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0.009 times its esd) with $R = 0.048$ and $R_w = 0.050$. A final difference-Fourier map showed no chemically significant features. Crystal data are $a = 16.027$ (2) Å, $b = 15.622$ (1) Å, $c = 16.228$ (1) Å, $\beta = 93.269$ (8)°, $V = 4056$ (1) Å^3, space group $P2_1/a$, $Z = 4$, mol wt = 816.05, and ρ(calcd) = 1.336 g/cm^3.

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Supplementary Material Available: Tables of positional parameters and final thermal parameters for (CdCp*[N(SiMe$_3$)$_2$])$_2$ (5 pages); a listing of final observed and calculated structure factors for (CdCp*[N(SiMe$_3$)$_2$])$_2$ (63 pages). Ordering information is given on any current masthead page.

Synthesis of Two Novel Pentanuclear Rhodium Clusters Bearing the Alkyl-like Ligands CH_2COOMe and CH_2CN. X-ray Structure of $[PPh_4]_2[Rh_5(\mu\text{-}CO)_6(CO)_8(CH_2CN)]$

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Summary: The reaction of $[PPh_4][Rh(CO)_4]$ (**1**) under CO with $BrCH_2COOMe$ or $BrCH_2CN$ in a 5:3 molar ratio gave high yields of the two novel clusters $[PPh_4]_2[Rh_5(CO)_{14}(CH_2COOMe)]$ (**3a**) and $[PPh_4]_2[Rh_5(CO)_{14}(CH_2CN)]$ (**3b**), respectively, which appear to be the first examples of rhodium clusters bearing an alkyl-like ligand. The first step of the reaction is the rapid formation of $[PPh_4][RhBr(CO)_2(CH_2R)]$ (R = COOMe (**2a**), CN (**2b**)), which further react, much more slowly, with an excess of $[Rh(CO)_4]^-$ to yield the cluster compounds. **3a**,**b** are indefinitely stable in the solid state under CO atmosphere. Crystals of **3b** suitable for an X-ray diffraction study could be obtained. **3b** is monoclinic, space group $P2_1/c$ with $a = 12.488$ (3) Å, $b = 43.585$ (9) Å, $c = 23.222$ (8) Å, $\beta = 91.46$ (4)°, $Z = 8$, and $R = 0.037$ for 8489 reflections having $I \geqslant 3\sigma(I)$. The $[Rh_5(CO)_{14}(CH_2CN)]^-$ anion contains an elongated trigonal-bipyramidal metallic framework bearing eight terminal and six edge-bridging carbonyls; the alkyl-like substituent is bonded to an apical Rh atom.

It has often been claimed that cluster compounds are possible models for heterogeneous catalysis, and they have even been proposed as homogeneous catalysts themselves.[1] Metal–alkyl species are often supposed to be formed at the active metal sites in many heterogeneously catalyzed reactions, but until recently, only a few osmium or rhenium clusters bearing an alkyl or alkyl-like ligand had been reported,[2] although many clusters with μ-carbene or -carbyne groups are known.

In a recent paper[3] we reported the synthesis of two iridium–alkyl clusters: $[PPh_4][Ir_4(CO)_{11}(CH_2COOMe)]$ and $[PPh_4]_2[Ir_4(CO)_{10}(CH_2COOMe)_2]$, starting from $Na[Ir(CO)_4]$ and $BrCH_2COOMe$. Here, we report our results concerning the related reaction of $[Cat][Rh(CO)_4]$ (Cat = Na, PPh_4) with a deficiency of $BrCH_2COOMe$ and $BrCH_2CN$ with respect to the 1:1 molar ratio. The reaction of $[PPN][Rh(CO)_4]$ [$PPN^+ = (PPh_3)_2N^+$] with a stoichiometric quantity of $BrCH_2COOMe$ or $BrCH_2CN$ has been previously reported by some of us as giving selectively the mononuclear compounds $[RhBr(CO)_2(CH_2R)]^-$ (R = COOMe, CN).[4]

Results and Discussion

When a THF solution of $[PPh_4][Rh(CO)_4]$[5] (**1**) is treated with a small amount of $BrCH_2COOMe$ or $BrCH_2CN$, an immediate reaction takes place, with vigorous CO evolution, yielding $[PPh_4][RhBr(CO)_2(CH_2R)]$ (R = COOMe (**2a**), CN(**2b**)).[4] All the organic bromide is consumed in a few minutes. This solution, still containing the excess **1**, upon standing reacts further (ca. 4 h in the case of **2a** and 2 h for **2b**), giving, as the only carbonyl products, two clusters (R = COOMe (**3a**), CN(**3b**)). Their IR absorption pattern is similar to that of the compounds of general formula $[Rh_5(CO)_{14}X]^{2-}$[6] (X = halide or pseudo-halide), thus suggesting structural similarity (vide infra).

$$\underset{\mathbf{1}}{[PPh_4][Rh(CO)_4]} \xrightarrow[-CO]{BrCH_2R} \underset{\mathbf{2a,b}}{[PPh_4][RhBr(CO)_2(CH_2R)]} \xrightarrow{Rh(CO)_4^-} \underset{\mathbf{3a,b}}{[PPh_4]_2[Rh_5(CO)_{14}(CH_2R)]} \quad (1)$$

The IR spectrum of **3a** also displayed an absorption band at 1675 cm^{-1}, assigned to the ν_{CO} stretching of the COOMe group, while **3b** showed an absorption at 2183

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(2) (a) Zoet, R.; Koten, G. v.; Vrieze, K.; Jansen, J.; Goubits, K.; Stam, C. H. *Organometallics* **1988**, *7*, 1565. (b) Bassner, S. L.; Morrison, E. D.; Geoffroy, G.; Rheingold, A. *Organometallics* **1987**, *6*, 2207. (c) Zuffa, J. L.; Gladfelter, W. L. *J. Am. Chem. Soc.* **1986**, *108*, 4669. (d) Morrison, E. D.; Bassner, S. L.; Geoffroy G. L. *Organometallics* **1986**, *5*, 408. (e) Cree-Uchiyama, M.; Shapley, J. R.; St. George, G. M. *J. Am. Chem. Soc.* **1986**, *108*, 1316. (f) Churchill, M. R.; Lashewycz, R. A. *Inorg. Chem.* **1978**, *17*, 1291. (g) Masters, A. F.; Mertis, K.; Gibson, J. F.; Wilkinson, G. *Nouv. J. Chim.* **1977**, *1*, 389. (h) Edwards, P. G.; Felix, F.; Mertis, K.; Wilkinson, G. *J. Chem. Soc., Dalton Trans.* **1979**, 361. (i) Hursthouse, M. B.; Malik, K. M. A. *J. Chem. Soc., Dalton Trans.* **1978**, 1334. (j) A $\sigma + \pi$ alkenyliridium cluster has also been reported: Pierpont, C. G. *Inorg. Chem.* **1979**, *18*, 2972.

(3) Ragaini, F.; Porta, F.; Demartin, F. *Organometallics* **1991**, *10*, 185.

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(5) Garlaschelli, L.; Chini, P.; Martinengo, S. *Gazz. Chim. Ital.* **1982**, *112*, 285.

(6) Fumagalli, A.; Martinengo, S.; Galli, D.; Allevi, C.; Ciani, G.; Sironi, A. *Inorg. Chem.* **1990**, *29*, 1408.

0276-7333/91/2310-3785$02.50/0

Table I. IR Data in THF Solution

compound	ν_{CO}, cm^{-1}								ref
$[PPh_4]_2[Rh_5(CO)_{14}(CH_2COOMe)]^a$ (**3a**)	2050 w	2016 s	1968 vs	1859 vw	1816 ms	1772 sh	1758 m		this work
$[PPh_4]_2[Rh_5(CO)_{14}(CH_2CN)]^b$ (**3b**)	2048 w	2018 s	1969 vs	1862 vw	1819 ms	1770 sh	1760 m		this work
$[PPh_4]_2[Rh_5(CO)_{14}(CH_2Ph)]$ (**3c**)	2049 w	2012 s	1961 vs	1856 vw	1812 ms		1753 m		this work
$[PPN]_2[Rh_5(CO)_{14}Cl]$	2059 w	2022 s	1979 vs		1828 ms	1822 sh	1767 m	1753 mw	6
$[PPN]_2[Rh_5(CO)_{14}Br]$	2053 w	2022 s	1977 vs		1827 ms		1768 m	1756 mw	6

[a] Other absorption bands: 1688 sh, 1675 w (γ_{COOMe}). [b] Other absorption bands: 2184 m (γ_{CN}).

Table II. Crystallographic Data

formula	$C_{64}H_{42}NO_{14}P_2Rh_5$
fw	1625.52
crystal system	monoclinic
space group	$P2_1/c$
a (Å)	12.488 (3)
b (Å)	43.585 (9)
c (Å)	23.222 (8)
β (deg)	91.46 (4)
V (Å^3)	12635 (9)
Z	8
D_{calcd} (g cm^{-3})	1.709
crystal dimensions (mm)	0.25 × 0.10 × 0.12
μ(Mo Kα) (cm^{-1})	13.71
min transmissn factor	0.90
scan mode	ω
ω-scan width (deg)	$1.0 + 0.35 \tan \theta$
θ range (deg)	3–22
octants of reciprocal space explored	$+h,+k,\pm l$
measd reflcns	11712
no. of unique obsd reflcns with $I > 3\sigma(I)$	8489
final R and R_w indices^a	0.037, 0.052
no. of variables	1069
GOF^b	1.993

[a] $R = [\sum(F_o - k|F_c|)/\sum F_o]$; $R_w = [\sum w(F_o - k|F_c|)^2/\sum wF_o^2]^{1/2}$. [b] $\mathrm{GOF} = [\sum w(F_o - k|F_c|)^2/(N_{observns} - N_{var})]^{1/2}$; $w = 1/(\sigma(F_o))^2$; $\sigma(F_o) = [\sigma^2(I) + (0.04I)^2]^{1/2}/2F_oLp$.

cm^{-1}, due to the CN moiety.[7] No intermediate could be observed, by IR spectroscopy, during the second step of the reaction.

In order to obtain selectively the clusters, it is necessary to use a molar ratio of bromide to **1** of 3:5. The only observed organic byproducts of the two reactions were, respectively, methyl acetate and acetonitrile (as evidenced by gas chromatographic analysis). No coupling products such as RCH_2CH_2R or $RCH_2C(O)CH_2R$ (R = COOMe, CN) could be detected. An abundant white precipitate of $[PPh_4]Br$ formed during the reaction.

Compounds **3a,b** could also be obtained in a two-step synthesis, by adding **1**, in a 2:3 molar ratio, to a preformed solution of **2a,b**, thus confirming the reaction path proposed.

Crystals of **3b** suitable for X-ray diffraction analysis were obtained by slow diffusion of a $[PPh_4]Br$-saturated 2-propanol solution into a concentrated acetone solution of the cluster.[8] The formulation of **3b** as $[PPh_4]_2[Rh_5(CO)_{14}(CH_2CN)]$, postulated on the basis of the IR spectra, has been confirmed by X-ray diffraction studies.

In the solid state, both **3a** and **3b** are indefinitely stable under a CO atmosphere, but slowly decompose under dinitrogen and very quickly in air, like the related $[Rh_5(CO)_{14}X]^{2-}$ clusters.[6] Given the necessity for a CO atmosphere, crystals of clusters **3** can be dried in vacuo only for very short periods.

Reaction of **3a,b** with an excess of the corresponding organic bromide (10:1 molar amount) resulted in a further slow reaction, which, in ca. 1 day, yielded $[RhBr_2(CO)_2]^-$[9] and methyl acetate or acetonitrile. Again, no intermediate was observed during the reaction.

Neither cluster reacts with CO (1 atm, 25 °C) to any detectable extent (IR evidence).

The ^{1}H NMR spectra of **3a,b** were also recorded. The signal of the CH_3 protons of **3b** is clearly visible as a sharp singlet at δ 3.29 (in THF-d_8). The signals due to the CH_2 groups in both **3a** and **3b** show, as expected, a fine structure because of the coupling with the rhodium atoms (^{103}Rh spin $^1/_2$, 100% natural abundance). At 80 MHz the signals for both compounds appear as broad doublets (**3a**, 1.91 ppm, J = 3.05 Hz; **3b**, 1.06 ppm, J = 1.52 Hz). At 200 MHz the signals show further splitting, due to coupling with the three rhodium atoms of the equatorial plane (see Figure 1), but the pattern of couplings is still unresolved.

$BrCH_2COOMe$ and $BrCH_2CN$ were chosen as substrates because the electron-withdrawing character of the COOMe or CN groups makes them reactive toward nucleophiles and, at the same time, stabilizes the Rh–C bond in the products. This last characteristic is useful to allow isolation of the clusters but hinders further reactivity. Accordingly, we attempted to effect reaction 1 using $PhCH_2Br$ or CH_3I as the alkylating agent. When $PhCH_2Br$ was used, the first step of the reaction was slower than in the case of the other organic halides. In contrast, the second step was faster. So the first product to be observed was a cluster (**3c**) whose IR absorption bands are shown in Table I together with those of other $[Rh_5(CO)_{14}X]^{2-}$ derivatives. Unfortunately, decomposition to $[RhBr_2(CO)_2]^-$ and toluene, caused by the still unreacted $PhCH_2Br$, started before all the $Rh(CO)_4^-$ had been consumed, thus preventing isolation of **3c** in a pure state. However, the close similarity of the IR absorption bands of **3c** with those of **3a,b**, in both shape and relative intensity (all absorptions for **3c** being at lower frequencies of the corresponding ones for **3a,b**), strongly indicates that the product is $[PPh_4]_2[Rh_5(CO)_{14}(CH_2Ph)]$.[10]

CH_3I reacted with **1** in a different way. The reaction is fast, but mixtures of clusters are obtained. The IR spectra of the solutions were very different from those of compounds **3**, so none of the obtained clusters seem to have the structure $[Rh_5(CO)_{14}R]^{2-}$ (R = CH_3, $C(O)CH_3$). Sep-

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[7] (a) The low values for both of these last stretching frequencies are typical for unsaturated groups bearing in β a transition metal. This shift has been denoted "β effect".[7b,c] For some examples of this effect in compounds related to those reported here, see refs 3 and 4. (b) Green, M. L. H. In *Organometallic Compounds*; Coates, G. E., Green, M. L. H., Wade, K., Eds.; Methuen: London, 1968; Vol. II. (c) Flood, T. C.; Di Santi, F. J.; Miles, D. L. *Inorg. Chem.* **1976**, *15*, 1910.

[8] (a) The saturation of the 2-propanol layer with $[PPh_4]Br$ decreased the solubility of the cluster in the mixed solution and allowed the rapid growth of large crystals. In the absence of the added $[PPh_4]Br$, growth of the crystals was very slow, even starting from almost saturated acetone solutions. Under these conditions almost all the cluster decomposed (see later). Use of lower polarity solvents such as toluene or n-hexane in place of 2-propanol gave only oily residues. This procedure has already been described by some of us and used to obtained crystals of $[PPh_4]_2[Ir_4(CO)_{10}(CH_2COOMe)_2]$.[3] (b) Much of the same chemistry was performed using PPN$^+$ (PPN$^+$ = $(PPh_3)_2N^+$) in place of PPh_4^+. The results are always identical.

[9] Vallarino, L. M. *Inorg. Chem.* **1965**, *5*, 433.

[10] **3c** cannot be $[PPh_4]_2[Rh_5(CO)_{14}(C(O)CH_2Ph)]$ as the IR absorption bands of the latter complex should be at higher frequencies with respect to those of **3a,b**, given the greater electronegativity of the acyl group. Moreover, no absorption around 1600 cm^{-1} due to the acyl group is detectable in the IR spectrum.

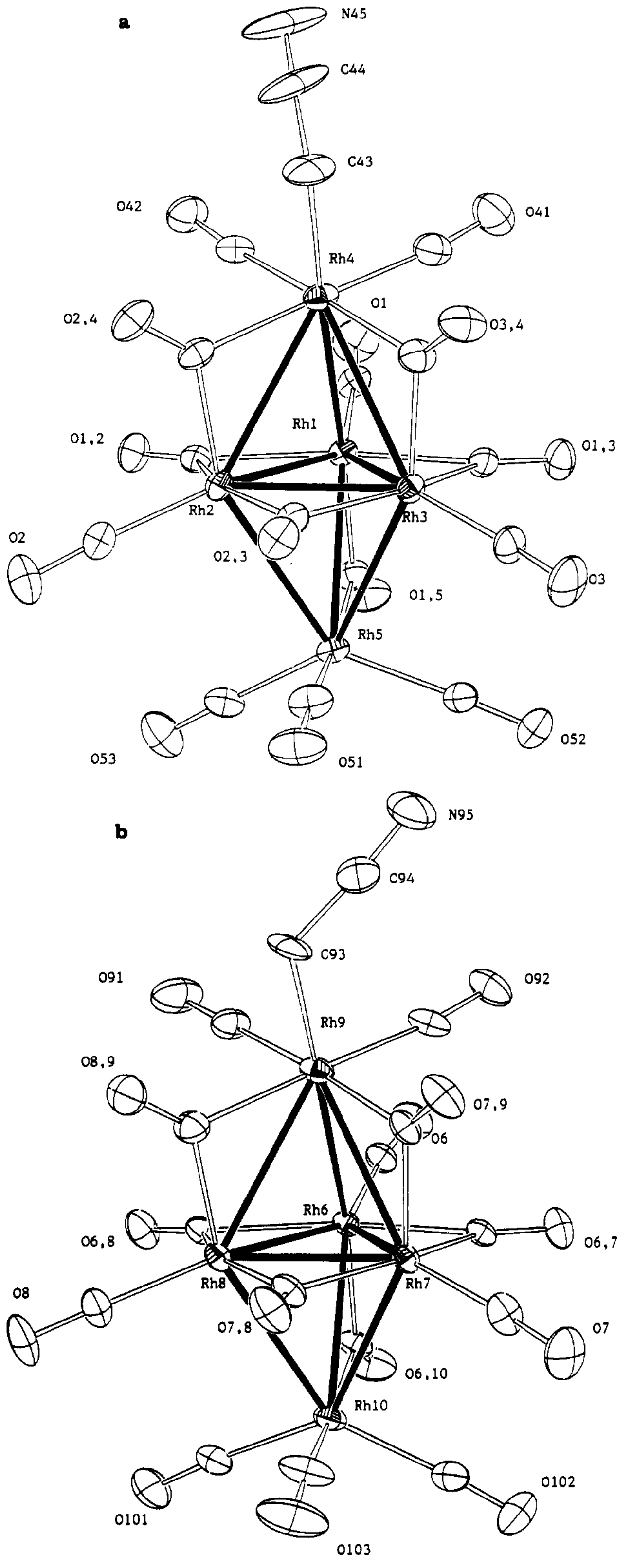

Figure 1. (a) ORTEP view of the first independent anion in the crystals of **3b**. Thermal ellipsoids are drawn at 30% probability. (b) ORTEP drawing of the second independent anion in the crystals of **3b**.

aration of these quite unstable mixtures was not attempted.

We have also tried to perform reaction 1 using the sodium salt of $[\mathrm{Rh(CO)_4}]^-$.[11] The same products as with the $\mathrm{PPh_4^+}$ or $\mathrm{PPN^+}$ countercations are obtained, but with the second step of the reaction running now faster, so that the intermediate formation of **2a,b** is no longer observable, though still probably occurring.[12]

Whatever the mechanism of formation of clusters **3**, it is surely different from that of the related $[\mathrm{Rh_5(CO)_{14}X}]^{2-}$ (X = Cl, Br, I, SCN) compounds. In this last case, the intermediate formation of $[\mathrm{Rh_5(CO)_{15}}]^-$ and the subsequent attack of $\mathrm{X^-}$ on it to yield the final product are clearly evident. In the present case, on the other hand, clustering seems to proceed by steps, starting from an already substituted mononuclear fragment.

It should be noted that although individual oxidation states for each rhodium atom cannot be easily assigned, the mean oxidation state of the rhodium atoms of the clusters **3** is $-^1/_5$. No mononuclear rhodium–alkyl complexes have ever been reported in which the oxidation state of the rhodium atom is lower than +1 and, furthermore, it is difficult to even imagine their synthesis. So these clusters represent, at least for the moment, a unique opportunity to have an alkyl group bound to a rhodium atom in such a low oxidation state.

Crystals of **3b** contain two independent $[\mathrm{Rh_5(CO)_{14}(CH_2CN)}]^{2-}$ anions, differing essentially in the conformational parameters of the $\mathrm{CH_2CN}$ moiety, and four $\mathrm{PPh_4^+}$ cations per asymmetric unit. Perspective views of the two anions are shown in parts a and b of Figure 1. Selected bond distances and angles are given in Table III. Both anions contain an elongated trigonal-bipyramidal rhodium cluster having a ligand stereogeometry similar to that previously observed in other pentanuclear 76 CVE substituted rhodium carbonyl clusters such as $[\mathrm{Rh_5(CO)_{14}X}]^{2-}$ (X = I, SCN) or $[\mathrm{Rh_5(CO)_{14}PPh_3}]^-$.[6] The alkyl-like substituent is almost trans to an unbridged Rh–Rh interaction (see the Rh(1)–Rh(4)–C(43) and Rh(6)–Rh(9)–C(93) angles, 176.7 (7) and 177.7 (3)°, respectively), as already observed in the $[\mathrm{Rh_5(CO)_{14}PPh_3}]^-$ anion, but not in the $[\mathrm{Rh_5(CO)_{14}X}]^{2-}$ (X = I, SCN) derivatives, where the substituent is trans to a bridging CO. The preference of the substituent for a given site within the $\mathrm{Rh(CO)_4X}$ moiety has already been discussed and ascribed to different steric requirements.[6]

Conclusions

As a conclusion to our investigation on the reactivity of the carbonyl anions $\mathrm{Rh(CO)_4^-}$ and $\mathrm{Ir(CO)_4^-}$ with organic halides, we can now present a general scheme showing the influence of the metal and the countercation on the reaction[13] (Scheme I). Only the most important points are discussed.

A common intermediate ($[\mathrm{MBr(CH_2)(CO)_2}]^-$) is always formed. In the case of iridium this can give a second oxidative addition, which is not observed for rhodium. The presence of a small cation ($\mathrm{Na^+}$) favors the formation of clusters, probably via the formation of ionic couples. This effect is essential for iridium, but not in the case of rhodium, for which no other reaction pathway is available under the proper experimental conditions. The formation of the rhodium clusters probably proceeds in a way analogous to that of the iridium ones.[3] The difference in

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[11] Chini, P.; Martinengo, S. *Inorg. Chim. Acta* **1969**, *3*, 21.

[12] During the reaction some NaBr precipitated. The clusters can then be isolated as $\mathrm{PPh_4^+}$ or $\mathrm{PPN^+}$ salts by exchange with a 2-propanol solution of the corresponding bromide or chloride. Although the reaction of $[\mathrm{Na}][\mathrm{Rh(CO)_4}]$ is much quicker than that of $[\mathrm{PPh_4}][\mathrm{Rh(CO)_4}]$, its preparation from $\mathrm{RhCl_3}$ gives much lower yields (40–50% against 80–90%) and the complex is less pure. Moreover, working up of reaction 1 is more complicated, and so the use of an organic countercation is preferable on a preparative scale.

[13] All reactions not described in this paper have been reported in refs 3 and 4.

Table III. Selected Bond Distances (Å) and Angles (deg) within the Two Independent $[Rh_5(CO)_{14}(CH_2CN)]^{2-}$ Anions

anion 1		anion 2	
Rh(1)–Rh(2)	2.723 (1)	Rh(6)–Rh(7)	2.722 (1)
Rh(1)–Rh(3)	2.733 (1)	Rh(6)–Rh(8)	2.735 (1)
Rh(2)–Rh(3)	2.671 (1)	Rh(7)–Rh(8)	2.671 (1)
Rh(4)–Rh(1)	2.937 (1)	Rh(9)–Rh(6)	2.953 (1)
Rh(4)–Rh(2)	2.971 (1)	Rh(9)–Rh(7)	2.973 (1)
Rh(4)–Rh(3)	2.985 (1)	Rh(9)–Rh(8)	2.971 (1)
Rh(5)–Rh(1)	2.920 (1)	Rh(10)–Rh(6)	2.919 (1)
Rh(5)–Rh(2)	3.050 (1)	Rh(10)–Rh(7)	3.054 (1)
Rh(5)–Rh(3)	3.008 (1)	Rh(10)–Rh(8)	3.021 (1)
Rh(1)–C(1)	1.875 (8)	Rh(6)–C(6)	1.875 (6)
Rh(2)–C(2)	1.844 (9)	Rh(7)–C(7)	1.863 (9)
Rh(3)–C(3)	1.862 (8)	Rh(8)–C(8)	1.865 (8)
Rh(4)–C(41)	1.931 (10)	Rh(9)–C(91)	1.940 (9)
Rh(4)–C(42)	1.951 (9)	Rh(9)–C(92)	1.949 (8)
Rh(5)–C(51)	1.913 (9)	Rh(10)–C(101)	1.947 (10)
Rh(5)–C(52)	1.918 (9)	Rh(10)–C(102)	1.915 (11)
Rh(5)–C(53)	1.923 (10)	Rh(10)–C(103)	1.919 (11)
C(1)–O(1)	1.139 (8)	C(6)–O(6)	1.147 (7)
C(2)–O(2)	1.165 (8)	C(7)–O(7)	1.139 (8)
C(3)–O(3)	1.140 (8)	C(8)–O(8)	1.144 (8)
C(41)–O(41)	1.129 (9)	C(91)–O(91)	1.109 (8)
C(42)–O(42)	1.135 (8)	C(92)–O(92)	1.126 (8)
C(51)–O(51)	1.156 (8)	C(101)–O(101)	1.107 (9)
C(52)–O(52)	1.136 (8)	C(102)–O(102)	1.122 (10)
C(53)–O(53)	1.128 (9)	C(103)–O(103)	1.153 (10)
Rh(1)–C(1,2)	2.084 (7)	Rh(6)–C(6,7)	2.079 (7)
Rh(1)–C(1,3)	2.108 (7)	Rh(6)–C(6,8)	2.084 (8)
Rh(1)–C(1,5)	1.990 (8)	Rh(6)–C(6,10)	1.984 (7)
Rh(2)–C(1,2)	2.119 (7)	Rh(7)–C(6,7)	2.081 (7)
Rh(2)–C(2,3)	2.075 (7)	Rh(7)–C(7,8)	2.065 (7)
Rh(2)–C(2,4)	2.000 (7)	Rh(7)–C(7,9)	2.008 (8)
Rh(3)–C(1,3)	2.092 (7)	Rh(8)–C(6,8)	2.126 (7)
Rh(3)–C(2,3)	2.091 (7)	Rh(8)–C(7,8)	2.065 (7)
Rh(3)–C(3,4)	1.983 (8)	Rh(8)–C(8,9)	2.000 (8)
Rh(4)–C(2,4)	2.087 (8)	Rh(9)–C(7,9)	2.082 (7)
Rh(4)–C(3,4)	2.084 (8)	Rh(9)–C(8,9)	2.073 (8)
Rh(5)–C(1,5)	2.075 (7)	Rh(10)–C(6,10)	2.071 (7)
C(1,2)–O(1,2)	1.154 (7)	C(6,7)–O(6,7)	1.178 (7)
C(1,3)–O(1,3)	1.167 (7)	C(6,8)–O(6,8)	1.161 (7)
C(1,5)–O(1,5)	1.179 (7)	C(6,10)–O(6,10)	1.180 (7)
C(2,3)–O(2,3)	1.166 (7)	C(7,8)–O(7,8)	1.175 (7)
C(2,4)–O(2,4)	1.176 (8)	C(7.9)–O(7,9)	1.182 (7)
C(3,4)–O(3,4)	1.167 (8)	C(8,9)–O(8,9)	1.160 (8)
Rh(4)–C(43)	2.211 (7)	Rh(9)–C(93)	2.201 (7)
C(43)–C(44)	1.438 (18)	C(93)–C(94)	1.411 (12)
C(44)–N(45)	1.082 (21)	C(94)–N(95)	1.197 (11)
Rh(4)–C(43)–C(44)	110.0 (7)	Rh(9)–C(93)–C(94)	108.0 (6)
C(43)–C(44)–N(45)	175.6 (19)	C(93)–C(94)–N(95)	176.3 (12)
Rh(1)–Rh(4)–C(43)	176.7 (3)	Rh(6)–Rh(9)–C(93)	177.7 (3)

the nuclearity of the final products is probably due to intrinsic instability of the tetranuclear rhodium[14] and pentanuclear iridium[15] anionic clusters under CO atmosphere.

Table IV. Fractional Atomic Coordinates for the Atoms of the Two Independent $[Rh_5(CO)_{14}(CH_2CN)]^{2-}$ Anions (Esd's in Parentheses)

atom	*x*	*y*	*z*
Rh(1)	0.27841 (5)	0.16757 (2)	0.24224 (3)
Rh(2)	0.40729 (6)	0.20197 (2)	0.31315 (3)
Rh(3)	0.30105 (6)	0.15460 (2)	0.35707 (3)
Rh(4)	0.48239 (6)	0.13982 (2)	0.28048 (3)
Rh(5)	0.16465 (6)	0.20824 (2)	0.31971 (3)
Rh(6)	0.02746 (5)	0.08479 (2)	0.81070 (3)
Rh(7)	−0.11370 (6)	0.05676 (2)	0.73657 (3)
Rh(8)	−0.00077 (6)	0.10458 (2)	0.69960 (3)
Rh(9)	−0.17277 (6)	0.11810 (2)	0.78192 (3)
Rh(10)	0.12645 (6)	0.04679 (2)	0.72326 (3)
O(1)	0.2678 (7)	0.1441 (2)	0.1202 (3)
O(2)	0.4811 (7)	0.2669 (2)	0.3332 (4)
O(3)	0.2031 (7)	0.1325 (2)	0.4661 (3)
O(6)	0.0525 (6)	0.0960 (2)	0.9385 (3)
O(7)	−0.2091 (6)	−0.0039 (2)	0.7023 (4)
O(8)	0.1019 (7)	0.1336 (2)	0.5973 (3)
O(1,2)	0.3900 (5)	0.2221 (2)	0.1861 (3)
O(1,3)	0.1453 (6)	0.1135 (2)	0.2867 (3)
O(1,5)	0.0743 (5)	0.1933 (2)	0.2008 (3)
O(2,3)	0.4353 (5)	0.1925 (2)	0.4437 (3)
O(2,4)	0.6369 (5)	0.1885 (2)	0.3240 (3)
O(3,4)	0.4550 (6)	0.1087 (2)	0.3950 (3)
O(41)	0.3859 (7)	0.0810 (2)	0.2299 (4)
O(42)	0.5616 (6)	0.1592 (2)	0.1612 (3)
O(51)	0.2211 (7)	0.2303 (2)	0.4419 (3)
O(52)	−0.0353 (6)	0.1734 (2)	0.3553 (4)
O(53)	0.1583 (8)	0.2716 (2)	0.2640 (4)
O(6,7)	−0.0914 (5)	0.0290 (2)	0.8579 (3)
O(6,8)	0.1714 (5)	0.1381 (2)	0.7737 (3)
O(6,10)	0.2281 (5)	0.0535 (2)	0.8417 (3)
O(7,8)	−0.1473 (6)	0.0736 (2)	0.6096 (3)
O(7,9)	−0.3402 (5)	0.0752 (2)	0.7308 (3)
O(8,9)	−0.1481 (6)	0.1549 (2)	0.6741 (3)
O(91)	−0.0561 (7)	0.1751 (2)	0.8258 (4)
O(92)	−0.2380 (6)	0.0954 (2)	0.9012 (3)
O(101)	0.3289 (6)	0.0803 (2)	0.6876 (4)
O(102)	0.1313 (9)	−0.0193 (2)	0.7645 (5)
O(103)	0.0573 (7)	0.0305 (3)	0.5998 (4)
N(45)	0.716 (1)	0.0949 (4)	0.2170 (7)
N(95)	−0.4396 (8)	0.1442 (3)	0.8525 (5)
C(1)	0.2705 (7)	0.1520 (2)	0.1669 (4)
C(2)	0.4553 (8)	0.2415 (2)	0.3253 (4)
C(3)	0.2381 (8)	0.1401 (2)	0.4236 (4)
C(6)	0.0457 (7)	0.0937 (2)	0.8894 (4)
C(7)	−0.1760 (8)	0.0193 (3)	0.7163 (4)
C(8)	0.0653 (8)	0.1229 (2)	0.6372 (4)
C(1,2)	0.3697 (7)	0.2062 (2)	0.2240 (4)
C(1,3)	0.2080 (7)	0.1332 (2)	0.2926 (4)
C(1,5)	0.1418 (7)	0.1910 (2)	0.2370 (4)
C(2,3)	0.3995 (7)	0.1872 (2)	0.3979 (4)
C(2,4)	0.5490 (7)	0.1806 (2)	0.3120 (4)
C(3,4)	0.4261 (8)	0.1265 (2)	0.3605 (4)
C(41)	0.4158 (9)	0.1032 (3)	0.2494 (5)
C(42)	0.5275 (8)	0.1532 (2)	0.2047 (4)
C(43)	0.6336 (9)	0.1166 (3)	0.3062 (6)
C(44)	0.684 (1)	0.1040 (4)	0.2564 (7)
C(51)	0.2078 (8)	0.2205 (3)	0.3959 (4)
C(52)	0.0398 (8)	0.1859 (2)	0.3415 (5)
C(53)	0.1615 (9)	0.2481 (2)	0.2842 (4)
C(6,7)	−0.0715 (6)	0.0470 (2)	0.8219 (4)
C(6,8)	0.1031 (7)	0.1203 (2)	0.7674 (4)
C(6,10)	0.1596 (7)	0.0596 (2)	0.8077 (4)
C(7,8)	−0.1061 (7)	0.0760 (2)	0.6555 (4)
C(7,9)	−0.2502 (7)	0.0807 (2)	0.7439 (4)
C(8,9)	−0.1209 (8)	0.1348 (2)	0.7038 (4)
C(91)	−0.0952 (8)	0.1533 (2)	0.8125 (5)
C(92)	−0.2101 (7)	0.1022 (3)	0.8572 (4)
C(93)	−0.3194 (8)	0.1445 (3)	0.7624 (5)
C(94)	−0.3845 (9)	0.1434 (3)	0.8111 (5)
C(101)	0.2543 (9)	0.0691 (3)	0.7015 (5)
C(102)	0.126 (1)	0.0052 (3)	0.7497 (5)
C(103)	0.0734 (9)	0.0386 (3)	0.6465 (5)

Just for comparison, it is interesting to mention that the cobalt–carbonyl anion, $Co(CO)_4^-$, reacts in a different way with respect to both the rhodium and iridium analogues, still being sensitive to the nature of the countercation. $NaCo(CO)_4$ reacts with CH_3I to yield $CH_3Co(CO)_4$ or $CH_3C(O)Co(CO)_4$, depending on the CO pressure, and the $RCH_2Co(CO)_4$ derivatives (R = COOMe, CN) have been synthesized.[16] On the other hand, use of $[PPN][Co(CO)_4]$ in the reaction with CH_3I led to the formation of $[CH_3C(O)Co(CO)_3I]^-$.[17] In the first case, formation of an ionic couple between Na^+ and I^- probably deactivates the iodide anion toward nucleophilic attack on $CH_3Co(CO)_4$. No

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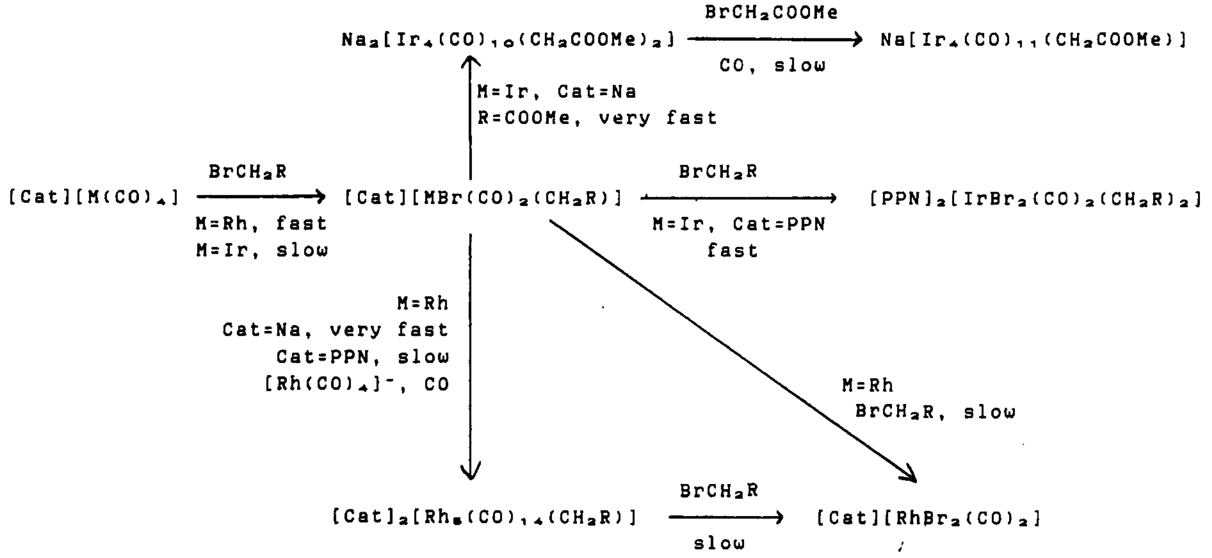
Scheme I



clusters are formed in any case.

Experimental Section

General Procedure. All reactions and manipulations were conducted at room temperature under CO atmosphere with a standard Schlenk-tube apparatus. All solvents were dried, distilled, and stored under dinitrogen before use. The organic reagents were all commercial products and were used as received. [PPN][Rh(CO)$_4$]^5 and Na[Rh(CO)$_4$]^{11} were prepared by the methods reported in the literature. IR spectra were recorded on a Perkin-Elmer 781 infrared spectrophotometer; ^{1}H NMR spectra were recorded on a Bruker VP 80 or on a Bruker AC-200 spectrometer, with reference to internal solvent. Elemental analyses were performed in the Analytical Laboratories of Milan University. Gas chromatographic analyses were conducted on a Dani 8520 packed gas chromatograph coupled to a Hewlett-Packard HP 3396 integrator or on a Perkin-Elmer 8420 capillary gas chromatograph.

Synthesis of [PPh$_4$]$_2$[Rh$_5$(CO)$_{14}$(CH$_2$COOMe)] (3a). [PPh$_4$]$_2$[Rh(CO)$_4$] (1) (800 mg, 1.44 mmol) was weighed in a Schlenk-tube under dinitrogen and dissolved in THF (4 mL). When 1 is stored for prolonged periods, it gives a crystalline form only slightly soluble in THF. However, even this form will react with the organic bromides dissolving into the solution. BrCH$_2$COOMe (132.6 mg, 80 μL, 0.87 mmol) was then added by a microsyringe, and the solution was left under stirring. The reaction was followed by IR until all 1 (ν_{CO} = 1895 cm^{-1}) and the intermediate formed, [PPh$_4$][RhBr(CO)$_2$(CH$_2$COOMe)] (2a) (ν_{CO} = 2035, 1957 cm^{-1}), disappeared. Given the high sensitivity of [PPh$_4$][Rh(CO)$_4$] to air, it is rarely perfectly pure, so a preferred procedure consisted of adding only 90% of the theoretical BrCH$_2$COOMe at the beginning of the reaction. Decreasing amounts of the organic bromide were then added. The reaction was followed by IR spectroscopy (letting the solution stand for 4 h after each addition) until the reaction was complete. During the reaction, the solution color turned from green (due to small amounts of a very intensely colored impurity) to red. An abundant white precipitate ([PPh$_4$]Br) was filtered off and washed with THF (2 × 2 mL) prior to discharge. The solution and the collected washings were evaporated in a CO stream up to Nujol consistence, and 2-propanol (3 × 10 mL) was added, trituring the residue with a glass rod until it became a powder. The solid was then washed with n-hexane (2 × 10 mL) to eliminate completely the 2-propanol and dried in a CO stream (334 mg, 70% isolated yield). Anal. Calcd for C$_{65}$H$_{45}$O$_{16}$P$_2$Rh$_5$: C, 47.0; H, 2.7. Found: C, 46.1; H, 2.4.

Synthesis of [PPh$_4$]$_2$[Rh$_5$(CO)$_{14}$(CH$_2$CN)] (3b). The synthesis is performed in the same way as the preceding one, but with use of BrCH$_2$CN (104.4 mg, 61 μL, 0.87 mmol) in place of BrCH$_2$COOMe. In this case, allowing the solution to stand for only 2 h is necessary after each addition ([PPh$_4$][RhBr(CO)$_2$(CH$_2$CN)], ν_{CO} 2041, 1961 cm^{-1}). 3b (370 mg, 79% yield) was isolated after workup. Anal. Calcd for C$_{64}$H$_{42}$O$_{14}$NP$_2$Rh$_5$: C, 47.3; H, 2.6; N, 0.9. Found: C, 47.0; H, 2.3; N, 0.9.

X-ray Data Collection and Structure Determination. Crystal data and other experimental details are summarized in Table II. The diffracted intensities were collected at variable scan speed (maximum scan time 120 s) on an Enraf-Nonius CAD-4 diffractometer at room temperature, using graphite-monochromated Mo Kα radiation (λ = 0.710 73 Å). The calculations were performed on a PDP11/73 computer using the SDP-Plus structure determination package.[18] The diffracted intensities were corrected for Lorentz, polarization, and absorption (empirical correction),[19] but not for extinction. Scattering factors for all the atomic species and anomalous dispersion corrections for scattering factors of non-hydrogen atoms were taken from ref 20. The structure was solved by direct methods (MULTAN)[21] and refined by full-matrix least-squares, minimizing the function $\sum w(F_0 - k|F_c|)^2$.

An anisotropic thermal factor was assigned to all the atoms of the anions and to the phosphorus atoms of the cations. All the hydrogen atoms of the cations were introduced in the structure model at calculated positions (C–H = 0.95 Å), and not refined. The final difference Fourier synthesis showed maximum residuals of 0.5 e/Å^3. The final atomic coordinates of the two independent anions are listed in Table IV; those of the PPh$_4^+$ cations are deposited as supplementary material.

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Registry No. 1, 74364-66-2; **2a**, 125519-32-6; **2b**, 125519-34-8; **3a**, 135952-70-4; **3b**, 135929-19-0; BrCH$_2$COOMe, 96-32-2; BrCH$_2$CN, 590-17-0; [PPh$_4$][RhBr$_2$(CO)$_2$], 135929-20-3; [PPh$_4$]$_2$[Rh$_5$(CO)$_{14}$(CH$_2$Ph)], 135929-22-5; PhCH$_2$Br, 100-39-0; CH$_3$I, 74-88-4; [Na][Rh(CO)$_4$], 57373-05-4.

Supplementary Material Available: Listings of fractional atomic coordinates of the cations and hydrogen atoms, thermal parameters, and interatomic distances and angles for **3b** (34 pages); tables of observed and calculated structure factors (57 pages). Ordering information is given on any current masthead page.

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