554 *Inorg. Chem.* **1993**, *32*, 554–560

Oxidative Addition of Methyl Iodide to Monosubstituted and Disubstituted Derivatives of Ruthenium Pentacarbonyl: Preparation of Neutral and Ionic Complexes of Ruthenium

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Received June 25, 1992

The oxidative addition of CH_3I to $Ru(CO)_4PMe_3$ (**1**) gives the methyl complex $Ru(CO)_3PMe_3(CH_3)I$ (**3**); with PMe_3 complex **3** gives the acetyl complexes $Ru(CO)_2(PMe_3)_2(COCH_3)I$ (isomers **10a** and **10b**), which, by decarbonylation, give $Ru(CO)_2(PMe_3)_2(CH_3)I$ (**4**). Complex **4** can also be obtained by oxidative addition of CH_3I to $Ru(CO)_3(PMe_3)_2$ (**2**). Complex **4** reacts at room temperature with the nucleophiles CO, PMe_3, and $P(OMe)_3$ giving the acetyl complexes (structures **7**, **15**, and **18**, respectively), which at higher temperatures isomerize to **8**, **16**, and **19**, respectively. Decarbonylation of these complexes gives complex **4** (in the case of CO), complex **12** (in the case of PMe_3), and complex **13** (in the case of $P(OMe)_3$). This last complex reacts with different nucleophiles (PMe_3, $P(OMe)_3$) and gives the ionic tetraphosphine complexes $[Ru(CO)(PMe_3)_3P(OMe)_3(CH_3)]I$ (**22**) and $[Ru(CO)(PMe_3)_2(P(OMe)_3)_2(CH_3)]BPh_4$ (**24**), respectively. The trisubstituted cyano derivative $Ru(CO)(PMe_3)_2P(OMe)_3(CH_3)CN$ (**14**) is obtained by the reaction of complex **22** with KCN in acetone. The structures of the various complexes were assigned, in most cases, on the basis of spectroscopic (IR, ^1H, ^{31}P, ^{13}C) information.

Introduction

Organometallic complexes of ruthenium are very active catalysts in homogeneous catalysis,[1] more active[2] than the corresponding complexes of iron[3] and osmium.[4] This behavior may depend on the different rates of oxidative addition,[5] insertion,[6] and reductive elimination,[7] which are essential steps of the homogeneous catalysis.

The direct oxidative addition of alkyl halides on monosubstituted and disubstituted derivatives of $Ru(CO)_5$ is complex,[8] but the dihalide derivatives, conveniently obtained by the reaction of $RuCl_3$ with L (phosphine ligands) in the presence of CO,[9] were used with electrophiles such as SnR_4 or HgR_2 and HgRX to form a series of alkyl and aryl derivatives.[10–13]

The oxidative addition reactivity of the ruthenium derivatives is anomalous compared with the behavior of the other metals of the same group.[2]

The reactivity of monosubstituted and disubstituted phosphine derivatives of $Ru(CO)_5$ toward methyl iodide has been investigated to compare their reactivities with similar derivatives of iron[14] and osmium.[15] Some preliminary results were previously communicated.[16]

We tried to prepare alkyl carbonyl complexes of ruthenium with various phosphine ligands in order to complete the series of $M(CO)_nL_{4-n}RY$ complexes. The alkyl tetraphosphine substituted derivatives of ruthenium were recently prepared[17] and their reductive elimination was studied.[18]

Experimental Section

The solvents (*n*-hexane, *n*-heptane, benzene, CH_2Cl_2, diethyl ether, acetone) were dehydrated by conventional methods[19] and deaerated by bubbling with nitrogen. Tetrahydrofuran (THF) was purified as described in ref 20 and freshly distilled before use. CH_3I was purified as described in ref 21 and stabilized with Hg. Trimethylphosphine was prepared by following the method described by Schmidbaur.[22] $Ru_3(CO)_{12}$ and other phosphine ligands are commercial products.

The IR spectra were carried out with a 1725X FT IR Perkin-Elmer spectrophotometer or with a 983 Perkin-Elmer dispersive spectrophotometer. The ^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectra were recorded

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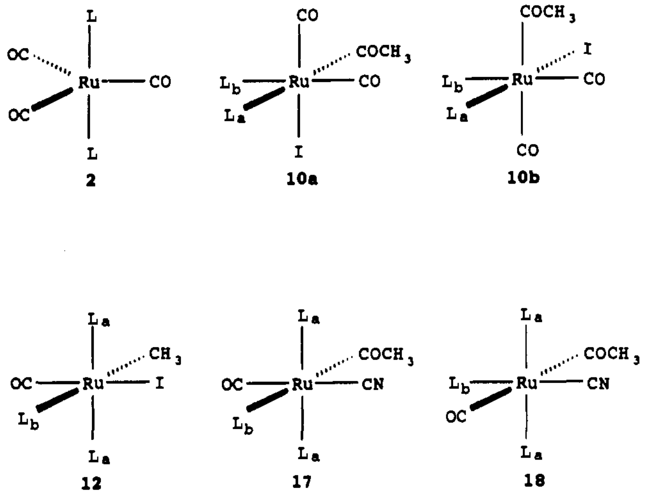

2 10a 10b

12 17 18

Figure 1. Structures of the complexes (L = PMe_3).

with a Bruker AC 200 spectrometer. The ^1H and $^{13}C\{^1H\}$ NMR chemical shifts are relative to tetramethylsilane as internal reference, and the $^{31}P\{^1H\}$ NMR chemical shifts are relative to 85% H_3PO_4 in D_2O as external reference with a positive sign indicating a shift to lower field. The elemental analyses were carried out with a Carlo Erba 1106 elemental analyzer.

The structure of the complexes are given in Figure 1 and in Schemes I–IV; their IR and NMR characterization is given in Tables I–III.

Preparation of $Ru(CO)_4PMe_3$ (1) and $Ru(CO)_3(PMe_3)_2$ (2). $Ru_3(CO)_{12}$ (3.03 g) was dissolved in diethyl ether (200 mL); an excess of an ether solution of PMe_3 (50 mL) was added. The reaction was completed after 15 h at room temperature and under stirring; then the solvent was evaporated under reduced pressure. The solid residue contained $Ru(CO)_4PMe_3$[23] (**1**), $Ru(CO)_3(PMe_3)_2$[24] (**2**), and $[Ru(CO)_3PMe_3]_3$,[25] which were purified by fractional sublimation. $Ru(CO)_4PMe_3$ (1.78 g, yield 43%) was sublimed at room temperature and at 10^{-2} mmHg; $Ru(CO)_3(PMe_3)_2$ (0.72 g, yield 15%) was sublimed at 60 °C and at 10^{-2} mmHg; the residue contained $[Ru(CO)_3PMe_3]_3$ (1.42 g, yield 38%).

With an increase of the reaction temperature to 65 °C and operation in a Carius tube in diethyl ether, the yield of **1** decreased (21%) and the yields of **2** and $[Ru(CO)_3PMe_3]_3$ increased (24% and 50%, respectively).

Preparation of $Ru(CO)_3PMe_3(CH_3)I$ (3). $Ru(CO)_4PMe_3$ (**1**) (2.2 g) was reacted with CH_3I (8 mL) at 0 °C. The reaction was completed in 12 h. The solvent was evaporated by a flux of nitrogen. The solid residue was dissolved in diethyl ether and crystallized by adding *n*-hexane at −18 °C. A yellow powder of complex **3** was obtained (1.5 g, yield 49%). It analyzed as $C_7H_{12}IPO_3Ru$. Anal. Found: C, 21.1; H, 3.11. Calcd: C, 20.86; H, 3.00.

Reaction of Complex 3 with Carbon Monoxide. Complex **3** reacted in solution (*n*-hexane, CH_2Cl_2) with CO at P = 1 atm, giving two acetyl complexes $Ru(CO)_3PMe_3(COCH_3)I$ (the CO and $COCH_3$ stretching frequencies are given in Table I); one of these was clearly characterized by NMR. ^1H NMR in CD_2Cl_2: δ_{PMe_3} = 1.7 ppm (d) ($^2J_{HP}$ = 10.1 Hz); δ_{COCH_3} = 2.50 ppm (s). $^{31}P\{^1H\}$NMR in CD_2Cl_2: δ_P = −14.7 ppm (s). The other was observed by $^{31}P\{^1H\}$NMR spectrum at δ_P = −15.4 ppm (s). The other bands were not clearly assigned. The reaction was reversible, and by N_2 flux complex **3** was obtained. The acetyl complexes were not isolated and characterized.

The mixture of acetyl complexes did not react with $NaBPh_4$ in CH_3OH. It reacted with $AgBF_4$ giving an intermediate which showed the CO stretching bands at ν = 2167 cm^{-1} (s), 2120 cm^{-1} (s), and 2086 cm^{-1} (vs). This intermediate is very unstable and decomposes. The IR spectrum suggests the structure $[Ru(CO)_4PMe_3(CH_3)]BF_4$, described for the isoelectronic osmium derivative.[15a]

Reaction of Complex 3 with PMe_3. Complex **3** (1.0 g) in ethyl ether (50 mL) was reacted with an excess of PMe_3 (2 g). A fast reaction was observed with formation of a mixture of acetyl complexes. The solvent was removed at reduced pressure, and the solid residue was dissolved in CH_2Cl_2 and crystallized by addition of *n*-hexane at room temperature as a yellow powder (0.84 g, yield 80%). ^1H and $^{31}P\{^1H\}$ NMR spectra in CD_2Cl_2 indicated the presence of two acetyl isomers (**9** and **10a** or **10b**).

Table I. IR CO, $COCH_3$, and CN Stretching Bands of the Complexes

complex	ν_{CO}, cm^{-1}	ν_{COCH_3}, cm^{-1}	ν_{CN}, cm^{-1}
1[c]	2058 s, 1982 s, 1944 vs		
2[c]	1890		
3[a]	2096 s, 2041 s, 2000 s		
4[a]	2022 s, 1955 s		
$[Ru(CO)_3(PMe_3)(COCH_3)I]$[a]	2117, 2096, 2049, 2031, 2015, 1999	1635	
5[b]	2026 s, 1970 s		2121
6[b]	2114 vw, 2044 vs		
7[a]	2037 s, 1978 s	1613	
8[a]	2080 vw, 1988 vs	1611	
9[a]	2043 s, 1994 s	1625	
10a,b[a]	2041 s, 1977 s	1623	
11[d]	2043 s, 1984 s		
12[a]	1926		
13[b]	1940		
14[b]	1958		2107
15[a]	1966	1589	
16[a]	1974	1592	
17, 18[b]	1962	1605	2108, 2097
21[b]	2055 s, 1996 s		
22[b]	1984		
23[c]	1956		
24[b]	2000		
25[b]	2004	1607	

[a] *n*-Hexane. [b] CH_2Cl_2. [c] Ethyl ether. [d] Acetone.

The mixture of the two acetyl isomers (0.5 g) was dissolved in *n*-hexane at 68 °C. After 1 h the equilibrium between the two acetyl isomers shifted and one isomer was observed in solution. By cooling of the solution to −18 °C a yellow solid precipitated (0.3 g, yield 60%). It was separated by filtration and dried. It analyzed as $C_{10}H_{21}IP_2O_3Ru$. Anal. Found: C, 24.8; H, 4.5. Calcd: C, 25.06; H, 4.42. The structure of **9** was assigned on the basis of spectroscopic characterization (Tables I–III).

If the mixture of acetyl complexes was heated to 68 °C in *n*-hexane with N_2 flux, a slow decarbonylation process occurred and the formation of $Ru(CO)_2(PMe_3)_2(CH_3)I$ (**4**) was observed. Complex **4** is isolated and characterized by comparison with a specimen prepared by another method (vide infra).

Preparation of $[Ru(CO)_3(PMe_3)_2CH_3]BPh_4$ (6). A mixture of the acetyl complexes (0.29 g), obtained as described previously, dissolved in CH_3OH (30 mL) was reacted with a solution of $NaBPh_4$ (0.5 g) in CH_3OH (10 mL). An immediate precipitation was observed with formation of a white microcrystalline solid, which was separated by filtration (0.25 g, yield 90%). It analyzed as $C_{34}H_{41}BP_2O_3Ru$. Anal. Found: C, 60.5; H, 6.25. Calcd: C, 60.81; H, 6.15. Its structure was assigned by comparison with a specimen prepared as described in ref 26.

Preparation of Complex $Ru(CO)_2(PMe_3)_2(CH_3)I$ (4). $Ru(CO)_3(PMe_3)_2$ (**2**) (0.72 g) was dissolved in CH_3I (15 mL) at 0 °C. The reaction was completed in a few minutes. The solvent was removed by N_2 flux, and the solid residue was dissolved in *n*-hexane and decarbonylated with N_2 flux at the boiling temperature of *n*-hexane. After 1 h the decarbonylation was completed and the complex **4** was crystallized at −18 °C as a white-yellow solid (0.79 g, yield 79%). It analyzed as $C_9H_{21}IO_2P_2Ru$. Anal. Found: C, 23.80; H, 4.75. Calcd: C, 23.96; H, 4.69.

Reaction of Complex 4 with the Nucleophiles PMe_3, $P(n\text{-}Bu)_3$, and $P(OMe)_3$. (a) PMe_3. An excess of an ether solution of PMe_3 (10 mL) was added to a solution in *n*-hexane (50 mL) of complex **4** (0.52 g) at room temperature. An immediate precipitation of a white-yellow solid (0.54 g, yield 89%) was observed. It analyzed as $C_{12}H_{30}IP_3O_2Ru$. Anal. Found: C, 27.00; H, 5.62. Calcd: C, 27.33; H, 5.74. The structure was tentatively assigned as complex **15** (Scheme II). Complex **15** at 60 °C, in *n*-hexane, gave an equilibrium with the isomer **16**.

Attempts to decarbonylate these complexes in *n*-hexane and in *n*-heptane in the temperature range 30–90 °C were unfruitful. The formation of a complex (**12**) with a stretching CO at 1926 cm^{-1} was observed only in *n*-heptane at 80–90 °C. Structure **12** was tentatively assigned to this complex by comparison with the well-characterized

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Table II. ^{1}H NMR Spectral Data (δ, ppm, and J, Hz) for the Complexes in CD_2Cl_2

complexes	δ_{CH_3} and $^3J_{HP}$	δ_{COCH_3} and $^4J_{HP}$	δ_{PMe_3} and J	$\delta_{P(OMe)_3}$ and $^3J_{HP}$
1			1.64, $\lvert ^2J_{HP}\rvert = 10.2$	
2			1.59, $\lvert ^2J_{HP} + {}^4J_{HP}\rvert = 7.6$	
3	0.38 d, 7.8		1.71, $\lvert ^2J_{HP}\rvert = 9.7$	
4	−0.03 t, 8.1		1.61, $\lvert ^2J_{HP} + {}^4J_{HP}\rvert = 7.6$	
5	−0.46 t, 7.9		1.47, $\lvert ^2J_{HP} + {}^4J_{HP}\rvert = 6.7$	
6	−0.18 t, 7.1		1.61, $\lvert ^2J_{HP} + {}^4J_{HP}\rvert = 7.9$	
7		2.57 s		
8		2.30 s	1.68, $\lvert ^2J_{HP} + {}^4J_{HP}\rvert = 7.6$	
9		2.47 s	1.59,[a] $\lvert ^2J_{HP}\rvert = 9.7$, $\lvert ^4J_{HP}\rvert = 0.9$, $\lvert ^2J_{PP}\rvert = 57$	
10a,b[b]		2.83 s		
11	−0.44 q, 8.0		1.55 (L_a), $\lvert ^2J_{HP} + {}^4J_{HP}\rvert = 6.8$, 1.42 d ($L_b$), $\lvert ^2J_{HP}\rvert = 8.2$	
13	0.04 q, 6.9		1.54, $\lvert ^2J_{HP} + {}^4J_{HP}\rvert = 7.0$	3.68 d, 10.4
14	−0.38 td, 7.1 (L), 5.7 (L′)		1.45, $\lvert ^2J_{HP} + {}^4J_{HP}\rvert = 7.0$	3.65 d, 11.0
15		2.33 d, 0.4 (L_b)	1.61 (L_a), $\lvert ^2J_{HP} + {}^4J_{HP}\rvert = 6.6$, 1.49 d ($L_b$), $\lvert ^2J_{HP}\rvert = 7.7$	
17, 18		2.24 s	1.49 (L_a), $\lvert ^2J_{HP} + {}^4J_{HP}\rvert = 6.6$	
17, 18		2.40 s	1.47 (L_a), $\lvert ^2J_{HP} + {}^4J_{HP} = 6.7$, 1.39 d ($L_b$), $\lvert ^2J_{HP}\rvert = 6.6$	
19		2.57 s	1.59, $\lvert ^2J_{HP} + {}^4J_{HP}\rvert = 7.3$	3.73 d, 10.0
20		2.31 s	1.61, $\lvert ^2J_{HP} + {}^4J_{HP}\rvert = 7.3$	3.82 d, 10.0
21	−0.35 q, 7.7		1.54, $\lvert ^2J_{HP} + {}^4J_{HP}\rvert = 7.5$	3.75 d, 10.8
22	−0.43 dq, 7.4 (L), 5.1 (L′)		1.48 (L_a), $\lvert ^2J_{HP} + {}^4J_{HP}\rvert = 6.7$, 1.40 d ($L_b$), $\lvert ^2J_{HP}\rvert = 8.1$	3.77 d, 10.6
24[c]	−0.30 dq, 6.8 (L), 6.8 (L'_a), 5.1 (L'_b)		1.49, $\lvert ^2J_{HP} + {}^4J_{HP}\rvert = 7.5$	3.80 d, 10.7, 3.84 d, 10.3
25		2.34 d, 0.6 (L'_b)	1.50, $\lvert ^2J_{HP} + {}^4J_{HP}\rvert = 7.6$	3.74 d, 10.3, 3.90 d, 10.1

[a] Completely solved $H_9PP'H_9'$ system.[30] [b] Toluene-d_8. [c] Acetone-d_6.

complex **13** (vide infra). This complex was not isolated since the decarbonylation equilibrium was shifted toward complex **4**.

(b) P(*n*-Bu)₃. An excess of P(n-Bu)$_3$ (molar ratio 7/1) was added to a solution of complex **4** (0.3 g) in n-hexane (35 mL) at room temperature. The reaction proceeded slowly. After 1 week the precipitation of complex **15**, previously characterized in part **a** of this section, and the formation of $Ru(CO)_2(PMe_3)P(n\text{-}Bu)_3(CH_3)I$ and $Ru(CO)_2(P(n\text{-}Bu)_3)_2(CH_3)I$ suggested a scrambling process of P(n-Bu)$_3$ and PMe$_3$. The insertion reaction occurred only in complex $Ru(CO)_2(PMe_3)_2(CH_3)I$. The formation of the $Ru(CO)_2(PMe_3)P(n\text{-}Bu)_3(CH_3)I$ and $Ru(CO)_2(P(n\text{-}Bu)_3)_2(CH_3)I$ complexes was supported by the IR spectrum of the residue solution that showed a downshift and a broadening of the two CO stretching bands. The reaction carried out at 60 °C proceeded in the same manner.

(c) P(OMe)₃. Complex **4** (0.2 g) in n-hexane (50 mL) at room temperature was reacted with P(OMe)$_3$ (1 mL). An instantaneous formation of a white precipitate was observed. The solid was filtered and washed with n-hexane. The solid (0.21 g, yield 82%) analyzed as $C_{12}H_{30}IP_3O_5Ru$. Anal. Found: C, 24.6; H, 5.52. Calcd: C, 25.05; H, 5.26. The ^{1}H and ^{31}P{^{1}H} NMR spectra indicate the presence of two isomers, probably structures **19** and **20**.

Preparation of Complexes [Ru(CO)(PMe₃)₂(P(OMe)₃)₂COCH₃]I (25) and Ru(CO)(PMe₃)₂P(OMe)₃(CH₃)I (13). The mixture of the acetyl isomers **19** and **20** (1 g) was added to n-hexane (100 mL) containing an excess of P(OMe)$_3$ (1 g). The suspension was vigorously stirred and fluxed with nitrogen at 60 °C. During the process the acetyl complexes were dissolved and the precipitation of a yellow crystalline solid was observed (0.2 g). The solid was filtered out and analyzed as $C_{15}H_{39}IP_4O_8Ru$. Anal. Found: C, 25.6; H, 5.51. Calcd: C, 25.75; H, 5.62. On the basis of the IR and ^{1}H and ^{31}P{^{1}H} NMR spectra (Tables I–III), structure **25** was attributed to the solid.

The mother solution was further crystallized at −18 °C. A yellow solid was obtained (0.25 g). It was filtered out and analyzed as $C_{11}H_{30}IP_3O_4Ru$. Anal. Found: C, 24.5; H, 5.35. Calcd: C, 24.14; H, 5.53. On the basis of the IR and ^{1}H and ^{31}P{^{1}H} NMR spectra, structure **13** was attributed to this solid.

Preparation of Complex [Ru(CO)₂(PMe₃)₃CH₃]BPh₄ (11). Complex **15** (0.2 g) was dissolved with a solution of CH_3OH (25 mL) containing $NaBPh_4$ (0.5 g). An instantaneous precipitation of a white microcrystalline solid was observed (complex **11**). The solid was washed with CH_3OH (0.25 g, yield 92%). It analyzed as $C_{36}H_{50}BO_2P_3Ru$. Anal. Found: C, 59.5; H, 7.21. Calcd: C, 60.09; H, 7.00.

Preparation of Complex [Ru(CO)₂(PMe₃)₂P(OMe)₃(CH₃)]BPh₄ (21). Complex **4** (0.20 g) and $NaBPh_4$ (0.5 g) were dissolved in CH_3OH (100 mL). A solution 0.19 M of P(OMe)$_3$ in CH_3OH (2.3 mL) was added (molar ratio 1/1). After a few seconds the formation of a white precipitate was observed. The solid (complex **21**) was filtered out, washed with CH_3OH, and dried (0.32 g; yield 90%). It analyzed as $C_{36}H_{50}BO_5P_3Ru$. Anal. Found: C, 56.5; H, 6.82. Calcd: C, 56.33; H, 5.53.

Table III. ^{31}P{^{1}H} NMR Spectral Data for the Complexes in CD_2Cl_2

complexes	δ_L, ppm	$\delta_{L'}$, ppm	$^2J_{PP}$, Hz
1	2.2 s		
2	5.2 s		
3	−14.2 s		
4[a]	−9.9 s		
5	−3.8 s		
6	−9.6 s		
9	−19.5 s		
10a,b[a]	−14.5 d, −34.6 d		27
11[c]	−10.3 d (L_a), −12.3 d (L_b)		39
13	−9.2 d	114.8 t	33
14	−1.3 d	102.2 t	32
15	−13.8 d (L_a), −25.5 t (L_b)		44
17, 18	−7.8 d (L_a), −17.1 t (L_b)		43
17, 18	−6.4 d (L_a), −20.3 t (L_b)		22
19	−10.6 d	132.4 t	56
20	−7.2 d	130.3 t	51
21	−7.4 d	122.9 t	51
22	−7.7 dd (L_a), −13.4 dt (L_b)	114.3 dt	47 (LL'_b), 42 (L_aL_b), 31 (L_aL')
24[b]	−1.6 dd	137.7 q (L'_a), 143.3 dt (L'_b)	55 (LL'_a), 55 ($L'_aL'_b$), 33 (LL'_b)
25	−7.1 dd	122.0 dt (L'_a), 133.9 dt (L'_b)	54 (LL'_a), 62 ($L'_aL'_b$), 33 (LL'_b)

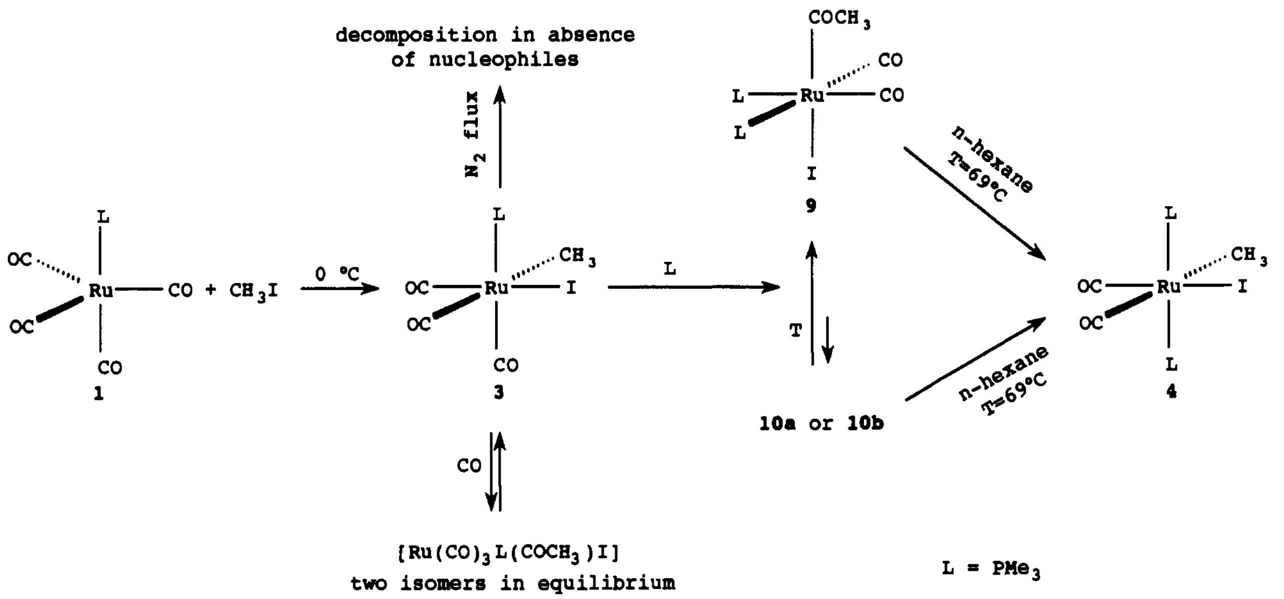
[a] Toluene-d_8. [b] Acetone-d_6. [c] A_2B system.

Complex **21** was also prepared in a different way from complex **13**. The latter (0.1 g) was dissolved in a solution of $NaBPh_4$ (0.2 g) in CH_3OH (50 mL). By the fluxing of CO in the solution, an immediate precipitation of the complex **21** (0.24 g; yield 86%) was observed.

Preparation of Complex [Ru(CO)(PMe₃)₃P(OMe)₃(CH₃)]I (22). Complex **13** (0.3 g) was dissolved in ethyl ether (20 mL); a solution of an excess of PMe$_3$ (molar ratio 10/1 with respect to complex **13**) in ethyl ether (20 mL) was added. The mixture was reacted for 1 day under magnetic stirring. The formation of a white crystalline precipitate (complex **22**) was observed. The solid was filtered out, washed with ethyl ether, and dried (0.22 g; yield 64%). It analyzed as $C_{14}H_{39}IO_4P_4Ru$. Anal. Found: C, 27.2; H, 6.15. Calcd: C, 26.98; H, 6.31.

Complex **22** (0.3 g) was dissolved in CH_3OH (25 mL), containing $NaBPh_4$ (1 g). A slow precipitation of a white solid (0.35 g; yield 90%) was observed which analyzed as $C_{38}H_{59}BO_4P_4Ru$. Anal. Found: C, 55.5; H, 7.40. Calcd: C, 55.96; H, 7.29. It shows the same structure as complex **22** with the BPh_4^- anion.

Scheme I



Preparation of Complex $[Ru(CO)(PMe_3)_4CH_3]I$ (23). Complex **22** (0.22 g) was suspended in ethyl ether (50 mL). An excess of PMe_3 (molar ratio 10/1) was added to the vigorously stirred solution. The exchange of $P(OMe)_3$ with PMe_3 was complete after 3 days, and the formation of $[Ru(CO)(PMe_3)_4CH_3]I$ (**23**) was observed. Its purification was not possible, since the phosphine was reexchanged during the purification.

Preparation of Complex $[Ru(CO)(PMe_3)_2(P(OMe)_3)_2CH_3]BPh_4$ (24). Complex **13** (0.10 g) and $NaBPh_4$ (0.60 g) were dissolved in CH_3OH (40 mL). $P(OMe)_3$ (1 mL) was added. After a few minutes the formation of a white precipitate was observed (complex **24**). The precipitate was filtered out and dried (0.14 g; yield 89%). It analyzed as $C_{36}H_{59}BO_7P_4$-Ru. Anal. Found: C, 51.9; H, 6.95. Calcd: C, 51.44; H, 7.09.

Preparation of Complex $Ru(CO)(PMe_3)_2P(OMe)_3(CH_3)CN$ (14). Complex **22** (0.20 g) was reacted with KCN (0.50 g) (molar ratio 1/30) in acetone (50 mL). The reaction was completed in 2 days. The solvent was evaporated, and the solid was extracted with benzene. The benzene was evaporated, and the white solid was analyzed spectroscopically (Tables I–III).

Preparation of the $Ru(CO)(PMe_3)_3(COCH_3)CN$ Complexes (Isomers 17 and 18). Complex **11** (0.25 g) was reacted with KCN (0.7 g) in THF (50 mL) under strong magnetic stirring. The reaction was completed in 1 day. The solvent was evaporated under reduced pressure, and the solid was extracted with benzene. The benzene was evaporated; the solid residue was dissolved in CH_2Cl_2 and crystallized with *n*-hexane. A mixture of the two isomers **17** and **18** was obtained in the ratio 1/1.8, which was measured by the intensity ratio of the $COCH_3$ resonances in the ^1H NMR spectrum.

Results

The oxidative addition of CH_3I to $Ru(CO)_4PMe_3$ (**1**) and the reactivity of the reaction products are shown in Scheme I. The oxidative addition of CH_3I to $Ru(CO)_3(PMe_3)_2$ (**2**) and the reactivity of the reaction products are shown in Scheme II. The reactivity of $Ru(CO)(PMe_3)_2P(OMe)_3(CH_3)I$ (**13**) is given in Scheme III. The formation reactions of the cyano complexes are given in Scheme IV. In all the schemes L = PMe_3 and L′ = $P(OMe)_3$.

The IR characterization of the complexes is given in Table I. The ^1H NMR and $^{31}P\{^1H\}$ NMR characterization of the complexes is given in Tables II and III, respectively.

Discussion

(a) Reaction of $Ru(CO)_4PMe_3$ with CH_3I (Scheme I). $Ru(CO)_4PMe_3$ reacts with CH_3I at 0 °C giving $Ru(CO)_3PMe_3(CH_3)I$ (**3**). The structure of complex **3** was assigned on the basis of IR and ^1H NMR and $^{31}P\{^1H\}$ NMR spectra. The IR spectrum (Table I) shows three CO stretching bands of equal intensity. This supports a facial structure: in fact an equatorial structure shows three CO stretching bands, one of which with very low intensity.[27,28] The ^1H NMR spectrum (Table II) shows a doublet for the CH_3 bonded to ruthenium with a coupling constant (7.8 Hz) typical of a cis structure for the phosphorus ligand.[29]

Complex **3** is very unstable in the absence of nucleophiles. Under nitrogen flux in *n*-hexane a fast decomposition is observed. In the presence of CO an equilibrium without decomposition with acetyl complexes $Ru(CO)_3PMe_3(COCH_3)I$ is observed. At least two isomers were observed: only one of them was characterized by spectroscopic techniques. These techniques are not sufficient to assign the structure. The behavior indicates that the decomposition is due to the dissociation of the Ru–CO bond in complex **3**. Complex **3** reacts with PMe_3 to give a mixture of two isomers (**10a** or **10b**) and **9**. Both isomers show two CO stretching bands of equal intensity (Table I), indicating a cis structure between these ligands. When the solution is heated, the equilibrium between the acetyl complexes is shifted toward isomer **9**, which was crystallized and characterized. The ^1H NMR spectrum shows a singlet for the COMe ligand and a multiplet of the Harris type[30] ($X_9AA'X'_9$), indicating a magnetic equivalence of the two phosphorus atoms. This is confirmed by the $^{31}P\{^1H\}$ NMR spectrum, which shows a singlet. In IR the complex shows two CO stretching bands of equal intensity. This pattern supports the structure **9** because the structure of the acetyl complexes with two trans phosphine ligands is assigned with certainty on the basis of ^{13}C NMR of the CO ligands.[26] The other acetyl complex shows two CO stretching bands of equal intensity and two doublets in the $^{31}P\{^1H\}$ NMR spectrum. This pattern is in agreement with structure **10a** or **10b**.

The decarbonylation of the acetyl complexes in *n*-hexane at 69 °C gives the methyl complex **4**, which can also be prepared via oxidative addition of CH_3I to the disubstituted $Ru(CO)_3(PMe_3)_2$ complex.[16,26]

(b) Reaction of $Ru(CO)_3(PMe_3)_2$ with CH_3I (Scheme II). $Ru(CO)_3(PMe_3)_2$ reacts instantaneously with CH_3I at 0 °C. When

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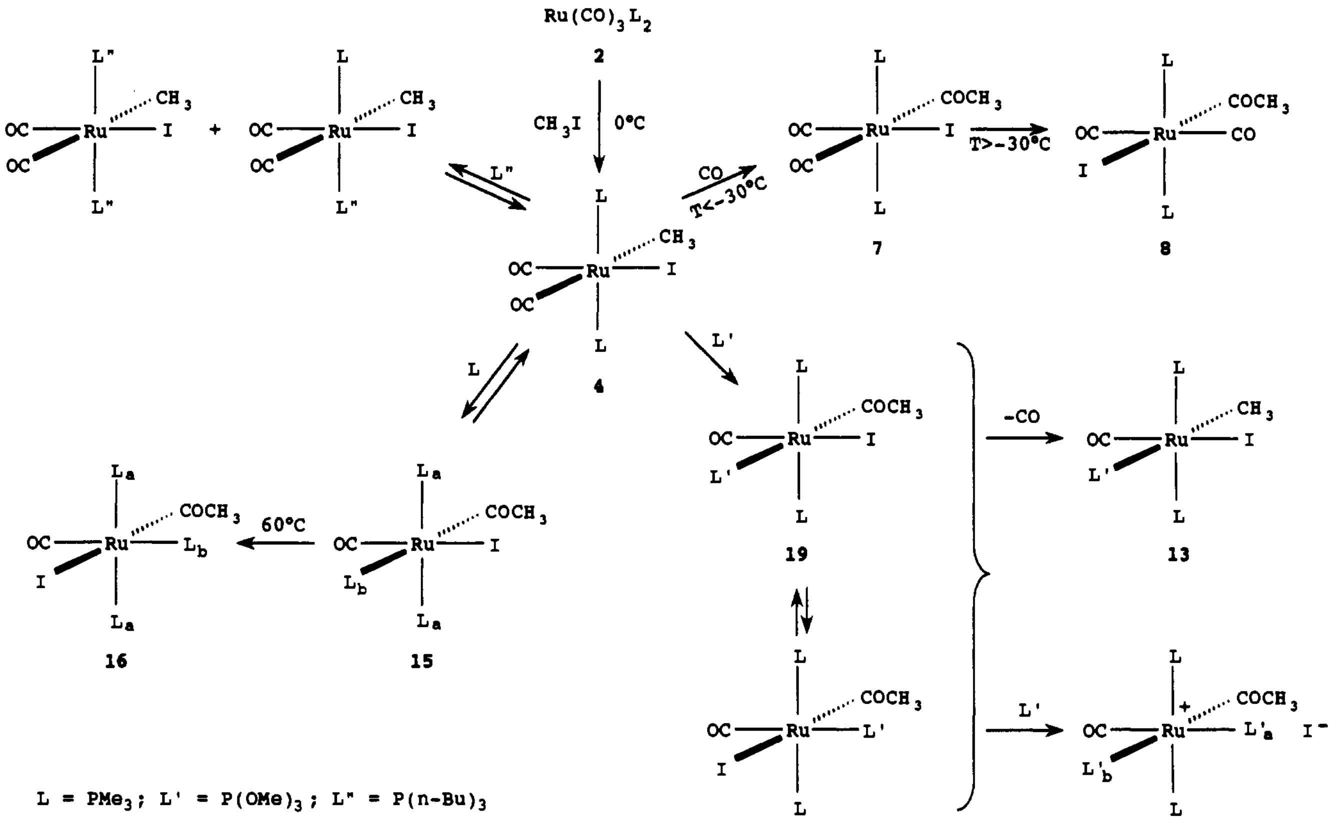
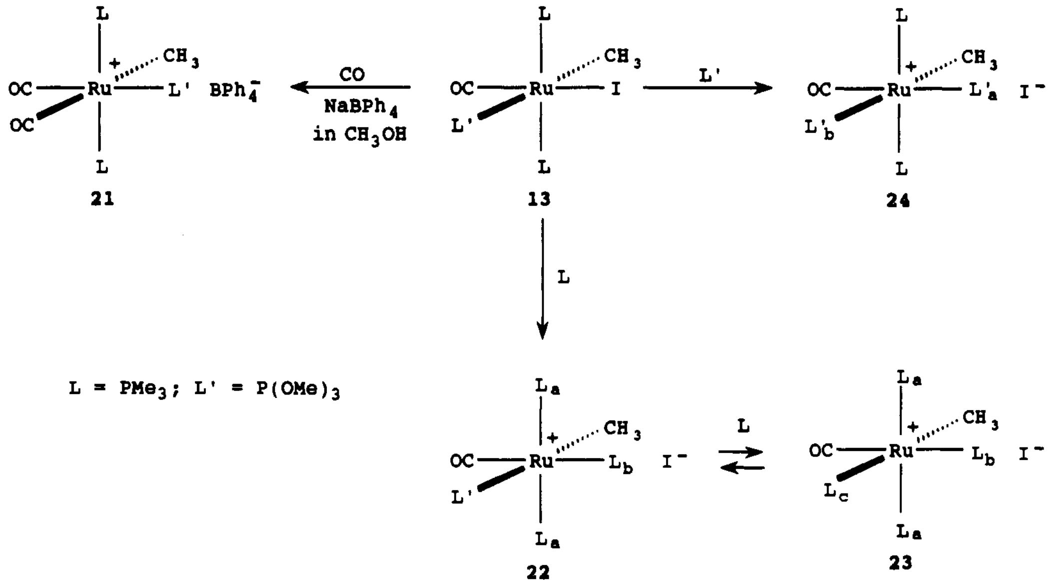
Scheme II



L = PMe$_3$; L' = P(OMe)$_3$; L" = P(n-Bu)$_3$

Scheme III



L = PMe$_3$; L' = P(OMe)$_3$

L is different from PMe$_3$ the reaction of Ru(CO)$_3$L$_2$ with CH$_3$I does not occur.[8,10] This behavior may be due to a notable effect of the steric hindrance of the ligand on the oxidative addition[31] as also observed with iron.[14,32]

The structure of the methyl complex **4** was previously assigned[16] on the basis of IR and ^{1}H NMR and ^{13}C{^{1}H} NMR spectra and on the basis of the results of the reaction with ^{13}CO.[26]

Complex **4** reacts very fast with CO at -30 °C to give the formation of acetyl complex **7** with two CO ligands in the cis position and the two phosphines in the trans position. Structure **7** was assigned on the basis of the similar behavior of the iron complexes[32] and of the ruthenium complexes, described previously by Mawby.[33] By an increase of the temperature, the acetyl complex **7** isomerizes to the acetyl complex **8**, which shows two CO groups in the trans position. The relative position of the two phosphine ligands is maintained during these transformations as observed with the isoelectronic complexes of iron.[32,34]

Complex **4** reacts with PMe$_3$ at room temperature giving the acetyl complex **15**. By an increase of the temperature, an equilibrium with the isomer **16** is observed. In IR both complexes

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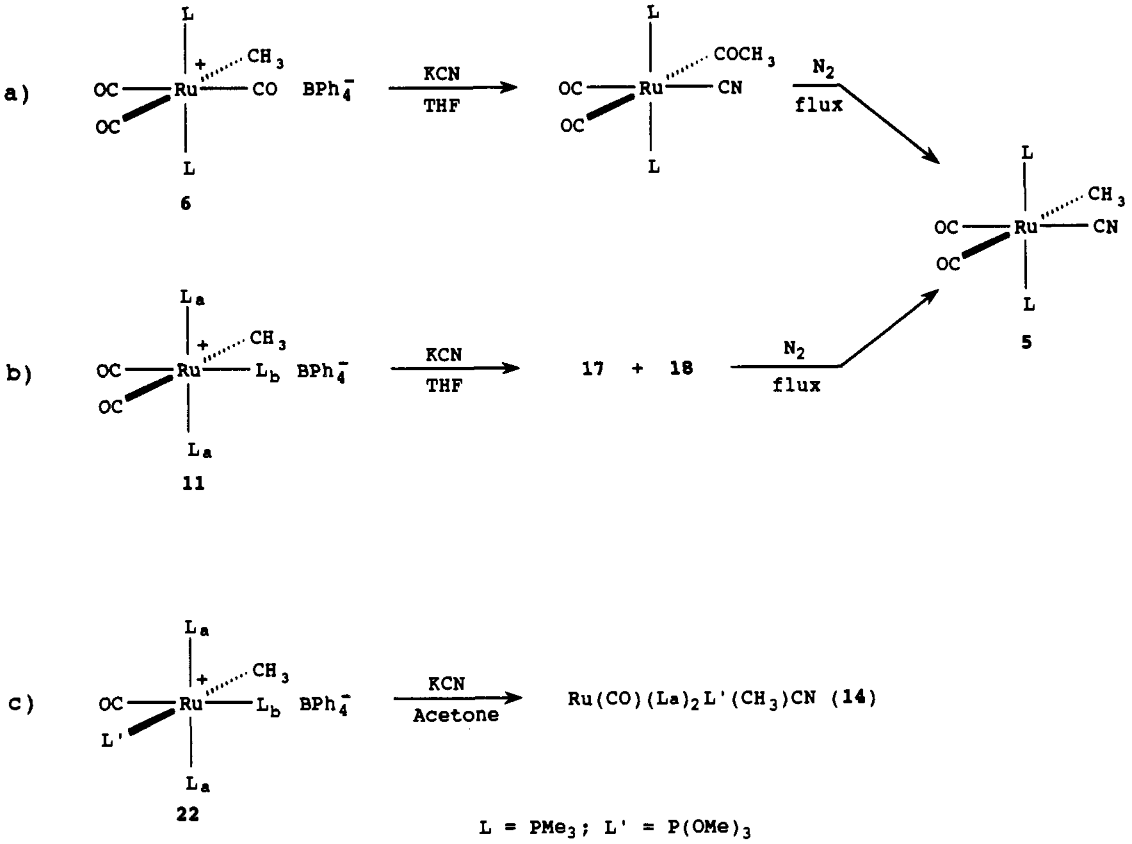
Scheme IV



show a CO stretching band. The $^{31}P\{^1H\}$ NMR spectra of complex **15** show two bands (a doublet due to L_a ligands and a triplet due to the L_b ligand), and they do not allow the discrimination between structures **15** and **16**. The position of the CO stretching bands may be useful in this aim. In fact the iodide ligand shows more electron-withdrawing power and less π-electron back-bonding[35] than the L_b ligand. Therefore, structure **15** is assigned to the complex showing the CO stretching band at the lower frequency (ν_{CO} = 1966 cm^{-1} in *n*-hexane) and structure **16** is assigned to the other complex (ν_{CO} = 1974 cm^{-1}). This assignment corresponds to that made by Mawby for other isoelectronic ruthenium complexes.[33]

The assignment is in agreement with the very strong trans effect of the $COCH_3$ ligand, which kinetically activates the trans coordination position giving complex **15**. At higher temperature complex **15** gives the thermodynamically more stable complex **16** as observed in many ruthenium[33] and iron complexes.[34,36]

Attempts to decarbonylate the mixture of acetyl complexes **15** and **16** always give complex **4**. In the IR spectrum traces of the methyl complex $Ru(CO)(PMe_3)_3(CH_3)I$ (**12**) are observed only at high temperature (80–90 °C). The structure of complex **12** is tentatively assigned by comparing it with complex **13**.

Complex **4** reacts at room temperature with $P(OMe)_3$ to give an equilibrium mixture of two acetyl isomers whose structures can be **19** and **20** as observed for the PMe_3 ligand. The ^1H NMR spectrum indicates that the two PMe_3 ligands are equivalent and they occupy a trans position and the $P(OMe)_3$ ligand is cis to these PMe_3 ligands.

In the presence of an excess of $P(OMe)_3$ the equilibrium mixture of the acetyl complexes ionizes to give complex **25**. A similar behavior was observed by Mawby with isocyanide complexes.[37]

In the $^{31}P\{^1H\}$ NMR spectrum, complex **25** shows a doublet of doublet due to the two PMe_3 ligands and two doublets of triplets due to the two magnetically nonequivalent L'_a and L'_b ligands. The $^2J_{PP}$ coupling constants are in agreement with a cis structure[38] between L'_a and L'_b and between the phosphite and phosphine ligands. This pattern is in agreement with the proposed structure.

Under nitrogen flux and at 60 °C the *n*-hexane solution of acetyl complexes **19** and **20** gives the methyl complex **13**. The structure of complex **13** was assigned on the basis of the $^{13}C\{^1H\}$ NMR spectrum. In fact notwithstanding the ^1H NMR spectrum which shows a quartet for the CH_3 bonded to ruthenium indicating a cis structure between CH_3 and the three phosphorus atoms, the $^{13}C\{^1H\}$ NMR spectrum shows a doublet ($^2J_{CP}$ = 97.6 Hz) of triplet ($^2J_{CP}$ = 9.9 Hz) at $\delta = -10.89$ ppm for the CH_3 carbon. The strong difference between the coupling constants indicates a different position of the CH_3 group with respect to the phosphorus atoms. Two phosphorus ligands are cis and correspond to the two phosphine ligands, and one phosphorus is trans and corresponds to the phosphite in the structure **13**. This situation has been observed in other tri- and tetraphosphine derivatives of ruthenium.[39–41]

Complex **4** reacts with $P(n\text{-}Bu)_3$ without forming acetyl complexes; scrambling between L and L′ is only observed with the formation of $Ru(CO)_2(PMe_3)P(n\text{-}Bu)_3(CH_3)I$ and $Ru(CO)_2(P(n\text{-}Bu)_3)_2(CH_3)I$.

(c) Reactivity of $Ru(CO)(PMe_3)_2P(OMe)_3(CH_3)I$ (13) with Nucleophiles (Scheme III). Complex **13** reacts with carbon

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monoxide giving complex **21**. The structure of complex **21** is assigned on the basis of the IR and NMR spectra. The IR spectrum shows two CO stretching bands of similar intensity; the ^1H NMR spectrum shows a quartet due to the coupling with all the three phosphorus atoms for the methyl bonded to ruthenium, a deceptive triplet[30] for the two trans PMe_3 ligands and a doublet for the $P(OMe)_3$ ligand; the $^{31}P\{^1H\}$ NMR spectrum shows a doublet at −7.2 ppm due to the two equivalent PMe_3 ligands and a triplet at 103.3 ppm due to the $P(OMe)_3$ ligand; the $^2J_{PP}$ coupling constant is in the range of the cis structure between the L and L′ ligands.

Complex **13** reacts with PMe_3 and $P(OMe)_3$ giving $[Ru(CO)(PMe_3)_3P(OMe)_3(CH_3)]I$ (**22**) and $[Ru(CO)(PMe_3)_2(P(OMe)_3)_2(CH_3)]I$ (**24**), respectively. The structure of complex **22** was assigned on the basis of the ^1H and $^{31}P\{^1H\}$ NMR spectra. The ^1H NMR spectrum shows a doublet of quartet at −0.43 ppm due to the CH_3 ligand, two signals in the range of the methyl of the PMe_3 ligand, and a band due to the $P(OMe)_3$ ligand. The $^{31}P\{^1H\}$ NMR spectrum shows a doublet of doublets for the two L_a ligands and a doublet of triplets for the L_b ligand; the L′ ligand shows a doublet of triplets. All the $^2J_{PP}$ coupling constants are in the 30–50-Hz range, typical for the cis phosphine group.

The structure of complex **24** was assigned on the basis of the arguments used for complex **25** discussed in the previous section.

Complex **22** in an excess of PMe_3 scrambles $P(OMe)_3$ with PMe_3 giving complex **23**. This complex shows a CO stretching band in the IR at lower frequency with respect to complex **22** (Table I), indicating a substitution of a phosphite with a phosphine ligand.[42]

(d) Derivatives with the Cyano Ligand (Scheme IV). The formation of the cyano derivatives can be obtained by reaction of the tetraphenylborate salts with KCN in THF.

The bis(phosphine) derivatives can be obtained by starting from complex **6** (Scheme IVa). This reaction was used to prepare complex **5**, previously described in ref 26. Attempts to prepare the tris(phosphine) derivatives $Ru(CO)L_3(CH_3)CN$ by starting from complex **11** were unsuccessful: in fact the reaction proceeds toward a mixture of acetyl derivatives **17** and **18**. On the contrary the successive deinsertion gives the bis(phosphine) complex **5** (Scheme IVb).

The tris(phosphine) methyl complex **14** was obtained by starting from complex **22** with KCN in acetone; no acetyl complex was observed in this case. This indicates a direct substitution of an L ligand by the CN^- ligand. The spectroscopic information is not sufficient to assign the structure of this complex; only the two phosphine ligands are in the trans position: in fact the $^{31}P\{^1H\}$ NMR spectrum shows a doublet due to the two magnetically equivalent phosphine ligands and a triplet due to the phosphite ligand.

Conclusions

Using the preparative methods described in this work the series of alkyl iodide complexes $Ru(CO)_{4-n}L_n(CH_3)I$ (I) with $n = 1–3$ were prepared; the complex with $n = 4$ was previously described with the chloride ligand.[43]

The series of cationic complexes $[Ru(CO)_{5-n}L_n(CH_3)]X$ (II) with $n = 2–4$ can also be prepared; it is not possible to prepare the complex with $n = 5$ owing to the steric hindrance of the five phosphorus ligands;[44] only the hydride $[RuL_5H]X$ complexes are described in the literature.[45] The complex with $n = 1$, $[Ru(CO)_4PMe_3(CH_3)]BF_4$, was only observed as an intermediate during the reaction of $Ru(CO)_3PMe_3(COCH_3)I$ with $AgBF_4$. It could not be isolated owing to its instability.

The structure of the alkyl complexes depends on the number of phosphine ligands. The structure of complexes I and II with $n = 1$ shows a cis position between the σ ligands and the phosphine; with two phosphine ligands the complexes prefer the structure with the two phosphines in the trans position; with three phosphine ligands the equatorial structure is preferred; with four phosphine ligands the complexes prefer the structure with the two nonphosphine ligands in the cis position.

The stability of the acetyl isomers is comparable to that found with the isoelectronic iron derivatives,[14] and therefore various isomers are often observed. With $n = 1$, different acetyl isomers are obtained; with two phosphine ligands, both the structures with these ligands in the cis and in the trans positions are observed. With three phosphine ligands two of the three possible structures are observed.

Acknowledgment. This work was supported by grants from the Consiglio Nazionale delle Ricerche (CNR, Rome, Italy) and the Ministero dell'Università e della Ricerca Scientifica e Tecnologica (MURST, Rome, Italy).

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