ever, the absence of complexes containing less than three chlorides may mean that this number is necessary to form the bridges in the dimeric structure. Whether these complexes should be viewed as containing ruthenium(II) and -(III) or two equivalent metal atoms is moot. However, the other similar ruthenium complexes on which structural data are available would favor the latter interpretation. Supporting this is the very broad, intense absorption in the visible spectrum and the diamagnetism of the corresponding ruthenium(III) dimers. In the absence of hyperfine splitting by the nuclei, the single resonance observed in the esr spectrum is consistent with both interpretations of the oxidation state. However, it should be pointed out that this resonance was assumed to arise from ruthenium(III) chloride complexes by Garif'yanov.[21] We have shown that neither the monomeric nor dimeric ruthenium(III) chloride complexes have an absorption at room temperature in aqueous solution.

The relation between our blue complexes and the ion identified by Wilkinson,[4] *et al.*, as $Ru_5Cl_{12}^{2-}$ is not clear. He assigned the oxidation state as 2+ on the basis of chemical and electrochemical reduction of ruthenium(III) chlorides. Our coulometric experiments show that this criterion may be insufficient to assign the oxidation state in the final blue complexes. Furthermore, as Wilkinson pointed out, the weak paramagnetism and esr signal which he observed is not consistent with a complex containing only ruthenium(II).

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CONTRIBUTION FROM THE CENTRO NAZIONALE DI CHIMICA DEI COMPOSTI DI COORDINAZIONE ED ELEMENTO ORGANICI DEL CNR,
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Preparation and Reactivity of Some Ruthenium Carbonyl Hydrides

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Triruthenium dodecacarbonyl reacts with CO and H_2 under convenient pressure to give $Ru(CO)_5$ and $H_4Ru_4(CO)_{12}$. Appropriate conditions are indicated for a quantitative synthesis of $H_4Ru_4(CO)_{12}$. By reaction of $H_4Ru_4(CO)_{12}$ with $P(C_4H_9)_3$ and $P(C_6H_5)_3$ the corresponding mono-, di-, tri-, and tetraphosphine-substituted ruthenium carbonyl hydrides were synthesized. The properties of $H_4Ru_4(CO)_{12}$ are compared with those reported in the literature and discussed.

Several ruthenium carbonyl hydrides have been described up to now: besides the mononuclear *cis*-$H_2Ru(CO)_4$,[1] the tri- and tetranuclear hydrides $H_4Ru_3(CO)_{10}$,[2] α-$H_2Ru_4(CO)_{13}$,[3] β-$H_2Ru_4(CO)_{13}$,[4] $H_nRu_4(CO)_{12}$,[5] α-$H_4Ru_4(CO)_{12}$,[3,4] β-$H_4Ru_4(CO)_{12}$,[4] and $H_2Ru_6(CO)_{18}$[6] have been reported. Very little however is known on their reactivity and stability.

As a result of some investigations on the catalytic activity of $Ru_3(CO)_{12}$ (I) we became interested in the stability and reactivity of ruthenium carbonyl hydrides. We had in fact found that I was an effective catalyst in the carbonylation of olefins[7-9] and acetylene[10,11] and in the hydrogenation of olefins and aldehydes.[9] By analogy with what was already suggested to rationalize the course of the hydroformylation of olefins in the presence of $Co_2(CO)_8$[12] and $RhCl[P(C_6H_5)_3]_3$[13] we have tentatively attributed this catalytic activity to the presence of one or more catalytically active ruthenium carbonyl hydrides.

In order to give experimental support to this hypothesis we started investigating the behavior of I in the presence of carbon monoxide and hydrogen at various temperatures and pressures.

Our aim was to detect, recover, and identify the ruthenium carbonyl hydrides eventually formed under hydroformylation conditions.[14]

Infrared spectroscopy was the technique chosen to detect the presence of the carbonyl derivatives in the reaction medium. By the use of a cell capable of withstanding high pressures and temperatures the deter-

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mination could actually be done under reaction conditions.

Results

Dodecacarbonyltriruthenium in the presence of carbon monoxide up to pressures of 150 atm and temperatures below 80° does not undergo any appreciable alteration even after 24 hr. At temperatures above 80°, better 100°, and pressures of carbon monoxide exceeding 10 atm the ir spectrum of I starts changing, and while new bands appear, which may be attributed to the formation of $Ru(CO)_5$ (II), the intensity of those due to I decreases.

The influence of the carbon monoxide partial pressure on the intensity of the bands due to I and II is an indication of the existence, under these conditions, of the equilibrium

$$[Ru(CO)_4]_3 + 3CO \rightleftharpoons 3Ru(CO)_5 \qquad (1)$$

The absence, in the ir spectrum of this solution, of other bands besides those of I and II may be taken as an indication that no other ruthenium carbonyl is stable, in the range of conditions explored, in appreciable concentrations.

Compound I is found unaltered after 24 hr of heating in the presence of hydrogen at temperatures below 80° and pressures up to 120 atm. At higher temperatures, 100–110°, and at hydrogen pressures exceeding 50 atm the ir spectrum of the solution shows a gradual weakening of the bands due to I while new bands appear. The relative intensity of the bands observed remains constant after 10–12 hr. However, if the gas present in the autoclave is purged and replaced with pure hydrogen, the intensity of the new bands further increases. After two to three of these treatments the ir spectrum of the solution is the one reported in Figure 1 where the bands due to I have completely disappeared. By addition of carbon monoxide under pressure (P_{CO} = 15 atm, P_{H_2} = 70 atm, T = 150°) the spectrum of the solution after a while shows, together with the new bands, also the bands characteristic of I and II.

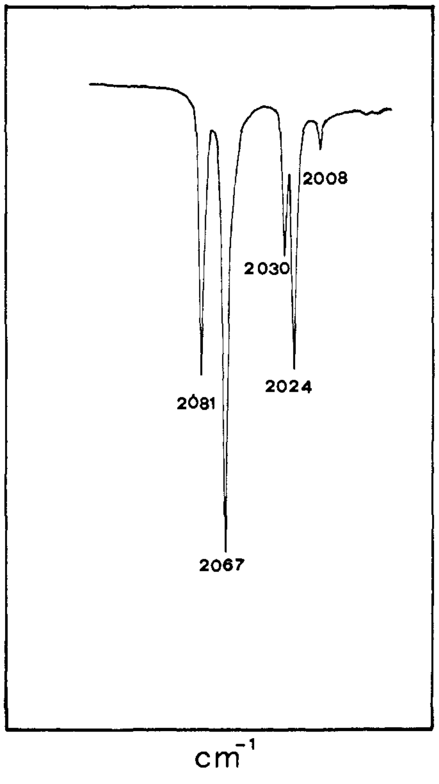

Figure 1.—Ir spectrum of $H_4Ru_4(CO)_{12}$ in cyclohexane solution.

The presence of carbon monoxide in the gas recovered from the autoclave and the technique necessary to induce the reported modifications in the ir spectrum are an indication that the reaction taking place is a partial decomposition of I controlled by carbon monoxide partial pressure. The best conditions to perform this reaction are 150° and a hydrogen partial pressure of 100 atm.

By cooling the solution obtained in such a way a microcrystalline yellow solid may be recovered in quantitative yield, which is only slightly soluble in organic solvents. Even after crystallization from tetrahydrofuran its ir spectrum is equal to that of the solution recovered from the autoclave.

Its elemental analysis suggests the minimum formula $HRu(CO)_3$.

The mass spectrum shows 13 rather complex envelopes corresponding to ions containing 4 Ru atoms and a number of CO groups varying from 0 to 12. Because of the low intensity of the spectra and of the not too good signal:noise ratio it was not possible to detect with certainty the presence of hydrogen-containing ions. The information thus acquired suggested for our hydride the formulation $H_xRu_4(CO)_{12}$.

The presence of hydrogen indicated by elemental analysis was confirmed by the presence of a resonance at τ 27.9 in the nmr spectrum.

The number of hydrogen atoms present was first determined by analyzing the mixture of carbon monoxide and hydrogen obtained by thermal decomposition of the hydride. The results of these experiments were in agreement with the formula $H_3Ru_4(CO)_{12}$. A further attempt to confirm the number of hydrogen atoms, done by nmr spectroscopy using $H_2Os(CO)_3P(C_6H_5)_3$ as internal standard, led to the formulation $H_4Ru_4(CO)_{12}$ (III) which was later proved to be the correct one.

In an effort to increase the solubility of the hydride the synthesis of its triphenyl- and tributylphosphine-substituted derivatives was attempted. The hydrogen of the phosphine could moreover act as internal standard in the determination of the hydridic hydrogens by nmr spectroscopy. The reactivity of the hydride would be tested at the same time.

Triphenylphosphine reacts with III giving rise to the formation of the products deriving from the substitution of one, two, three, and four carbon monoxide groups in III (Scheme I).

The gradual displacement of carbon monoxide is dependent on the ratio between reagents, reaction temperature, and carbon monoxide partial pressure (Scheme I). Reactions at temperatures above 100° were generally carried out in an autoclave, under pressure of hydrogen.

When III is allowed to react with an excess of triphenylphosphine at temperatures just below 70°, generally 60–70°, a mixture of $H_4Ru_4(CO)_{10}[P(C_6H_5)_3]_2$ (IV) and $H_4Ru_4(CO)_9[P(C_6H_5)_3]_3$ (V) is formed; the same compounds, IV and V, are obtained by treating $[Ru(CO)_3P(C_6H_5)_3]_3$ with hydrogen under pressure.

At higher temperatures (130°), $H_4Ru_4(CO)_8[P$-

SCHEME I

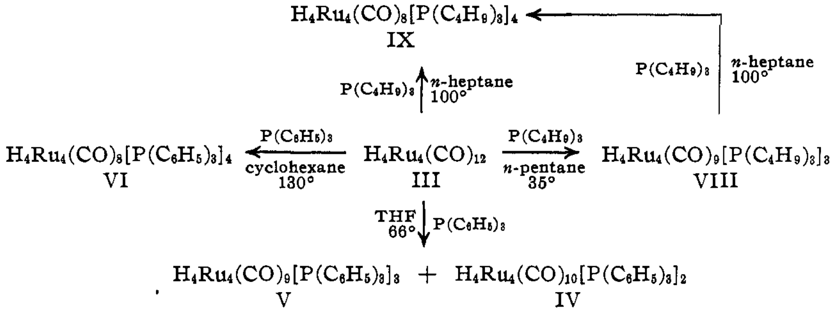

TABLE I

NMR DATA OF RUTHENIUM HYDRIDE DERIVATIVES

Compound	Chem shift[a] [H(hydride)]	Multiplicity	H(hydride)/ H(organic)	Medium
$H_4Ru_4(CO)_{12}$	27.9	Singlet	. . .	Octadeuteriofuran
$H_4Ru_4(CO)_{11}P(C_4H_9)_3$	27.7	Multiplet	3.95/27	Benzene
$H_4Ru_4(CO)_9[P(C_4H_9)_3]_3$	26.5	Multiplet	3.90/81	Hexadeuteriobenzene
$H_4Ru_4(CO)_8[P(C_4H_9)_3]_4$	26.8	Multiplet	4.10/108	Hexadeuteriobenzene
$H_4Ru_4(CO)_{11}P(C_6H_5)_3$	27.7	Multiplet	4.0/15	Tetrahydrofuran
$H_4Ru_4(CO)_{10}[P(C_6H_5)_3]_2$	26.1, 26.9	Multiplet	4.1/30	Tetrahydrofuran
$H_4Ru_4(CO)_9[P(C_6H_5)_3]_3$	26.1, 27.1	Multiplet	4.1/45	Tetrahydrofuran
$H_4Ru_4(CO)_8[P(C_6H_5)_3]_4$	25.65	Multiplet	3.9/60	Tetrahydrofuran

[a] In ppm from tetramethylsilane (10τ) as internal standard.

$(C_6H_5)_3]_4$ (VI) is obtained in almost quantitative yields.

Compounds IV and V are most conveniently obtained by displacement of a phosphine molecule with carbon monoxide under pressure from V and VI, respectively. The monosubstituted derivative $H_4Ru_4(CO)_{11}P(C_6H_5)_3$ (VII) is best prepared by an exchange reaction (eq 2), which was carried out under hydrogen pressure to prevent decomposition of the hydrides at reaction temperature (100°).

$$\underset{\text{III}}{H_4Ru_4(CO)_{12}} + \underset{\text{IV}}{H_4Ru_4(CO)_{10}[P(C_6H_5)_3]_2} \longrightarrow \underset{\text{VII}}{2H_4Ru_4(CO)_{11}P(C_6H_5)_3} \quad (2)$$

When III is allowed to react with tributylphosphine, only $H_4Ru_4(CO)_9[P(C_4H_9)_3]_3$ (VIII) and $H_4Ru_4(CO)_8[P(C_4H_9)_3]_4$ (IX) are obtained as reported in Scheme I.

The monotributylphosphine-substituted derivative of III, $H_4Ru_4(CO)_{11}P(C_4H_9)_3$ (X), is obtained by an exchange reaction from III and VIII as reported in eq 3.

$$2H_4Ru_4(CO)_{12} + H_4Ru_4(CO)_9[P(C_4H_9)_3]_3 \longrightarrow 3H_4Ru_4(CO)_{11}P(C_4H_9)_3 \quad (3)$$

Also, this reaction was carried out under hydrogen pressure.

All triphenyl- and tributylphosphine-substituted derivatives of III show a good solubility in most organic solvents and a good thermal stability even in the presence of air. They react however with halogenated solvents at room temperature.

The nmr and ir spectra of these compounds are reported in Tables I and II.

Discussion

Dodecacarbonyltriruthenium (I) under convenient pressures of carbon monoxide and hydrogen is in equilibrium with $Ru(CO)_5$ (II) and $H_4Ru_4(CO)_{12}$ (III).

The infrared spectrum of this hydride is similar to that reported by Pichler and coworkers for the compound formulated[2] as $H_4Ru_3(CO)_{10}$. The analogies between the ir spectra and the synthetic methods of the compounds obtained by Pichler and by us are a strong indication that these two products are really the same.

TABLE II

INFRARED SPECTRUM IN THE 2200–1800-CM^{-1} REGION[a]

$H_4Ru_4(CO)_{12}$	2081 s, 2067 s, 2030 m, 2024 s, 2008 w
$H_4Ru_4(CO)_{11}P(C_4H_9)_3$	2093 m, 2086 s, 2064 s, 2056 sh, 2052 vs, 2045 sh, 2032 s, 2024 s, 2007 s, 1988 s, 1973 w, 1968 m, 1959 w
$H_4Ru_4(CO)_9[P(C_4H_9)_3]_3$	2052 s, 2045 sh, 2014 vs, 1996 s, 1977 s, 1951 s, 1932 m, 1924 sh
$H_4Ru_4(CO)_8[P(C_4H_9)_3]_4$	1998 vs, 1958 s, 1938 vs, 1928 sh
$H_4Ru_4(CO)_{11}P(C_6H_5)_3$	2094 m, 2086 w, 2067 s, 2057 s, 2053 sh, 2038 w, 2032 m, 2027 s, 2015 m, 2008 s, 1998 w, 1994 w, 1966 mw
$H_4Ru_4(CO)_{10}[P(C_6H_5)_3]_2$	2082 m, 2077 s, 2058 vs, 2050 s, 2033 s, 2017 vs, 2009 s, 2000 s, 1989 m, 1973 m, 1954 m
$H_4Ru_4(CO)_9[P(C_6H_5)_3]_3$	2068 s, 2024 vs, 2003 s, 1993 s, 1987 sh, 1963 s, 1945 sh, 1940 m
$H_4Ru_4(CO)_8[P(C_6H_5)_3]_4$	2016 s, 1984 m, 1952 m, 1930 w

[a] Cyclohexane solution.

The analytical and spectroscopic results collected on both the hydride III and its phosphine-substituted derivatives do not allow doubts as to the $H_4Ru_4(CO)_{12}$ formulation. The nmr spectrum of III shows a hydride resonance at τ 27.9, very near that found for α-$H_4Ru_4(CO)_{12}$ (τ 27.6)[3,4] and for $H_nRu_4(CO)_{12}$ (τ 27.5).[5]

The ir spectrum of α-$H_4Ru_4(CO)_{12}$ reported by Johnson[3] shows, besides the bands common to the spectrum of the hydride we have prepared, a strong band at 2061 cm^{-1} and two very weak ones at 1984 and 1973 cm^{-1}. While we have no good explanation for the two weak bands, the strong band seems due to the presence of I.

A sample of α-$H_4Ru_4(CO)_{12}$ prepared as described by Johnson, *et al.*,[3,4] had in fact the ir spectrum reported for it by these authors; however the relative intensity of the various bands changed by chromatographic purification of the sample, and, carrying on the purification, a sample of α-$H_4Ru_4(CO)_{12}$ having an ir spectrum equal to that of the product prepared by us could be obtained. Moreover the ir spectrum of a mixture of approximately equal amounts of I and III is identical with that of the sample of α-$H_4Ru_4(CO)_{12}$ prepared according to Johnson, *et al.*[15]

All the physical–chemical properties of the hydride we have prepared are in agreement with those suggested by Johnson, *et al.*,[4] for a tetrahedral arrangement of four ruthenium atoms surrounded by terminal carbonyl groups and bridging hydrogens. The bands at 2081, 2067, 2030, 2024, and 2008 cm^{-1} are in agreement with a D_{2d} structure, as proposed by Johnson, *et al.*, for which five infrared-active bands are predicted in the carbonyl stretching region (2 B_2 + 3 E).

The number (4) and position of the bands present in the ir spectra of the tetrasubstituted phosphine derivatives $H_4Ru_4(CO)_8P_4$ [P = $P(C_6H_5)_3$ or $P(C_4H_9)_3$] are indicative of an even distribution of the phosphines on the ruthenium atoms. The possibility of formation of different isomeric species due to the relative position of the phosphine however exists even in this case.

The ir spectrum is in near agreement with a D_{2d} structure for which three infrared-active CO stretching vibrations (B_2 + 2 E) are predicted. The weak band at 1928 cm^{-1} present in the spectrum of both VI and IX may be due to ^{13}C isotopic effect.

The ir spectra of the di- and trisubstituted phosphine derivatives IV, V, and VIII are so complex that no conclusion may be drawn on the location of the phosphine on the cluster.

A phosphine disposition on different ruthenium atoms is suggested by the consecutive formation of the di- and trisubstituted derivatives IV and V by displacement of the phosphine with carbon monoxide from VI.

The consecutive substitution of CO groups in III by phosphines may be carried out gradually by controlling both reaction temperature and reagent concentration. Under a convenient pressure of carbon monoxide the reverse reaction may be obtained. This behavior is quite different from that of $[Ru(CO)_3P(C_6H_5)_3]_3$ which reacts with carbon monoxide to form $Ru(CO)_4P(C_6H_5)_3$.[16] While $[Ru(CO)_3P(C_6H_5)_3]_3$ reacts with carbon monoxide with fission of the metal–metal bond, the phosphine ligand is displaced by carbon monoxide in V and VI.

Fission of the metal–metal bond by carbon monoxide may be obtained in this class of compounds when IV is treated with carbon monoxide: $Ru(CO)_4P(C_6H_5)_3$ is in fact the product.

The synthesis of VII by reaction of equimolar amounts of III and IV is analogous to that described by Szabò, *et al.*,[17] to prepare $Co_2(CO)_7P(C_6H_5)_3$ from $Co_2(CO)_8$ and $[Co(CO)_3P(C_6H_5)_3]_2$.

The catalytic activity of these ruthenium carbonyl hydrides is actually under investigation.

The very low concentration of III under the conditions most suited for the carbonylation of olefins and acetylene in the presence of I is however a strong argument against its contribution to the activity of the ruthenium carbonyl catalytic system in these reactions.

Experimental Section

Infrared spectra were measured in the specified solvents with a Perkin-Elmer Model 225 spectrometer. Infrared spectra under pressure were recorded using a cell having NaCl optics, developed by us, capable of withstanding high pressures (200 atm) and temperatures (up to 150°). The sample was transferred from the autoclave into the cell through a stainless steel coil kept at the required temperature. Proton nmr spectra were observed on a JEOL 60 instrument, on solutions in specified solvents using tetramethylsilane as an internal standard. Mass spectra were recorded on a LKB 9000 instrument (ionizing voltage 70 V, ion-source temperature 150°, direct-inlet system temperature 60°). Both nmr and ir data are reported in Tables I and II.

Molecular weights were determined either by differential vapor pressure measurements performed at 25° using a Mechrolab osmometer in specified solvents or from mass spectra. Carbon and hydrogen determinations were carried out by the Laboratorio di Microanalisi della Facolta di Farmacià della Università di Pisa. The composition of H_2–CO mixtures was determined by vapor phase chromatography using a Perkin-Elmer Model 154 B instrument equipped with a silica gel column and argon as carrier gas.

Chemicals.—Triruthenium dodecacarbonyl was prepared according to the method described by Pino, *et al.*;[18] $H_2Os(CO)_3P(C_6H_5)_3$ was synthesized according to L'Eplattenier, *et al.*[19]

Preparation of Complexes. $\mathbf{H_4Ru_4(CO)_{12}}$.—$Ru_3(CO)_{12}$ (0.600 g, 0.94 mmol) and 50 ml of *n*-heptane were heated in a 125-ml stainless steel autoclave at 150° under a hydrogen pressure of 150 atm. Small portions of the solution were transferred from time to time through a stainless steel coil into the high-pressure cell kept at 150°, and the ir spectrum was recorded.

After 4 hr the spectrum characteristic of $Ru_3(CO)_{12}$ had completely disappeared. The autoclave was then cooled, the gas vented, and the yellow solution collected together with 0.500 g of $H_4Ru_4(CO)_{12}$ as a yellow solid. From the mother liquor, evaporated to dryness, 0.020 g of the same solid was recovered; yield 99%. $H_4Ru_4(CO)_{12}$ was recrystallized from tetrahydrofuran. *Anal.* Calcd for $H_4Ru_4(CO)_{12}$: C, 19.36; H, 0.54; Ru, 54.31. Found: C, 19.43; H, 0.50; Ru, 54.59.

A 0.0982-g sample of $H_4Ru_4(CO)_{12}$ heated at 500° for 2 hr evolved 39.97 cm^3 (n.c.) of gas. Its composition, by gc analysis, appeared to be 8:1 = CO:H_2.

A solution of 0.0037 g (4.97 × 10^{-6} mol) of $H_4Ru_4(CO)_{12}$ and 0.0045 g (8.35 × 10^{-6} mol) of $H_2Os(CO)_3P(C_6H_5)_3$ in octadeuteriofuran (0.8 ml) gave an nmr spectrum where the intensity of the resonances at τ 27.9 and τ 18.0 due to the hydridic hydrogens of the ruthenium and osmium complexes, respectively, indicated the presence of four hydrogen atoms for each $Ru_4(CO)_{12}$ group.

$\mathbf{H_4Ru_4(CO)_9[P(C_4H_9)_3]_3}$.—A suspension of 0.50 g (0.67 mmol) of $H_4Ru_4(CO)_{12}$ in 0.75 g (3.7 mmol) of $P(C_4H_9)_3$ and 50 ml of *n*-pentane was refluxed for 15 hr under nitrogen. The red solution formed was evaporated to dryness. The residue was first washed with cool (−20°) methanol and then slowly crystallized from methanol giving 0.70 g of $H_4Ru_4(CO)_9[P(C_4H_9)_3]_3$ as deep red, long needles (82% yield). *Anal.* Calcd for $H_4Ru_4(CO)_9[P(C_4H_9)_3]_3$: C, 42.64; H, 6.76; mol wt 1267.4. Found: C, 42.64; H, 6.73; mol wt 1298 (benzene solution).

$\mathbf{H_4Ru_4(CO)_8[P(C_4H_9)_3]_4}$.—A suspension of 0.500 g (0.67 mmol) of $H_4Ru_4(CO)_{12}$ in 0.75 g (3.7 mmol) of $P(C_4H_9)_3$ and 30 ml of *n*-heptane was refluxed for 10 hr under nitrogen. The red solution formed was evaporated to dryness. The residue was washed with cool methanol (−20°) and then dissolved in 70 ml of hot methanol. From this solution $H_4Ru_4(CO)_8[P(C_4H_9)_3]_4$ crystallized as long orange needles (0.794 g, 82% yield). *Anal.* Calcd for $H_4Ru_4(CO)_8[P(C_4H_9)_3]_4$: C, 46.65; H, 7.83; mol wt 1441.7. Found: C, 46.95; H, 7.84; mol wt 1395 (benzene solution).

From an *n*-heptane solution (10 ml) of 0.100 g of $H_4Ru_4(CO)_9[P(C_4H_9)_3]_3$ (0.079 mmol) and 0.05 g of $P(C_4H_9)_3$ (0.24 mmol) refluxed for 3 hr and worked up as described above, 0.096 g of $H_4Ru_4(CO)_8[P(C_4H_9)_3]_4$ (84% yield) was obtained.

$\mathbf{H_4Ru_4(CO)_{11}P(C_4H_9)_3}$.—In a 125-ml autoclave were placed 0.100 g (0.079 mmol) of $H_4Ru_4(CO)_9[P(C_4H_9)_3]_3$, 0.120 g (0.161 mmol) of $H_4Ru_4(CO)_{12}$, 20 ml of tetrahydrofuran, and finally hydrogen up to 90 atm. The autoclave was then heated at 100° for 8 hr. After cooling, the gas was vented and a red solution was recovered and evaporated to dryness. The residue was purified by thin layer chromatography on silica gel using pentane as the eluent. A 0.05-g amount of $H_4Ru_4(CO)_{11}P(C_4H_9)_3$ was recovered as orange-red crystals after crystallization from pentane

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at −20° (23% yield). *Anal.* Calcd for $H_4Ru_4(CO)_{11}P(C_4H_9)_3$: C, 30.06; H, 3.40; mol wt 918.7. Found: C, 30.4; H, 3.40; mol wt 985 (benzene solution).

$H_4Ru_4(CO)_{10}[P(C_6H_5)_3]_2$ and $H_4Ru_4(CO)_9[P(C_6H_5)_3]_3$.—(a) A suspension of 0.50 g (0.67 mmol) of $H_4Ru_4(CO)_{12}$ in 50 ml of tetrahydrofuran and 0.80 g (3.06 mmol) of $P(C_6H_5)_3$ was refluxed for 10 hr under nitrogen. The red solution obtained was evaporated and the solid residue, dissolved in the minimum amount of CH_2Cl_2, was separated into its components by thin layer chromatography. The solid phase was silica gel. A 2.3:1 mixture of pentane and benzene was initially used to get rid of the excess of phosphine while with a 1:1 mixture of the same solvents the solid could be split into two red bands. The two components could be recovered by elution with CH_2Cl_2 and were then both recrystallized from a CH_2Cl_2 solution by addition of pentane. We thus recovered 0.285 g (0.235 mmol) of $H_4Ru_4(CO)_{10}[P(C_6H_5)_3]_2$ as brown-red plates (35% yield) and 0.389 g (0.269 mmol) of $H_4Ru_4(CO)_9[P(C_6H_5)_3]_3$ as deep red crystals (40% yield).

(b) A solution of 0.100 g (0.074 mmol) of $[Ru(CO)_3P(C_6H_5)_3]_3$ in 10 ml of tetrahydrofuran was heated in a 125-ml autoclave at 100° for 4 hr under a hydrogen pressure of 130 atm. The red solution obtained was worked up as described in procedure (a) giving 0.039 g (0.032 mmol) of $H_4Ru_4(CO)_{10}[P(C_6H_5)_3]_2$ (60% yield) and 0.026 g (0.018 mmol) of $H_4Ru_4(CO)_9[P(C_6H_5)_3]_3$ (34% yield).

$H_4Ru_4(CO)_{10}[P(C_6H_5)_3]_2$.—A tetrahydrofuran (7 ml) solution of $H_4Ru_4(CO)_9[P(C_6H_5)_3]_3$ (0.10 g, 0.069 mmol) was heated at 130° for 2 hr in a 125-ml autoclave under pressure of carbon monoxide (100 atm) and hydrogen (40 atm). From the solution obtained, 0.081 g (0.067 mmol) of $H_4Ru_4(CO)_{10}[P(C_6H_5)_3]_2$ was recovered by addition of *n*-pentane (96.8% yield). *Anal.* Calcd for $H_4Ru_4(CO)_{10}[P(C_6H_5)_3]_2$: C, 45.5; H, 2.82; mol wt 1213. Found: C, 45.46; H, 2.85; mol wt 1202 (methyl ethyl ketone solution).

$H_4Ru_4(CO)_9[P(C_6H_5)_3]_3$.—A tetrahydrofuran (8 ml) solution of 0.100 g (0.0595 mmol) of $H_4Ru_4(CO)_8[P(C_6H_5)_3]_4$ was heated in a 125-ml autoclave at 130° for 2 hr under pressure of carbon monoxide (110 atm) and hydrogen (40 atm). By addition of pentane to the solution obtained 0.0835 g (0.0577 mmol) of $H_4Ru_4(CO)_9[P(C_6H_5)_3]_3$ was recovered (97% yield). *Anal.* Calcd for $H_4Ru_4(CO)_9[P(C_6H_5)_3]_3$: C, 52.28; H, 3.41; mol wt 1447.2. Found: C, 52.28; H, 3.95; mol wt 1514 (methyl ethyl ketone solution).

$H_4Ru_4(CO)_8[P(C_6H_5)_3]_4$.—In a 125-ml autoclave were placed 0.100 g (0.134 mmol) of $H_4Ru_4(CO)_{12}$, 0.300 g (1.14 mmol) of $P(C_6H_5)_3$, 20 ml of cyclohexane, and then hydrogen up to the pressure of 100 atm. The autoclave was heated at 130° for 2 hr. After cooling, the gases were vented and the pressure was restored with new hydrogen. The heating of the autoclave was continued for 14 hr. After cooling, a pale red solution and a red microcrystalline solid (0.220 g; 97%) were recovered. After crystallization of the solid from CH_2Cl_2 and pentane 0.177 g (0.105 mmol) of $H_4Ru_4(CO)_8[P(C_6H_5)_3]_4$ was recovered (78% yield). This product has a low solubility in aliphatic solvents and a better one in the aromatic ones. *Anal.* Calcd for $H_4Ru_4(CO)_8[P(C_6H_5)_3]_4$: C, 57.14; H, 3.89. Found: C, 57.60; H, 3.65.

$H_4Ru_4(CO)_{11}P(C_6H_5)_3$.—In a 125-ml autoclave were placed 0.124 g (0.167 mmol) of $H_4Ru_4(CO)_{12}$, 0.200 g (0.165 mmol) of $H_4Ru_4(CO)_{10}[P(C_6H_5)_3]_2$, 20 ml of tetrahydrofuran, and finally hydrogen up to 90 atm. The autoclave was heated at 100° for 8 hr. After cooling, the gas was vented and a red solution was recovered which was evaporated to dryness. The residue was purified by thin layer chromatography on silica gel using pentane as the eluent. A 0.060-g (0.061-mmol) amount of $H_4Ru_4(CO)_{11}P(C_6H_5)_3$ was recovered as yellow-brown crystals after crystallization from a cyclohexane–pentane mixture (yield 18.5%). *Anal.* Calcd for $H_4Ru_4(CO)_{11}P(C_6H_5)_3$: C, 35.59; H, 1.96; mol wt 978.7. Found: C, 35.99; H, 2.00; mol wt 943 (benzene solution).

$Ru(CO)_4P(C_6H_5)_3$.—In a 125-ml autoclave a solution of 0.12 g (0.1 mmol) of $H_4Ru_4(CO)_{10}[P(C_6H_5)_3]_2$ in 7 ml of tetrahydrofuran was treated with CO under pressure (100 atm) in the presence of hydrogen (40 atm) at 150° for 3 hr. After cooling, the gas was vented and a yellow solution was recovered which was evaporated to dryness. The residue was purified by chromatography on an alumina column using a benzene–pentane mixture as the eluent and gave 0.08 g of $Ru(CO)_4P(C_6H_5)_3$[16] (84% yield).

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Electronic Spectra of Some Pentacarbonyl Compounds of Manganese and Rhenium

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The electronic spectra of some $LM(CO)_5$ compounds of C_{4v} or related symmetry are reported in the range 5000–1900 Å in the vapor and solution phases. L may be CF_3, CH_3, H, Cl, Br, or I and M may be Mn or Re. The compounds have been classified according to the σ and π properties of the ligand. Band assignments are made and qualitative molecular orbital energy diagrams are given to account for charge-transfer bands. The low-energy spectra of the tetracarbonyl dimers of Mn are reported and related to those of C_{4v} compounds.

Introduction

In recent years a large number of metal carbonyl compounds have been prepared and examined. For most of these, structural interpretations based on the ir spectra and assignments have been published.[1-5] Only a limited amount of uv and visible spectral data has appeared and a small number of assignments and interpretations have been made.[6-8] Photoelectron (pe) spectra have appeared for a number of these compounds[9] and recent MO calculations have been published for $HMn(CO)_5$ and the pentacarbonyl halides.[10]

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