Organometallic Chemistry

Synthesis of neutral tri- and tetranuclear organometallic clusters of group VIII transition metals

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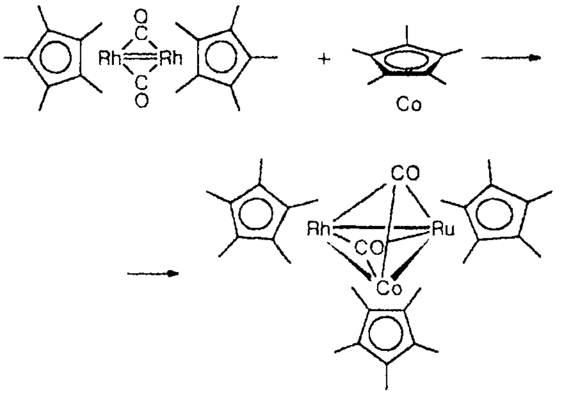
A number of earlier unknown tri- and tetranuclear organometallic clusters of group VIII transition metals was synthesized by the addition of coordinatively unsaturated species to a single metal—metal bond. A number of novel heteronuclear clusters, $CpCp'_2RhM_2(\mu\text{-}CO)_3(\mu_3\text{-}CO)$, ($Cp' = Cp, Cp^*$; $M_2 = Ru_2, Fe_2, RuFe$); $Cp_2Cp^*_2Rh_2M_2(\mu_3\text{-}CO)_3$ ($M = Ru, Fe$); $Cp_3Cp^*Rh_3M(\mu_3\text{-}CO)_2(\mu_3\text{-}$[illegible]$)$ ($M = Ru, Fe$); $Cp_2Cp^*_2Rh_2Co_2(\mu_3\text{-}CO)_2$, *etc.*, was obtained.

Key words: clusters, binuclear complexes, addition, coordinatively unsaturated species.

Literature data on the synthesis of neutral tri- and tetranuclear clusters of transition metals have been summarized in detailed reviews.[1—3] Most of the described compounds are carbonyl clusters, their *n*-substituted analogs, and various derivatives of these clusters. We have been mostly interested in clusters with organic ligands of the cyclopentadienyl type at each metal atom. The metallacycles in such clusters should have increased electron density and could be used in reactions with cationic coordinatively unsaturated species to obtain cationic clusters of higher nuclearity. However, synthetic methods for the compounds we needed have not been adequately developed. The clusters obtained in Refs. 4—6 by the addition of coordinatively unsaturated species to binuclear organometallic complexes with multiple (usually double) metal—metal bonds had permethylated cyclopentadienyl ligands only.



Thus, the potential of the method appeared to be limited. We used another approach based on the addition of coordinatively unsaturated species to binuclear complexes with a single metal—metal bond. Such complexes, both with methylated and unsubstituted cyclopentadienyl rings ($Cp = \eta^5\text{-}C_5H_5$ and $Cp^* = \eta^5\text{-}C_5Me_5$),

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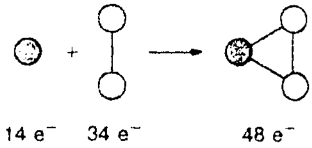
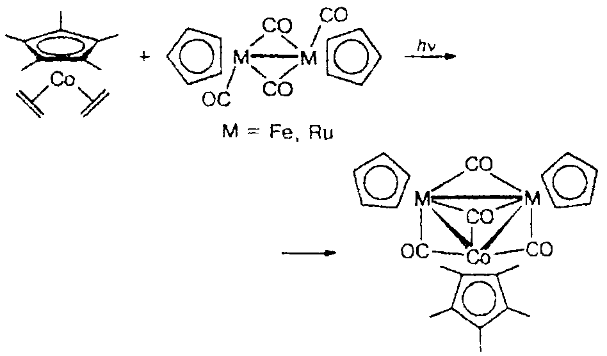
are readily available. This approach is based on the following electronic scheme:



In accordance with this scheme, three-membered metallacycles with a stable 48-electron shell can be obtained by the addition of 14-electron coordinatively unsaturated species to binuclear 34-electron organometallic complexes. This type of reaction was first described in 1983.[7] In this case photoirradiation of the compound $CoCp^*(C_2H_4)_2$ in the presence of complexes of Fe and Ru was used to generate a coordinatively unsaturated species [CoCp*]. The following trinuclear clusters were obtained as a result:



It should be noted that the reaction was only described in a short communication. Later,[8] an analogous approach was used to synthesize a wide range of trinuclear compounds.

$$M_2Cp_2(CO)_n + RhCp(C_2H_4)_2 \xrightarrow[\text{or } \Delta]{h\nu} M_2RhCp_3(CO)_n$$

M = Mo, n = 6
M = Fe, n = 4
M = Ni, n = 2

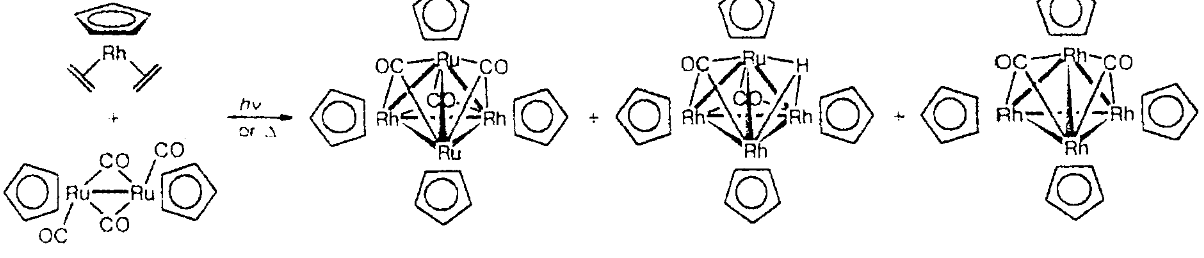
Results and Discussion

Our attempt to obtain a three-membered $RhRu_2Cp_3(\mu\text{-}CO)_3(\mu_3\text{-}CO)$ metallacycle by the addition of a coordinatively unsaturated species [RhCp] to the ordinary bond of a binuclear complex $[RuCp(CO)_2]_2$ under conditions analogous to those described in Ref. 8 (heating in toluene or UV-irradiation) failed. A mixture of tetrahedral clusters **1**—**3** (Scheme 1) was isolated instead in 6, 11, and 11% yields, respectively. Column chromatography on Al_2O_3 was used to separate the mixture.

Cluster **3** has been previously described in the literature[9] and identified by means of spectral data, which were identical with those previously published.[9] The structures of clusters **1** and **2** were confirmed by elemental analyses, and by IR, NMR, and mass spectra. The two absorption ν(CO) bands at 1704 (sh) and 1672 cm^{-1} (vs) observed in the IR spectrum of cluster **1** can be assigned to the vibrations of the μ_3-CO group. Three signals in the region of the cyclopentadienyl protons at δ 5.38, 5.23, and 5.03 are observed in the ^1H NMR spectrum; the ratio of their integrated intensities is 1 : 2 : 1. The first and the last signals correspond to cyclopentadienyl rings bonded to ruthenium atoms in different ligand environments. The signal at δ 5.23 is assigned to two cyclopentadienyl rings bonded to rhodium atoms. A molecular ion peak with m/z = 752 $[M]^+$ is observed in the mass-spectrum.

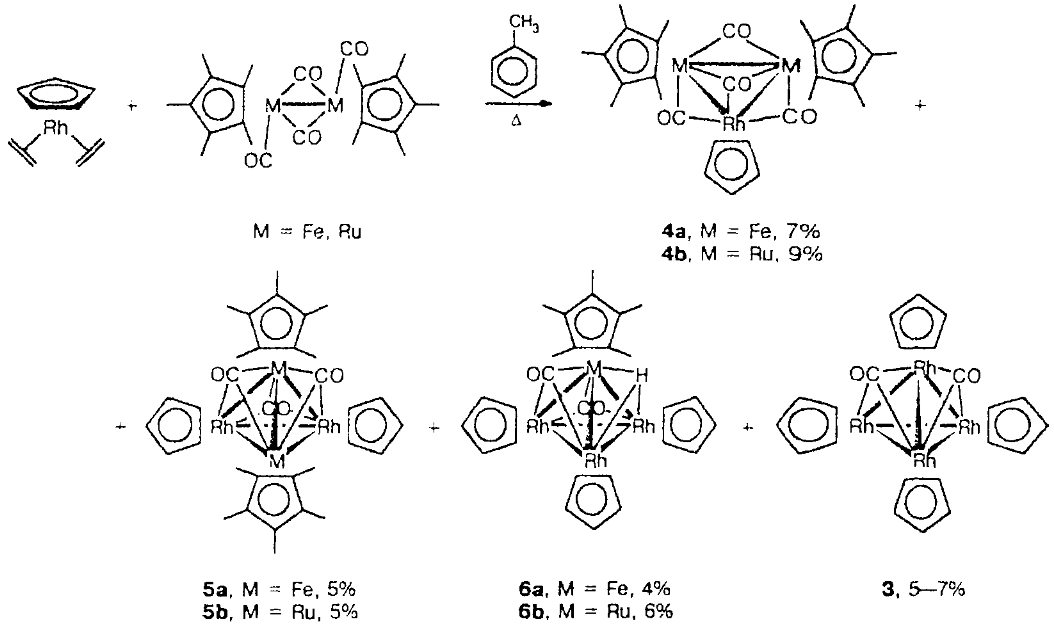
The ν(CO) bands at 1730 (m), 1688 (sh), and 1670 cm^{-1} (vs) observed in the IR spectrum of cluster **2** can be assigned to the vibrations of the μ_3-CO group. The ^1H NMR spectrum contains signals in the region of cyclopentadienyl rings and hydride hydrogen atoms. The signal of the protons of the Cp group at two Rh atoms in an identical environment detected at δ 5.37 substantially differs in spectral position from those of the protons of the Cp groups at the Rh atom (at δ 5.30) and at the ruthenium atom (at δ 5.20). The signals of the protons of the Cp groups bonded to Rh can be identified by the line broadening due to the splitting at the ^{103}Rh atoms ($^2J_{Rh-H}$ ~0.6 Hz for the rhodium atoms of both types). The intensities of these signals are in a 2 : 1 : 1 ratio. The signal of the hydride hydrogen atom appears

Scheme 1



1, 6% **2**, 11% **3**, 11%

Scheme 2



M = Fe, Ru

4a, M = Fe, 7%
4b, M = Ru, 9%

5a, M = Fe, 5%
5b, M = Ru, 5%

6a, M = Fe, 4%
6b, M = Ru, 6%

3, 5–7%

as a high-field triplet at δ −10.58 due to interaction with two rhodium atoms ($^1J_{Rh-H}$ = 65 Hz). A molecular ion peak with *m/z* = 727 $[M]^+$ is observed in the mass-spectrum.

We succeeded in isolating a number of tetranuclear clusters, **3**, **5a,b**, and **6a,b** (Scheme 2) along with trinuclear clusters $RhM_2CpCp_2^*(\mu_2\text{-}CO)_3(\mu_3\text{-}CO)$ (**4a,b**) in the reaction with more sterically hindered binuclear complexes with pentamethylcyclopentadienyl ligands $[MCp^*(CO)_2]_2$ (M = Fe, Ru) (boiling in toluene or xylene). The products were separated by column chromatography on Al_2O_3.

The structures of complexes **4**, **5**, and **6** were confirmed by the elemental analyses and the IR, ^{1}H NMR, and mass-spectral data. Three ν(CO) absorption bands are observed in the IR spectra for each of the clusters **4a,b** in the region of metallocarbonyl ligands, at 1810 (vs), 1744 (s), and 1652 cm^{-1} (s) (**4a**) and at 1810 (vs), 1746 (s), and 1648 cm^{-1} (s) (**4b**). They can be assigned to the absorption bands of bridging μ_2- (~1810 and 1750 cm^{-1}) and μ_3- (~1650 cm^{-1}) carbonyl ligands. One signal of methyl protons of the Cp* group bonded to Fe or Ru atoms (at δ 1.62 (**4a**) and 1.75 (**4b**)) and the signal of protons of Cp rings at a rhodium atom (at δ 5.33 (**4a**) and 5.26 (**4b**)) broadened due to the proton splitting at the ^{103}Rh atoms ($^2J_{Rh-H}$ ~0.7 Hz for **4a** and **4b**) are observed in the ^{1}H NMR spectra of **4a,b**. The ratio of the integrated intensities of the signals of the protons of the two pentamethylcyclopentadienyl rings and one unsubstituted Cp ring for **4a,b** is 6 : 1. Peaks of molecular ions with *m/z* = 662 $[M]^+$ (**4a**) and 752 $[M]^+$ (**4b**) are present in the mass-spectra.

Bands corresponding to ν(CO) of the μ_3-CO groups are observed in the IR spectra of clusters **5a,b** at 1674 (sh) and 1640 cm^{-1} (vs) (**5a**) and at 1670 (sh) and 1640 cm^{-1} (vs) (**5b**). One signal from the Cp rings bonded to Rh atoms (at δ 5.18 (**5a**) and 5.16 (**5b**)) and two signals from Cp* rings coordinated to Fe or Ru atoms (at δ 1.77 and 1.72 (**5a**), and at δ 1.79 and 1.68 (**5b**), in the ratio 1 : 1) are observed in the ^{1}H NMR spectra of **5a,b**.

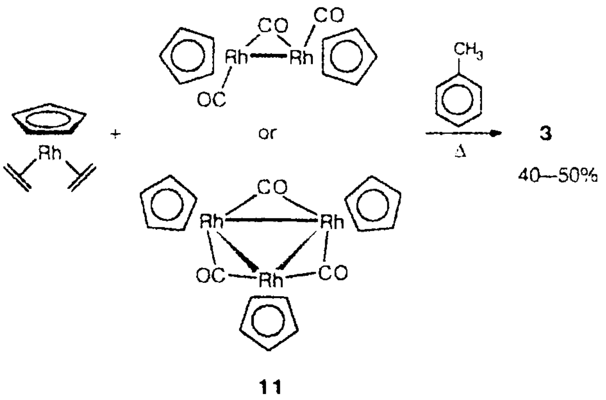
On the basis of the ^{1}H NMR spectral data, it is impossible to decide to which of the atoms, Ru or Fe, the Cp*-rings are bonded. Intense peaks of molecular ions with *m/z* = 802 $[M]^+$ (**5a**) and 893 $[M]^+$ (**5b**) are observed in the mass-spectra.

Absorption bands corresponding to ν(CO) of the μ_3-CO groups are detected in the IR spectra of complexes **6a,b** at 1708 (m), 1666 (s), and 1644 cm^{-1} (vs) (**6a**) and at 1706 (m), 1668 (s), and 1646 cm^{-1} (vs) (**6b**). Two signals are observed in the ^{1}H NMR spectra of **6a** and **6b** in the region characteristic of the Cp rings. One of them (at δ 5.27 (**6a**) or 5.31 (**6b**)) is assigned to Cp rings bonded to two Rh atoms in an identical ligand environment, and the other (at δ 5.03 (**6a**) or 5.14 (**6b**)) corresponds to Cp rings bonded to a single Rh atom. The ratio of the intensities of these signals is 2 : 1. Additionally, one signal of the methyl protons of the Cp* rings bonded to an Fe or Ru atom (at δ 1.68 (**6a**) or 1.87 (**6b**)) is observed. The signals of the hydride hydrogen split into triplets at two rhodium atoms (at δ −17.40, $^1J_{Rh-H}$ = 61.5 Hz (**6a**) or at δ −11.99, $^1J_{Rh-H}$ = 66.6 Hz (**6b**)) also appear in the high-field region. Peaks of molecular ions with (*m/z* = 752 $[M]^+$

(**6a**) and 797 $[M]^+$ (**6b**)) are observed in the mass-spectra.

As can be seen from Schemes 1 and 2, we obtained a previously described[9] rhodium cluster **3**. However, the yields of this cluster were low. Since we had used this cluster previously,[10] a new preparative method for the synthesis of this compound based on the addition of the [RhCp] species to bi- and trinuclear rhodium complexes (Scheme 3) was developed.

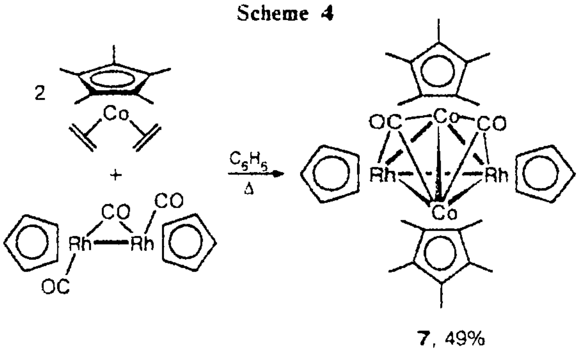
Scheme 3



The tetranuclear rhodium cluster **3** was obtained in 40—50 % yields.[*] This new synthetic route was used to obtain other tetranuclear clusters. Thus, a tetranuclear heterometallic cluster **7** was isolated as the only product in 30—50% yield (Scheme 4) by the reaction of bis-ethylene cobalt complex $CoCp^*(C_2H_4)_2$ with binuclear rhodium complex $Rh_2Cp_2(CO)_3$ in boiling benzene.

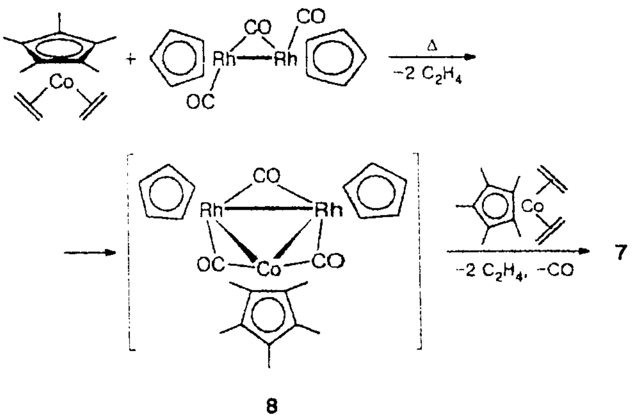
Cluster **7** is a dark-green crystalline substance readily soluble in both nonpolar and polar solvents. Its structure was confirmed by its elemental analysis and IR, ^1H NMR, and mass spectra. The IR spectrum of cluster **7** contains two ν(CO) absorption bands at 1668 (m, sh) and 1640 cm^{-1} (vs) which are characteristic of μ_3-CO groups. A signal from protons of Cp rings at a rhodium atom (at δ 5.25) and one from Me groups at a Cp* ligand at a Co atom (at δ 1.55) are observed in the ^1H NMR spectrum. The ratio of the intensities of the signals is 1 : 3. A molecular ion peak with m/z = 780 $[M]^+$ is observed in the mass spectrum.

Scheme 4



It should be noted that an attempt to obtain trinuclear cluster **8** from equimolar amounts of complexes $CoCp^*(C_2H_4)_2$ and $Rh_2Cp_2(CO)_3$ again resulted in the tetranuclear cluster **7**. It was not possible to detect even traces of compound **8**. We suggest that complex **8**, formed as an intermediate, is more active than $Rh_2Cp_2(CO)_3$ in the reaction with the initial $CoCp^*(C_2H_4)_2$ and further reacts to form cluster **7** and eliminate one CO group (Scheme 5).

Scheme 5



Scheme 5 was indirectly confirmed by the reaction between $CoCp^*(C_2H_4)_2$ and the trinuclear cluster $Rh_3(\eta\text{-}C_5H_4CH_3)_3(\mu\text{-}CO)_3$ (cluster $Rh_3(\eta\text{-}C_5H_4CH_3)_3(\mu\text{-}CO)_3$[*] was used instead of cluster $Rh_3Cp_3(\mu\text{-}CO)_3$ as it is readily soluble in benzene) (Scheme 6).

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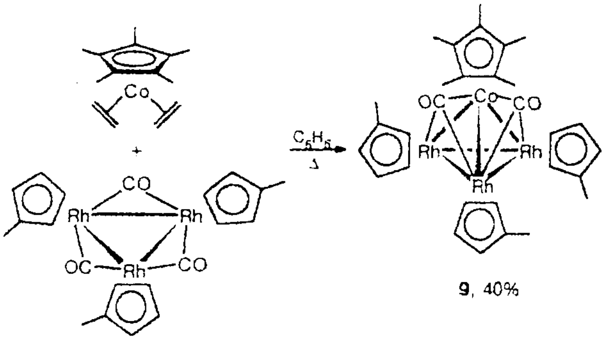
[*] Along with complex **3**, a cationic product, isolated as hexafluorophosphate, is formed in this reaction. On the basis of spectral data, the structure of an octahedron with an interstitial carbon atom, $[Rh_6Cp_6(\mu_6\text{-}C)](PF_6)_2$, was ascribed to it. The IR spectrum (in nitromethane) of this product contains no absorption bands in the carbonyl region. The ^1H NMR spectrum (CD_3NO_2) contains only one signal at δ 5.85 (s, C_5H_5). A molecular ion peak and peaks of its fragments with m/z 1020 $[M]^+$, 840 $[M-CpRh-C]^+$, and 510 $[M]^{2+}$ are present in the mass spectrum. Unfortunately, we failed to grow a crystal appropriate for X-ray analysis.

[*] To obtain the trirhodium cluster $Rh_3Cp_3(\mu\text{-}CO)_3$, the reaction of trimethylamine oxide with mononuclear complex $RhCp(CO)_2$, mentioned in Ref. 9, was used. A previously unknown complex with the μ_3-oxygen ligand, $Rh_3Cp_3(\mu_3\text{-}CO)(\mu_3\text{-}O)$, was isolated as a reaction product along with complexes $Rh_2Cp_2(CO)_3$, $Rh_3Cp_3(\mu\text{-}CO)_3$, and **3** described in Ref. 9. The use of the complex $Rh(\eta^5\text{-}C_5H_4CH_3)(CO)_2$ as a starting compound in this reaction resulted in new complexes, $Rh_2(\eta^5\text{-}C_5H_4CH_3)_2(CO)_3$, $Rh_3(\eta^5\text{-}C_5H_4CH_3)_3(\mu\text{-}CO)_3$, $Rh_4(\eta^5\text{-}C_5H_4CH_3)_4(\mu_3\text{-}CO)_2$, and $Rh_3(\eta^5\text{-}C_5H_4CH_3)_3(\mu_3\text{-}CO)(\mu_3\text{-}O)$ (see Experimental).

Scheme 6



11a

9, 40%

Cluster **9** was isolated as the only reaction product. It is a green substance readily soluble in both polar solvents and solvents of low polarity. The structure of cluster **9** was confirmed by its elemental analysis, and IR, ^{1}H NMR, and mass spectra. The IR spectrum of compound **9** contains ν(CO) absorption bands of μ_3-CO groups at 1660 (m, sh) and 1642 cm^{-1} (vs). Signals of (η-$C_5H_4CH_3$) rings at rhodium atoms (at δ 4.93 (br) and δ 4.75 (br)) and those of methyl groups of η-$C_5H_4CH_3$ (at δ 1.53) and Cp* rings (at δ 1.68) at rhodium and cobalt atoms, respectively, are observed in the ^{1}H NMR spectrum. The ratio of the intensities of the signals is 12 : 9 : 15. A molecular ion peak with (m/z = 796 [M]$^+$) is observed in the mass spectrum.

As can be seen from Schemes 1—6, it was possible to isolate trinuclear clusters only as complex mixtures with other products in the course of the reactions of addition of coordinatively unsaturated species to single metal—metal bonds under rather severe conditions (in a boiling solvent). Therefore we tried to develop a method for synthesizing clusters under milder conditions that would allow us to stop the reaction at the stage of the formation of three-membered cycles. For this purpose, rhodium complexes [Rh(μ-Cl)(C_2H_4)$_2$]$_2$ and Rhacac(C_2H_4)$_2$ (acac is acetylacetonate) capable of replacing the ethylene ligands at ~20 °C were chosen. The reactions of these compounds with binuclear complexes of transition metals were carried out in ether at room temperature. Trinuclear complexes **10**, **12**, **14**, and **15** containing acac and Cl ligands were formed at the first stage. To obtain the required trinuclear clusters, these ligands must be replaced by cyclopentadienyl ligands. For this purpose, the products of the first reaction stage were treated with TlCp without isolation (Scheme 7).

No side products are formed in any of the reactions described.

The advantage of the suggested reaction scheme is that the substituents (Cl and acac) contained in the products formed at the first stage (**10**, **12**, **14**, **15**) slightly decrease the donor properties of these clusters and impede further addition of coordinatively unsaturated species. The products of the first reaction stages shown in Scheme 7 were detected in the IR spectra containing the following ν(CO) absorption bands, cm^{-1}: 1880 (s) and 1812 (vs) (**10**), 1878 (s), 1810 (vs), and 1690 (m) (**12**), 1886 (s), 1828 (vs), and 1696 (s) (**14**), 1880 (s), 1810 (vs), and 1695 (s) (**15**). However, the reactions are never brought to completion, so the absorption bands of the CO groups of the initial binuclear complexes are always present in the IR spectra along with the bands of the products. The addition of TlCp to solutions of these compounds results in a shift of the absorption bands of the CO groups by Δν ~25—50 cm^{-1} to the low-frequency region, which is in agreement with replacement of an acceptor substituent (Cl or acac) by a donor (Cp). Chromatography on Al_2O_3 allows one to separate the reaction products from the initial binuclear complexes.

In this way we obtained a trinuclear cluster **13**, which we previously failed to isolate from the reaction shown in Scheme 1. Additionally, a potentially optically active trinuclear cluster **16**, containing the atoms of three different metals (Fe, Ru, and Rh), was obtained. Cluster **11**, which has been described previously,[9] was synthesized for comparison. The spectral characteristics of isolated cluster **11** are identical with those reported in the literature.[9]

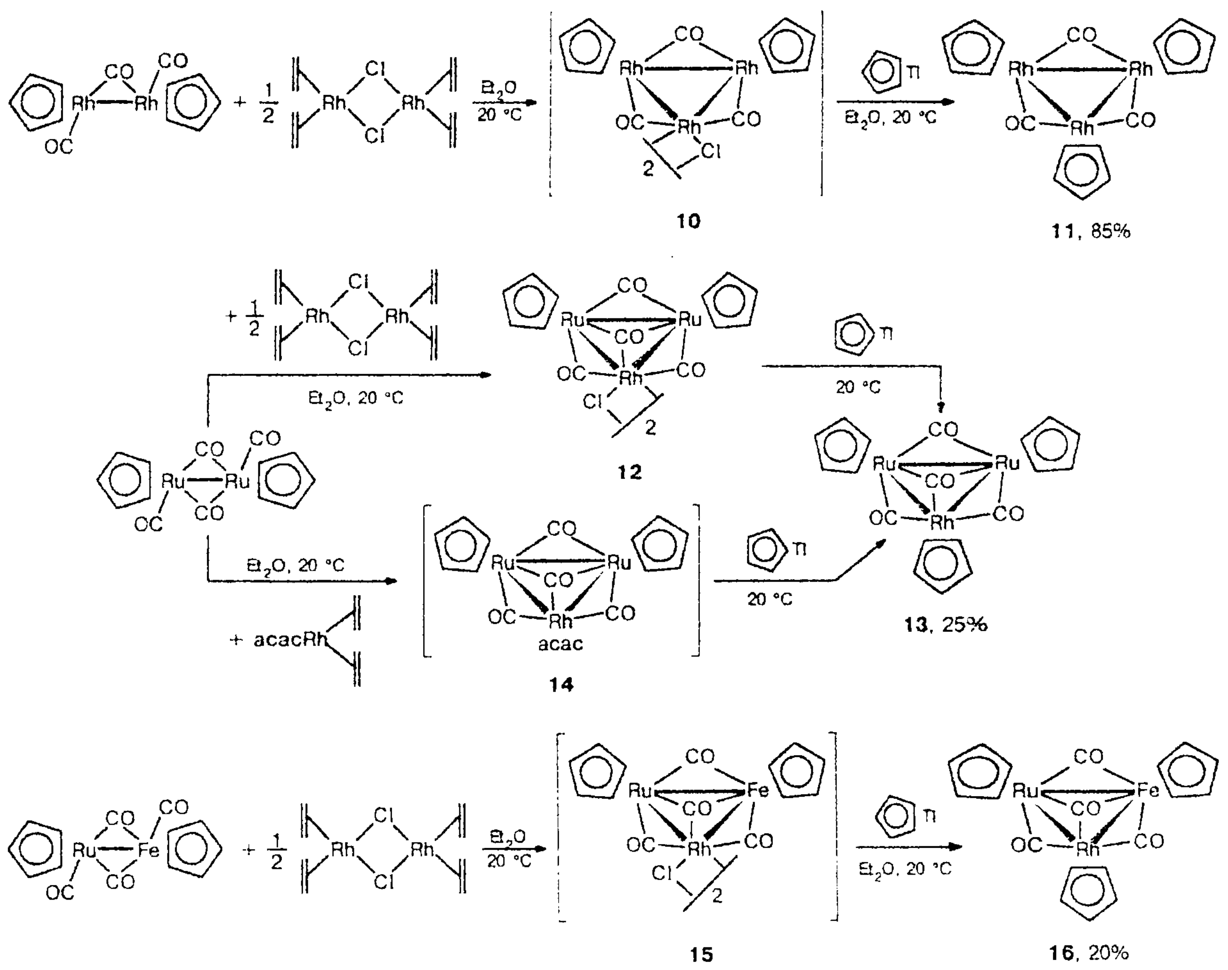
The yield of complex **11** is 85%, whereas compounds **13** and **16** are formed in a much lower yield, which is likely associated with the fact that the reactivity of [MCp(CO)$_2$]$_2$ complexes of metals of the iron subgroup is lower than that of the rhodium complex $Rh_2Cp_2(CO)_3$. The method we have developed is of interest for the synthesis of various heteronuclear three-membered clusters. It is particularly important for obtaining clusters with three different metals which is the case of cluster **16**. The use of other methods for synthesizing this cluster can cause problems.

Clusters **13** and **16** are dark-green substances stable as solids and in solution in the absence of air. They are poorly soluble in benzene, but are readily soluble in CH_2Cl_2 or acetone. The structures of **13** and **16** were confirmed by the elemental analyses, and by IR, ^{1}H NMR, and mass spectra.

The ν(CO) absorption bands at 1836 (vs) and 1774 cm^{-1} (s) and the band at 1670 cm^{-1} (s) in the IR spectrum (CH_2Cl_2) of compound **13** correspond to the μ_2-CO and μ_3-CO groups, respectively. The ^{1}H NMR spectrum contains signals in the region of protons of Cp groups (at δ 5.52 and 5.38, the ratio of the intensities is 1 : 2) corresponding to Cp groups bonded to Rh and Ru atoms. The signal of the protons of the Cp group at the rhodium atom is split at the ^{103}Rh atoms ($^2J_{Rh-H}$ = 0.87 Hz). A molecular ion peak with m/z = 612 [M]$^+$ is observed in the mass spectrum.

The IR spectrum of compound **16** contains ν(CO) absorption bands at 1838 (vs) and 1778 cm^{-1} (s) and a band at 1670 cm^{-1} (s) corresponding to the μ_2-CO and μ_3-CO groups, respectively. Proton signals at δ 5.51

Scheme 7



(br), 5.40, and 4.77, corresponding to Cp groups bonded to Rh, Ru, and Fe atoms, respectively, are observed in the ^1H NMR spectrum. The ratio of the intensities of the signals is 1 : 1 : 1. The signal of the Cp protons at the rhodium atom is broadened due to the splitting at the ^{103}Rh atom ($^2J_{Rh-H}$ = ~0.8 Hz). A molecular ion peak with m/z = 567 $[M]^+$ is observed in the mass spectrum.

Thus, several new methods for the synthesis of neutral tri- and tetranuclear clusters of group VIII transition metals are suggested in the present work. The methods are based on the addition of coordinatively unsaturated species to a single metal—metal bond. As a result, a number of previously inaccessible heteronuclear clusters has been obtained.

Experimental

The syntheses were carried out under an argon atmosphere using anhydrous solvents. Column chromatography on alumina, Al_2O_3 (Brockmann II activity), was used to isolate individual substances.

Mass spectra were recorded on Varian MAT AEI-MS-30 and Varian MAT CH-5-FD spectrometers using the fast atom bombardment method.

^1H NMR spectra of solutions of the compounds in $CDCl_3$ were recorded on a Bruker WP-200-SY spectrometer operating at 200.13 MHz. Chemical shifts were measured relative to the internal Me_4Si. IR spectra of solutions of the compounds in CH_2Cl_2 were recorded on an UR-20 instrument.

Commercially available chemical reagents were used in the experiments.

The following initial substances were obtained using procedures described in the literature: $RhCp(C_2H_4)_2$,[11] $Ru_2Cp_2(CO)_4$,[12] $Ru_2Cp^*_2(CO)_4$,[13] $Fe_2Cp^*_2(CO)_4$,[14] $CoCp^*(C_2H_4)_2$,[15] $[Rh(C_2H_4)_2(\mu\text{-}Cl)]_2$,[16] $Rh(C_2H_4)_2(acac)$,[17] $FeRuCp_2(CO)_4$,[18] $(CH_3)_3NO \cdot 2H_2O$,[19] and $C_5H_4CH_3Si(CH_3)_3$.[20]

Reaction of $RhCp(C_2H_4)_2$ with $Ru_2Cp_2(CO)_4$. A solution of $RhCp(C_2H_4)_2$ (0.896 g, 4 mmol) and $Ru_2Cp_2(CO)_4$ (1.776 g, 4 mmol) in *m*-xylene (50 mL) was refluxed for 30 h. The solvent was distilled off, and the residue was chromatographed on a column with Al_2O_3 (2×40 cm) using CH_2Cl_2 as the eluent. A yellow fraction containing 0.178 g (10%) of unreacted initial complex $Ru_2Cp_2(CO)_4$ was isolated. Further elution was performed with a CH_2Cl_2—acetone mixture (20 : 1). A gray fraction was collected first. The solvent was distilled off, and a black crystalline substance (0.160 g, 11%) was isolated, which was identified as complex $Rh_4Cp_4(\mu_3\text{-}CO)_2$ (**3**) on the basis of its spectral data. Further elution resulted in a crimson fraction followed by a violet-blue one. They were concentrated to ~10 mL, a hexane layer was added atop with caution, and the mixture was kept in the refrigerator for 48 h. $Ru_2Rh_2Cp_4(\mu_3\text{-}CO)_3$ (**1**) (0.090 g, 6%) and $RuRh_3Cp_4(\mu_3\text{-}CO)_2H$ (**2**) (0.184 g, 11%), were obtained as dark crimson and black-violet fine crystals, respectively. Complex **1**. Found (%): C, 36.55; H, 2.50. $C_{23}H_{20}Rh_2Ru_2O_3$. Calculated (%): C, 36.72; H, 2.68. Complex **2**. Found (%): C, 36.22; H, 2.84. $C_{22}H_{21}Rh_3RuO_2$. Calculated (%): C, 36.33; H, 2.92.

Reaction of $RhCp(C_2H_4)_2$ with $Fe_2Cp^*{}_2(CO)_4$. A mixture of $RhCp(C_2H_4)_2$ (0.896 g, 4 mmol) and $Fe_2Cp^*{}_2(CO)_4$ (1.976 g, 4 mmol) in 50 mL of *m*-xylene was refluxed for 30 h. The solvent was distilled off, and the residue was chromatographed on a column with Al_2O_3 (2×40 cm). Using benzene as the eluent, a red fraction containing unreacted starting complex $Fe_2Cp^*{}_2(CO)_4$ (0.237 g, 12%) was collected. Further elution with a benzene—ether mixture (5 : 1) resulted in two poorly separating fractions, one brown-green and one green, which were evaporated. In the case of incomplete separation of substances chromatography was repeated. Solid substances were dried *in vacuo*. $Fe_2RhCp^*{}_2Cp(\mu\text{-}CO)_3(\mu_3\text{-}CO)$ (**4a**) (0.185 g, 7%) and $Fe_2Rh_2Cp^*{}_2Cp_2(\mu_3\text{-}CO)_3$ (**5a**) (0.080 g, 5%) were obtained as brown and dark green powders, respectively. Complex **4a**. Found (%): C, 53.09; H, 5.60. $C_{29}H_{35}Fe_2RhO_4$. Calculated (%): C, 52.61; H, 5.33. Complex **5a**. Found (%): C, 49.96; H, 5.34. $C_{33}H_{40}Fe_2Rh_2O_3$. Calculated (%): C, 49.42; H, 5.02. Further elution with ether resulted in a dark green product $FeRh_3Cp^*Cp_3(\mu_3\text{-}CO)_2H$ (**6a**) (0.040 g, 4%). Found (%): C, 43.41; H, 4.34. $C_{27}H_{31}FeRh_3O_2$. Calculated (%): C, 43.09; H, 4.15. Further elution with a CH_2Cl_2—acetone mixture (20 : 1) afforded complex **3** (0.036 g, 5%).

Reaction of $RhCp(C_2H_4)_2$ with $Ru_2Cp^*{}_2(CO)_4$. A mixture of $RhCp(C_2H_4)_2$ (0.896 g, 4 mmol) and $Ru_2Cp^*{}_2(CO)_4$ (2.336 g, 4 mmol) in 50 mL of *m*-xylene was refluxed for 30 h. The solvent was distilled off, and the residue was chromatographed on a column with Al_2O_3 (2×40 cm). Using benzene as the eluent, an orange fraction containing unreacted starting complex $Ru_2Cp^*{}_2(CO)_4$ (0.374 g, 16%) was collected. Further elution with a benzene—ether mixture (5 : 1) resulted in two poorly separating fractions, one yellow-brown and one crimson, which were evaporated. In the case of incomplete separation of substances chromatography was repeated. Solid substances were dried *in vacuo*, and $Ru_2RhCp^*{}_2Cp(\mu\text{-}CO)_3(\mu_3\text{-}CO)$ (**4b**) (0.271 g, 9%) and $Ru_2Rh_2Cp^*{}_2Cp_2(\mu_3\text{-}CO)_3$ (**5b**) (0.089 g, 5%) were obtained as brown and dark crimson powders, respectively. Complex **4b**. Found (%): C, 46.32; H, 5.10. $C_{29}H_{35}RhRu_2O_4$. Calculated (%): C, 46.28; H, 4.69. Complex **5b**. Found (%): C, 44.94; H, 4.80. $C_{33}H_{40}Rh_2Ru_2O_3$. Calculated (%): C, 44.41; H, 4.51. Further elution with ether gave $RuRh_3Cp^*Cp_3(\mu_3\text{-}CO)_2H$ (**6b**) (0.064 g, 6%) as a violet product. Found (%): C, 40.89; H, 4.08. $C_{27}H_{31}Rh_3RuO_2$. Calculated (%): C, 40.68; H, 3.91. Further elution with a CH_2Cl_2—acetone mixture (20 : 1) afforded complex **3** (0.051 g, 7%).

Synthesis of $Rh_4Cp_4(\mu_3\text{-}CO)_2$ (3). *A*. From $Rh_2Cp_2(CO)_3$ and $RhCp(C_2H_4)_2$. A solution of $Rh_2Cp_2(CO)_3$ (0.420 g, 1 mmol) and $RhCp(C_2H_4)_2$ (0.448 g, 2 mmol) in 30 mL of *m*-xylene was refluxed for 20 h. The solvent was evaporated, and the residue was chromatographed on a column with Al_2O_3 (2×30 cm). Using CH_2Cl_2 as the eluent, trace amounts of impurities (including unreacted starting $Rh_2Cp_2(CO)_3$ and $Rh_3Cp_3(\mu\text{-}CO)_3$ (**11**)) were isolated. Further elution with a CH_2Cl_2—acetone mixture (20 : 1) resulted in a gray fraction which was concentrated to a small volume. A hexane layer was added atop, and the mixture was kept in the refrigerator at −20 °C for 48 h. The black crystals **3** that formed were filtered off and dried *in vacuo*; the yield was 0.328 g (45%). Cluster **3** was identified with the help of its spectral data, which were identical with those reported in the literature.[9]

***B*. From $Rh_3Cp_3(\mu\text{-}CO)_3$ (11) and $RhCp(C_2H_4)_2$.** Cluster **3** (0.280 g, 39%) was obtained analogously from $Rh_3Cp_3(\mu\text{-}CO)_3 \cdot 0.5CH_2Cl_2$ (**11**) (0.630 g, 1 mmol) and $RhCp(C_2H_4)_2$ (0.224 g, 1 mmol).

Synthesis of $Co_2Rh_2Cp^*{}_2Cp_2(\mu_3\text{-}CO)_2$ (7) from $Rh_2Cp_2(CO)_3$ and $CoCp^*(C_2H_4)_2$ in a 1 : 1 ratio. A solution of $Rh_2Cp_2(CO)_3$ (0.210 g, 0.5 mmol) and $CoCp^*(C_2H_4)_2$ (0.125 g, 0.5 mmol) in 30 mL of benzene was refluxed for 10 h. The solvent was evaporated, and the residue was chromatographed on a column with Al_2O_3 (2×30 cm). Elution with benzene resulted in a small red fraction (containing traces of unreacted starting complex $Rh_2Cp_2(CO)_3$) followed by a dark green fraction that was evaporated. The solid substance obtained was dried *in vacuo* to give a dark green fine-crystalline product **7** (0.090 g, 23% with respect to $Rh_2Cp_2(CO)_3$). Found (%): C, 48.58; H, 4.92. $C_{32}H_{40}Co_2Rh_2O_2$. Calculated (%): C, 49.26; H, 5.16. Further elution with CH_2Cl_2 gave a pale green fraction containing traces of $Rh_3Cp_3(\mu\text{-}CO)_3$ (**11**).

The yield of complex **7** was 49% when starting reagents were used in a 1 : 2 ratio.

Synthesis of $CoRh_3Cp^*(\eta\text{-}C_5H_4Me)_3(\mu_3\text{-}CO)_2$ (9). A solution of $Rh_3(\eta\text{-}C_5H_4Me)_3(\mu\text{-}CO)_3$ (**11a**) (0.315 g, 0.5 mmol) and $CoCp^*(C_2H_4)_2$ (0.125 g, 0.5 mmol) in 30 mL of benzene was refluxed for 16 h. The solvent was evaporated, and the residue was chromatographed on a column with Al_2O_3 (2×30 cm). Elution with benzene resulted in a green fraction which was evaporated to give a dark green product **9** (0.159 g, 40%). Found (%): C, 45.51; H, 4.72. $C_{32}H_{36}CoRh_3O_2$. Calculated (%): C, 45.25; H, 4.56. Further successive elution with benzene and a benzene—CH_2Cl_2 mixture gave a pale green fraction containing traces of $Rh_3(\eta\text{-}C_5H_4Me)_3(\mu\text{-}CO)_3$ (**11a**) and a dark gray fraction containing traces of $Rh_4(\eta\text{-}C_5H_4Me)_4(\mu_3\text{-}CO)_2$, respectively.

Reaction of $Rh_2Cp_2(CO)_3$ with $[Rh(C_2H_4)_2(\mu\text{-}Cl)]_2$. A mixture of $Rh_2Cp_2(CO)_3$ (0.210 g, 0.5 mmol) and $[Rh(C_2H_4)_2(\mu\text{-}Cl)]_2$ (0.097 g, 0.25 mmol) in 30 mL of ether was stirred for 16 h at 25 °C. Then TlCp (0.269 g, 1 mmol) was added, and the reaction mixture was stirred for an additional 3 h and filtered. The precipitate obtained was washed with CH_2Cl_2 (3×10 mL), the combined filtrates were evaporated to dryness, and the residue was chromatographed on a column with Al_2O_3 (2×30 cm). Elution with benzene resulted in a light yellow fraction containing traces of complex $RhCp(C_2H_4)_2$ (the complex is formed in the reaction of unreacted starting complex $[Rh(C_2H_4)_2(\mu\text{-}Cl)]_2$ with TlCp) followed by a pale red fraction containing traces of unreacted starting complex $Rh_2Cp_2(CO)_3$. Further elution with CH_2Cl_2 resulted in a yellow-green fraction which was evaporated to give cluster $Rh_3Cp_3(\mu\text{-}CO)_3$ (**11**) (0.250 g, 85%).

Reaction of $Ru_2Cp_2(CO)_4$ with $[Rh(C_2H_4)_2(\mu\text{-}Cl)]_2$. A mixture of $Ru_2Cp_2(CO)_4$ (0.444 g, 1 mmol) and $[Rh(C_2H_4)_2(\mu\text{-}Cl)]_2$ (0.194 g, 0.5 mmol) in 30 mL of ether was stirred at 25 °C for 16 h. Then TlCp (0.539 g, 2 mmol) was added, and the reaction mixture was stirred for an additional 3 h and filtered. The precipitate obtained was washed with CH_2Cl_2 (3×10 mL), the combined filtrates were evaporated to dryness, and the residue was chromatographed on a column with Al_2O_3 (2×30 cm). Elution with benzene resulted in a light yellow fraction containing the complex $RhCp(C_2H_4)_2$ (0.134 g, 60%; the complex is formed in the reaction of unreacted starting complex $[Rh(C_2H_4)_2(\mu\text{-}Cl)]_2$ with TlCp) followed by a yellow fraction containing unreacted starting complex $Ru_2Cp_2(CO)_4$ (0.250 g, 56%). Further elution with CH_2Cl_2 resulted in a dark green fraction that was evaporated to give the cluster $Ru_2RhCp_3(\mu\text{-}CO)_3(\mu_3\text{-}CO)$ (**13**) (0.153 g, 25%). Found (%): C, 37.55; H, 2.61. $C_{19}H_{15}RhRu_2O_4$. Calculated (%): C, 37.27; H, 2.47.

Reaction of $FeRuCp_2(CO)_4$ with $[Rh(C_2H_4)_2(\mu\text{-}Cl)]_2$. A mixture of $FeRuCp_2(CO)_4$ (0.120 g, 0.3 mmol) and $[Rh(C_2H_4)_2(\mu\text{-}Cl)]_2$ (0.058 g, 0.15 mmol) in 30 mL of ether was stirred at 25 °C for 16 h. Then TlCp (0.162 g, 0.6 mmol) was added, and the reaction mixture was stirred for an additional 3 h and filtered. The precipitate obtained was washed with CH_2Cl_2 (3×10 mL), the combined filtrates were evaporated to dryness, and the residue was chromatographed on a column with Al_2O_3 (2×30 cm). Elution with benzene resulted in a light yellow fraction containing the complex $RhCp(C_2H_4)_2$ (0.043 g, 65%; the complex is formed in the reaction of unreacted starting $[Rh(C_2H_4)_2(\mu\text{-}Cl)]_2$ with TlCp) followed by a red fraction containing unreacted starting complex $FeRuCp_2(CO)_4$ (0.08 g, 67%). Further elution with CH_2Cl_2 resulted in a green fraction. The eluate was collected, the solvent was evaporated, and the cluster $FeRuRhCp_3(\mu\text{-}CO)_3(\mu_3\text{-}CO)$ (**16**) (0.034 g, 20%) was obtained as a dark green powder. Found (%): C, 40.41; H, 2.70. $C_{19}H_{15}FeRhRuO_4$. Calculated (%): C, 40.24; H, 2.67.

Reaction of $Ru_2Cp_2(CO)_4$ with $Rh(C_2H_4)_2(acac)$. A mixture of $Ru_2Cp_2(CO)_4$ (0.133 g, 0.3 mmol) and $Rh(C_2H_4)_2(acac)$ (0.077 g, 0.3 mmol) in 30 mL of ether was stirred at 25 °C for 16 h. Then TlCp (0.162 g, 0.6 mmol) was added, and the reaction mixture was stirred for an additional 3 h and filtered. The precipitate obtained was washed with CH_2Cl_2 (3×10 mL), the combined filtrates were evaporated to dryness, and the solid substance obtained was chromatographed on a column with Al_2O_3 (2×30 cm). Elution with benzene resulted in a light yellow fraction containing the complex $RhCp(C_2H_4)_2$ (0.039 g, 58%; the complex is formed in the reaction of unreacted starting $Rh(C_2H_4)_2(acac)$ with TlCp) followed by a yellow fraction, containing unreacted starting complex $Ru_2Cp_2(CO)_4$ (0.074 g, 56%). Further elution with CH_2Cl_2 resulted in a green fraction, which was evaporated, and the cluster $Ru_2RhCp_3(\mu\text{-}CO)_3(\mu_3\text{-}CO)$ (**13**) (0.042 g, 23%) was obtained as a dark green powder.

Reaction of $RhCp(CO)_2$ with trimethylamine *N*-oxide. $(CH_3)_3NO \cdot 2H_2O$ (2.23 g, 20 mmol) was added to a solution of $RhCp(CO)_2$ (4.48 g, 20 mmol) in 50 mL of benzene. The mixture was refluxed until gas evolution had ceased (~3—5 h), evaporated *in vacuo* to dryness, and chromatographed on a column with Al_2O_3 (2×40 cm). Elution with benzene resulted in a red fraction, which was evaporated and recrystallized from a CH_2Cl_2—pentane mixture (1 : 4) at −50 °C to give dark red crystals of $Rh_2Cp_2(CO)_3$ (0.81 g, 19%). Further elution with CH_2Cl_2 resulted in a yellow-green fraction of $Rh_3Cp_3(\mu\text{-}CO)_3$ (**11**). The eluate was collected, evaporated *in vacuo*, and complex **11** (2.44 g, 58%) was obtained. Further successive elution with a CH_2Cl_2—methanol mixture (20 : 1) resulted in two fractions, one black and one pink. They were collected, evaporated *in vacuo*, and cluster **3** (0.182 g, 5%) and $Rh_3Cp_3(\mu_3\text{-}CO)(\mu_3\text{-}O) \cdot CH_2Cl_2$ (0.211 g, 5%) were obtained as a black powder and glittering green crystals, respectively. Found (%): C, 32.05; H, 2.74. $C_{17}H_{17}Cl_2Rh_3O_2$. Calculated: C, 32.26; H, 2.70. IR (CH_2Cl_2), ν/cm^{-1}: 1688 (vs) (CO). ^1H NMR ($CDCl_3$), δ: 5.17 (s, Cp). MS, *m/z*: 548 $[M]^+$.

Synthesis of $Rh(\eta\text{-}C_5H_4CH_3)(CO)_2$. A mixture of $[Rh(CO)_2(\mu\text{-}Cl)]_2$ (1.94 g, 5 mmol) and $C_5H_4CH_3Si(CH_3)_3$ (0.84 g, 1 mmol) in 20 mL of pentane was stirred for 2 h. The initial complex completely dissolved, and the solution turned orange. The solvent was evaporated *in vacuo*, and the orange oil obtained was chromatographed on a column with Al_2O_3 (2×30 cm). Elution with pentane resulted in a bright orange fraction, which was collected, evaporated, and $Rh(\eta\text{-}C_5H_4CH_3)(CO)_2$ (1.08 g, 91%) was obtained as an orange oil. IR (pentane), ν/cm^{-1}: 2030 (vs), 1970 (vs) (CO). ^1H NMR ($CDCl_3$), δ: 5.46 (m, 2 H, Cp), 5.27 (m, 2 H, Cp), 2.08 (s, 3 H, Me). MS, *m/z*: 238 $[M]^+$.

Reaction of $Rh(\eta\text{-}C_5H_4CH_3)(CO)_2$ with trimethylamine *N*-oxide. $(CH_3)_3NO \cdot 2H_2O$ (0.333 g, 3 mmol) was added to a solution of $Rh(\eta\text{-}C_5H_4CH_3)(CO)_2$ (0.714 g, 3 mmol) in 50 mL of benzene. The mixture was refluxed until gas evolution had ceased (~2—3 h), evaporated *in vacuo* to dryness, and chromatographed on a column with Al_2O_3 (2×40 cm). Elution with benzene resulted in a red fraction $Rh_2(\eta\text{-}C_5H_4CH_3)_2(CO)_3$. The eluate was collected, evaporated and a dark red fine-crystalline substance (0.081 g, 12%) was obtained. Further elution with a benzene—CH_2Cl_2 mixture (10 : 1) resulted in a yellow-green fraction of $Rh_3(\eta\text{-}C_5H_4CH_3)_3(\mu\text{-}CO)_3$ (**11a**). The eluate was collected and evaporated, and a brown-green fine-crystalline substance **11a** (0.39 g, 62%) was obtained. Further elution with a CH_2Cl_2—methanol mixture (20 : 1) resulted in two fractions: one black and one pink. They were collected, the solvent was evaporated, and the products were dried *in vacuo*. The cluster $Rh_4(\eta\text{-}C_5H_4CH_3)_4(\mu_3\text{-}CO)_2$ (**3a**) (0.024 g, 4%) and $Rh_3(\eta\text{-}C_5H_4CH_3)_3(\mu_3\text{-}CO)(\mu_3\text{-}O)$ (0.030 g, 5%) were obtained as a black powder and glittering green crystals, respectively.

The substances were identified by comparison of their spectral data with those for the known nonmethylated analogs.

Complex $Rh_2(\eta\text{-}C_5H_4CH_3)_2(CO)_3$. IR ($CH_2Cl_2$), ν/cm^{-1}: 1970 (vs), 1825 (vs) (CO). ^1H NMR ($CDCl_3$), δ: 5.45 (m, 4 H, Cp), 5.30 (m, 4 H, Cp), 1.85 (s, 6 H, Me). MS, *m/z*: 448 $[M]^+$.

Cluster **11a**. IR (CH_2Cl_2), ν/cm^{-1}: 1838 (vs), 1783 cm^{-1} (s), (CO). ^1H NMR ($CDCl_3$), δ: 5.45 (m, 6 H, Cp), 5.33 (m, 6 H, Cp), 1.85 (s, 9 H, Me). MS, *m/z*: 630 $[M]^+$.

Cluster **3a**. IR (CH_2Cl_2), ν/cm^{-1}: 1696 (sh, m), 1660 (vs), (CO). ^1H NMR ($CDCl_3$), δ: 5.52 (m, 8 H, Cp), 5.33 (m, 8 H, Cp), 1.82 (s, 12 H, Me). MS, *m/z*: 784 $[M]^+$.

Cluster $Rh_3(\eta\text{-}C_5H_4CH_3)_3(\mu_3\text{-}CO)(\mu_3\text{-}O)$. IR ($CH_2Cl_2$), ν/cm^{-1}: 1690 (vs), (CO). ^1H NMR ($CDCl_3$), δ: 5.22 (m, 6 at 25 °CH, Cp), 5.05 (m, 6 H, Cp); 1.80 (s, 9 H, Me). MS, *m/z*: 590 $[M]^+$.

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