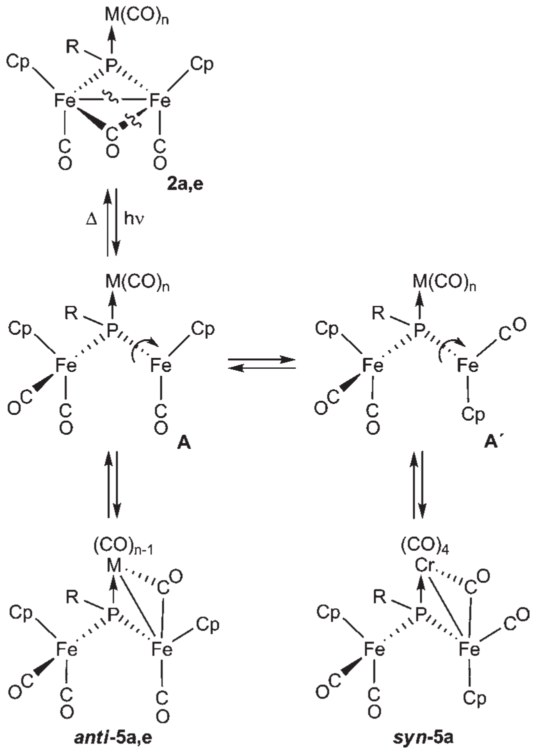
Chart 3



PR_2 ligand. Indeed, the bond distances and angles around the M−Fe center in **5e** are shorter (ca. 2.26 Å) and comparable to those in diiron complexes of the type $[Fe_2Cp(\mu\text{-}PR_2)(\mu\text{-}CO)(CO)_4]$.[30,31] The positioning of the μ_3-PCy ligand over the M−Fe center is rather symmetric (after allowing for the different covalent radii of Cr and Fe in **5a**), and this requires that the bridging carbonyl is asymmetrically placed (closer to M) so as to balance the electron density around the M and Fe centers. In fact, the actual structures of compounds **5a,e** can be viewed as intermediate between the extreme distributions implied by structures A and B in Chart 3. We finally note that the Fe−Cr distance of 2.7370(3) Å in **5a** is consistent with the formulation of a single bond and comparable to those measured for compounds bearing two bridging ligands between these metal atoms.[32]

The spectroscopic data in solution for compounds **5** are in good agreement with the structures found in the solid state, except for the fact that the chromium complex exhibits two isomers in solution, in a ratio of ca. 6:1. Presumably, the major species is the *syn* isomer found in the solid state, while the minor species would be the *anti* isomer. In line with this, the IR spectrum of **5a** in solution exhibits a large number of bands. Moreover, the relative intensities of the two bands at higher frequency change with the solvent, suggesting that the isomers are linked by a solvent-dependent equilibrium. In contrast, the triiron compound **5e** displays a single isomer in solution and gives rise to bands that can be assigned to independent $FeCp(CO)_2$ (2003 and 1984 cm^{-1}) and $(CO)Fe(\mu\text{-}CO)Fe(CO)_3$ oscillators, with the bands of the latter being comparable to those measured for compounds of the formula $[Fe_2Cp(\mu\text{-}PR_2)(\mu\text{-}CO)(CO)_4]$.[30,33]

Scheme 3. Reaction Pathways in the Formation of Compounds 5



The $^{31}P\{^1H\}$ NMR spectra of compounds **5a,e** show resonances in the range 240−300 ppm, ca. 100 ppm lower than those of the precursors of type **2**. At 213 K, the chromium complex exhibits two different resonances at 301.1 and 304.3 ppm that we assign to the *syn* and *anti* isomers, respectively, on the basis of their relative intensity. When increasing the temperature, these resonances broaden, but coalescence is never reached since the tautomerization to give back **2a** takes place rapidly above 253 K.

Unlike **5a**, the triiron compound **5e** displays just one isomer in solution, but the $^{13}C\{^1H\}$ NMR spectrum indicates the presence of dynamic effects at room temperature. Thus, although the appearance of two doublets around 213 ppm can be attributed to the CO ligands of a conventional $FeCp(CO)_2$ moiety, all other carbonyl ligands give rise to just one broad resonance at 226.0 ppm. This implies the operation of a fast exchange process between the bridging and terminal ligands of the $(CO)_3Fe(\mu\text{-}CO)FeCp(CO)$ moiety, but we could not observe separated resonances even at 188 K.

Proposed Pathways for the Formation of Compounds 5a,e. To account for the photochemical tautomerization of compound **2**, we propose a first step in which the Fe−Fe bond is cleaved homolytically (Scheme 3), thus resembling the well-known behavior of $[Fe_2Cp_2(CO)_4]$.[34] This would be accompanied with a rearrangement of the bridging CO ligand to a terminal position, thus leading to an intermediate (**A**) having 18-electron $FeCp(CO)_2$ and 16-electron $FeCp(CO)$ fragments. The formation of compounds **5a,e** would follow from the binding to this unsaturated center of the other 18-electron fragment present in the molecule ($M(CO)_n$), this being accompanied by the rearrangement of a CO ligand to the bridging position and leading specifically to the *anti* isomer. All of these steps are expectedly reversible, thus accounting for the thermal rearrangement of

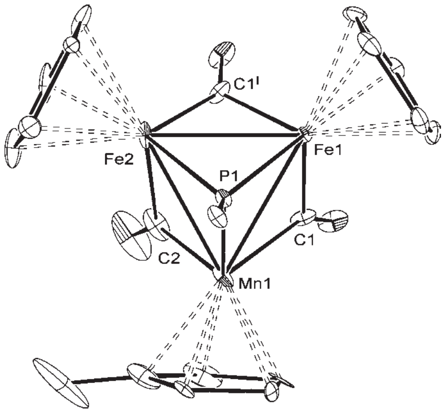


Figure 5. ORTEP diagram for compound **7**, with H atoms and the Cy group (except the C^1 atom) omitted for clarity. Only one of the two (symmetry related) disordered molecules is shown.

compounds **5a**,**e** back to their precursors **2a**,**e**. Moreover, the intermediate **A** would easily account for the *syn*/*anti* isomerization observed for the chromium compound, since that would only require a rotation around the Fe—P bond of the unsaturated FeCp(CO) fragment.

Photochemical Decarbonylation of Compound 2d. The photochemical treatment of **2d** does not lead to compounds of the type **5**. Instead, decarbonylation takes place easily to give, depending on the conditions of the photolysis, the tetracarbonyl derivative $[Fe_2MnCp_2Cp'(\mu_3\text{-PCy})(\mu\text{-CO})_2(CO)_2]$ (**6**) or the tricarbonyl $[Fe_2MnCp_2Cp'(\mu_3\text{-PCy})(\mu\text{-CO})_3]$ (**7**) (Scheme 2). Thus, when just visible light is used, only the tetracarbonyl **6** is formed. However, under visible—UV light irradiation, a mixture of **6** and **7** is obtained if using a Pyrex flask, the latter filtering off most of the UV radiation. Finally, the tricarbonyl **7** can be obtained selectively under the latter conditions but using a quartz flask instead. All of these processes are reversible, and compound **7** gives back **2d** under a CO atmosphere at room temperature, via the tricarbonyl **6**, as indicated by IR and $^{31}P\{^1H\}$ NMR monitoring. As discussed below, compound **6** is formed as a mixture of six isomers grouped in two sets (N and E in Scheme 2), with their relative ratio being the same regardless of the reaction conditions or purification procedures, thus suggesting that all of them are in equilibrium.

The tricarbonyl complex **7** is isoelectronic with the 48-electron clusters $[Fe_2MnCp(\mu_3\text{-PR})(\mu\text{-CO})_2(CO)_6]$ mentioned previously.[7] Interestingly, the latter clusters also have been shown to react stepwise with two-electron donors such us CO, phosphines, and phosphites, to give Fe_2Mn derivatives isoelectronic with compounds **6** and **2d**, respectively, via the progressive opening of their Fe—Mn bonds.[35] We finally note that a phenylphosphinidene Fe_2Mn cluster comparable to compound **7** has been previously prepared in low yield through the reaction of $[MnCoCp(\mu\text{-PHPh})(CO)_5]$ with $K[FeCp(CO)_2]$.[36]

Structural Characterization of 6. The structures we propose for the isomers observed for the 50-electron complex **6** are derived from that of the 48-electron cluster **7** (Scheme 2) after adding a CO ligand, with this resulting in the opening of one of the carbonyl bridges and cleavage of the corresponding metal—metal bond. In all cases, the PCy ligand would bridge a V-shaped trimetal skeleton, and two carbonyls would bridge each of the remaining metal—metal bonds from a side of the intermetallic plane opposite the phosphinidene ligand, while there would be a terminal carbonyl at the external metal centers. This is consistent with the fact that the IR spectrum of **6** displays two low-frequency C—O stretching bands, due to bridging carbonyls, with relative intensities (strong and weak in order of decreasing frequency) indicative of a cisoid arrangement.[23] The differences between isomers would arise from the two possible positions of the manganese atom, either in the middle (isomers N) or at the end of the trimetal chain (isomers E), from the two relative positions of the terminal carbonyls with respect to the intermetallic plane (*cis* and *trans*), and from the two relative positions of the Cp′ or Cp rings at the external metal center with respect to the PCy ligand (*syn* and *anti*). This gives a total of four possible isomers of type **E** and three possible isomers of type **N**. Further details of the structures and spectroscopic characterization of these isomers are given in the Supporting Information.

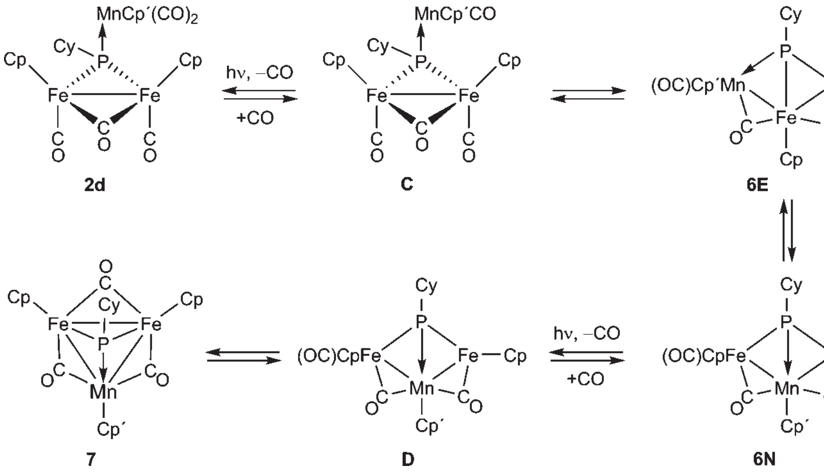
Table 5. Selected Bond Lengths (Å) and Angles (deg) for Compound 7

Fe(1)—Fe(2)	2.568(7)	Fe(1)—C(1)	1.985(3)
Fe(1)—Mn(1)	2.684(8)	Fe(1)—C(1′)	1.985(3)
Fe(2)—Mn(1)	2.66(1)	Mn(1)—C(1)	1.990(8)
Fe(1)—P(1)	2.139(1)	Mn(1)—C(2)	1.826(7)
Fe(2)—P(1)	2.153(8)	Fe(2)—C(2)	2.087(7)
Mn(1)—P(1)	2.149(9)	Fe(2)—C(1′)	1.835(7)
C(1)—Fe(1)—P(1)	98.76(9)	C(1)—Fe(1)—C(1′)	80.5(2)
C(2)—Mn(1)—P(1)	103.8(4)	C(1)—Mn(1)—C(2)	82.0(4)
C(1′)—Fe2—P(1)	103.2(3)	C(2)—Fe(2)—C(1′)	79.2(3)

Structural Characterization of Compound 7. Our data for **7** are not very accurate, because the molecule is placed on a crystallographic plane of symmetry containing one of the Fe atoms, resulting in an imposed disorder between the other FeCp fragment and the MnCp′ one. Yet, the essential features of the molecule are well-defined (Figure 5, Table 5). The cluster displays a trimetal core held by a face-bridging PCy ligand and a carbonyl ligand bridging each of the edges from the opposite side of the intermetallic plane (C—M—P angles ca. 100°). The M—P distances are similar to each other and short (ca. 2.15 Å), indicating a strong coordination of the PCy group, while the heterometallic distances of ca. 2.67 Å are similar to those measured in the isoelectronic cluster $[Fe_2MnCp(\mu_3\text{-PPh})(\mu\text{-CO})_2(CO)_6]$[37] and consistent with the formulation of single bonds between Mn and Fe atoms in any case. The latter appears to be the only other phosphinidene-bridged Fe_2Mn cluster structurally characterized before. We note that the Fe—Fe length in **7** (2.568(7) Å) is significantly shorter than the corresponding length in the mentioned cluster (2.686 Å), but this difference can be attributed to the presence of a bridging carbonyl over that bond in **7**. For instance, the intermetallic length in the complex $[Fe_2Cp_2(\mu\text{-PPh})(\mu\text{-CO})(CO)_2]$ is comparably short (2.5879(4) Å).[12a]

The IR spectrum of **7** denotes a local symmetry even higher than in the crystal, since only two bands are observed in the C—O stretching region of the bridging carbonyls, with the relative intensities (very strong and medium, in order of decreasing frequencies) expected for a $M_3(\mu\text{-CO})_3$ oscillator under C_{3v} symmetry.[22] This means that the replacement of FeCp with MnCp′ fragments has little effect, as far as the C—O stretches are concerned. Finally, we note that its $^{31}P\{^1H\}$ NMR spectrum displays one resonance at 558.4 ppm, a value similar to those measured for the mentioned isoelectronic clusters $[Fe_2MnCp(\mu_3\text{-PR})(\mu\text{-CO})_2(CO)_6]$ (R = Et, Bu, ^{t}Bu, Cy).[7]

Scheme 4. Reaction Pathways in the Formation of Compounds 6 and 7



Reaction Pathways in the Formation of Compounds 6 and 7.

The most plausible pathway would involve the loss of a terminal CO from the unique dicarbonyl fragment in **2d** (MnCp′(CO)$_2$) to give the intermediate **C**, with a 16-electron MnCp′(CO) fragment (Scheme 4). The formation of a Mn−Fe bond in **C** with a simultaneous rearrangement of a terminal CO to a bridging position would give compound **6** specifically as an isomer of type **E**. As noted above, our data suggest that these isomers are in equilibrium with those of type **N**. The implied tautomerization would just require the cleavage of an Fe−Fe bond and simultaneous formation of a new Fe−Mn bond, along with the pertinent rearrangement of the CO ligands between terminal and bridging sites. The formation of **7** from **6** requires the loss of another CO from one of the external FeCp(CO) or MnCp′(CO) moieties. This would yield intermediates of type **D** having 16-electron FeCp or MnCp′ centers (only one of them shown in Scheme 4) that would rearrange spontaneously to give the electron-precise cluster **7** after formation of a new metal−metal bond and movement of the remaining terminal CO ligand to a bridging position. All of these steps should be reversible, since compound **7** reacts with CO to regenerate the tetracarbonyl **2d** via the tricarbonyls **6**, as noted above.

We should also remark that the reversible transformation between compounds **6** and **7** is completely analogous to the reversible reaction of the mentioned clusters [Fe$_2$MnCp(μ_3-PR)(μ-CO)$_2$(CO)$_6$] (isoelectronic with **7**) with simple two-electron donors L (CO, phosphines, phosphites) to give 50-electron derivatives [Fe$_2$MnCp(μ_3-PR)(CO)$_8$L] (isoelectronic with **6**) and even 52-electron derivatives [Fe$_2$MnCp(μ_3-PR)(CO)$_8$L$_2$] (isoelectronic with **2d**) in some cases.[35] Interestingly, kinetic measurements on the first step of the above reaction support the involvement of intermediates having a 16-electron iron center (isoelectronic with intermediates of type **D**) that would easily add any two-electron donor ligand.

■ CONCLUDING REMARKS

The phosphinidene complex **1** is a good precursor of heterometallic derivatives of the type [Fe$_2$ML$_n$Cp$_2$(μ_3-PR)(μ-CO)(CO)$_2$] bearing a phosphinidene ligand bridging three metal atoms, since it reacts selectively under mild conditions with metal carbonyls of the groups 6−8 and metal halides of group 11 by coordinating its strongly nucleophilic phosphorus atom to the corresponding metal fragment, reminiscent of the reactivity of phosphines with the same substrates. The reaction of **1** with [Co$_2$(CO)$_8$] induces a disproportionation process of the Co(0) species to give [{Co(CO)$_3$}{(μ_3-PCy)Fe$_2$Cp$_2$(μ-CO)(CO)$_2$}$_2$][Co(CO)$_4$], with Co(+1) and Co(−1) centers, respectively. This type of reactivity is also known for phosphines and further stresses the analogy in chemical behavior between the latter ligands and the “dimetallaphosphine” **1**. The photochemical treatment of the new trinuclear compounds can induce reversible decarbonylation processes, leading to the formation of new metal−metal bonds (ML$_n$ = MnCp′(CO)$_2$), or a reversible tautomerization derived from the cleavage of the Fe−Fe bond of **1** and formation of a new M−Fe bond (ML$_n$ = Cr(CO)$_5$ or Fe(CO)$_4$). The above reactions illustrate the efficiency of the binuclear complex **1** in the rational synthesis of polynuclear complexes and clusters stabilized by μ_3-phosphinidene ligands.

■ EXPERIMENTAL SECTION

General Procedures and Starting Materials. All manipulations and reactions were carried out under a nitrogen (99.995%) atmosphere using standard Schlenk techniques. Solvents were purified according to literature procedures and distilled prior to use.[38] Petroleum ether refers to that fraction distilling in the range 338−343 K. Compound **1**,[12a,c] [M(CO)$_5$(THF)] (M = Cr, Mo, W),[15] [MnCp′(CO)$_2$(THF)] (Cp′ = η^5-C$_5$H$_4$Me),[16] and [AuCl(THT)][39] were prepared according to literature procedures. All other reagents were obtained from the usual commercial suppliers and used as received. Photochemical experiments were performed using jacketed quartz or Pyrex Schlenk tubes, cooled by tap water (ca. 288 K) or by a closed 2-propanol circuit, kept at the desired temperature with a cryostat. A 400 W high-pressure mercury lamp was used for the experiments with visible−UV light, whereas a conventional 200 W lamp was used in the experiments with visible light. In both cases, the lamp was placed ca. 1 cm away from the Schlenk tube. Chromatographic separations were carried out using jacketed columns cooled as described for the Schlenk tubes. Commercial aluminum oxide (activity I, 150 mesh) was degassed under vacuum conditions prior to use. The latter was mixed under nitrogen with the appropriate amount of water to reach the activity desired. IR C−O stretching frequencies were measured in solution and are referred to as ν(CO). Nuclear magnetic resonance (NMR) spectra were routinely recorded at 400.13 (^{1}H), 162.00 (^{31}P{^{1}H}), or 100.62 MHz (^{13}C{^{1}H}) at 290 K in CD$_2$Cl$_2$ solutions unless otherwise stated. Chemical shifts (δ) are given in parts per million, relative to internal tetramethylsilane (^{1}H, ^{13}C) or external 85% aqueous H_3PO_4 (^{31}P). Coupling constants (J) are given in Hz.

Preparation of [$CrFe_2Cp_2(\mu_3$-PCy)(μ-CO)(CO)$_7$] (2a). A tetrahydrofuran (THF) solution (4 mL) of freshly prepared [$Cr(CO)_5$(THF)] (ca. 0.15 mmol) was added to a toluene solution (4 mL) of compound **1** (0.040 g, 0.091 mmol). The mixture was stirred for 1 min, and the solvents were then removed under vacuum conditions to give a red solid that was dissolved in the minimum amount of dichloromethane/petroleum ether (1/6) and chromatographed on alumina (activity IV) at 288 K. Elution with dichloromethane/petroleum ether (1/8) gave a red fraction, yielding, after removal of solvents under vacuum conditions, compound **2a** as a red microcrystalline solid (0.055 g, 96%). X-ray quality crystals of **2a** were grown by the slow diffusion of a layer of petroleum ether into a dichloromethane solution of the compound at 253 K. Anal. Calcd for $C_{24}H_{21}CrFe_2O_8P$: C, 45.60; H, 3.35. Found: C, 45.33; H, 3.15. ^{1}H NMR: δ 5.12 (s, 10H, Cp), 2.20 (m, 2H, Cy), 1.85−1.80 (m, 4H, Cy), 1.60 (m, 1H, Cy), 1.39 (m, 2H, Cy), 1.15 (m, 2H, Cy). ^{13}C{^{1}H} NMR: δ 266.2 (s, μ-CO), 225.2 (d, J_{CP} = 5, CrCO), 220.9 (d, J_{CP} = 12, 4CrCO), 212.9 (d, J_{CP} = 8, FeCO), 88.2 (s, Cp), 62.5 [d, J_{CP} = 13, C^{1}(Cy)], 33.7 [s, C^{2}(Cy)], 27.5 [d, J_{CP} = 10, C^{3}(Cy)], 25.8 [s, C^{4}(Cy)].

Preparation of [$Fe_2MoCp_2(\mu_3$-PCy)(μ-CO)(CO)$_7$] (2b). A THF solution (4 mL) of compound **1** (0.030 g, 0.068 mmol) and [$Mo(CO)_6$] (0.036 g, 0.136 mmol) was irradiated for 25 min with visible−UV light in a Pyrex Schlenk tube at 288 K while gently bubbling N_2 through the mixture, to give a red wine solution. The solvent was then removed under vacuum conditions, the residue dissolved in the minimum amount of dichloromethane/petroleum ether (1/2), and the solution chromatographed on alumina (activity IV) at 253 K. Elution with the same solvent mixture gave a red fraction, yielding, after removal of solvents under vacuum conditions, compound **2b** as a red microcrystalline solid (0.041 g, 89%). Anal. Calcd for $C_{24}H_{21}Fe_2MoO_8P$: C, 42.64; H, 3.13. Found: C, 42.38; H, 3.15. ^{1}H NMR (tol-d_8): δ 4.41 (s, 10H, Cp), 2.30 (m, 2H, Cy), 2.12 (m, 1H, Cy), 1.90−1.86 (m, 4H, Cy), 1.57 (m, 2H, Cy), 1.30 (m, 2H, Cy).

Preparation of [$Fe_2WCp_2(\mu_3$-PCy)(μ-CO)(CO)$_7$] (2c). The procedure is completely analogous to that described for **2b**, but using [$W(CO)_6$] (0.048 g, 0.136 mmol) and an irradiation time of 40 min. After a similar workup, compound **2c** was isolated as a dark red microcrystalline solid (0.047 g, 90%). Anal. Calcd for $C_{24}H_{21}Fe_2O_8PW$: C, 37.73; H, 2.77. Found: C, 37.48; H, 2.62. ^{1}H NMR (C_6D_6): δ 4.38 (s, 10H, Cp), 2.24−1.21 (m, 11H, Cy).

Preparation of [$Fe_2MnCp_2Cp'(\mu_3$-PCy)(μ-CO)(CO)$_4$] (2d). A THF solution (4 mL) of freshly prepared [MnCp′(CO)$_2$(THF)] (ca. 0.10 mmol) was added to a toluene solution (4 mL) of compound **1** (0.030 g, 0.068 mmol). The mixture was stirred for 1 min, and the solvents then were removed under vacuum conditions to give a green residue. The latter was extracted with dichloromethane/petroleum ether (1/4), and the extract was chromatographed on alumina (activity IV) at 288 K. Elution with the same solvent mixture gave a green fraction, yielding, upon removal of solvents under vacuum conditions, compound **2d** as a green microcrystalline solid (0.040 g, 93%). Anal. Calcd for $C_{27}H_{28}Fe_2MnO_5P$: C, 51.47; H, 4.48. Found: C, 51.39; H, 4.50. ^{1}H NMR (tol-d_8): δ 4.76 (br, s, 2H, C_5H_4), 4.57 (s, 10H, Cp), 4.34 (br, s, 2H, C_5H_4), 1.84 (s, 3H, Me), 2.40−1.15 (m, 11H, Cy).

Reaction of Compound 1 with [$Fe_2(CO)_9$]. Solid [$Fe_2(CO)_9$] (0.087 g, 0.239 mmol) was added to a solution of compound **1** (0.070 g, 0.159 mmol) in THF (4 mL), and the mixture was stirred in the dark for 1 h. The solvent was then removed under vacuum conditions. The residue was extracted with dichloromethane/petroleum ether (1/2), and the extract was chromatographed on alumina (activity IV) at 253 K. Elution with dichloromethane/petroleum ether (1/4) gave a red fraction, yielding, upon removal of solvents under vacuum conditions, complex [$Fe_3Cp_2(\mu_3$-PCy)(μ-CO)(CO)$_6$] (**2e**) as a red microcrystalline solid (0.073 g, 76%). X-ray quality crystals of **2e** were grown from a concentrated petroleum ether solution of the compound at 253 K. Elution with dichloromethane/petroleum ether (1/3) gave a yellow-brownish fraction, yielding analogously compound [{Fe(CO)$_3$}{(μ_3-PCy)Fe_2Cp_2(μ-CO)(CO)$_2$}$_2$] (**3**) as a microcrystalline solid (0.008 g, 10%). X-ray quality crystals of **3** were grown by the slow diffusion of a layer of petroleum ether into a toluene solution of the compound at 253 K. *Data for compound* ***2e***: Anal. Calcd for $C_{23}H_{21}Fe_3O_7P$: C, 45.44; H, 3.48. Found: C, 45.38; H, 3.29. ^{1}H NMR: δ 5.10 (s, 10H, Cp), 2.50, 1.96 [2 m, 2 × 2H, HC^{2}(Cy)], 1.79 [m, 2H, HC^{3}(Cy)], 1.60 [m, 1H, HC^{4}(Cy)], 1.45 [m, 1H, HC^{1}(Cy)], 1.32 [m, 1H, HC^{4}(Cy)], 1.10 [m, 2H, HC^{3}(Cy)]. ^{13}C{^{1}H} NMR: δ 265.6 (s, μ-CO), 216.8 (d, J_{CP} = 15, 4FeCO), 212.0 (d, J_{CP} = 11, 2FeCO), 90.4 (s, Cp), 68.6 [s, C^{1}(Cy)], 36.2 [s, C^{2}(Cy)], 27.8 [d, J_{CP} = 11, C^{3}(Cy)], 26.4 [s, C^{4}(Cy)]. The assignment of the ^{1}H NMR resonances of the Cy ring was made on the basis of a standard $^{1}J(^{13}C-^{1}H)$ correlation experiment (HSQC). *Data for compound* ***3***: Anal. Calcd for $C_{41}H_{42}Fe_5O_9P_2$: C, 48.28; H, 4.15. Found: C, 48.12; H, 4.11. ^{1}H NMR (C_6D_6): δ 4.79 (s, 20H, Cp), 3.11−1.23 (m, 22H, Cy).

Preparation of [$CuFe_2ClCp_2(\mu_3$-PCy)(μ-CO)(CO)$_2$] (2f). Solid CuCl (0.006 g, 0.061 mmol) was added to a solution of compound **1** (0.020 g, 0.045 mmol) in toluene (4 mL), and the mixture was stirred for 5 min to yield an orange-reddish solution. The solvent was then removed under vacuum conditions. The residue was extracted with dichloromethane/petroleum ether (1/1), and the extract was chromatographed on alumina (activity IV) at 288 K. Elution with the same solvent mixture gave an orange-reddish fraction, yielding, after removal of solvents under vacuum conditions, compound **2f** as an orange microcrystalline solid (0.022 g, 91%). Anal. Calcd for $C_{19}H_{21}ClCuFe_2O_3P$: C, 42.34; H, 3.93. Found: C, 42.25; H, 3.79. ^{1}H NMR (300.13 MHz): δ 5.03 (s, 10H, Cp), 2.00−1.03 (m, 11H, Cy).

Preparation of [$AuFe_2ClCp_2(\mu_3$-PCy)(μ-CO)(CO)$_2$] (2g). Solid [AuCl(THT)] (0.022 g, 0.069 mmol) was added to a solution of compound **1** (0.030 g, 0.068 mmol) in dichloromethane (4 mL), and the mixture was stirred for 5 min to yield a cherry-red solution. The solvent was then removed under vacuum conditions, and the residue was washed with petroleum ether (5 × 4 mL) and dried under vacuum conditions to give compound **2g** as a red microcrystalline solid (0.044 g, 96%). X-ray quality crystals of **2g** were grown by the slow diffusion of a layer of petroleum ether and a layer of toluene into a dichloromethane solution of the compound at 253 K. Anal. Calcd for $C_{19}H_{21}AuClFe_2O_3P$: C, 33.94; H, 3.15. Found: C, 33.76; H, 3.07. ^{1}H NMR (300.13 MHz): δ 5.06 (d, J_{HP} = 1, 10H, Cp), 2.21−2.12 (m, 4H, Cy), 1.90 (m, 2H, Cy), 1.68, 1.54, 1.41 (3 m, 3 × 1H, Cy), 1.32 (m, 2H, Cy). ^{13}C{^{1}H} NMR (75.48 MHz): δ 263.6 (s, μ-CO), 210.2 (d, J_{CP} = 14, FeCO), 89.2 (s, Cp), 54.1 [d, J_{CP} = 13, C^{1}(Cy)], 36.7 [s, C^{2}(Cy)], 27.3 [d, J_{CP} = 13, C^{3}(Cy)], 26.1 [s, C^{4}(Cy)].

Preparation of [{Co(CO)$_3$}{(μ_3-PCy)Fe_2Cp_2(μ-CO)(CO)$_2$}$_2$][Co(CO)$_4$] (4). Solid [$Co_2(CO)_8$] (0.044 g, 0.129 mmol) was added to a dichloromethane solution (5 mL) of compound **1** (0.040 g, 0.091 mmol) at 273 K, and the mixture was stirred at that temperature for 10 min to give a yellow-brown solution. The solvent was then removed under vacuum conditions, and the residue was washed with petroleum ether (6 × 5 mL) and dried under vacuum conditions to yield compound **4** as a microcrystalline solid (0.052 g, 96%). X-ray quality crystals of **4** were grown by the slow diffusion of a layer of petroleum ether into a dichloromethane solution of the compound at 253 K. Anal. Calcd for $C_{45}H_{42}Co_2Fe_4O_{13}P_2$: C, 45.27; H, 3.55. Found: C, 45.03; H, 3.38. ^{1}H NMR (acetone-d_6): δ 5.53 (s, 20H, Cp), 2.83−1.17 (m, 22H, Cy).

Preparation of [$CrFe_2Cp_2(\mu_3$-PCy)(μ-CO)(CO)$_7$] (5a). A toluene solution (4 mL) of compound **2a** (0.040 g, 0.063 mmol) was irradiated for 40 min with visible−UV light in a Pyrex Schlenk tube refrigerated at 253 K while gently bubbling N_2 through the mixture, to

Table 6. Crystal Data for New Compounds

	2a	2e	2g·0.5CH$_2$Cl$_2$	3·2CH$_2$Cl$_2$.
mol formula	$C_{24}H_{21}CrFe_2O_8P$	$C_{23}H_{21}Fe_3O_7P$	$C_{19.5}H_{22}AuCl_2Fe_2O_3P$	$C_{43}H_{46}Cl_4Fe_5O_9P_2$
mol wt	632.08	607.92	714.91	1189.79
cryst syst	monoclinic	triclinic	tetragonal	triclinic
space group	$P2_1/c$	$P\bar{1}$	$P4_2/n$	$P\bar{1}$
radiation (λ, Å)	0.71073	0.71073	0.71073	0.71073
a, Å	21.4980(7)	11.055(1)	17.9569(2)	9.0577(17)
b, Å	14.5527(5)	14.844(1)	17.9569(2)	11.669(2)
c, Å	15.8604(5)	16.036(2)	13.6231(2)	22.175(4)
α, deg	90	109.399(8)	90	94.591(3)
β, deg	93.547(2)	109.268(7)	90	99.170(3)
γ, deg	90	90.931(9)	90	95.294(3)
V, Å^3	4952.5(3)	2319.6(4)	4392.77(9)	2293.2(7)
Z	8	4	8	2
calcd density, g cm^{-3}	1.695	1.741	2.162	1.723
absorp coeff, mm^{-1}	1.699	1.963	8.301	1.901
temperature, K	100(2)	120(2)	100(2)	100(2)
θ range (deg)	0.95−26.42	1.47−26.73	1.88−25.24	0.93−26.43
index ranges (h, k, l)	−26, 26; 0, 18; 0, 19	−13, 13; −18, 17; 0, 20	0, 21; 0, 21; 0, 16	−11, 11; −14, 14; 0, 27
no. of reflns collected	67596	27935	34685	26016
no. of indep reflns (R_{int})	10149 (0.0556)	9792 (0.0245)	3977 (0.0325)	9381 (0.0569)
reflns with $I > 2\sigma(I)$	7984	8569	3486	6234
R indexes	R_1 = 0.0291	R_1 = 0.0219	R_1 = 0.0223	R_1 = 0.0429
[data with $I > 2\sigma(I)$][a]	wR_2 = 0.0553[b]	wR_2 = 0.0552[c]	wR_2 = 0.0482[d]	wR_2 = 0.0843[e]
R indexes (all data)[a]	R_1 = 0.0472, wR_2 = 0.0619[b]	R_1 = 0.0269, wR_2 = 0.0570[c]	R_1 = 0.0267, wR_2 = 0.0510[d]	R_1 = 0.0793, wR_2 = 0.0933[e]
GOF	1.036	1.063	1.144	1.011
no. of restraints/params	0/640	0/613	0/258	0/568
$\Delta\rho$ (max., min.), e·Å^{-3}	0.880, −0.628	0.375, −0.255	1.208, −1.111	0.676, −0.566
	4·CH$_2$Cl$_2$	5a	5e	7
mol formula	$C_{46}H_{44}Cl_2Co_2Fe_4O_{13}P_2$	$C_{24}H_{21}CrFe_2O_8P$	$C_{23}H_{21}Fe_3O_7P$	$C_{25}H_{28}Fe_2MnO_3P$
mol wt	1278.91	632.08	607.92	574.08
cryst syst	trigonal	monoclinic	monoclinic	orthorhombic
space group	$R\bar{3}$	$P2_1/n$	$P2_1/c$	$Pnma$
radiation (λ, Å)	1.54184	0.71073	1.54184	1.54184
a, Å	37.8398(6)	9.7622(2)	11.9840(2)	14.0485(2)
b, Å	37.8398(6)	18.5003(3)	13.8562(3)	12.4050(2)
c, Å	19.7609(4)	13.3338(2)	17.5092(4)	13.3384(3)
α, deg	90	90	90	90
β, deg	90	95.024(1)	123.355(1)	90
γ, deg	120	90	90	90
V, Å^3	24503.9(7)	2398.88(7)	2428.53(9)	2324.50(7)
Z	18	4	4	4
calcd density, g cm^{-3}	1.560	1.750	1.663	1.640
absorp coeff, mm^{-1}	14.923	1.754	15.168	15.084
temperature, K	100(2)	100(2)	295(2)	120(2)
θ range (deg)	2.61−74.12	1.89−27.88	4.40−70.06	4.57−67.50
index ranges (h, k, l)	−45, 44; −42, 37; −24, 24	−12, 12; 0, 24; 0, 17	−14, 13; −16, 0; −21, 13	0, 16; 0, 14; 0, 15
no. of reflns collected	60488	78988	17577	14856
no. of indep reflns (R_{int})	10549 (0.0927)	5730 (0.037)	4471 (0.0891)	2125 (0.0618)
reflns with $I > 2\sigma(I)$	7453	5050	3510	1870
R indexes	R_1 = 0.0473	R_1 = 0.0214	R_1 = 0.0604	R_1 = 0.0350
[data with $I > 2\sigma(I)$][a]	wR_2 = 0.1014[f]	wR_2 = 0.0508[g]	wR_2 = 0.1519[h]	wR_2 = 0.0870[i]
R indexes (all data)[a]	R_1 = 0.0753, wR_2 = 0.1151[f]	R_1 = 0.0270, wR_2 = 0.0530[g]	R_1 = 0.0721, wR_2 = 0.1656[h]	R_1 = 0.0409, wR_2 = 0.0939[i]
GOF	1.016	1.043	1.024	1.054
no. of restraints/params	0/622	0/325	0/307	0/205
$\Delta\rho$(max., min.), e·Å^{-3}	0.495, −0.457	0.366, −0.310	0.728, −1.213	0.443, −0.525

[a] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. $wR = [\Sigma w(|F_o|^2 - |F_c|^2)^2/\Sigma w|F_o|^2]^{1/2}$. $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$ where $P = (F_o^2 + 2F_c^2)/3$. [b] a = 0.0150, b = 7.1684. [c] a = 0.0281, b = 0.5678. [d] a = 0.0176, b = 11.4744. [e] a = 0.0381, b = 0. [f] a = 0.0567, b = 0. [g] a = 0.0242, b = 1.3570. [h] a = 0.1183, b = 0. [i] a = 0.0507, b = 2.7246.

give an orange solution. The solvent was then removed under vacuum conditions. The residue was extracted with dichloromethane/petroleum ether (1/6), and the extract was chromatographed on alumina (activity IV) at 253 K. Elution with dichloromethane/petroleum ether (1/4) gave an orange fraction that was collected at 253 K. Removal of solvents at this temperature yielded compound **5a** as an orange microcrystalline solid (0.039 g, 98%). This species is stable in solution only below 253 K, and it isomerizes back to the starting complex **2a** in ca. 15 min at room temperature. In solution, compound **5a** exists as an equilibrium mixture of *syn* and *anti* isomers. X-ray quality crystals of *syn*-**5a** were grown by the slow diffusion of a layer of petroleum ether into a dichloromethane solution of the compound at 253 K. Anal. Calcd for $C_{24}H_{21}CrFe_2O_8P$: C, 45.60; H, 3.35. Found: C, 45.44; H, 3.28. ν_{CO}(THF): 2034 (m), 2024 (w), 2006 (vs), 1981 (m, sh), 1968 (s), 1944 (m, sh), 1932 (vs), 1909 (vs), 1788 (m). ν_{CO}(toluene): 2037 (w), 2025 (w), 2006 (vs), 1968 (s), 1943 (vs), 1911 (s), 1792 (m). *Spectroscopic data for syn-5a*: ^{1}H NMR (213 K): δ 5.55, 4.96 (2s, 2 × 5H, Cp), 2.23−1.05 (m, 11H, Cy). ^{13}C{^{1}H} NMR (213 K): δ 274.2 (s, μ-CO), 230.1 (s, CO), 226.0 (d, J_{CP} = 10, CO), 215.7 (d, J_{CP} = 18, CO), 214.7 (s, CO), 214.3 (d, J_{CP} = 9, CO), 213.8 (d, J_{CP} = 8, CO), 212.9 (d, J_{CP} = 11, CO), 87.9, 86.1 (2s, Cp), 66.7 [s, C^1(Cy)], 37.3, 36.4 [2s, C^2(Cy)], 27.7 [s, $2C^3$(Cy)], 26.3 [s, C^4(Cy)]. *Spectroscopic data for anti-5a*: ^{1}H NMR (213 K): δ 5.52, 4.87 (2s, 2 × 5H, Cp), 2.23−1.05 (m, 11H, Cy). ^{13}C{^{1}H} NMR (213 K): δ 271.9 (s, μ-CO), 228.8 (s, CO), 225.1 (d, J_{CP} = 13, CO), 87.9, 85.4 (2s, Cp); other resonances of this minor isomer were obscured by those of the major isomer. Ratio *syn*/*anti* = 6 at 213 K (from the ^{1}H NMR spectrum).

Preparation of [$Fe_3Cp_2(\mu_3$-PCy)(μ-CO)(CO)$_6$] (5e). A THF solution (4 mL) of compound **2e** (0.030 g, 0.049 mmol) was irradiated for 1.5 h with visible light in a Pyrex Schlenk tube refrigerated at 288 K while gently bubbling N_2 through the mixture, to give a green solution. The solvent was then removed under vacuum conditions. The residue was extracted with dichloromethane/petroleum ether (1/3), and the extract was chromatographed on alumina (activity IV) at 288 K. Elution with dichloromethane/petroleum ether (1/2) gave a green fraction, yielding, after removal of solvents under vacuum conditions, compound **5e** as a green microcrystalline solid (0.027 g, 91%). X-ray quality crystals of **5e** were grown by the slow diffusion of a layer of petroleum ether and a layer of toluene into a dichloromethane solution of the compound at 253 K. Anal. Calcd for $C_{23}H_{21}Fe_3O_7P$: C, 45.44; H, 3.48. Found: C, 45.25; H, 3.38. ^{1}H NMR: δ 5.13, 4.86 (2s, 2 × 5H, Cp), 2.60, 2.33, 2.11 (3 m, 3 × 1H, Cy), 1.95−1.25 (m, 8H, Cy). ^{13}C{^{1}H} NMR: δ 226.0 (br, s, μ-CO and 4FeCO), 213.3 [d, J_{CP} = 20, FeCp(CO)$_2$], 212.4 [d, J_{CP} = 18, FeCp(CO)$_2$], 85.6, 84.0 (2s, Cp), 64.1 [d, J_{CP} = 12, C^1(Cy)], 37.0 [s, C^2(Cy)], 36.5 [d, J_{CP} = 5, C^2(Cy)], 28.3, 27.7 [2d, J_{CP} = 9, C^3(Cy)], 26.8 [s, C^4(Cy)]. The resonance at 226.0 ppm remained broad down to 183 K.

Preparation of [$Fe_2MnCp_2Cp'(\mu_3$-PCy)(μ-CO)$_2$(CO)$_2$] (6). A toluene solution (4 mL) of compound **2d** (0.080 g, 0.127 mmol) was irradiated for 7 h with visible light in a Pyrex Schlenk tube refrigerated at 288 K while gently bubbling N_2 through the mixture, to give a brown-greenish solution. The solvent was then removed under vacuum conditions; the residue was extracted with dichloromethane/petroleum ether (1/3), and the extract was chromatographed on alumina (activity IV) at 263 K. Elution with dichloromethane/petroleum ether (1/1) gave a green fraction possibly containing the isomers **E** of compound **6**, these quickly isomerizing outside the column to give the corresponding equilibrium ratio with the isomers **N** of this compound. Elution with dichloromethane/petroleum ether (3/1) gave a brown fraction possibly containing the isomers **N**, these also isomerizing rapidly outside the column to give the corresponding equilibrium ratio with the isomers **E**. Both fractions were combined, and the solvents were removed under vacuum conditions to give compound **6** as a brown solid (0.069 g, 90%). Low temperature NMR spectra revealed the presence in solution of two isomers of type **N** and four different isomers of type **E** (see the Supporting Information). The latter are arbitrarily labeled as **A**, **B**, **C**, and **D** in order of increasing δ_P, since we were unable to assign their individual resonances in the ^{1}H NMR spectra. Anal. Calcd for $C_{26}H_{28}MnFe_2O_4P$: C, 51.86; H, 4.69. Found: C, 51.62; H, 4.38. *Spectroscopic data for trans-**6N***: ^{1}H NMR: δ 4.57, 4.32 (2s, 2 × 5H, Cp), 4.15, 4.05 (2 m, 2 × 2H, C_5H_4), 2.32 (s, 3H, Me), 3.09−1.52 (m, 11H, Cy). ^{1}H NMR (213 K): δ 4.59 (s, 5H, Cp), 4.35 (m, 1H, C_5H_4), 4.33 (s, 5H, Cp), 4.18, 4.06, 4.03 (3 m, 3 × 1H, C_5H_4), 2.32 (s, 3H, Me), 3.09−1.52 (m, 11H, Cy). ^{13}C{^{1}H} NMR (213 K): δ 272.0, 269.0 (2s, μ-CO), 219.0, 213.1 (2s, FeCO), 87.0, 84.5 (2s, Cp), 11.7 (s, Me). Other resonances in the spectrum were obscured due to the presence of the resonances corresponding to the other isomers; these resonances could not be individually assigned either. The relative ratio for the six different isomers, according to the ^{31}P{^{1}H} NMR spectrum at 213 K, was *cis*-**6N**/*trans*-**6N**/**A**/**B**/**C**/**D** = 2:30:5:2:2:10 (see see the Supporting Information).

Preparation of [$Fe_2MnCp_2Cp'(\mu_3$-PCy)(μ-CO)$_3$] (7). A toluene solution (5 mL) of compound **2d** (ca. 0.080 g, 0.127 mmol) was irradiated for 1.5 h with visible−UV light in a quartz Schlenk tube refrigerated at 288 K while gently bubbling N_2 through the mixture, to give a red solution that yielded a solid of the same color after removal of the solvent under vacuum conditions. The residue was then extracted with dichloromethane/petroleum ether (1/2), and the extract was chromatographed on alumina (activity IV) at 288 K. Elution with dichloromethane gave a red fraction, yielding, after removal of solvents under vacuum conditions, compound **7** as a red microcrystalline solid (0.047 g, 86%). X-ray quality crystals of **7** were grown by the slow diffusion of a layer of petroleum ether and a layer of toluene into a dichloromethane solution of the compound at 253 K. Anal. Calcd for $C_{25}H_{28}Fe_2MnO_3P$: C, 52.30; H, 4.92. Found: C, 51.93; H, 4.62. ^{1}H NMR: δ 5.15 (m, 1H, Cy), 4.30 (s, 10H, Cp), 4.30 (br, s, 2H, C_5H_4), 4.09 (br, s, 2H, C_5H_4), 2.32 (s, 3H, Me), 3.22, 2.71, 2.33 (3 m, 3 × 2H, Cy), 2.15 (m, 1H, Cy), 2.02 (m, 2H, Cy), 1.75 (m, 1H, Cy), 1.55 (m, 3H, Me).

X-Ray Structure Determination for Compounds 2a, 2e, 2g, 3, 4, 5a, 5e and 7. The main crystallographic data are collected in the Table 6. Further details of the data adquisition, structure solution, and refinements are given in the Supporting Information.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information. A CIF file giving the crystallographic data for compounds **2a**, **2e**, **2g**, **3**, **4**, **5a**, **5e**, and **7** and a PDF file with text describing details of the data adquisition, structure solution, and refinements for these compounds, as well as details of the structural characterization of the isomers of compound **6**. This material is available free of charge via the Internet at http://pubs.acs.org.

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