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The reductive carboxylation of mixtures of Na2PtCl4 and RhCl3·xH2O (at room temperature and 1 atm CO) are reported. From the reaction mixtures [PtRh5(CO)16]− and [PtRh4(CO)15]2− have been isolated; the latter is in equilibrium, through the release and absorption of CO, with [PtRh4(CO)13]3−. Solution structures and fluxional behavior of all these anions have been established by multinuclear (13C, 1H,[103Rh, 109Rh, 199Pt] variable-temperature NMR measurements.

Introduction

We reported, in a preliminary communication,2 the isolation of [PtRh4(CO)13]−, which reacted further under CO with an alkaline methanolic solution or Na–anthracene in THF to give an orange-yellow anion. This was formulated on the basis of partial analytical data to be [PtRh4(CO)13]−, which we now show to be [PtRh4(CO)15]2−. This reversibly loses CO to give the related dianion [PtRh5(CO)15]4−. The general features of the reductive carboxylation of mixtures containing Na2PtCl4 and RhCl3·xH2O are discussed in connection with the preparation of the above clusters. Multinuclear NMR studies (13C, 1H,[103Rh, 109Rh, 199Pt] are reported which establish their structures and fluxional behavior in solution.

Acknowledgment. We thank the Microanalytical Service Unit, The Australian National University, and F. Galsbø, Ørsted Institute, University of Copenhagen, for an authentic sample of [Ir(en)3]Cl3 and a preliminary account of its synthesis. We are also grateful to Dr. N. J. Curtis for helpful discussions.

Registry No. [Rh(NH3)3(OSO2CF3)](CF3SO3)3, 2801-72-0; [Cr(NH3)5(OSO2CF3)](CF3SO3)3, 2801-73-1; [Ir(NH3)5Cl3](CF3SO3)3, 1260-59-5.

Results and Discussion

1. Generalities on the Reductive Carboxylation of Pt–Rh Systems. In an attempt to develop synthetic routes to mixed Pt–Rh clusters in good yields from readily available materials, we have carried out a systematic investigation of the reductive carboxylation of mixtures of Na2PtCl4 and RhCl3·xH2O in methanol under CO (1 atm pressure) at room temperature. The reduction was carried out by a stepwise addition of NaOH (1 M in methanol) to a vigorously stirred solution with various ratios of Pt:Rh (1:1, 1:2, 1:4, 1:5) under an atmosphere of CO; the reactions were monitored by IR after each addition of NaOH or at regular intervals. When an unambiguous interpretation of the spectra was not possible, excess bulky cations were added to precipitate the equilibrium mixture, which was then subjected to fractional crystallization. In every case, the same species were always formed first, though in different proportions. The final distribution of products, however, depends on both the ratios of OH−:metals and Pt:Rh;
Scheme I. Carbonyl Species Observed in the Stepwise Reductive Carbonylation of \([\text{PtCl}_6]^{3-}\) and RhCl\(_3\) in \(\text{H}_2\text{O}\)

\[
\begin{align*}
\text{OH}^- + \text{CO} &\rightarrow [\text{Pt}([\text{CO}]_2\text{Cl})^-] \rightarrow [\text{Pt}([\text{CO}]_3\text{Cl})^-] + \\
[\text{Rh}([\text{CO}]_2\text{Cl})]^- + [\text{Pt}([\text{CO}]_3\text{Cl})^-] &\rightarrow [\text{Pt}([\text{CO}]_5\text{Cl})^-] + [\text{Rh}([\text{CO}]_3\text{Cl})]^- + \text{OH}^- + \text{CO}
\end{align*}
\]

\(a\) Performed in methanol at room temperature under 1 atm CO with stepwise addition of NaOH. \(b\) Byproducts A: \([\text{Rh}([\text{CO}]_2\text{Cl})]^-\) and \([\text{Rh}([\text{CO}]_3\text{Cl})]^-\) if Pt:Rh \(\leq 1:5\); \(c\) Byproducts B: \([\text{Rh}([\text{CO}]_2\text{Cl})]^-\) and \([\text{Rh}([\text{CO}]_3\text{Cl})]^-\) if Pt:Rh \(\leq 1:4\); \(d\) if Pt:Rh > 1:5. \(e\) Byproducts C: \([\text{Rh}([\text{CO}]_2\text{Cl})]^-\) and \([\text{Rh}([\text{CO}]_3\text{Cl})]^-\) if Pt:Rh < 1:4. \(f\) If Pt:Rh > 1:4. 

slowly (2–3 days) because of the immediate formation of a buffer, CO\(_2\)/HCO\(_3^-\), which significantly slows the reductive process. Method c provides a high-yield synthesis in a reasonable time (12–18 h) but has to be performed in such a way that the evolved CO\(_2\) does not escape; this gives, but only near the end of the reaction, the above mentioned CO\(_2\)/HCO\(_3^-\) buffer in which the mixed-metal cluster is stable. The formal stoichiometry of this reaction is

\[
\begin{align*}
[\text{PtCl}_6]^{3-} + 5\text{RhCl}_3 + 20\text{CO}_2^- + 2\text{CO} &\rightarrow 25\text{CO} + 10\text{H}_2\text{O} \\
\text{MeOH}, \text{room temp} &\rightarrow 1 \text{ atm CO} \\
[\text{PtRh}_5(\text{CO})_{21}]^- + 21\text{Cl}^- + 20\text{HCO}_3^- + 10\text{CO}_2 &\rightarrow \text{1 atm CO}
\end{align*}
\]

The product can be obtained directly as the sodium salt or, by metathesis, as a bulky cation salt, in yields up to 80–85%.

Solutions of \([\text{PtRh}_5(\text{CO})_{21}]^-(\text{THF}, \text{CH}_2\text{Cl}_2, \text{acetone})\) at room temperature are decomposed within minutes in air, but the solid is somewhat more stable, especially the large crystals of the \([\text{PPN}]^+\) salt, which can be obtained by slow diffusion of pentane into THF solutions.

We have previously reported\(d\) that the dodecacarboxylic species of Pt\(^{3+}\) and Rh\(^{3+}\) react according to eq 2. Because it requires previous preparation of both reactants, this reaction is of little synthetic interest but it is important in understanding the peculiar reactivity of the mixed anion toward CO. It has been observed that the reaction does not proceed under a nitrogen atmosphere, while there is a slow reaction (ca. 12 h) under CO. With \([N_{-}n\text{-Bu}_{4}]^+\) or \([\text{PPN}]^+\) as counterions, \([\text{PtRh}_5(\text{CO})_{21}]^-\) seems to be the only product present and indefinitely stable under these conditions. However, a THF solution of \((\text{M})[\text{PtRh}_5(\text{CO})_{21}]\) (M = Na or \([\text{NEt}_4]\)) under 1 atm CO undergoes slow precipitation of \([\text{Rh}_3(\text{CO})_{13}]^2\)–, which is rather insoluble in THF as a salt of these cations. This suggests that reaction 2 is reversible and should be regarded as an equilibrium. The situation is, however, more complicated because under CO \([\text{Rh}_3(\text{CO})_{13}]^2\)– is known to be in equilibrium with \([\text{Rh}_5(\text{CO})_{21}]^2\)– which is thus very probably involved as an intermediate in eq 2, and this would explain the lack of reaction under \(\text{N}_2\). Further evidence for the involvement of \([\text{Rh}_5(\text{CO})_{21}]^2\)– in the formation and degradation of \([\text{PtRh}_5(\text{CO})_{21}]^-\) comes from the reaction of this mixed anion under a slightly higher pressure of CO (3–5 atm); the original brown solution becomes grayish and the IR spectrum shows the presence of mainly \([\text{Rh}_5(\text{CO})_{21}]^2\)– along with \([\text{Pt}([\text{CO}]_3\text{Cl})]^-\) (n = 4–5). This mixture reverts back to \([\text{PtRh}_5(\text{CO})_{21}]^-\) within a few hours if the CO pressure is released to 1 atm. The similar behavior toward CO of the analogous species \([\text{NiRh}_5(\text{CO})_{21}]^2\)– should be noted, since this also gives \([\text{Rh}_5(\text{CO})_{21}]^2\)– along with \([\text{Ni}(\text{CO})_4]\).

Thermogravimetric measurements on solid \((\text{M})[\text{PtRh}_5(\text{CO})_{21}]\) (M = \([\text{PPN}]^+\) or \([\text{NEt}_4]\)^+) indicate a two-step decomposition. The first, which starts between 120 and 140 °C and ends at about 200 °C (depending upon the cation and the \(\text{N}_2\) or CO atmosphere), is consistent with loss of about 4–5 mol of CO/mol of compound; subsequently, a further progressive loss occurs in the range 250–400 °C, leaving an essentially, but not entirely, metallic residue. The product obtained in the first step has been found to be a complex mixture of presently unidentified species, which are very likely high-nuclearity clusters. A similar result is obtained when solutions of \([\text{PtRh}_6(\text{CO})_{23}]^2\)– are heated, under both \(\text{N}_2\) and CO: mix-
tues of brown anions are obtained, and their identification is still in progress.

The reaction of an aqueous solution of Na[PtRh4(CO)14] with slight excess of aqueous HCl gives precipitation of a product that we believe to be [HPrRh4(CO)14]. Unfortunately, both its poor stability and solubility prevented us from obtaining a 1H NMR spectrum. This formulation, however, is supported by the IR spectrum in CH2Cl2, which has bands at 2065 s, 2035 m, and 1810 ms cm−1. Both the shift to higher wavenumbers (20–30 cm−1) and the pattern, almost identical with that of the parent compound, are in keeping with the existence of such hydric species.

Attempts to obtain neutral species by controlled oxidation with FeCl3, Ag2SO4, AgBF4, or I2, in THF under N2 or CO, gave mixtures that contained [Rh6(CO)16], [Pt3(CO)6]: three distinct products, each containing a mixture of metal carbonyls, and with slight excess of aqueous HCl gives precipitation of a product that we believe to be [HF'tRh3(CO),,]. Unfortunately, the reaction is not fast under vacuum, and a few cycles of evacuation to dryness followed by redissolution in THF or acetone results in complete conversion to the related species [PtRh4(CO)12]2− (eq 4). The stoichiometry of the reaction has been confirmed by gas-volumetric measurements (see Experimental Section). The CO evolution results in a shift of the IR absorptions to lower wavenumbers that is particularly evident in the terminal-CO region (a decrease of 5–15 cm−1 depending on the counterion; see Table I). This is consistent with the loss of ligands and consequent increased back-donation toward the remaining CO's.

The brown-red [PtRh4(CO)12]2− dianion has been crystallized as [N-n-Bu4N]+ and [PPN]+ salts from acetone or THF solution by slow diffusion of 2-propanol under nitrogen. All the salts, obtained with a variety of cations, are soluble in acetone and acetonitrile, moderately soluble in THF (but less than those of the parent [PtRh4(CO)14]2− anion), and insoluble in 2-propanol. They are sensitive to air, which causes decomposition in both the solid and solution, to as yet uncharacterized brown species.

5. Reactivity of [PtRh4(CO)12]2− (n = 12 and 14).

The behavior of these two species with respect to carbon monoxide is rather interesting. In fact, through the absorption and release of CO, the two clusters appear to be in reversible equilibrium (eq 4). At room temperature and 1 atm CO there is IR evidence only of the species at the left, and in fact only this one is recovered by precipitation under these conditions, although we cannot exclude the presence of trace amounts of [PtRh4(CO)12]2− in solution. However, under a nitrogen atmosphere or vacuum, complete conversion to [PtRh4(CO)12]2− occurs and these reactions may be continuously recycled.

The reactivity of both anions was also studied in order to synthesize other mixed clusters and to understand the equilibria between heteronuclear and homonuclear species. One particular type of reaction, designed to build up larger clusters by means of condensation of small fragments, was tried. Thus, both [PtRh4(CO)14]2− and [PtRh4(CO)12]2− react with the cationic species [Rh(CO)9(CH2CN)3]+ to give [PtRh5(CO)14]2− when the reaction is carried out under CO (eq 5), whereas under nitrogen significant amounts of unknown side products are formed together with the hexanuclear mixed cluster.

Table I. IR Data

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<th>700</th>
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<td>ms</td>
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a Legend: (a) MeOH; (b) THF; (c) dimethoxyethane; (d) MeCN.  b Abbreviations: vv, very weak; w, weak; m, medium; s, strong; sh, shoulder.
reaction is particularly interesting in that there is a redistribution of both metal atoms and charge between clusters. Reaction with electrophilic agents such as Ag⁺ and mineral acids (H₂SO₄, H₃PO₄) resulted in oxidation to mixtures of brown, as yet uncharacterized products.

Further reduction of the two anions is difficult and under severe conditions (i.e. with KOH in dimethyl sulfoxide) leads, under a CO atmosphere, to disruption of the clusters with formation of [Rh(CO)₆]⁻, [Pt₃(CO)₆]²⁻, and perhaps [Pt₃(CO)₃]²⁻.

Attempts to obtain higher nuclearity species by thermal treatment in CH₃CN solution gave, after prolonged reflux under nitrogen, mixtures of dark brown anions, which are under investigation.

6. IR Spectra. Reference IR spectra of all the anions as PPN salts in THF solution are reported in Figure 1. Frequencies in the CO region of a variety of salts are tabulated in Table I. IR spectra of [PtRh₆(CO)₁₄]²⁻ are negligibly affected on changing the cation and the solvent; the shape and position of the bands are very similar to those found in the series [Rh₆(CO)₁₆X]⁻ (X = Cl, Br, I, SCN, CN), which are closely related structurally (vide infra). In contrast, the two pentanuclear clusters show, particularly in the bridging carbonyl region, a remarkable dependence upon the cation and/or the solvent, probably because of ion-pairing effects. The IR spectra of [PtRh₄(CO)₁₄]²⁻ were recorded under CO, while all the other species were under N₂.

7. Multinuclear NMR Studies. (a) [PtRh₆(CO)₁₄]²⁻. The structure of this cluster (Figure 2) is related to that of [Rh₆(CO)₁₆]³⁻ by replacing a Rh(CO)₂ group with a Pt(CO)₆ group. The ¹³C NMR spectrum at -90 °C (Figure 3) is completely consistent with this structure and, except for our inability to distinguish between the two well-resolved doublets at 189.8 and 188.4 ppm due to CbO and CcO, has been unambiguously assigned by ¹³C{'bRh} measurements; the data are summarized in Table II.

At -50 °C (Figure 3), partial fluxionality occurs as evidenced by the collapse of the resonances due to CO, C₆O, and C₇O with all the other resonances remaining essentially unchanged (Table II). It is not easy to envisage this migratory motion, but at room temperature all the carbonyls clearly become involved in exchange as shown by the presence of a broad resonance at about 198 ppm (δ(CO)meas = 201.3), which also exhibits satellites due to J(¹⁹⁵Pt-CO), ca. 600 Hz. However, the ¹⁹⁵Pt NMR spectrum clearly shows the metal skeleton is intact since a doublet of quintets is observed at +36.2 ppm; ¹⁹⁵J(Rh₆-Pt) = 24 Hz, and ¹⁹⁵J(Rh₄-Pt) = 73 Hz. It should be noted that ¹⁹⁵J(Pt₆-Pt) < ¹⁹⁵J(Pt₄-Pt), which may arise from a change in sign or, if the one- and two-bond coupling constants have the same sign, from the greater number of pathways for transmission of coupling in the two-bond case.

(b) [PtRh₄(CO)₁₄]²⁻. The structure of this anion is shown schematically in Figure 4. It is closely related to the solid-state structure of [Rh₆(CO)₁₆]⁻ by replacing the unique Rh(CO)₆ group in the equatorial plane. Consistent with this structure, which has a C₂ axis incorpo-
as a doublet with associated $^{195}$Pt satellites ($\delta(C'O) = 245.5$), $^1J(Rh_{eq}-C'O) = 34.4$ Hz, $^1J(Pt-C'O) = 654$ Hz); $C'O$ occurs as a triplet ($\delta(C'O) = 256.6$, $^1J(Rh_{eq}-C'O) = 31.7$ Hz), and $C'O$ appears as a doublet of doublets ($\delta(C'O) = 247.4$, $^1J(Rh_{eq-C'O}) = 37.1$ Hz, $^1J(Rh_{eq-C'O}) = 25.8$ Hz). These assignments have been unambiguously confirmed by specifically decoupling $Rh_{eq}$, which also allowed $C'O$ to be assigned ($\delta(C'O) = 205.9$, $^1J(Rh_{eq-C'O}) = 93.4$ Hz). Similarly, decoupling $Rh_{sp}$ confirmed the assignment of $C'O$, $C'O$, and $C'O$ ($\delta(C'O) = 207.7$, $^1J(Rh_{eq-C'O}) = 73.6$ Hz; $\delta(C'O) = 199.9$, $^1J(Rh_{eq-C'O}) = 76.2$ Hz; $\delta(C'O) = 197.5$, $^1J(Rh_{sp-C'O}) = 79.5$ Hz), but they could not be distinguished.

The variable-temperature $^{13}$C NMR spectra of [PtRh$_4$(CO)$_{14}$]$^{2-}$ (Figure 5) are interesting and clearly show that at

$-75^\circ C$ there is a rocking motion of the carbonyls on the upper and lower halves of the trigonal-bipyramidal metallic skeleton as was proposed for [Rh$_5$(CO)$_{15}$]$^{2-}$; there is clearly no exchange of $C'O-C'O$. At room temperature, all the carbonyls except $C'O$, $C'O$, and $C'O$ are involved in exchange and give a broad resonance at 211.7 ppm exactly in the calculated position (Figure 5, 25 $^\circ C$). The same nonfluxionality of edge-bridging carbonyls in the Rh$_3$ equatorial plane was also found in [Rh$_5$(CO)$_{15}$]$^{2-}$ and probably stems from them being coplanar...
Table II. NMR Data for [NEt₄][PtRh₄(CO)₁₂] in Acetone-d₆ (See Figures 2 and 3)²

<table>
<thead>
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<th>δ (ppm)</th>
<th>J/Hz</th>
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<tr>
<td>C₅O³</td>
<td>192.5 s + d</td>
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<td>C₅O¹</td>
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<td>C₅O⁰</td>
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<td>C₅O⁻</td>
<td>235.8 s + d, t</td>
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For 13C NMR spectra. At -30 °C, two broad peaks are observed at 249.7 and 216.9 ppm in the ratio ca. 3:9, which may be attributed to C₅O³/C₅O⁰ (mean 256.0 ppm) and the remaining CO's (mean 216.7 ppm), respectively.

(c) [PtRh₄(CO)₁₂]²⁺. The 90-MHz ¹³C NMR spectrum of this anion (Figure 6) has been completely assigned by ¹³C-¹⁹⁵Pt and ¹⁹⁵Rh NMR measurements (Table III) and is completely in accord with the solid-state structure, which is also shown schematically in Figure 6. The two distinct resonances labeled 4 and 4' (which may be interchanged) are also in keeping with the nonequivalence of these two carbonyls in the crystal structure. At -90 °C, there are three rhodium resonances at +233.7, -432.6, and -475.9 ppm in the ratio 1:1:2 due to Rh¹, Rh², and Rh³, respectively; surprisingly only Rh¹ shows coupling to platinum (1/₂(J(Rh¹-Pt)) = 44 Hz). We have no good explanation for 1/₂(J(Rh²-Pt) not being observed, but it is perhaps significant that the observation of 1/₂(J(Rh²-Pt)) involves the non-carbonyl-bridged edge and this direct interaction would reasonably be expected to be stronger than the Rh(C₅O⁰)Pt interactions. At higher temperatures, carbonyl exchange occurs, which results in Rh¹ and Rh² eventually becoming equivalent. However, at -55 °C the carbonyls are obviously at some intermediate rate of exchange since the direct ¹⁹⁵Rh NMR spectrum shows only a single sharp resonance at -435 ppm due to Rh¹. This is confirmed by measuring variable-temperature ¹³C NMR spectra. At -30 °C, two broad peaks are observed at 249.7 and 216.7 ppm in the ratio ca. 3:9, which may be attributed to C₅O³/C₅O⁰ (mean 256.0 ppm) and the remaining CO's (mean 216.7 ppm), respectively. The nonfluxuality of the μ-CO's in the equatorial plane is again similar to the behavior found for [PtRh₄(CO)₁₂]²⁺, but the involvement of the Pt-CO is different. However, [PtRh₄(CO)₁₂]²⁺ is more flexible than [PtRh₄(CO)₁₂]²⁺ since at room temperature the ¹³C NMR consists of a broad but clearly resolved 1:4:1 resonance at 225.7 ppm, J(Pt-CO) = ca. 380 Hz; the position of this resonance is also in good agreement with the calculated δ(CO)mean, 225.7. The platinum resonance does not show any dramatic shift with the Rh²Pt plane, since the related carbonyl arrangement Rh₃(C₅O²)(μ-CO) in [Rh₄(C₅O₁₄)₁²⁻] and [NiRh₄(CO)₁₆]²⁻ exhibits CO ← μ-CO because, in these cases, the carbonyls are not coplanar with the Rh₃ triangle. The nonfluxuality of the Pt-CO group probably arises because of the greater Pt-CO bond strength and the particular geometry around Pt (vide infra).

Table III. NMR Data for [N+n-Bu₄][PtRh₄(CO)₁₂] in THF-d₈ (See Figure 6) at -98 °C for ¹³C and ¹⁹⁵Pt Data and at -90 °C for ¹⁹⁵Rh Data²

<table>
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<th>δ (ppm)</th>
<th>J/Hz</th>
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<tr>
<td>Pt</td>
<td>+36.2 q, d</td>
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<td>RhA</td>
<td>-243.0</td>
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<tr>
<td>RhB</td>
<td>-495.0</td>
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a Abbreviations: s, singlet; d, doublet; t, triplet; q, quintet. b At 25 °C.
temperature (-98 °C, +386 ppm; +25 °C, +421 ppm), and it therefore seems unlikely that the metal skeleton rearranges in solution at room temperature in the absence of CO.

8. Concluding Remarks. The equilibrium (4) between [PtRh6(CO)14]2- and [PtRh4(CO)12]2- is the first example of a facile interconversion between two trigonal-bipyramidal clusters with 76 and 72 CVE's (cluster valence electrons), respectively. The fact that pentanuclear clusters, with such a geometry, can occur with 76 or 72 CVE's has been rationalized with semiempirical extended-Hückel MO calculations, but it remains difficult to account for the site occupancy of platinum in these two different clusters. Over the last few years several trigonal-bipyramidal clusters have been characterized, but they mostly have 76 CVE's, except for a few osmium compounds such as Os5(CO)1518 and [H2Os2(CO)13]19 which have 72 CVE's. However, these osmium compounds seem reluctant to coordinate two additional CO's to give the 76-CVE clusters and only react with CO under forcing conditions, which result in opening of the cluster to give Os5(CO)1920 with a "bow-tie" structure. Moreover, all other known 76-CVE species, on loss of CO, generally rearrange to higher nuclearity clusters.521

Experimental Section

All the reactions and subsequent manipulations were carried out under nitrogen or carbon monoxide atmosphere in carefully purified solvents. Na2PtCl6 was recrystallized and used both in the hexahydrated form and in the anhydrous form obtained by vacuum drying at 100 °C; RhCl3·xH2O was used as commercially available with ca. 40% Rh.

11CO-enriched samples (ca. 20–30%) were obtained by direct exchange at room temperature with 90% 13CO, using standard vacuum-line techniques, on various salts of [PtRh6(CO)13]2- and [PtRh4(CO)12]2-. [PtRh4(CO)12]2- was obtained from the latter by vacuum removal of CO.

1H, 13C, 31P, and 19F NMR measurements were carried out as described previously.22-25 under CO. A mixture of 13CO for [PtRh4(CO)12]2- and under N2 for the other samples. Infrared spectra were recorded on Perkin-Elmer 457 and 297 grating spectrophotometers and on a Nicolet MX-1 FT IR instrument with subtraction of the solvent, using 0.1-mm calcium fluoride cells previously purged with nitrogen or carbon monoxide.

1. Preparation of [PtRh6(CO)14]2- by Reductive Carboxylation. RhCl3·xH2O (39% Rh: 2.500 g, 9.475 mmol) and anhydrous Na2PtCl6 (0.859 g, 1.692 mmol) were placed in a two-necked 500-mL round-bottomed flask equipped with an inlet stopcock, a stopper, and a Teflon-covered stirring magnetic bar; methanol (60 mL) was then added and a solution of NaOH (0.87 M in methanol, 46 mL, 40 mmol) was added and the resulting solution, with some suspended material, was briefly evacuated and submitted to approximately 1 atm CO through a mercury valve placed before the inlet in such a way as to allow accumulation of the CO2 evolved during the reaction. After about 10 min, when saturation of the solution with CO was complete, anhydrous Na2CO3 (4.0 g, 37.74 mmol) was added and the mixture stirred vigorously. The maximum CO absorption was observed within the first 4 or 5 h, and special attention had to be paid in order to avoid a decrease of the pressure. The reduction slowed down as the medium became progressively buffer, and in about 18–24 h a brown solution was obtained with a white precipitate, primarily of NaCl and NaHCO3. The solution was filtered (through a medium-porosity glass frit) under CO, and the precipitate was washed with 10 mL of methanol to recover most of the product.

(a) Recovery of the Sodium Salt Na[PtRh6(CO)14]. The methanolic solution of Na[PtRh6(CO)14], obtained according to the procedure above described, was checked by IR to confirm the presence of CO (band at 2330 cm⁻¹), which assures no residual alkalinity to be present (in cases where absent, the bubbling of CO in the presence of solid CO2 was added), and then evaporated in vacuum without any heating. The solid obtained was treated with THF (20 mL), and the resulting solution was separated from a light-brown insoluble residue by filtration under N2; this precipitate, prior to discharge, was washed with THF (2 × 5 mL), and the washings were collected together with the main solution. Evaporation under vacuum gave the product as a light brown, extremely air-sensitive powder of good purity, according to IR, which makes it suitable starting material for most reactions, without further purification; yield 1.9 g (87%).

(b) Metathesis of Na[PtRh6(CO)14] with Bulky Cations. Salts of several bulky cations were obtained by metathesis performed directly on the filtered methanolic solution obtained as previously described; best results were obtained by addition of methanolic solutions containing a 5–10-fold excess of [N(C2H5)4]Br or [PPN]Cl and water to complete the precipitation. The product, as brown flakes, was recovered by filtration under N2 carefully washed with water (5 × 10 mL and 2-propanol (10 mL)), vacuum-dried and stored under nitrogen. Purification was made by extraction with a 1:1 mixture of THF/n-pentane (or n-heptane) followed by further addition of n-pentane (or n-heptane). With the slow-diffusion technique sodium derivative afforded black crystals suitable for X-ray diffraction studies. Anal. (Found (calcd) for the [N(C2H5)]4[PtRh6(CO)14] salt: [N(C2H5)4] CO (gravimetric), 10.13 (10.33). Pt, 15.87 (15.48). Rh, 41.39 (40.83). CO (gas volumetric), 33.67 (33.34).

2. Preparation of [PtRh4(CO)12]2- by Reaction of [PtRh4(CO)12]2- and RhC13-xH2O. A solution of [N-n-Bu4]+[Rh3(CO)12] (0.190 g, 0.0742 mmol in 10 mL of THF) was treated with [N-n-Bu4]+[PtRh4(CO)12] (10 mL of a THF solution 1.49 × 10⁻¹⁷ M) under N2. The resulting grayish solution was divided in two portions, one being submitted to CO. This same portion slowly turned brown and gave IR evidence after 17 h of [PtRh6(CO)14]2- together with some [Rh5(CO)12]2-; within a few days the mixed anion appeared almost pure. In contrast the portion left under nitrogen gave no evidence of reaction after several days.

3. Reaction of Na[PtRh6(CO)14] with Aqueous HCl. Na[PtRh6(CO)14] (0.489 g, 0.42 mmol) was dissolved in water (30 mL), and concentrated aqueous HCl (4–5 mL) was added dropwise with stirring; the precipitated brown flakes were centrifuged, separated from the mother liquor, washed with dilute HCl (1:10), and centrifuged to give a colorless washing. The resulting vacuum-dried product dissolved only sparingly in CH2Cl2 and toluene. IR absorptions in CH2Cl2: 1985, 1203, 1035 m, and 1824 cm⁻¹.

4. Synthesis of [PtRh4(CO)12]2-. RhCl3·xH2O (40% Rh: 1.500 g, 5.83 mmol) and anhydrous Na2PtCl6 (0.659 g, 1.45 mmol) were placed in a two-necked 500-mL round-bottomed flask equipped with an inlet stopcock, a stopper, and a Teflon-covered magnetic stirring bar; methanol (50 mL) was then added, and the resulting solution with some suspended material was briefly evacuated and submitted to CO through a mercury valve maintaining a slightly positive pressure. After about 10 min, which was required to saturate the solution with CO, NaOH (0.87 M in methanol, 46 mL, 40 mmol) was added and the mixture was stirred vigorously. The maximum CO absorption was observed within the first 2 or 3 h, and special attention had to be paid in order to avoid a decrease of the CO pressure. In about 18 h an orange-yellow solution was obtained with a precipitate, primarily of NaCl and NaHCO3. The solution was filtered (through a medium-porosity glass frit) under CO, and the precipitate was washed with 10 mL of methanol to recover most of the product. The procedure is the same, and precipitation occurs on addition of an excess of the chosen cation and, if necessary, water to complete the recovery. The products obtained are generally of good purity, as can be easily

(21) Femagalli, A.; Martinengo, A.; unpublished results.
checked by IR and the color, which should be golden yellow or orange-yellow.

When the above reaction is carried out on a larger scale (6 g of RhCl₃·3H₂O), the best reaction is found to occur by slow addition of the NaOH solution (over ca. 2 h); this avoids a fast reduction and formation of brown insoluble products. Recrystallization to obtain high-purity compounds or a large crystalline specimen is performed by slow diffusion of 2-propanol (saturated with CO) into THF or acetone solutions, under a CO atmosphere.

Anal. Found (calcd) for the [Ni(C₅H₅)₄][PtRh₄(CO)₁₂] salt: C, 28.58 (28.61); H, 3.25 (3.20); N, 2.22 (2.22); Pt, 14.70 (15.49); Rh, 34.26 (32.68).

5. Synthesis of [PtRh₄(CO)₁₂]²⁻. In a typical preparation, [PPN]₂[PtRh₄(CO)₁₂] (0.280 g, 0.135 mmol) was dissolved in THF (15 mL) under a nitrogen atmosphere. The solution was slowly evaporated under vacuum, and the reddish brown solid obtained was redissolved in THF (15 mL); and IR spectrum revealed complete conversion to [PPN]₂[PtRh₄(CO)₁₂]. Recovery was accomplished by addition of 2-propanol (30 mL); the microcrystalline precipitate was filtered, washed with 2-propanol (5 + 5 mL), vacuum-dried, and stored under nitrogen; yield 0.250 g (92%). The same procedure can be used to obtain any other salt using the corresponding salt of the parent compound. When larger amounts of products are worked up, more than one cycle of evaporation and redissolution may be necessary; in any case purity should be checked by IR. Recrystallization from acetone/2-propanol using the slow-diffusion technique gives good crystals of the product.

Gas Volumetric Analysis of Evolved CO. A sample of [PPN]₂[PtRh₄(CO)₁₂] (0.8502 g, 0.037 mmol) was dissolved in THF (10 mL). The evolved CO (reduced to STP conditions) was 0.7875 mL, corresponding to 1.923 mol of starting material.

6. Reaction of [PtRh₄(CO)₁₂]²⁻ with CO. A THF or acetone solution of any salt of [PtRh₄(CO)₁₂]²⁻ prepared under nitrogen is briefly evacuated and submitted to 1 atm CO; within minutes the color turns yellow from the original reddish brown and the IR spectrum taken under CO shows complete conversion to [PtRh₄(CO)₁₂]²⁻.

7. Reaction of [PtRh₄(CO)₁₂]²⁻ with [Rh(CO)₂(CH₃CN)]⁺. [NEt₃]₂[PtRh₄(CO)₁₂] (0.050 g, 0.037 mmol) was dissolved in acetonitrile under CO. Addition of [Rh(CO)₂(CH₃CN)]⁺[BF₄]⁻ (2 mL of a 0.0185 M solution in acetonitrile) gave immediate reaction, yielding a brown solution of [NEt₃]₂[PtRh₄(CO)₁₂] (IR bands at 2035, 2004, and 1785 ms cm⁻¹).

8. Reaction of [PtRh₄(CO)₁₂]²⁻ with Rh₆(CO)₁₆. Finely powdered Rh₆(CO)₁₆ (0.051 g, 0.048 mmol) was reacted under CO with [PPN]₂[PtRh₄(CO)₁₂] (4.8 mL of a 0.01 M THF solution). After 1 h of stirring, a dark red solution was obtained, which showed the characteristic IR bands of [Rh₆(CO)₁₆]²⁻ (2035 s, 2004 vs, 1838 m, and 1785 ms cm⁻¹) superimposed on those of [PtRh₄(CO)₁₂]²⁻.

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Registry No. Na[PtRh₄(CO)₁₂], 67954-67-0; [NEt₃]₂[PtRh₄(CO)₁₂], 68034-57-1; PPN[PtRh₄(CO)₁₂], 68034-56-0; Na[PtRh₄(CO)₁₂], 91238-53-8; [PPN]₂[PtRh₄(CO)₁₂], 91238-55-0; [PPh₄]₂[PtRh₄(CO)₁₂], 91238-56-1; [NEt₃-n-Pr]₂[PtRh₄(CO)₁₂], 91238-57-2; [PPh₄]₂[PtRh₄(CO)₁₂], 91265-29-1; [NEt₃-n-Pr]₂[PtRh₄(CO)₁₂], 91286-54-9; [NEt₃-n-Pr]₂[PtRh₄(CO)₁₂], 91286-55-0; [PPN]₂[PtRh₄(CO)₁₂], 91286-52-1; [PPh₄]₂[PtRh₄(CO)₁₂], 91286-57-2; [Na(n-Bu₄)₂][PtRh₄(CO)₁₂], 97706-02-6; Na[PPh₄]₂[PtRh₄(CO)₁₂], 16923-58-3; [Na(n-Bu₄)₂][PtRh₄(CO)₁₂], 68034-57-1; [PPh₄]₂[PtRh₄(CO)₁₂], 61084-51-3; [Rh(CO)₂(CH₃CN)]⁺[BF₄]⁻, 3513-97-6; Rh(CO)₁₆, 28407-51-4; [Rh₆(CO)₁₆]²⁻, 72826-87-0; Rh, 7440-16-6; Pt, 7440-06-4.

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Synthesis of M₂Pt(CO)₁₂ (M = Re, Mn). Crystal Structure of Re₂Pt(CO)₁₂

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The heterobimetallic carbonyl compounds M₂Pt(CO)₁₂ (M = Re, Mn) have been synthesized in high yield from the reaction of M₂Pt(COD) (COD = 1,5-cyclooctadiene) with excess HM(CO)₆ (M = Re, Mn) in the presence of CO at room temperature. The concomitant formation of M₂(CO)₁₀ is suggested as evidence of a radical pathway for this reaction. The molecular structure of Re₂Pt(CO)₁₂ is reported and compared to the structure of Re₂(CO)₁₆. Crystals of Re₂Pt(CO)₁₂ form in the triclinic space group PI with a = 7.225 (2) Å, b = 10.116 (2) Å, c = 6.503 (2) Å, α = 94.57 (2)°, β = 91.86 (2)°, γ = 71.59 (2)°, V = 449.5 (2) Å³, and ρ(calcd) = 3.383 g cm⁻³, for mol wt 903.61 and Z = 1. The structure can best be described as a platinum atom in a square-planar environment, bound to two carbonyl ligands and two Re(CO)₅ moieties in the trans configuration. Anisotropic refinement of all atoms has resulted in final discrepancy factors of R = 0.030 and Rₛ = 0.038 for 1094 observed reflections. The observed Pt-Re bond distance is 2.8309 (5) Å.

Introduction

As part of a program to evaluate oxide-supported heterobimetallic compounds as heterogeneous catalysts, we have sought high-yield pathways to new mixed-metal compounds that contain catalytically important metals. One of the most important commercial bimetallic catalysts is alumina-supported platinum-rhenium, which is used in the catalytic reforming of petroleum naphtha.s To date, however, only a few bimetallic compounds of platinum–rhenium have been reported, and all of them contain phosphate ligands. This is an undesirable feature for a catalyst precursor, in that supported metal particles generated from such compounds may be poisoned by phosphorus. The preparation of platinum–rhenium bimetallic compounds that contain easily removable ligands is therefore a desirable goal.

We have previously shown that mixed-metal clusters could be prepared by the addition of metal hydride complexes to...