complexes, which substantiate and extend the ideas discussed here, will be communicated shortly.[19]

Conclusions

Lewis bases will react with $CH_3Mn(CO)_5$, most likely by a methyl-migration mechanism, to yield *cis*-$CH_3COMn(CO)_4L$ as the preferred product. Whether or not partial conversion of a *cis*-acetylmanganese complex to the *trans* isomer will occur is apparently a function of particular steric, nucleophilic, and π-acceptor properties of that ligand. The decarbonylation of *cis*-$CH_3COMn(CO)_4L$ complexes to *cis*-$CH_3Mn(CO)_4L$ can be rationalized on the basis of a modified methyl-migration mechanism.

[19] P. K. Maples and C. S. Kraihanzel, *J. Am. Chem Soc.*, in press.

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On the Reactivity of Tris(triphenylphosphine)triruthenium Enneacarbonyl

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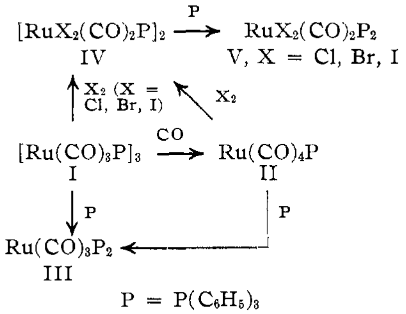
By reaction of $[Ru(CO)_3P(C_6H_5)_3]_3$ with CO, $Ru(CO)_4P(C_6H_5)_3$ has been prepared from which, with halogens (X = Cl, Br, I) or $CHCl_3$, $[RuX_2(CO)_2P(C_6H_5)_3]_2$ complexes were obtained. These last compounds could also be formed from $[Ru(CO)_3P(C_6H_5)_3]_3$ and halogens. From the ir spectral data a structure with bridging halogens is suggested for the dimeric compounds $[RuX_2(CO)_2P(C_6H_5)_3]_2$. $[Os(CO)_3P(C_6H_5)_3]_3$ reacts with CO with displacement of $P(C_6H_5)_3$ and formation of $[Os(CO)_4]_3$.

Investigating the chemical behavior of cluster ruthenium carbonyls,[1,2] the reactivity of $[Ru(CO)_3P(C_6H_5)_3]_3$ (I) with CO and halogens has been studied. At 150°, in benzene solution, I reacts with CO (150 atm) to give, in quantitative yield, a pale yellow crystalline compound which analyzes as $Ru(CO)_4P(C_6H_5)_3$ (II), the first example of a monosubstituted derivative of $Ru(CO)_5$ (eq 1).



(1)

The cleavage of the metal–metal bonds in I by CO is analogous to the one performed by $P(C_6H_5)_3$ on I and $P(C_4H_9)_3$ on $[Ru(CO)_3P(C_4H_9)_3]_3$ to obtain $Ru(CO)_3[P(C_6H_5)_3]_2$ and $Ru(CO)_3[P(C_4H_9)_3]_2$ previously reported.[1] These reactions, like the formation of $RuI_2(CO)_3P(C_6H_5)_3$ from $[Ru(CO)_3P(C_6H_5)_3]_3$ and I_2,[2,3] support a symmetrical structure for I, with a phosphine molecule attached to each Ru atom.

By heating II with an excess $P(C_6H_5)_3$, in benzene solution at 100°, $Ru(CO)_3[P(C_6H_5)_3]_2$ (III) is formed in quantitative yield.

By reaction of II with an equimolecular amount of I_2 in refluxing acetone $[Ru(CO)_2P(C_6H_5)_3I_2]_2$ (IVc) is obtained. The same compound (identical ir spectrum) is obtained by treating I with I_2 (1:3 mol) under the same conditions.

$[Ru(CO)_2P(C_6H_5)_3Br_2]_2$(IVb) and $[Ru(CO)_2P(C_6H_5)_3Cl_2]_2$ (IVa), analogous to IVc, are obtained by treating I with a stoichiometric amount of the corresponding halogen.

The formation of IVa is obtained also by reaction of II with CCl_4 or $CHCl_3$ at room temperature and from I in refluxing CCl_4 with a behavior analogous to the one observed when CCl_4 or $CHCl_3$ reacts with $[Ru(CO)_4]_3$.[4] The fate of the residue of the CCl_4 and $CHCl_3$ molecules after chlorine abstraction is not clear: in the case of $CHCl_3$ small amounts of CH_2Cl_2 have been detected by vpc.

The binuclear ruthenium carbonyls IVa, IVb, and IVc react at 30–50° with an excess of $P(C_6H_5)_3$ to give the corresponding $Ru(CO)_2[P(C_6H_5)_3]_2X_2$ (V) derivatives described by Collman and Roper.[5]

The ir spectrum of II (Table I) in the C=O stretching region is analogous to that of $Fe(CO)_4P(C_6H_5)_3$[6] and suggests also for II a trigonal-bipyramidal structure. The weak band at 1906 cm^{-1} might be related to the ^{13}C isotopic shift associated with the strong band appearing at 1940 cm^{-1}.

The ir spectra of the binuclear ruthenium carbonyls

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[1] (a) F. Piacenti, M. Bianchi, E. Benedetti, and G. Sbrana, *Chim. Ind* (Milan), **48**, 762 (1966); (b) F. Piacenti, M. Bianchi, E. Benedetti, and G. Sbrana, *J. Inorg. Nucl. Chem.*, **29**, 1389 (1967).

[2] J. P. Candlin, K. K. Joshi, and D. T. Thompson, *Chem. Ind.* (London), 1960 (1966).

[3] D. Seyferth and R. B. King, "Annual Surveys of Organometallic Chemistry," Elsevier Publishing Co., Amsterdam, 1967, p 370.

[4] G. Braca, G. Sbrana, P. Pino, and E. Benedetti, *Chim. Ind.* (Milan), **49**, 1381 (1967).

[5] J. P. Collman and W. R. Roper, *J. Am. Chem. Soc.*, **87**, 4008 (1965).

[6] F. A. Cotton and R. V. Parish, *J. Chem. Soc.*, 1440 (1960).

Table I

Compound	Medium	CO stretching, cm^{-1}
$Ru(CO)_4P(C_6H_5)_3$	Nujol	2060 s, 1980 m, 1940 vs, 1906 vw
$[RuI_2(CO)_2P(C_6H_5)_3]_2$	CH_2Cl_2	2061 s, 2005 s
$[RuBr_2(CO)_2P(C_6H_5)_3]_2$	CH_2Cl_2	2068 s, 2011 s
$[RuCl_2(CO)_2P(C_6H_5)_3]_2$	CH_2Cl_2	2074 s, 2013 s
$[Os(CO)_3P(C_6H_5)_3]_3$[a]	CH_2Cl_2	2053 w, 1998 sh, 1985 s, 1972 s, 1940 m
$[Os(CO)_3P(C_4H_9)_3]_3$	CH_2Cl_2	1962 vs, 1917 m
$Os(CO)_3[P(C_6H_5)_3]_2$[b]	CH_2Cl_2	1885 s

[a] C. W. Bradford and R. S. Nyholm, *Chem. Commun.*, 384 (1967), report 2053 w, 1988 s, 1969 s, 1927 s, 1957 sh cm^{-1} for the spectrum in Nujol mull. [b] J. P. Collman and W. R. Roper, *J. Am. Chem. Soc.*, **88**, 3504 (1966), report 1890 cm^{-1} in KBr pellets.

IVa, IVb, and IVc show, in the C═O stretching region, only two bands, in keeping with the formulation proposed, suggesting the presence of only terminal carbonyl groups. These bands, as expected,[7,8] are progressively shifted toward lower wave numbers in passing from Cl to Br to I derivatives.

No definite evidence is at present available to assign a structure to compounds IVa, IVb, and IVc. However the ir spectrum in the low-frequency region of IVa, showing three bands at 321, 268, and 240 cm^{-1}, seems to suggest for this compound a dimeric structure with both bridging and terminal halogens. The ir spectrum in the same region of $[Ru(CO)_3Cl_2]_2$[9] which has two halogen bridges and two terminal halogens shows three bands at 332, 295, and 262 cm^{-1} of which the first might be assigned to the terminal ruthenium–chlorine stretching vibration[10] and the other two bands to the stretching vibration of M–Cl–M bonds on the basis of what is known on Pt, Pd,[11] and Rh[12] complexes. Assuming then that the difference in frequency between the bands appearing in the spectrum of IVa and $[Ru(CO)_3Cl_2]_2$ is due to $P(C_6H_5)_3$[12] in the molecule of IVa, the same type of metal–halogen bonds seems to be present in both compounds.

$[Os(CO)_3P(C_6H_5)_3]_3$ (VI) recently described by Bradford and Nyholm[13] and $[Os(CO)_3P(C_4H_9)_3]_3$ (VII) were prepared from $[Os(CO)_4]_3$ and the corresponding phosphine in refluxing toluene.

By treating VI and VII, respectively, with an excess of $P(C_6H_5)_3$ and $P(C_4H_9)_3$ in benzene solution at 200–220°, $Os(CO)_3[P(C_6H_5)_3]_2$ (VIII) and $Os(CO)_3[P(C_4H_9)_3]_2$ (IX) were obtained. More severe conditions were in fact necessary to obtain the same reaction on the Os than on the Ru derivatives.

While VIII could be isolated and analyzed and did show in the ir spectrum a band at 1885 cm^{-1} as described by Collman and Roper for *trans*-$Os(CO)_3[P(C_6H_5)_3]_2$,[14] evidence for the formation of IX is based on the presence in the ir spectrum of the reaction mixture of only one strong band at 1864 cm^{-1} in the C═O stretching region.

The difference in reactivity of I and VI toward CO is shown in eq 2.

$$\begin{gathered}[Ru(CO)_3P(C_6H_5)_3]_3 + 3CO \longrightarrow 3Ru(CO)_4P(C_6H_5)_3 \\ [Os(CO)_3P(C_6H_5)_3]_3 + 3CO \longrightarrow [Os(CO)_4]_3 + 3P(C_6H_5)_3\end{gathered} \qquad (2)$$

In fact, while in the case of the ruthenium derivative the metal–metal bonds are broken with formation of the mononuclear species, in the case of the Os derivative the phosphine is replaced by CO with formation of $[Os(CO)_4]_3$.

This different behavior of I and VI should be attributed to the different strength of the metal–metal bonds in these carbonylic derivatives and to the different affinity of Ru and Os for CO and $P(C_6H_5)_3$.

Experimental Section

Chemicals.—Triruthenium dodecacarbonyl was prepared according to the method described by Pino, *et al.*;[15] triosmium dodecacarbonyl was obtained by the procedure of Bradford and Nyholm.[13]

Spectral Measurements.—Infrared spectra in Nujol and CH_2Cl_2 solutions of the complexes were recorded with a Perkin-Elmer Model 225 spectrophotometer.

Molecular Weight Determinations.—Molecular weights were determined by differential vapor pressure measurements carried out at 25° using a Mechrolab osmometer. Benzene, CCl_4, and CH_2Br_2 were used as solvents.

Analysis.—Carbon and hydrogen determinations were performed by "Laboratorio di Microanalisi della Facoltà di Farmacia della Università di Pisa;" halogen and P determinations were done by A. Bernhardt-Mikroanalytisches Laboratorium, Max-Planck-Institut.

Preparation of Complexes. **$[Ru(CO)_3P(C_6H_5)_3]_3$.**—A solution of 0.644 g (2.47 mmol) of $P(C_6H_5)_3$ in 30 ml of methanol was mixed with 0.46 g (0.72 mmol) of $[Ru(CO)_4]_3$ and then refluxed for 7 hr. A dark violet precipitate was formed (0.93 g, 99% yield) which recrystallized from benzene–pentane as needles having a melting point of 174–176° under vacuum. *Anal.* Calcd for $[Ru(CO)_3P(C_6H_5)_3]_3$: C, 56.29; H, 3.37; P, 6.91; Ru, 22.7; mol wt, 1344.0. Found: C, 56.15; H, 3.31; P, 6.76; Ru, 21.8; mol wt, 1403. In an analogous experiment carried out in a gas volumetric apparatus, heating for 8 hr at 65° a mixture of 0.1436 g (0.22 mmol) of $[Ru(CO)_4]_3$ and 0.39 g (1.5 mmol) of $P(C_6H_5)_3$ in 25 ml of *n*-butyl alcohol, 0.293 g (97% yield) of $[Ru(CO)_3P(C_6H_5)_3]_3$ was obtained and 15.5 cm^3 (normal conditions) of CO was evolved (CO expected for the loss of a CO molecule per Ru atom, 15.15 cm^3).

$Ru(CO)_4P(C_6H_5)_3$.—One gram (0.74 mmol) of $[Ru(CO)_3P(C_6H_5)_3]_3$ and 40 ml of benzene were placed in a 125-ml autoclave and heated at 150° for 4 hr under a CO pressure of 160 atm. After cooling the autoclave, the residual gas was vented and a pale yellow solution was collected which, after concentration (to 3 ml) at room temperature and reduced pressure, was passed through a chromatographic column prepared with Al_2O_3 in *n*-pentane. By eluting with a benzene–pentane (1:1) mixture a pale yellow compound was recovered (0.98 g, 92.5% yield) which recrystallized from benzene–pentane as prisms decomposing above 120° without melting. *Anal.* Calcd for $Ru(CO)_4P(C_6H_5)_3$: C, 55.58; H, 3.18; P, 6.52; Ru, 21.26;

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(14) J. P. Collman and W. R. Roper, *J. Am. Chem. Soc.*, **88**, 3504 (1966).

(15) G. Braca, G. Sbrana, and P. Pino, *Chim. Ind.* (Milan), **46**, 206 (1964).

mol wt, 475.38. Found: C, 55.31; H, 3.14; P, 6.70; Ru, 21.40; mol wt, 485 (benzene solution).

$Ru(CO)_3[P(C_6H_5)_3]_2$.—A solution of 0.55 g (2.1 mmol) of $P(C_6H_5)_3$ and 0.30 g (0.22 mmol) of $[Ru(CO)_3P(C_6H_5)_3]_3$ in 20 ml of methyl isobutyl ketone was heated at 125° for 4 hr. From this solution, by cooling at −30°, 0.36 g (76% yield) of $Ru(CO)_3[P(C_6H_5)_3]_2$ was recovered as pale yellow crystals which, after crystallization from benzene–pentane, melted at 250–251°. $Ru(CO)_3[P(C_6H_5)_3]_2$ was also obtained by heating for 3 hr at 100° in a pressure vessel a solution of 0.1 g (0.21 mmol) of $Ru(CO)_4P(C_6H_5)_3$ and 0.06 g (0.23 mmol) of $P(C_6H_5)_3$ in 7 ml of benzene. After cooling, by addition of 10 ml of pentane, 0.07 g (47% yield) of $Ru(CO)_3[P(C_6H_5)_3]_2$ was collected.

$[RuI_2(CO)_2P(C_6H_5)_3]_2$.—(I) A solution of 0.450 g (0.335 mmol) of $[Ru(CO)_3P(C_6H_5)_3]_3$ in 20 ml of acetone was treated at room temperature with a solution of 0.250 g (1 mmol) of I_2 in 8 ml of acetone and then heated to reflux for 2 hr. A yellow solid was formed and collected after evaporation of most of the solvent. By recrystallization from CH_2Br_2–pentane, 0.6 g (89% yield) of $[RuI_2(CO)_2P(C_6H_5)_3]_2$ as light brown crystals was recovered, mp 235–240°. *Anal.* Calcd for $[RuI_2(CO)_2P(C_6H_5)_3]_2$: C, 35.68; H, 2.24; P, 4.60; I, 37.71; mol wt, 1346.34. Found: C, 35.65; H, 2.14; P, 4.59; I, 37.57; mol wt, 1275 (in CH_2Br_2).

(II) A solution of 0.47 g (1 mmol) of $Ru(CO)_4P(C_6H_5)_3$ in 25 ml of acetone was treated with 0.27 g (1.06 mmol) of I_2 and then refluxed for 2 hr. Working up the solution as described above, 0.6 g (90% yield) of light brown crystals, was collected, identified as $[RuI_2(CO)_2P(C_6H_5)_3]_2$ from its spectrum.

$[RuBr_2(CO)_2P(C_6H_5)_3]_2$.—A solution of 0.3 g (0.223 mmol) of $[Ru(CO)_3P(C_6H_5)_3]_3$ in 5 ml of CH_2Br_2 was treated with 0.11 g (0.69 mmol) of Br_2 in 2 ml of CH_2Br_2 at room temperature and then heated to 60° for 2 hr. After cooling, by addition of 10 ml of *n*-pentane 0.3 g (78% yield) of pale yellow crystals was recovered which could be recrystallized from CH_2Br_2–pentane. *Anal.* Calcd for $[RuBr_2(CO)_2P(C_6H_5)_3]_2$: C, 41.47; H, 2.61; Br, 27.60; P, 5.35; mol wt, 1158.39. Found: C, 40.40; H, 2.54; Br, 27.66; P, 5.51; mol wt, 1033 (in CH_2Br_2).

$[RuCl_2(CO)_2P(C_6H_5)_3]_2$.—This compound could be obtained from $[Ru(CO)_3P(C_6H_5)_3]_3$ and $Ru(CO)_4P(C_6H_5)_3$ in the following ways.

(I) A stream of Cl_2 was bubbled through a solution of 0.2 g (0.15 mmol) of $[Ru(CO)_3P(C_6H_5)_3]_3$ in 5 ml of CH_2Cl_2 at room temperature up to decoloration. The solvent was then evaporated and the solid residue was crystallized from CH_2Cl_2–*n*-pentane. White crystals (0.15 g, 63% yield) of $[RuCl_2(CO)_2P(C_6H_5)_3]_2$ were obtained, mp >250°. *Anal.* Calcd for $[RuCl_2(CO)_2P(C_6H_5)_3]_2$: C, 48.99; H, 3.08; P, 6.31; Cl, 14.46. Found: C, 48.63; H, 3.04; P, 6.34; Cl, 14.56.

(II) By refluxing a solution of 0.1 g (0.074 mmol) of $[Ru(CO)_3P(C_6H_5)_3]_3$ in 3 ml of CCl_4 for 30 min a pale yellow solution was obtained from which, on cooling, 0.10 g (84% yield) of a white crystalline precipitate was recovered, identified as $[RuCl_2(CO)_2P(C_6H_5)_3]_2$ by its ir spectrum. An analogous experiment carried out using $CHCl_3$ as solvent gave the same solid product. By vpc analysis of the residual solvent the formation of a small amount of CH_2Cl_2 was recognized.

(III) From a solution of 0.2 g (0.42 mmol) of $Ru(CO)_4P(C_6H_5)_3$ in 6 ml of CCl_4, on standing at room temperature, a white crystalline precipitate (0.15 g 67% yield) was formed and was identified, after crystallization from CH_2Cl_2–pentane, as $[RuCl_2(CO)_2P(C_6H_5)_3]_2$ from its ir spectrum.

$RuI_2(CO)_2[P(C_6H_5)_3]_2$.—By heating 0.16 g (0.12 mmol) of $[RuI_2(CO)_2P(C_6H_5)_3]_2$ with 0.1 g (0.38 mmol) of $P(C_6H_5)_3$ dissolved in 5 ml of CH_2Br_2 at 70° for 1 hr, the solution was discolored. On cooling and addition of *n*-pentane, white crystals were recovered which, after crystallization from benzene–*n*-pentane, did show in the $C{=}O$ stretching region of the ir spectrum two strong bands at 1993 and 2054 cm^{-1}, in good agreement with that reported for $RuI_2(CO)_2[P(C_6H_5)_3]_2$ by Collman and Roper.[5] *Anal.* Calcd for $RuI_2(CO)_2[P(C_6H_5)_3]_2$: C, 48.79; H, 3.23. Found: C, 48.71; H, 3.30.

$RuBr_2(CO)_2[P(C_6H_5)_3]_2$.—By treating 0.07 g (0.06 mmol) of $[RuBr_2(CO)_2P(C_6H_5)_3]_2$ with 0.06 g (0.23 mmol) of $P(C_6H_5)_3$ in 5 ml of CH_2Br_2 at 50° for 1 hr a colorless solution was obtained from which, by addition of *n*-pentane, 0.08 g (79% yield) of $RuBr_2(CO)_2[P(C_6H_5)_3]_2$ was recovered. Its ir spectrum in the $C{=}O$ stretching region showed two bands at 1997 and 2057 cm^{-1} (CH_2Cl_2 solution). Collman and Roper[5] reported for the same compound absorption bands in the ir spectrum at 2050 and 1990 cm^{-1} (KBr pellet). *Anal.* Calcd for $RuBr_2(CO)_2[P(C_6H_5)_3]_2$: C, 54.24; H, 3.59. Found: C, 54.02; H, 3.70.

$RuCl_2(CO)_2[P(C_6H_5)_3]_2$.—By treating 0.1 g (0.093 mmol) of $[RuCl_2(CO)_2P(C_6H_5)_3]_2$ with 0.06 g (0.22 mmol) of $P(C_6H_5)_3$ in 7 ml of CH_2Cl_2 at reflux temperature for 30 min a solution was obtained from which, by *n*-pentane addition, 0.12 g (80% yield) of $RuCl_2(CO)_2[P(C_6H_5)_3]_2$ was obtained as white crystals. The ir spectrum showed two strong bands in the $C{=}O$ stretching region at 2059 and 1996 cm^{-1} (CH_2Cl_2 solution). Collman and Roper[5] reported for the same compound two bands at 1990 and 2050 cm^{-1} (KBr pellet). *Anal.* Calcd for $RuCl_2(CO)_2[P(C_6H_5)_3]_2$: C, 60.64; H, 4.02. Found: C, 60.21; H, 3.92.

$[Os(CO)_3P(C_4H_9)_3]_3$.—In a gas volumetric apparatus a solution of 0.1 g (0.11 mmol) of $[Os(CO)_4]_3$ and 0.2 g (1 mmol) of $P(C_4H_9)_3$ in 20 ml of toluene under N_2 was heated at 110° for 3 hr; 7.3 cm^3 of CO (normal conditions) was evolved. After cooling the solution, the solvent was evaporated and the residue was crystallized from methanol three times obtaining 0.1 g (63% yield) of $[Os(CO)_3P(C_4H_9)_3]_3$ as orange needles, mp 81–82°. *Anal.* Calcd for $[Os(CO)_3P(C_4H_9)_3]_3$: C, 37.80; H, 5.71; P, 6.50; mol wt, 1429.65. Found: C, 37.61; H, 5.62; P, 6.61; mol wt, 1490.

$Os(CO)_3[P(C_6H_5)_3]_2$.—A mixture of 0.20 g (0.12 mmol) of $[Os(CO)_3P(C_6H_5)_3]_3$ and 0.3 g. (1.1 mmol) of $P(C_6H_5)_3$ was heated under N_2 at 220° for 2 hr. The brown liquid thus obtained was dissolved in CH_2Cl_2, and by addition of ethyl alcohol a white crystalline solid was obtained. After recrystallization from CH_2Cl_2–ethyl alcohol, its ir spectrum in the 2200–1800-cm^{-1} region showed only one strong band at 1885 cm^{-1} (CH_2Cl_2 solution) as described by Collman and Roper for *trans*-$Os(CO)_3[P(C_6H_5)_3]_2$.[14] *Anal.* Calcd for $Os(CO)_3[P(C_6H_5)_3]_2$: C, 58.64; H, 3.78; mol wt, 798.79. Found: C, 58.54; H, 3.85; mol wt, 795.

An analogous experiment carried out on a mixture of 0.2 g (0.14 mmol) of $[Os(CO)_3P(C_4H_9)_3]_3$ and 0.3 g (1.5 mmol) of $P(C_4H_9)_3$ gave a brown liquid which, dissolved in *n*-pentane, did show an ir spectrum with only one band at 1864 cm^{-1} in the 2200–1800-cm^{-1} region. $Os(CO)_3[P(C_4H_9)_3]_2$ could not however be isolated. For the reaction of $[Os(CO)_3P(C_6H_5)_3]_3$ with CO, in a 125-ml autoclave 0.1 g (0.062 mmol) of $[Os(CO)_3P(C_6H_5)_3]_3$ in 50 ml of isooctane was heated to 180° under a CO pressure of 150 atm. After 2 hr the autoclave was cooled and the residual gas was vented. $[Os(CO)_4]_3$ was recovered in almost quantitative yield.