

Vinylidene Transition-Metal Complexes, VI¹⁾The Rhodium Compounds $C_5H_5Rh(=C=CHR)P_iPr_3$ as Building Blocks for the Synthesis of Heterometallic Di- and Trinuclear Vinylidene-Bridged ComplexesHelmut Werner^{a*}, Francesco Javier Garcia Alonso^b, Heiko Otto^a, Karl Peters^c, and Hans Georg von Schnering^cInstitut für Anorganische Chemie der Universität Würzburg^a,
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Received March 21, 1988

The vinylidene rhodium complex $C_5H_5Rh(=C=CH_2)P_iPr_3$ (**1**) reacts with $C_6H_6Cr(CO)_3$ upon UV irradiation and with $C_5H_5Mn(CO)_2THF$ at room temperature to give the heterometallic dinuclear compounds $[C_5H_5(P_iPr_3)Rh(\mu-C=CH_2)(\mu-CO)Cr(CO)_3C_6H_6]$ (**4**) and $[C_5H_5(P_iPr_3)Rh(\mu-C=CH_2)(\mu-CO)Mn(CO)_2C_5H_5]$ (**6**), respectively. Treatment of **6** with HBF_4 in ether leads, after metathetical exchange of the anion with NH_4PF_6 , to the PF_6^- salt of the μ -ethylidyne cation $[C_5H_5(P_iPr_3)Rh(\mu-C=CH_2)(\mu-CO)Mn(CO)_2C_5H_5]^+$ (**7**). The reactions of **1** and $C_5H_5Rh(=C=CHR)P_iPr_3$ (**2**: R = Me; **3**: R = Ph) with $Fe_2(CO)_9$ give the dinuclear complexes $[C_5H_5(P_iPr_3)Rh(\mu-C=CHR)(\mu-CO)Fe(CO)_3]$ (**11–13**) as the main products. In addition, small amounts of the trinuclear clusters $[(\mu_3-\eta^1, \eta^2-C=CHR)(\mu-CO)_2Fe_2Rh(CO)_4(P_iPr_3)C_5H_5]$ (**14–16**) are formed. The protonation of **11–13** with HBF_4 gives the ionic compounds $[C_5H_5(P_iPr_3)Rh(\mu-C=CHR)(\mu-CO)Fe(CO)_3]BF_4$ (**17–19**). The crystal and molecular structures of **6**, **11**, and **14** have been determined. The two dinuclear complexes **6** and **11** contain unsymmetrical bridging ligands (CO and C=CH₂) probably as a consequence of the different electronic configuration of the metal atoms. The core of the trinuclear cluster **14** consists of an open Rh–Fe–Fe triangle which is triply bridged by the C=CH₂ unit.

Vinyliden-Übergangsmetallkomplexe, VI¹⁾. – Die Rhodiumverbindungen $C_5H_5Rh(=C=CHR)P_iPr_3$ als Bausteine für die Synthese von heterometallischen Vinyliden-verbrückten Zwei- und Dreikern-Komplexen

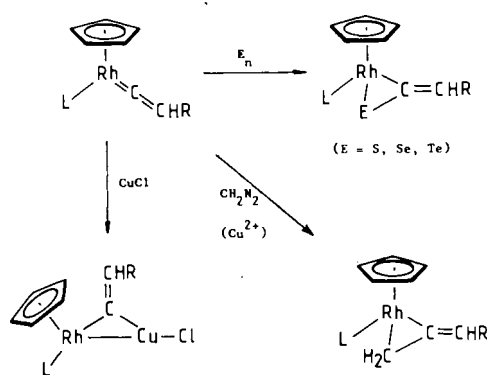
Der Vinyliden-Rhodiumkomplex $C_5H_5Rh(=C=CH_2)P_iPr_3$ (**1**) reagiert mit $C_6H_6Cr(CO)_3$ bei UV-Bestrahlung und mit $C_5H_5Mn(CO)_2THF$ bei Raumtemperatur zu den heterometallicischen Zweikernverbindungen $[C_5H_5(P_iPr_3)Rh(\mu-C=CH_2)(\mu-CO)Cr(CO)_3C_6H_6]$ (**4**) bzw. $[C_5H_5(P_iPr_3)Rh(\mu-C=CH_2)(\mu-CO)Mn(CO)_2C_5H_5]$ (**6**). Die Behandlung von **6** mit HBF_4 in Ether führt, nach Austausch des Anions mit NH_4PF_6 , zu dem PF_6^- -Salz des μ -Ethylidin-Kations $[C_5H_5(P_iPr_3)Rh(\mu-C=CH_2)(\mu-CO)Mn(CO)_2C_5H_5]^+$ (**7**). Die Reaktionen von **1** und $C_5H_5Rh(=C=CHR)P_iPr_3$ (**2**: R = Me; **3**: R = Ph) mit $Fe_2(CO)_9$ ergeben als Hauptprodukte die Zweikernkomplexe $[C_5H_5(P_iPr_3)Rh(\mu-C=CHR)(\mu-CO)Fe(CO)_3]$ (**11–13**). Daneben werden auch geringe Mengen der dreikernigen Cluster $[(\mu_3-\eta^1, \eta^2-C=CHR)(\mu-CO)_2Fe_2Rh(CO)_4(P_iPr_3)C_5H_5]$ (**14–16**) gebildet. Die Protonierung von **11–13** mit HBF_4 liefert die ionischen Verbindungen $[C_5H_5(P_iPr_3)Rh(\mu-C=CHR)(\mu-CO)Fe(CO)_3]BF_4$ (**17–19**). Die Kristall- und Molekülstrukturen von **6**, **11** und **14** wurden bestimmt. Die Zweikernkomplexe **6** und **11** enthalten unsymmetrisch gebundene Brückenliganden (CO und C=CH₂), was wahrscheinlich auf die unterschiedliche Elektronenkonfiguration der beiden Metallatome zurückzuführen ist. Das Gerüst des dreikernigen Clusters **14** besteht aus einem offenen Rh–Fe–Fe-Dreieck, das von der C=CH₂-Einheit überbrückt ist.

During our investigations on electron-rich half-sandwich type compounds C_5H_5MLL' (M = Co, Rh, Ir; L and L' = two-electron donor ligands) we previously observed that the reaction of *trans*- $[RhCl(RC\equiv CH)L_2]$ (L = P_iPr_3) with NaC_5H_5 not only leads to the formation of the expected alkyne complexes $C_5H_5Rh(RC\equiv CH)L$ but also to that of the unexpected vinylidene isomers $C_5H_5Rh(=C=CHR)L$ ^{2,3)}. These compounds reveal a remarkable reactivity towards electrophilic substrates as is illustrated with CH_2N_2 , the chalcogens⁴⁾, and $CuCl$ ⁵⁾ as examples in Scheme 1.

As a continuation of these studies, we were interested to learn whether not only $CuCl$ but also other metal-contain-

ing species that have a free coordination site are able to react with the $Rh=C$ bond of $C_5H_5Rh(=C=CHR)L$ to form heterometallic dinuclear complexes. Prior to our work⁶⁾ Antonova, Kolobova, and coworkers⁷⁾ as well as Berke⁸⁾ reported that mononuclear manganese, rhenium, and iron compounds of general composition $M(=C=CHR)L_n$ react, e.g., with $C_5H_5Mn(CO)_2(THF)$, $Fe_2(CO)_9$, or $M(CO)_6$ (M = Mo, W) under UV irradiation to give the corresponding dinuclear vinylidene-bridged products $[L_nM(\mu-C=CHR)M'L_n]$ (R = Ph, CO_2Me). A related complex of formula $[(dppm)Pt(\mu-C=CH_2)W(CO)_5]$ [$dppm = CH_2(PPh_2)_2$], in which the unsubstituted $:C=CH_2$

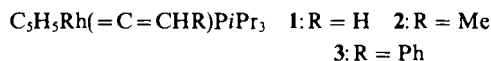
Scheme 1
(L = P1Pr₃)



unit bridges two different metal atoms was obtained by Stone et al.⁹ but was not prepared from a mononuclear vinylidene-containing precursor.

Heterometallic Dinuclear Complexes and Trinuclear Clusters Formed from C₅H₅Rh(=C=CHR)L

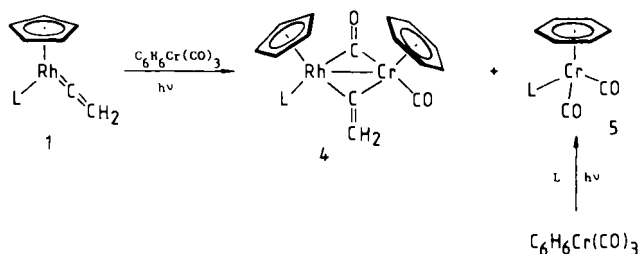
The primary attempts to use the complexes C₅H₅Rh(=C=CHR)L (L = P1Pr₃; 1: R = H; 2: R = Me; 3: R = Ph) as building blocks for vinylidene-bridged dirhodium compounds [C₅H₅(L)Rh(μ-C=CHR)Rh(L')C₅H₅] remained unsuccessful. Neither of the starting materials, C₅H₅Rh(CO)₂, C₅H₅Rh(CO)PMe₃ nor C₅H₅Rh(C₂H₄)PMe₃ which on thermolysis or photolysis could generate a [C₅H₅Rh(L')] species, reacted with 1–3 to form a product with the aforementioned composition.



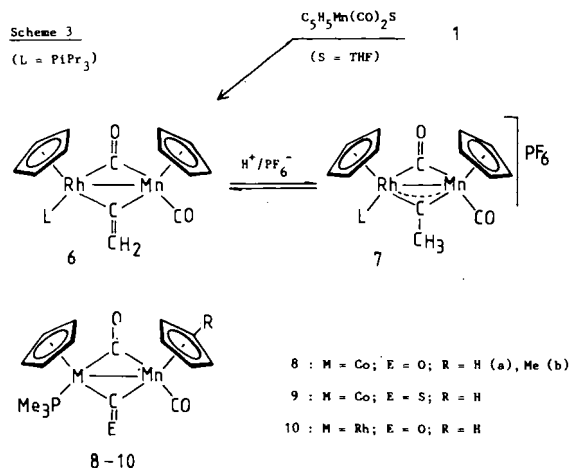
We therefore turned our interest to [C₆H₆Cr(CO)₂], [C₅H₅Mn(CO)₂], and [Fe(CO)₄] as 16-electron fragments which, like [C₅H₅Rh(L')], are also isolobal to CH₂¹⁰. The reaction of 1 with C₆H₆Cr(CO)₃ under UV irradiation in benzene at room temperature gives a mixture of products from which the expected dinuclear complex 4 is isolated in 30% yield. The structure proposed on the basis of the IR and ¹H-NMR data is shown in Scheme 2. Recently, the Stone group described the synthesis of a structurally similar compound, [C₅Me₅(CO)Rh(μ-CO)₂Cr(CO)C₆H₆], in which the two [C_nR_nM(L')] units are not linked by one carbonyl and one vinylidene but by two semi-bridging CO groups¹¹.

By using chromatographic techniques, the phosphane-substituted compound C₆H₆Cr(CO)₂L (5) has been separated in small amounts from the reaction mixture obtained from 1 and C₆H₆Cr(CO)₃. This result demonstrates that during the interaction between 1 and C₆H₆Cr(CO)₃ (or, more probably, [C₆H₆Cr(CO)₂]) partial migration of the phosphane ligand L from rhodium to chromium occurs that possibly proceeds via a dinuclear carbonyl-bridged intermediate. Complex 5 has independently been prepared by photolysis of a benzene solution of C₆H₆Cr(CO)₃ and L in nearly quantitative yield.

Scheme 2 (L = P1Pr₃)



The synthesis of the rhodium-manganese compound [C₅H₅(L)Rh(μ-C=CH₂)(μ-CO)Mn(CO)C₅H₅] (6) (see Scheme 3) follows a similar route, but uses the THF adduct C₅H₅Mn(CO)₂(THF) instead of C₅H₅Mn(CO)₃ as starting material. The molecular structure of 6 has been elucidated by X-ray analysis. Like that of 4 the IR spectrum in THF shows two CO stretching frequencies at 1895 and 1800 cm⁻¹, which indicates that the structure with one bridging CO group in the crystal is also present in solution. Some relatives of 6, the cobalt-manganese complexes 8a,b and 9^{12a,b} and the rhodium-manganese complex 10^{12c}, are known and have been prepared in our laboratory from C₅H₅Co(CE)PMe₃ (E = O, S) or C₅H₅Rh(CO)PMe₃, respectively, and (C₅H₄R)Mn(CO)₂(THF).

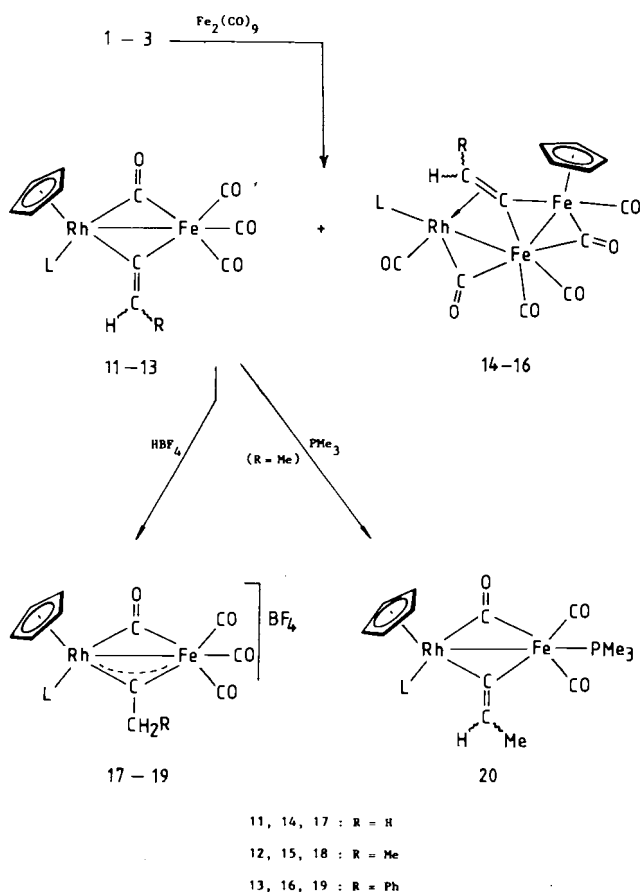


Complex 6 reacts with acids such as HBF₄ in ether to give the dark blue [C₅H₅(L)Rh(μ-C=CH₂)(μ-CO)Mn(CO)C₅H₅]⁺ cation. It has been isolated as the PF₆⁻ salt 7 in ca. 70% yield. The ¹³C-NMR spectrum of 7 is particularly notable for the very low-field resonance at δ = 452.7 which is characteristic of the ligated carbon atom of a bridging carbene group^{13–15}. Protonation of the symmetrical dinuclear μ-vinylidene complexes [C₅H₅(CO)₂Mn]₂(μ-C=CH₂)¹⁶, [C₅H₅(CO)Co]₂(μ-C=CH₂)¹⁷, and [C₅H₅(CO)M]₂(μ-CO)(μ-C=CH₂) (M = Fe¹⁴, Ru¹⁵) likewise yields μ-ethylidyne cations whereas the analogous indenyl rhodium compound [C₉H₇(CO)Rh]₂(μ-C=CH₂) on treatment with HBF₄ forms the unsymmetrical vinyl-bridged species [C₉H₇Rh(μ-CO)(μ-η²-CH=CH₂)Rh(CO)C₉H₇]⁺¹⁸. The observation that complex 7 is stable in the solid state but decomposes in acetone or methanol to reform the parent compound 6 indicates that

in solution an equilibrium between the neutral μ -vinylidene complex and the μ -carbyne cation exists.

The results illustrating the reactivity of the three vinylidene rhodium complexes **1–3** towards $\text{Fe}_2(\text{CO})_9$ are summarized in Scheme 4. We found that in all cases the expected dinuclear iron-rhodium compound **11–13** is the main product, but, in addition to this, small quantities of trinuclear RhFe_2 clusters **14–16** are formed. As far as the reaction mechanism is concerned we assume that both $[\text{Fe}(\text{CO})_4]$ as well as $[\text{Fe}_2(\text{CO})_x]$, $x = 7$ or 8 , are involved as reactive intermediates which are stabilized by the electron-rich vinylidene rhodium complex. The interesting facet of the cluster formation is that a trinuclear species such as $[\text{C}_5\text{H}_5(\text{L})\text{Rh}(\mu\text{-CO})(\mu\text{-C}=\text{CHR})\text{Fe}(\mu\text{-CO})_3\text{Fe}(\text{CO})_3]$ does not seem to be stable and rearranges by loss of CO and transfer of cyclopentadienyl from rhodium to iron to give the isolated product. A few examples of trinuclear homo- and heterometallic clusters containing triply bridging $\eta^1, \eta^2\text{-C}=\text{CHR}$ units are already known but have not been prepared from mononuclear vinylidene compounds as starting materials^{19–21}.

Scheme 4

(L = $\text{P}(\text{iPr})_3$)

The dinuclear complexes **11–13** smoothly react with HBF_4 in ether to give the corresponding μ -carbyne iron-rhodium cations (Scheme 4). The BF_4 salts **17–19**, which precipitate out of solution as dark brown powders within

seconds after addition of HBF_4 , are quite stable under nitrogen in the solid state but in acetone or methanol in absence of excess acid decompose rapidly to regenerate **11–13**. In nitromethane, solutions of **17–19** are stable at room temperature for ca. one hour and thus NMR spectra can be measured. The ^1H -NMR spectra show two signals for the diastereotopic methyl protons of the triisopropylphosphane ligand owing to the chirality of the cationic species. In the ^{13}C -NMR spectrum of **19** (which is the most stable of the dinuclear cations) the resonance of the μ -carbyne carbon atom is again found at very low field ($\delta = 416.54$) which is in agreement with earlier observations mentioned before^{13–15}.

Attempts to split the carbonyl and vinylidene bridges in the dinuclear Fe–Rh compounds by PMe_3 to eventually produce $\text{C}_5\text{H}_5\text{Rh}(\text{P}(\text{iPr})_3)\text{PMe}_3$ ²² and the unknown iron complex $\text{Fe}(=\text{C}=\text{CHR})(\text{CO})_4$ failed. Instead of cleavage of the bridge substitution of one terminal CO group by the phosphane occurs to give **20** in almost quantitative yield. The formation of **20** is noteworthy insofar as the related complexes **8** and **10** react with PMe_3 not by substitution but by fragmentation of the dinuclear framework to give mononuclear products^{12a,c}.

X-Ray Structural Analyses of Complexes **6**, **11**, and **14**

The molecular structures of the two dinuclear μ -vinylidene complexes **6** and **11** are shown in Figures 1 and 2. In both molecules the RhC_2M four-membered ring is bent along the Rh–M axis resulting in a dihedral angle between the $[\text{RhC}(\text{CH}_2)\text{M}]$ and $[\text{RhC}(\text{O})\text{M}]$ planes of 162.7° for **6** and 140.3° for **11**. The value of 162.7° for the rhodium-manganese compound is nearly identical to that found for the related cobalt-manganese complex **8a** (160.7°), in which the two metal atoms are bridged by two carbonyl groups²³.

The most characteristic feature of the structures of **6** and **11** undoubtedly is the presence of *unsymmetrical* CO and $\text{C}=\text{CH}_2$ bridging ligands (cf. Tables 1, 2). In **6**, the angles

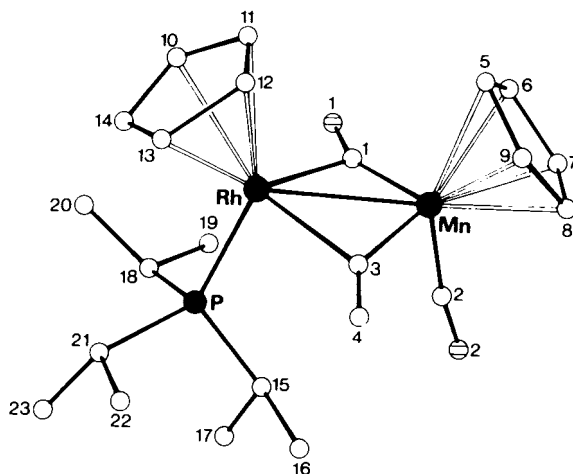


Figure 1. Perspective drawing of **6** with the numbering of atoms corresponding to Tables 1 and 2

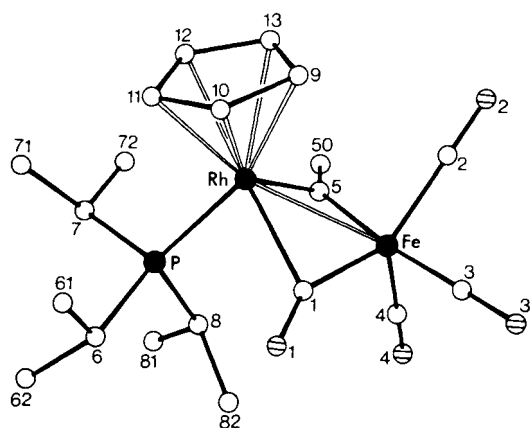


Figure 2. Perspective drawing of **11** with the numbering of atoms corresponding to Tables 3 and 4

Rh–C–X and Mn–C–X differ by 30.4° for $X = O$ and 14.6° for $X = CH_2$, with the oxygen atom and the carbon atom of the CH_2 group being bent towards rhodium and not to manganese. The corresponding values for **11** are 21.8° for $X = O$ and 5.7° for $X = CH_2$ (Tables 3, 4). There is also a significant difference in the $M-\mu-C(O)$ and $M-\mu-C(CH_2)$ distances which are shorter by 39.9 and 15.5 pm for $M = Mn$ than for $M = Rh$ in **6** and by 29.9 and 7.5 pm for $M = Fe$ than for $M = Rh$ in **11**. We conclude that these differences do not mainly arise from the non-equivalence of the two metal atoms, since, for example, the Rh–Mn bond length in **6** [266.7(1) pm] is only slightly different from the metal-metal distance in comparable homometallic Rh–Rh and Mn–Mn complexes, e.g., $[C_9H_7(CO)Rh]_2(\mu-C=CH_2)$ [Rh–Rh = 269.1(1) pm]¹⁸, $[C_5Me_5(CO)Rh]_2(\mu-C=CMe_2)$ [Rh–Rh = 268.4(0) pm]²⁴, $[C_5H_5(CO)Rh]_2(\mu-CH_2)$ [Rh–Rh = 266.2(1) pm]²⁵, $[C_5H_5(CO)_2Mn]_2(\mu-C=CH_2)$ [Mn–Mn = 275.9(1) pm]²⁶, and $[C_5H_5(CO)_2Mn]_2(\mu-CH_2)$ [Mn–Mn = 277.9(1) pm]²⁷. It is worth mentioning that the Rh–Mn bond length in **6** lies in the same range as that found in $[C_5Me_5(CO)Rh(\mu-CO)_2Mn(CO)C_5H_5]$ [270.3(2) pm]²⁸.

We believe that the reason for the remarkable dissymmetry of the central RhC_2M unit in **6** and **11** should be sought in the different electronic configuration of the two metal atoms. If the four electrons of the bridging ligands are

Table 1. Selected bond distances (pm) in **6** with estimated standard deviations

Rh–Mn	266.7(1)	C13–C14	138.7(9)	C5–C6	137.1(9)
Rh–P	231.7(1)	C14–C10	137.1(7)	C6–C7	136.8(8)
Rh–C1	222.4(4)	Mn–C1	183.3(3)	C7–C8	136.0(7)
Rh–C3	205.6(3)	Mn–C2	175.6(3)	C8–C9	137.3(8)
Rh–C10	231.4(4)	Mn–C3	190.1(3)	C9–C5	136.8(7)
Rh–C11	228.5(4)	Mn–C5	217.9(5)	C1–O1	119.0(4)
Rh–C12	225.6(6)	Mn–C6	213.7(6)	C2–O2	115.9(4)
Rh–C13	224.7(6)	Mn–C7	210.9(5)	C4–H1	67(5)
Rh–C14	225.5(5)	Mn–C8	211.2(4)	C4–H2	78(5)
C10–C11	135.1(8)	Mn–C9	214.3(5)	P–C15	185.8(3)
C11–C12	138.6(9)	C3–C4	129.4(6)	P–C18	187.0(4)
C12–C13	140.6(9)			P–C21	186.2(4)

Table 2. Selected bond angles ($^\circ$) in **6** with estimated standard deviations

Mn–Rh–P	107.34(2)	Rh–Mn–C3	50.8(1)	Mn–C3–C4	144.2(3)
Mn–Rh–C1	32.9(1)	C1–Mn–C2	93.6(2)	Rh–C3–C4	129.6(3)
Mn–Rh–C3	45.2(1)	C1–Mn–C3	104.0(1)	H1–C4–H2	118(6)
P–Rh–C1	96.4(1)	C2–Mn–C3	94.5(1)	Mn–C2–O2	172.2(3)
P–Rh–C3	96.8(1)	Rh–C1–Mn	81.6(1)	Rh–P–C15	120.2(1)
C1–Rh–C3	86.8(1)	Mn–C1–O1	153.8(3)	Rh–P–C18	114.9(1)
Rh–Mn–C1	55.6(1)	Rh–C1–O1	123.4(3)	Rh–P–C21	109.7(1)
Rh–Mn–C2	107.8(1)	Rh–C3–Mn	84.6(1)		

Table 3. Selected bond distances (pm) in **11** with estimated standard deviations

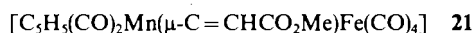
Rh–Fe	260.4(1)	C9–C10	141.2(6)	Fe–C5	193.6(3)
Rh–P	233.6(1)	C10–C11	138.6(5)	C1–O1	117.6(4)
Rh–C1	214.1(3)	C11–C12	143.4(5)	C2–O2	114.5(5)
Rh–C5	201.1(3)	C12–C13	139.2(6)	C3–O3	113.6(6)
Rh–C9	225.0(4)	C13–C9	142.1(6)	C4–O4	114.3(6)
Rh–C10	228.9(4)	Fe–C1	184.2(3)	C5–C50	132.0(5)
Rh–C11	225.0(4)	Fe–C2	180.8(4)	P–C6	186.6(3)
Rh–C12	223.7(3)	Fe–C3	179.1(4)	P–C7	186.4(3)
Rh–C13	225.9(3)	Fe–C4	175.9(4)	P–C8	187.0(3)

Table 4. Selected bond angles ($^\circ$) in **11** with estimated standard deviations

Fe–Rh–P	107.7(1)	Rh–Fe–C4	120.9(1)	C4–Fe–C5	87.1(2)
Fe–Rh–C1	44.4(1)	Rh–Fe–C5	50.0(1)	Rh–C1–O1	128.2(3)
Fe–Rh–C5	47.5(1)	C1–Fe–C2	141.0(2)	Rh–C5–C50	135.3(3)
P–Rh–C1	86.9(1)	C1–Fe–C3	86.5(2)	Fe–C5–C50	141.0(3)
P–Rh–C5	91.0(1)	C1–Fe–C4	104.5(2)	Fe–C1–O1	150.0(3)
C1–Rh–C5	85.1(1)	C1–Fe–C5	96.0(1)	Fe–C2–O2	178.4(4)
Rh–C1–Fe	81.3(1)	C2–Fe–C3	91.5(2)	Fe–C3–O3	177.9(4)
Rh–C5–Fe	82.5(1)	C2–Fe–C4	114.4(2)	Fe–C4–O4	177.5(4)
Rh–Fe–C1	54.4(1)	C2–Fe–C5	82.5(1)	Rh–P–C6	112.6(1)
Rh–Fe–C2	99.6(1)	C3–Fe–C4	98.7(2)	Rh–P–C7	114.7(1)
Rh–Fe–C3	128.4(1)	C3–Fe–C5	173.0(2)	Rh–P–C8	115.2(1)

equally divided between the two metals and the electrons of the metal-metal bond not considered for electron counting, the rhodium has 18 and the manganese or iron 16 electrons in the valence shell. This means that one side of the molecule is two electrons short which is probably compensated by a donor bond from rhodium to manganese or iron. MO calculations on the model compounds $[C_5H_5(PH_3)Rh(\mu-CO)_2CoC_5H_5]$ and $[C_5Me_5(CO)Rh(\mu-CO)_2Cr(CO)C_6H_6]$ are in good agreement with this hypothesis as they indicate that the $C_5H_5Co(CO)_2$ and $C_6H_6Cr(CO)_3$ moieties are excellent π -acid ligands for the electron-rich $[C_5R_5(L)Rh]$ fragments²⁹. We note that other structurally similar dinuclear homo- and heterometallic complexes with an [18 + 16]-electron configuration are already known, prominent examples besides **8–10** (Scheme 3), $[C_5Me_5(CO)Rh(\mu-CO)_2Mn(CO)C_5H_5]$ ²⁸, and $[C_5Me_5(CO)Rh(\mu-CO)_2Cr(CO)C_6H_6]$ ¹¹ being $[C_5H_5(PPh_3)Rh(\mu-CO)_2RhC_5H_5]$ ³⁰, $[C_5Me_5(P(OMe)_3)Rh(\mu-CO)_2RhC_5Me_5]$ ³¹, $[C_5H_4Me(PMe_2Ph)Co(\mu-$

$\text{CO})_2\text{CoC}_5\text{H}_4\text{Me}$]³², and $[\text{C}_5\text{H}_5(\text{PMe}_3)\text{Co}(\mu\text{-CS})_2\text{CoC}_5\text{H}_5]$]³³. It should be mentioned that in contrast to **11** the manganese-iron compound **21** described by Kolobova et al.^{7d} does not contain a CO bridge which could be due to the fact that two monodentate ligands (CO) are bound to the manganese atom in **21** but only one PiPr_3 to the rhodium atom in **11**.



The vinylidene C=C distances in **6** and **11** lie in the range 129–135 pm observed for several other vinylidene-bridged complexes^{9,18,20,24,26,34}. The Mn– $\mu\text{-C}(\text{CH}_2)$ bond length in **6** [190.1(3) pm] is significantly shorter than that found in the symmetrical compound $[\text{C}_5\text{H}_5(\text{CO})_2\text{Mn}]_2(\mu\text{-C}=\text{CH}_2)$ [197.9(7) pm]²⁶ which might be a consequence of the unequal electron distribution in the central RhC_2Mn fragment. Accordingly, the Rh– $\mu\text{-C}(\text{CH}_2)$ distance in **6** [205.6(3) pm] is somewhat longer than the distance found in $[\text{C}_9\text{H}_7(\text{CO})\text{Rh}]_2(\mu\text{-C}=\text{CH}_2)$ [198.2(3) and 198.8(3) pm]¹⁸ and $[\text{C}_5\text{Me}_5(\text{CO})\text{Rh}]_2(\mu\text{-C}=\text{CMe}_2)$ [197.8(1) and 204.3(1) pm]²⁴. The two hydrogens of the C=CH₂ bridge in **6** do not lie in the [Rh,C3,Mn] plane; the dihedral angle between the [Rh,C3,Mn] and [C4,H1,H2] planes is 11.1°. A similar observation has already been made for $[\text{C}_9\text{H}_7(\text{CO})\text{Rh}]_2(\mu\text{-C}=\text{CH}_2)$ ¹⁸ and other C=CH₂-bridged derivatives²⁰. Finally it should be pointed out that the cyclopentadienyl ligands in **6** are in a *cis* relationship which is in contrast to the related rhodium-manganese complex $[\text{C}_5\text{Me}_5(\text{CO})\text{Rh}(\mu\text{-CO})_2\text{Mn}(\text{CO})\text{C}_5\text{H}_5]$ where the two rings are *trans* to each other²⁸. The sterically demanding PiPr_3 ligand in **6** may be the source of this feature.

The molecular structure of the trinuclear complex **14** is shown in Figure 3. The three metal atoms define an open triangle which is bridged by the C=CH₂ unit. The α -carbon atom of the vinylidene (C12 in A and C22 in B) is σ -bound to the two irons and π -bound to rhodium, and thus a similar coordination of the vinylidene as that found in $[\text{Co}_2\text{Ru}(\text{CO})_9(\mu_3\text{-C}=\text{CHR})]$ (R = *t*Bu)^{21a} is present. The Fe– $\mu\text{-C}(\text{CH}_2)$ distances [185.8(6) and 192.7(8) pm in A, and

186.9(8) and 193.2(6) pm in B] are comparable to the corresponding Fe–C bond length in **11**. Owing to the (2 σ + π) coordination, the vinylidene C=C distance [136.5(10) pm in A and 135.9(10) pm in B] is somewhat longer than that found in **6** [129.4(6) pm], **11** [132.0(5) pm], and in the mononuclear complex **3** [129.5(2) pm]³.

The iron-rhodium bond length in **14** [259.5(1) pm in A and 259.7(1) pm in B] is nearly identical to the Fe–Rh distances found in $[(\text{C}_5\text{H}_5)_2\text{Rh}_2\text{Fe}_2(\text{CO})_8]$ (**22**) and $[\text{C}_5\text{H}_5\text{RhFe}_3(\text{CO})_{11}]$ (**23**). These two clusters which have been prepared from $\text{C}_5\text{H}_5\text{Rh}(\text{CO})_2$ and $\text{Fe}_2(\text{CO})_9$ ³⁵ contain a tetrahedral metal core with Fe–Rh linkages of 257.0(5) and 259.8(5) pm in **22** and 259.2 pm (mean value) in **23**^{36,37}. The Fe–Fe bond lengths in **22** and **23** range from 253.9(7) to 259.4(3) pm and thus differ only slightly from the Fe–Fe distance found in **14** (see Table 5).

Table 5. Selected bond distances (pm) in **14** with estimated standard deviations

Rh1 – Fe11	259.5(1)	Fe12–C12	192.7(8)	C11 –C12	136.5(10)
Rh1 – P1	232.5(2)	Fe12–C13	187.3(7)	C13 –O13	116.3(10)
Rh1 – C11	221.9(6)	Fe12–C18	176.6(8)	C14 –O14	116.3(11)
Rh1 – C12	218.3(6)	Fe12–C120	209.1(18)	C15 –O15	112.9(9)
Rh1 – C14	215.2(8)	Fe12–C121	209.4(18)	C16 –O16	114.1(10)
Rh1 – C15	185.3(7)	Fe12–C122	206.5(10)	C17 –O17	111.6(11)
Fe11–Fe12	255.8(1)	Fe12–C123	205.5(17)	C18 –O18	111.8(10)
Fe11–C12	185.8(6)	Fe12–C124	206.9(19)	C120–C121	133(3)
Fe11–C13	204.6(9)	P1 –C101	184.4(11)	C121–C122	133(2)
Fe11–C14	183.8(9)	P1 –C102	184.7(11)	C122–C123	133(2)
Fe11–C16	178.9(8)	P1 –C103	182.0(11)	C123–C124	136(3)
Fe11–C17	177.6(8)			C124–C120	137(2)
Rh2 – Fe21	259.7(1)	Fe22–C22	193.2(6)	C21 –C22	135.9(10)
Rh2 – P2	232.2(2)	Fe22–C23	186.3(10)	C23 –O23	117.4(11)
Rh2 – C21	221.2(8)	Fe22–C28	175.4(11)	C24 –O24	116.2(10)
Rh2 – C22	216.6(8)	Fe22–C220	208.2(17)	C25 –O25	112.2(12)
Rh2 – C24	216.8(8)	Fe22–C221	211.3(11)	C26 –O26	114.9(13)
Rh2 – C25	184.7(9)	Fe22–C222	209.0(11)	C27 –O27	113.6(11)
Fe21–Fe22	255.2(2)	Fe22–C223	208.5(16)	C28 –O28	112.8(13)
Fe21–C22	186.9(8)	Fe22–C224	205.4(17)	C220–C221	134(3)
Fe21–C23	204.3(9)	P2 –C201	181.9(23)	C221–C222	133(2)
Fe21–C24	184.6(9)	P2 –C202	178.8(23)	C222–C223	139(2)
Fe21–C26	179.2(10)	P2 –C203	187.1(19)	C223–C224	136(3)
Fe21–C27	177.5(9)			C224–C220	137(3)

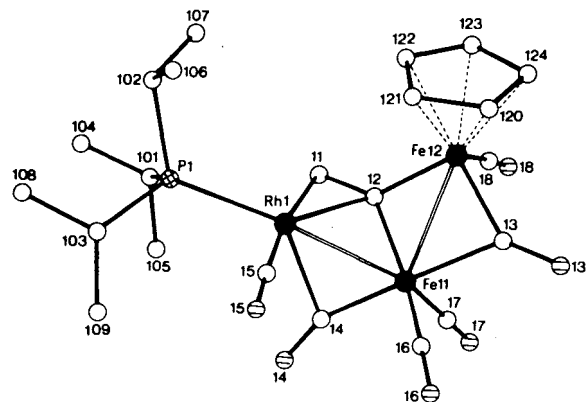


Figure 3. Perspective drawing of **14** with the numbering of atoms corresponding to Tables 5 and 6. **14** crystallizes with two independent molecules, A and B, in the asymmetric unit. Only the structure of one molecule is shown

The terminal and bridging M–CO distances in the trinuclear complex **14** are in agreement with expected values³⁶. It is interesting to note that although the coordination spheres of the rhodium and the central iron atom (Fe11 or Fe21) in **14** are not comparable to those in **11**, the Fe–C and Rh–C bond lengths and the Rh–C–Fe angle for the $\text{Rh}(\mu\text{-CO})\text{Fe}$ fragment of the two compounds are nearly the same. Owing to the difference of ca. 32° between the angles Fe–C–O and Rh–C–O in **14** (Table 6), the carbonyl group C14–O14 in A and C24–O24 in B is more semi-bridging than unsymmetrical in character³⁸. There is a significant increase of the Rh– $\mu\text{-C}(\text{CH}_2)$ distance in **14** compared to **11** which is a consequence of the additional linkage of the vinylidene α -carbon atom C12 or C22 to the $\text{Fe}(\text{CO})\text{C}_5\text{H}_5$ unit.

Table 6. Selected bond angles (°) in **14** with estimated standard deviations

Fe11-Rh1-P1	164.7(1)	C12-Fe12-C13	97.8(3)	Fe11-Fe12-C13	52.3(3)
P1-Rh1-C11	93.2(2)	C12-Fe12-C18	86.1(3)	Fe11-Fe12-C18	95.1(3)
P1-Rh1-C12	128.3(2)	Rh1-C11-C12	70.5(4)	C13-Fe12-C18	91.1(3)
Fe11-Rh1-C14	44.4(2)	Fe11-Rh1-C11	76.7(2)	Rh1-C12-Fe11	79.5(2)
C11-Rh1-C14	86.2(3)	Fe11-Rh1-C12	44.7(2)	Rh1-C12-Fe12	116.8(3)
Fe11-Rh1-C15	95.3(2)	C11-Rh1-C12	36.1(3)	Rh1-C12-C11	73.4(4)
C11-Rh1-C15	171.8(3)	C12-Rh1-C14	74.0(3)	Fe12-C12-C11	137.4(5)
C14-Rh1-C15	89.1(3)	C12-Rh1-C15	135.9(3)	Fe11-C13-C11	135.4(6)
Rh1-Fe11-C12	55.8(2)	Rh1-Fe11-Fe12	85.6(1)	Rh1-C14-Fe11	80.7(3)
Rh1-Fe11-C13	123.1(2)	Fe12-Fe11-C12	48.6(2)	Fe11-C14-C12	155.9(7)
C12-Fe11-C13	94.2(3)	Fe12-Fe11-C13	46.4(2)	Fe11-C16-C12	178.8(9)
Fe12-Fe11-C14	136.2(2)	Rh1-Fe11-C14	54.9(3)	Fe12-C18-C12	177.9(8)
C13-Fe11-C14	172.3(3)	Fe11-Fe11-C14	89.8(3)	Fe11-C12-Fe12	85.0(3)
Fe12-Fe11-C16	119.1(3)	Rh1-Fe11-C16	101.6(2)	Fe11-C12-C11	136.7(6)
C13-Fe11-C16	83.7(4)	C12-Fe11-C16	151.1(3)	Fe11-C13-Fe12	81.3(3)
Rh1-Fe11-C17	141.3(3)	C14-Fe11-C16	89.8(4)	Fe12-C13-C11	143.3(7)
C12-Fe11-C17	105.0(3)	Fe12-Fe11-C17	106.4(3)	Rh1-C14-C12	123.4(6)
C14-Fe11-C17	96.4(4)	C13-Fe11-C17	88.5(4)	Rh1-C15-C12	178.3(7)
Fe11-Fe12-C12	46.3(2)	C16-Fe11-C17	103.8(4)	Fe11-C17-C12	177.7(9)
Fe21-Rh2-P2	165.5(1)	C22-Fe22-C23	97.9(3)	Fe21-Fe22-C23	52.4(3)
P2-Rh2-C21	93.4(2)	C22-Fe22-C28	86.4(3)	Fe21-Fe22-C28	91.1(3)
P2-Rh2-C22	128.5(2)	Rh2-C21-C22	70.1(4)	C23-Fe22-C28	91.1(4)
Fe21-Rh2-C24	44.4(2)	Fe21-Rh2-C21	77.0(2)	Rh2-C22-Fe21	79.7(3)
C21-Rh2-C24	86.4(3)	Fe21-Rh2-C22	45.1(2)	Rh2-C22-Fe22	114.2(3)
Fe21-Rh2-C25	95.5(3)	C21-Rh2-C22	36.2(3)	Rh2-C22-C21	73.8(5)
C21-Rh2-C25	171.6(3)	C22-Rh2-C24	74.3(3)	Fe22-C22-C21	137.4(6)
C24-Rh2-C25	90.8(4)	C22-Rh2-C25	135.5(3)	Fe21-C23-C23	135.4(8)
Rh2-Fe21-C22	55.2(2)	Rh2-Fe21-Fe22	83.9(1)	Rh2-C24-Fe21	80.2(3)
Rh2-Fe21-C23	122.3(3)	Fe22-Fe21-C22	48.9(2)	Fe21-C24-C24	155.5(7)
C22-Fe21-C23	93.9(4)	Fe22-Fe21-C23	46.2(3)	Fe21-C26-C26	177.0(8)
Fe22-Fe21-C24	135.5(3)	Rh2-Fe21-C24	55.4(2)	Fe22-C28-C28	177.6(9)
C23-Fe21-C24	172.9(4)	C22-Fe21-C24	89.6(3)	Fe21-C22-Fe22	84.3(3)
Fe22-Fe21-C26	117.7(3)	Rh2-Fe21-C26	102.1(3)	Fe21-C22-C21	137.0(6)
C23-Fe21-C26	83.6(4)	C22-Fe21-C26	150.9(3)	Fe21-C23-Fe22	81.5(4)
Rh2-Fe21-C27	142.4(3)	C24-Fe21-C26	90.3(4)	Fe22-C23-C23	143.2(8)
C22-Fe21-C27	105.7(4)	Fe22-Fe21-C27	107.9(4)	Rh2-C24-C24	124.3(6)
C24-Fe21-C27	97.1(4)	C23-Fe21-C27	87.9(4)	Rh2-C25-C25	175.6(8)
Fe21-Fe22-C22	46.8(2)	C26-Fe21-C27	103.2(4)	Fe21-C27-C27	178.9(10)

This work has been supported by the *Deutsche Forschungsgemeinschaft*, the *Fonds der Chemischen Industrie*, and the *Ministerio de Educacion y Ciencia from Spain* (scholarship for F. J. G. A.). We thank *Degussa AG* for generous gifts of chemicals, *HM-Leasing* (Heidelberg) for instrumental support, Mrs. *U. Neumann* and Mrs. *R. Schedl* for elemental analyses, Dr. *G. Lange* and *F. Dadrach* for the mass spectra, and Dr. *W. Buchner* and Mrs. *M. Treiber* for NMR measurements. Invaluable experimental advice by and discussions with Dr. *J. Wolf* and Dr. *A. Höhn* are particularly acknowledged.

Experimental

All operations were carried out under either purified nitrogen or argon. The starting materials **1**–**3**³¹, $C_6H_6Cr(CO)_3$ ³⁹, $C_5H_5Mn(CO)_2(THF)$ ⁴⁰, $Fe_2(CO)_9$ ⁴¹, and $PiPr_3$ ⁴² were prepared by published procedures. Melting points were measured by DTA.

Preparation of $[C_5H_5(PiPr_3)Rh(\mu-CO)(\mu-C=CH_2)Cr(CO)_2C_6H_6]$ (4): A solution of 450 mg (1.27 mmol) of **1** in 10 ml of benzene was treated with 272 mg (1.27 mmol) of $C_6H_6Cr(CO)_3$ and irradiated at room temperature for 4 h with a mercury lamp Philips HPK 125 W. After the solvent and other volatile substances were removed in vacuo, a red oily residue remained which was dissolved in 10 ml of benzene and chromatographed on Al_2O_3 (Woelm, neutral, activity grade III). With benzene as solvent a yellow fraction was eluted which proved by IR and 1H NMR to contain $C_6H_6Cr(CO)_2(PiPr_3)$ (**5**). With THF a red fraction was obtained which was brought to dryness in vacuo. The residue was recrystallized from THF/pentane

(1:3) to give deep red, air-sensitive crystals. Yield 206 mg (30%); m.p. 93°C (dec.). – IR (C_6H_6): $\nu(CO)$ 1850, 1770 cm^{-1} . – 1H NMR (C_6D_6 , 100 MHz): δ = 6.70 (dd), $J(HH)$ = 7.0, $J(RhH)$ = 2.5 Hz [CH_2 , 1 H *cis* to Rh]; 6.50 (ddd), $J(HH)$ = 7.0, $J(RhH)$ = 3.5, $J(PH)$ = 1.2 Hz [CH_2 , 1 H *trans* to Rh]; 5.18 (dd), $J(PH)$ = 1.2, $J(RhH)$ = 0.4 Hz [C_5H_5]; 1.96 (m) [PCH]; 1.26 (dd), $J(PH)$ = 13.2, $J(HH)$ = 7.0 Hz and 1.05 (dd), $J(PH)$ = 12.8, $J(HH)$ = 7.0 Hz [PCHCH₃]. – ^{31}P NMR (C_6D_6 , 90 MHz): δ = 48.32 (d), $J(RhP)$ = 195.0 Hz. – ^{13}C NMR (C_6D_6 , 400 MHz): δ = 285.0 (d), $J(RhC)$ = 36.1 Hz [$C=CH_2$]; 259.0 (s) [$\mu-CO$]; 245.9 (s) [CO]; 120.3 (s) [$C=CH_2$]; 97.7 (s) [C_6H_6]; 91.5 (s) [C_5H_5]; 27.3 (d), $J(PC)$ = 17.6 Hz [PCH]; 20.85 (s) and 20.1 (s) [PCHCH₃].

$C_{24}H_{34}CrO_2PRh$ (540.4) Calcd. C 53.34 H 6.34 Rh 19.04
Found C 53.65 H 6.57 Rh 18.65
 M_r = 514 (osmometry in benzene)

Preparation of $C_6H_6Cr(CO)_2(PiPr_3)$ (5): A solution of 252.5 mg (1.18 mmol) of $C_6H_6Cr(CO)_3$ in 10 ml of benzene was treated with 0.26 ml (1.3 mmol) of $PiPr_3$ and irradiated at room temperature for 6 h with a mercury lamp Philips HPK 125 W. After the solvent and excess phosphane were removed in vacuo the residue was repeatedly washed with pentane and recrystallized from THF/pentane (+25 to –78°C) to give a yellow, moderately air-stable solid. Yield 302 mg (74%); m.p. 92°C (dec.). – IR (THF): $\nu(CO)$ 1881, 1827 cm^{-1} . – 1H NMR (C_6D_6 , 60 MHz): δ = 4.45 (d), $J(PH)$ = 1.8 Hz [C_6H_6]; 1.82 (m) [PCH]; 1.03 (dd), $J(PH)$ = 12.3, $J(HH)$ = 6.5 Hz [PCHCH₃]. – ^{31}P NMR (C_6D_6 , 90 MHz): δ = 92.44 (s).

$C_{17}H_{27}CrO_2P$ (346.4) Calcd. C 58.95 H 7.86
Found C 59.12 H 8.10

Preparation of $[C_5H_5(PiPr_3)Rh(\mu-CO)(\mu-C=CH_2)Mn(CO)_2C_5H_5]$ (6): A solution of 396.5 mg (1.12 mmol) of **1** in 10 ml of benzene was treated with a solution of 317.4 mg (1.30 mmol) of $C_5H_5Mn(CO)_2(THF)$ in 5 ml of tetrahydrofuran and stirred for 2 h at room temperature. After the solvent and other volatile substances were removed in vacuo a red oily residue remained which was dissolved in 5 ml of hexane and chromatographed on Al_2O_3 (Woelm, neutral, activity grade V). With hexane as solvent some as yet unidentified side products were separated. Subsequent elution with benzene gave a red fraction which was brought to dryness in vacuo. The residue was recrystallized from THF/pentane (1:2) to give deep red, moderately air-stable crystals. Yield 130 mg (22%); m.p. 129°C (dec.). – IR (THF): $\nu(CO)$ 1895, 1800 cm^{-1} . – 1H NMR (C_6D_6 , 100 MHz): δ = 6.55 (ddd), $J(HH)$ = 7.3, $J(RhH)$ = 3.2, $J(PH)$ = 1.0 Hz [CH_2 , 1 H *trans* to Rh]; 6.45 (dd), $J(HH)$ = 7.3, $J(RhH)$ = 2.7 Hz [CH_2 , 1 H *cis* to Rh]; 5.06 (d), $J(PH)$ = 1.0 Hz [C_5H_5Rh]; 4.33 (s) [C_5H_5Mn]; 1.95 (m) [PCH]; 1.23 (dd), $J(PH)$ = 13.5, $J(HH)$ = 7.0 Hz and 0.98 (dd), $J(PH)$ = 13.0, $J(HH)$ = 7.0 Hz [PCHCH₃]. – ^{31}P NMR (C_6D_6 , 90 MHz): δ = 48.18 (d), $J(RhP)$ = 189.0 Hz. – ^{13}C NMR (C_6D_6 , 400 MHz): δ = 278.9 (d), $J(RhC)$ = 33.3 Hz [$C=CH_2$]; 250.9 (s) [$\mu-CO$]; 234.9 (s) [CO]; 121.5 (s) [$C=CH_2$]; 91.05 (s) and 88.1 (s) [both C_5H_5]; 26.92 (d), $J(PC)$ = 20.5 Hz [PCH]; 20.85 (s) and 20.1 (s) [PCHCH₃].

$C_{23}H_{33}MnO_2PRh$ (530.3) Calcd. C 52.09 H 6.27
Found C 52.20 H 6.39
 M_r = 530 (MS)

Preparation of $[C_5H_5(PiPr_3)Rh(\mu-CO)(\mu-CCH_3)Mn(CO)_2C_5H_5]PF_6$ (7): A solution of 200 mg (0.38 mmol) of **6** in 100 ml of ether was treated dropwise with a solution of HBf_4 in ether (ca. 50%) until the formation of a dark blue precipitate was completed. The precipitate was repeatedly washed with ether and dissolved in ca. 10 ml of methanol. After an excess of NH_4PF_6 was added to the methanol solution, the reaction mixture was stirred for 2.5 h at room temperature and then stored for 2 h at –78°C. A dark blue

powder was formed which was separated from the mother liquor, repeatedly washed with small amounts of cold water and acetone, and dried in high vacuo. Yield 174 mg (68%); dec. temp. 153°C. — IR (Nujol): $\nu(\text{CO})$ 1963, 1855; $\nu(\text{PF}_6)$ 840 cm^{-1} . — ^1H NMR (CD_3NO_2 , 60 MHz): $\delta = 5.78$ (dd), $J(\text{PH}) = 1.2$, $J(\text{RhH}) = 0.4$ Hz [$\text{C}_5\text{H}_5\text{Rh}$]; 5.16 (s) [$\text{C}_5\text{H}_5\text{Mn}$]; 4.46 (s, br) [CCH_3]; 2.20 (m) [PCH]; 1.39 (dd), $J(\text{PH}) = 14.4$, $J(\text{HH}) = 6.8$ Hz and 1.27 (dd), $J(\text{PH}) = 14.4$, $J(\text{HH}) = 6.6$ Hz [PCHCH_3]. — ^{31}P NMR (CD_3NO_2 , 90 MHz): $\delta = 50.17$ (d), $J(\text{RhP}) = 171.2$ Hz [PiPr_3]; 145.51 (sept), $J(\text{PF}) = 707.1$ Hz [PF_6]. — ^{13}C NMR (CD_3NO_2 , 400 MHz): $\delta = 452.75$ (m) [$\mu\text{-C}$]; 243.2 (m) [$\mu\text{-CO}$]; 228.6 (s, br) [CO]; 95.9 (s) and 93.1 (s, br) [both C_5H_5]; 29.7 (d), $J(\text{PC}) = 22.8$ Hz [PCH]; 20.3 (s) and 20.15 (s) [PCHCH_3]; signal of CCH_3 carbon not observed.

$\text{C}_{23}\text{H}_{34}\text{F}_6\text{MnO}_2\text{P}_2\text{Rh}$ (676.3) Calcd. C 40.85 H 5.07 Rh 15.22
Found C 41.01 H 5.27 Rh 15.32

Preparation of [$\text{C}_5\text{H}_5(\text{PiPr}_3)\text{Rh}(\mu\text{-CO})(\mu\text{-C}=\text{CH}_2)\text{Fe}(\text{CO})_3$] (**11**) and [$(\mu_3\text{-}\eta^1, \eta^2\text{-C}=\text{CH}_2)(\mu\text{-CO})_2\text{Fe}_2\text{Rh}(\text{CO})_4(\text{PiPr}_3)\text{C}_5\text{H}_5$] (**14**): A solution of 170 mg (0.48 mmol) of **1** in 20 ml of THF was treated with 250 mg (0.69 mmol) of $\text{Fe}_2(\text{CO})_9$ and stirred for 4 h at room temperature. After the solvent was removed in vacuo the oily residue was dissolved in 10 ml of hexane, and the solution was chromatographed on Al_2O_3 (Woelm, neutral, activity grade V). With hexane as solvent a first fraction was eluted which contained small amounts of $\text{C}_5\text{H}_5\text{Rh}(\text{CO})(\text{PiPr}_3)^{43}$ besides some other unidentified side products. Further elution with hexane/benzene (12:1) first gave a deep red and subsequently a green fraction both of which were brought to dryness in vacuo. The dark red residue was recrystallized from THF/pentane (1:2) to give deep red, moderately air-stable crystals of **11**. The dark green residue was recrystallized from pentane (+25 to -78°C) to give green, fairly air-stable crystals of **14**.

11: Yield 95 mg (38%); m.p. 108°C (dec.). — IR (THF): $\nu(\text{CO})$ 2015, 1945, 1795 cm^{-1} . — ^1H NMR (C_6D_6 , 100 MHz): $\delta = 6.66$ (ddd), $J(\text{HH}) = 8.3$, $J(\text{RhH}) = 2.7$, $J(\text{PH}) = 2.3$ Hz [CH_2 , 1H *trans* to Rh]; 6.34 (ddd), $J(\text{HH}) = 8.3$, $J(\text{RhH}) = 2.5$, $J(\text{PH}) = 0.8$ Hz [CH_2 , 1H *cis* to Rh]; 5.10 (dd), $J(\text{PH}) = 1.2$, $J(\text{RhH}) = 0.6$ Hz [C_5H_5]; 2.22 (m) [PCH]; 0.96 (dd), $J(\text{PH}) = 14.2$, $J(\text{HH}) = 7.0$ Hz and 0.80 (dd), $J(\text{PH}) = 13.6$, $J(\text{HH}) = 7.0$ Hz [PCHCH_3]. — ^{31}P NMR (C_6D_6 , 90 MHz): $\delta = 50.28$ (d), $J(\text{RhP}) = 172.7$ Hz. — ^{13}C NMR (C_6D_6 , 400 MHz): $\delta = 250.6$ (d), $J(\text{RhC}) = 33.0$ Hz [$\text{C}=\text{CH}_2$]; 250.5 (d), $J(\text{RhC}) = 36.8$ Hz [$\mu\text{-CO}$]; 221.9 (s) [CO]; 124.7 (s) [$\text{C}=\text{CH}_2$]; 89.6 (s) [C_5H_5]; 23.6 (d), $J(\text{PC}) = 22.2$ Hz [PCH]; 20.0 (s) and 19.9 (s) [PCHCH_3].

$\text{C}_{20}\text{H}_{28}\text{FeO}_4\text{PRh}$ (522.2) Calcd. C 46.00 H 5.40
Found C 46.24 H 5.65
 $M_r = 522$ (MS)

14: Yield 15 mg (5%); m.p. 157°C (dec.). — IR (THF): $\nu(\text{CO})$ 2015, 1980 (sh), 1970, 1943, 1850, 1820 cm^{-1} . — ^1H NMR (C_6D_6 , 400 MHz): $\delta = 5.13$ (m) [$=\text{CH}_2$]; 4.03 (s) [C_5H_5]; 2.06 (m) [PCH]; 1.02 (dd), $J(\text{PH}) = 14.0$, $J(\text{HH}) = 7.0$ Hz and 1.01 (dd), $J(\text{PH}) = 14.0$, $J(\text{HH}) = 7.0$ Hz [PCHCH_3].

$\text{C}_{22}\text{H}_{28}\text{Fe}_2\text{O}_6\text{PRh}$ (634.0) Calcd. C 41.68 H 4.45
Found C 41.39 H 4.27
 $M_r = 606$ (osmometry in benzene)

Preparation of [$\text{C}_5\text{H}_5(\text{PiPr}_3)\text{Rh}(\mu\text{-CO})(\mu\text{-C}=\text{CHMe})\text{Fe}(\text{CO})_3$] (**12**) and [$(\mu_3\text{-}\eta^1, \eta^2\text{-C}=\text{CHMe})(\mu\text{-CO})_2\text{Fe}_2\text{Rh}(\text{CO})_4(\text{PiPr}_3)\text{C}_5\text{H}_5$] (**15**): As described for **11/14** starting with 200 mg (0.54 mmol) of **2** and 250 mg (0.69 mmol) of $\text{Fe}_2(\text{CO})_9$. Whereas **12** was obtained after recrystallization from THF/pentane (1:2) as deep red, moderately air-stable crystals, the green trinuclear complex **15** could not be isolated in analytically pure state.

12: Yield 231 mg (80%); m.p. 101°C (dec.). — IR (THF): $\nu(\text{CO})$ 2015, 1940, 1795 cm^{-1} . — ^1H NMR (C_6D_6 , 100 MHz): $\delta = 6.34$ (dd), $J(\text{HH}) = 6.5$, $J(\text{RhH}) = 2.2$, $J(\text{PH}) = 0.9$ Hz [$\text{C}=\text{CHMe}$]; 5.12 (dd), $J(\text{PH}) = 1.2$, $J(\text{RhH}) = 0.5$ Hz [C_5H_5]; 2.24 (dd), $J(\text{HH}) = 6.5$, $J(\text{PH}) = 0.6$ Hz [$\text{C}=\text{CHMe}$]; 2.20 (m) [PCH]; 0.95 (dd), $J(\text{PH}) = 13.6$, $J(\text{HH}) = 7.1$ Hz and 0.85 (dd), $J(\text{PH}) = 13.6$, $J(\text{HH}) = 7.1$ Hz [PCHCH_3]. — ^{31}P NMR (C_6D_6 , 90 MHz): $\delta = 50.45$ (d), $J(\text{RhP}) = 172.7$ Hz. — ^{13}C NMR (C_6D_6 , 400 MHz): $\delta = 248.4$ (d), $J(\text{RhC}) = 33.3$ Hz [$\text{C}=\text{CHMe}$]; 248.3 (d), $J(\text{RhC}) = 30.6$ Hz [$\mu\text{-CO}$]; 222.5 (s) [CO]; 130.5 (s) [$\text{C}=\text{CHMe}$]; 89.6 (s) [C_5H_5]; 23.7 (d), $J(\text{PC}) = 22.2$ Hz [PCH]; 22.4 (s) [$\text{C}=\text{CHCH}_3$]; 20.1 (s) and 19.85 (s) [PCHCH_3].

$\text{C}_{21}\text{H}_{30}\text{FeO}_4\text{PRh}$ (536.2) Calcd. C 47.04 H 5.64
Found C 47.50 H 5.97 $M_r = 536$ (MS)

15: IR (THF): $\nu(\text{CO})$ 2010, 1980 (sh), 1960, 1940, 1840, 1826 cm^{-1} . — ^1H NMR (C_6D_6 , 100 MHz): $\delta = 4.23$ (s) [C_5H_5]; 1.96 (d), $J(\text{HH}) = 6.0$ Hz [$\text{C}=\text{CHMe}$]; 1.93 (m) [PCH]; 0.80 (dd), $J(\text{PH}) = 14.0$, $J(\text{HH}) = 7.0$ Hz and 0.78 (dd), $J(\text{PH}) = 14.0$, $J(\text{HH}) = 7.0$ Hz [PCHCH_3]; signal of $\text{C}=\text{CHMe}$ proton not exactly located.

Preparation of [$\text{C}_5\text{H}_5(\text{PiPr}_3)\text{Rh}(\mu\text{-CO})(\mu\text{-C}=\text{CHPh})\text{Fe}(\text{CO})_3$] (**13**) and [$(\mu_3\text{-}\eta^1, \eta^2\text{-C}=\text{CHPh})(\mu\text{-CO})_2\text{Fe}_2\text{Rh}(\text{CO})_4(\text{PiPr}_3)\text{C}_5\text{H}_5$] (**16**): As described for **11/14** starting with 300 mg (0.69 mmol) of **3** and 300 mg (0.82 mmol) of $\text{Fe}_2(\text{CO})_9$; reaction time 2 h. The workup procedure was modified insofar as during the chromatography with hexane as solvent two fractions, the first containing some side products and the second containing the green trinuclear complex **16**, were eluted. As the yield of **16** was very low, the compound could be characterized only by IR and ^1H -NMR spectroscopy. The main product **13** was eluted with hexane/benzene (10:1). After removing the solvent the residue was recrystallized from THF/pentane (1:2) to give deep red, moderately air-stable crystals.

13: Yield 280 mg (77%); m.p. 106°C (dec.). — IR (THF): $\nu(\text{CO})$ 2015, 1940, 1795 cm^{-1} . — ^1H NMR (C_6D_6 , 100 MHz): $\delta = 7.76$ (dd), $J(\text{RhH}) = 2.8$, $J(\text{PH}) = 0.8$ Hz [$\text{C}=\text{CHPh}$]; 7.30 (m) [C_6H_5]; 5.11 (dd), $J(\text{PH}) = 1.3$, $J(\text{RhH}) = 0.5$ Hz [C_5H_5]; 2.10 (m) [PCH]; 0.87 (dd), $J(\text{PH}) = 13.6$, $J(\text{HH}) = 7.2$ Hz and 0.85 (dd), $J(\text{PH}) = 13.8$, $J(\text{HH}) = 7.2$ Hz [PCHCH_3]. — ^{31}P NMR (C_6D_6 , 90 MHz): $\delta = 48.93$ (d), $J(\text{RhP}) = 169.7$ Hz. — ^{13}C NMR (C_6D_6 , 400 MHz): $\delta = 238.8$ (d), $J(\text{RhC}) = 32.8$ Hz [$\text{C}=\text{CHPh}$]; 238.65 (d), $J(\text{RhC}) = 33.3$ Hz [$\mu\text{-CO}$]; 224.4 (m) [CO]; 140.0 (s) [$\text{C}=\text{CHPh}$]; 128.4 (s), 128.3 (s), 125.4 (s), 125.0 (s) [C_6H_5]; 90.3 (s) [C_5H_5]; 23.8 (d), $J(\text{PC}) = 24.7$ Hz [PCH]; 20.3 (s) and 20.0 (s) [PCHCH_3].

$\text{C}_{26}\text{H}_{32}\text{FeO}_4\text{PRh}$ (598.3) Calcd. C 52.20 H 5.39 Rh 17.20
Found C 52.56 H 5.55 Rh 17.08
 $M_r = 598$ (MS)

16: IR (THF): $\nu(\text{CO})$ 2015, 1970, 1945, 1846, 1825 cm^{-1} . — ^1H NMR (C_6D_6 , 100 MHz): $\delta = 7.20$ (m) [C_6H_5]; 4.30 (s) [C_5H_5]; 1.90 (m) [PCH]; 0.96 (dd), $J(\text{PH}) = 14.0$, $J(\text{HH}) = 7.0$ Hz and 0.94 (dd), $J(\text{PH}) = 14.0$, $J(\text{HH}) = 7.0$ Hz [PCHCH_3]; signal of $\text{C}=\text{CHPh}$ proton not exactly located.

Preparation of the complexes [$\text{C}_5\text{H}_5(\text{PiPr}_3)\text{Rh}(\mu\text{-CO})(\mu\text{-C}=\text{CCH}_2\text{R})\text{Fe}(\text{CO})_3$]/ BF_4 (**17–19**): A solution of 0.30 mmol of **11**, **12**, or **13** in 100 ml of ether was treated dropwise with a solution of HBF_4 in ether (ca. 50%) until the formation of a dark brown precipitate was complete. The precipitate was filtered off, repeatedly washed with ether, and dried in vacuo. Yield 95–98%. Complex **18** contained some impurities which could not be removed by recrystallization and thus no correct analytical values were obtained.

17: IR (Nujol): $\nu(\text{CO})$ 2070, 1990, 1850; $\nu(\text{BF}_4)$ 1050 cm^{-1} . — ^1H NMR (CD_3NO_2 , 60 MHz): $\delta = 6.08$ (dd), $J(\text{PH}) = 1.2$, $J(\text{RhH}) = 0.4$ Hz [C_5H_5]; 3.82 (m) [$\mu\text{-CCH}_3$]; 2.22 (m) [PCH]; 1.38 (dd), $J(\text{PH}) = 14.6$; $J(\text{HH}) = 6.8$ Hz and 1.28 (dd), $J(\text{PH}) = 15.3$, $J(\text{HH}) = 6.8$ Hz [PCHCH₃]. — ^{31}P NMR (CD_3NO_2 , 90 MHz): $\delta = 49.10$ (d), $J(\text{RhP}) = 157.8$ Hz.

$\text{C}_{20}\text{H}_{29}\text{BF}_4\text{FeO}_4\text{PRh}$ (610.0) Calcd. C 39.38 H 4.81
Found C 39.12 H 4.45

18: IR (Nujol): $\nu(\text{CO})$ 2060 cm^{-1} , 1990, 1835; $\nu(\text{BF}_4)$ 1050. — ^1H NMR (CD_3NO_2 , 60 MHz): $\delta = 6.03$ (dd), $J(\text{PH}) = 1.0$, $J(\text{RhH}) = 0.4$ Hz [C_5H_5]; 3.75 (m) [$\mu\text{-CCH}_2\text{CH}_3$]; 2.23 (m) [PCH]; 1.80 (t), $J(\text{HH}) = 7.2$ Hz [$\mu\text{-CCH}_2\text{CH}_3$]; 1.37 (dd), $J(\text{PH}) = 14.8$, $J(\text{HH}) = 6.8$ Hz and 1.28 (dd), $J(\text{PH}) = 15.0$, $J(\text{HH}) = 6.8$ Hz [PCHCH₃]. — ^{31}P NMR (CD_3NO_2 , 90 MHz): $\delta = 48.90$ (d), $J(\text{RhP}) = 159.3$ Hz.

19: IR (Nujol): $\nu(\text{CO})$ 2060, 1990, 1830, $\nu(\text{BF}_4)$ 1055 cm^{-1} . — ^1H NMR (CD_3NO_2 , 60 MHz): $\delta = 7.53$ (m) [C_6H_5]; 6.00 (d), $J(\text{PH}) = 0.8$ Hz [C_5H_5]; 4.90 (m) [$\mu\text{-CCH}_2\text{Ph}$]; 2.30 (m) [PCH]; 1.38 (dd), $J(\text{PH}) = 15.0$, $J(\text{HH}) = 7.0$ Hz and 1.32 (dd), $J(\text{PH}) = 15.3$, $J(\text{HH}) = 7.0$ Hz [PCHCH₃]. — ^{31}P NMR (CD_3NO_2 , 90 MHz): $\delta = 49.02$ (d), $J(\text{RhP}) = 157.8$ Hz. — ^{13}C NMR (CD_3NO_2 , 268 K, 400 MHz): $\delta = 416.5$ (m) [$\mu\text{-C}$]; 96.0 (s) [C_5H_5]; 85.3 (s) [CH_2Ph]; 26.9 (d), $J(\text{PC}) = 25.0$ Hz [PCH]; 20.4 (s) and 20.2 (s) [PCHCH₃]; signals of CO and phenyl carbons not exactly located due to raising decomposition during the measurement.

$\text{C}_{26}\text{H}_{33}\text{BF}_4\text{FeO}_4\text{PRh}$ (686.1) Calcd. C 45.51 H 4.85
Found C 45.37 H 4.65

Preparation of [$\text{C}_5\text{H}_5(\text{PiPr}_3)\text{Rh}(\mu\text{-C}=\text{CHMe})(\mu\text{-CO})\text{Fe}(\text{CO})_2\text{PMe}_3$] (20): A solution of 200 mg (0.34 mmol) of **12** in 30 ml of benzene was treated with 0.06 ml (0.59 mmol) of PMe_3 and stirred for 12 h at room temperature. The solvent and excess phosphane were removed in vacuo, and the residue was recrystallized from THF/pentane (1:2) to give deep blue, moderately air-stable crystals. Yield 169 mg (85%); m.p. 129°C (dec.). — IR (THF): $\nu(\text{CO})$ 1938, 1877, 1760 cm^{-1} . — ^1H NMR (C_6D_6 , 60 MHz): $\delta = 6.75$ (m)

Table 7. Crystallographic data for **6**, **11**, and **14**

crystallographic section			
compound	6	11	14
empirical formula	$\text{C}_{22}\text{H}_{22}\text{MnO}_4\text{PRh}$	$\text{C}_{20}\text{H}_{20}\text{O}_4\text{PFeRh}$	$\text{C}_{22}\text{H}_{22}\text{O}_4\text{PRhFe}_2$
a [pm]	1604.4(6)	1264.2(4)	1405.7(4)
b [pm]	843.3(3)	1817.8(8)	1726.1(4)
c [pm]	1677.0(7)	959.5(2)	1104.6(3)
α [deg]	90	90	87.81(2)
β [deg]	101.94(3)	95.94(2)	92.49(2)
γ [deg]	90	90	106.71(2)
V [pm ³ ×10 ⁻³]	2220(2)	2193(1)	2563.5(7)
Z	4	4	4
d(calcd) [gcm ⁻³]	1.587	1.581	1.723
crystal system	monoclinic	monoclinic	triclinic
space group	$\text{P}2_1/\text{c}$	$\text{P}2_1/\text{n}$	$\text{P}1$
data collection			
diffractometer	Syntax P2,	Syntax P3	Syntax P3
radiation	MoK α		
monochromator	graphite		
crystal size [mm]	0.3 × 0.4 × 0.4	0.5 × 0.8 × 0.2	0.35 × 0.5 × 0.25
data collection mode	ω -scan		
theta range [deg]	2.5 – 25.0	1.75 – 27.5	1.75 – 27.5
recip. latt. segment	h = 0 – 19 k = 0 – 10 l = 20 – 19	h = 0 – 16 k = 0 – 23 l = 12 – 12	h = 0 – 18 k = 22 – 21 l = 14 – 14
no. refl. measd.	3899	4939	8708
no. unique refl.	3531	4669	8708
no. refl. $F_0 > 3\sigma(F)$	3531	4465	7902
lin. abs. coeff. [cm ⁻¹]	14.10	14.81	18.90
abs. correction	ψ -scan		
structural analysis and refinement			
solution by	Patterson synthesis	direct methods	Patterson synthesis
method of refinement	anisotropic block diagonal least squares;		
	hydrogen positions were calculated and considered isotropically		
parameter/ F_0 ratio	0.074	0.055	0.070
R, R _w	0.026, 0.029	0.032, 0.033	0.054, 0.054
program used	SHELXTL		

[$\text{C}=\text{CHMe}$]; 5.40 (dd), $J(\text{PH}) = 1.5$, $J(\text{RhH}) = 0.6$ Hz [C_5H_5]; 2.50 (d), $J(\text{HH}) = 6.5$ Hz [$\text{C}=\text{CHMe}$]; 2.26 (m) [PCH]; 1.40 (d), $J(\text{PH}) = 9.3$ Hz [PMe_3]; 1.06 (dd), $J(\text{PH}) = 13.5$, $J(\text{HH}) = 7.3$ Hz and 1.04 (dd), $J(\text{PH}) = 13.8$, $J(\text{HH}) = 7.3$ Hz [PCHCH₃].

$\text{C}_{23}\text{H}_{39}\text{FeO}_3\text{P}_2\text{Rh}$ (584.3) Calcd. C 47.45 H 6.73

Found C 47.57 H 6.84 $M_r = 584$ (MS)

X-Ray Structural Analyses of 6, 11, and 14: Special X-ray operations and results are listed in Table 7 and special bond lengths and angles in Tables 1–6. Further details of the crystal structure investigations including tables with the final positional parameters are available on request from the Fachinformationszentrum Energie Physik Mathematik GmbH, D-7514 Eggenstein-Leopoldshafen 2, on quoting the depository number CSD 51388, the names of the authors, and the journal citation.

CAS Registry Numbers

1: 88000-17-3 / 2: 112421-62-2 / 3: 85452-98-8 / 4: 100219-04-3 / 5: 114674-81-6 / 6: 100238-03-7 / 7: 114674-83-8 / 11: 100219-05-4 / 12: 114674-84-9 / 13: 107860-07-1 / 14: 114674-85-0 / 15: 114674-86-1 / 16: 114674-87-2 / 17: 114674-89-4 / 18: 114674-91-8 / 19: 114674-93-0 / 20: 114674-94-1 / $\text{C}_6\text{H}_5\text{Cr}(\text{CO})_3$: 12082-08-5 / $\text{C}_5\text{H}_5\text{Mn}(\text{CO})_2(\text{THF})$: 12093-26-4 / Rh: 7440-16-6 / Mn: 7439-96-5 / Fe: 7439-89-6 / Cr: 7440-47-3

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