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Dinuclear ruthenium(II) carbonyl complexes bridged by a $C(O)CH_2C_5H_3NCH_2$ group: synthesis, characterization and crystal structures

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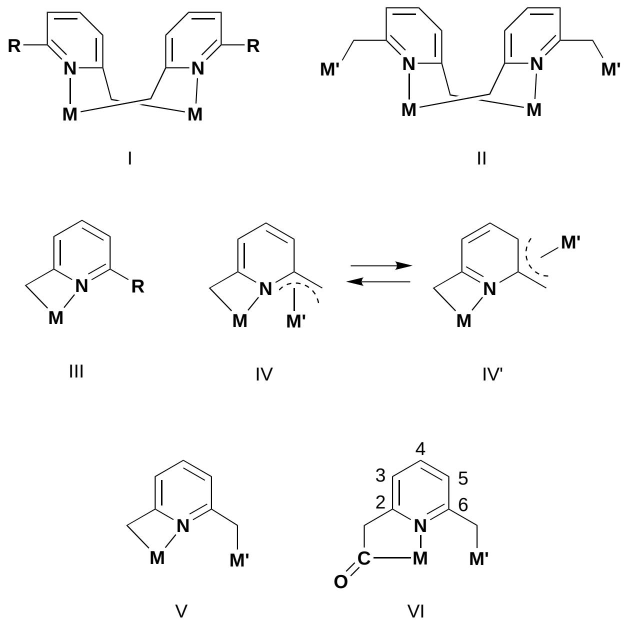
The reaction of $[Ru_3(CO)_{12}]$ with 2,6-bis(chloromethyl)pyridine ($ClCH_2C_5H_3NCH_2Cl$) gave the scarcely soluble complex **1**, $[Ru_2Cl_2\{C(O)CH_2C_5H_3NCH_2\}(CO)_4]$. Further reactions of **1** with MeOH and PPh_3 under appropriate conditions afforded organic-soluble complexes $[Ru_2(\mu\text{-}Cl)\{\mu\text{-}C(O)CH_2C_5H_3NCH_2\text{-}C,N,C'\}Cl(CO)_4(MeOH)_2]$ **2** and $[Ru_2(\mu\text{-}Cl)\{\mu\text{-}C(O)CH_2C_5H_3NCH_2\text{-}C,N,C'\}Cl(CO)_n(PPh_3)_m]$ ($n = 4$, $m = 1$ **3**; $n = 3$, $m = 2$ **4**), respectively. Complexes **2**–**4** were characterized by ^1H, ^{13}C and ^{31}P (for **3** and **4**) NMR spectroscopy and by single-crystal structure determinations. These complexes are dinuclear and two Ru atoms are doubly connected by a chlorine atom and a $C(O)CH_2C_5H_3NCH_2$ group. Each of the metal atoms in **2** has a distorted octahedral co-ordination, while in **3** and **4** one metal atom adopts a distorted octahedral geometry and the other pseudo-octahedral; the latter geometry is completed by a Ru · · · Cl secondary bonding interaction [2.855(2) in **3**; 2.941(2) Å in **4**].

We have found that 2,6-bis(chloromethyl)pyridine, which is potentially bifunctional in oxidative-addition reactions, reacts with low-valent transition metals to give mono-, di- and tetra-nuclear complexes with a variety of bonding types shown in Scheme 1.[1] Di- and tetra-nuclear complexes with bonding types **I** and **II** (M, M′ = Pd), respectively, have been obtained by the reaction with $[Pd(PPh_3)_4]$.[1a] A mixed-metal complex of type **II** (M = Pd, M′ = Pt) was prepared by reaction with $[Pd(PPh_3)_4]$ followed by $[Pt(PPh_3)_4]$. Mononuclear complexes of type **III** (M = Rh or Ir) have been obtained by reactions with $[RhCl(PPh_3)_3]$[1c] and $[IrCl(PPh_3)_3]$,[1d] respectively. Although the novel bonding type **IV** was previously assigned[1b,c] for a dinuclear complex obtained by reaction with $[RhCl(PPh_3)_3]$, X-ray single-crystal structure determination established a structure of type **V** for the complex.[1d] By reaction with $[IrCl(PPh)_3]$ and subsequent reaction of the product obtained with $[RhCl(PPh_3)_3]$, two kinds of mixed-metal dinuclear complexes of type **V** (M = Rh, M′ = Ir; M = Ir; M′ = Rh) have been prepared and their structures established by X-ray analyses.[1d]

Recently, much attention has been devoted to the reactivities of $[Ru_3(CO)_{12}]$ toward N-donor ligands, especially those containing N-heterocycles.[2] The reaction of the carbonyl cluster with pyridine gave cycloruthenated complexes $[Ru_3(\mu\text{-}H)(\mu\text{-}C_5H_4N)(CO)_{10}]$ and $[Ru_3(\mu\text{-}H)_2(\mu\text{-}C_5H_4N)_2(CO)_8]$.[3,4] The former complex could be obtained more conveniently using $[Ru_3(CO)_{12-n}(NCMe)_n]$ ($n = 1$ or 2)[5] as starting materials. The reaction of $[Ru_3(CO)_{10}(NCMe)_2]$ with 2-methylpyridine has been investigated and found to give the *ortho*-ruthenated cluster $[Ru_3(\mu\text{-}H)(\mu\text{-}2\text{-}MeC_5H_3N)(CO)_{10}]$.[6] Other reactions of $[Ru_3(CO)_{12}]$ with 2-substituted pyridines having acidic protons in the substituent, for example 2-aminopyridine[7] and pyridine-2-thiol,[8] also gave similar μ-hydrido-triruthenium cluster complexes, while the reaction with 2-(diphenylphosphino)pyridine afforded a trinuclear acyl complex with P–C bond cleavage and migratory CO insertion.[9] On the other hand, 2-pyridone reacted to give the polymeric $[\{Ru_2(\mu\text{-}OC_5H_4N)_2(CO)_4\}_n]$, which with neutral ligands (L) gave dinuclear complexes $[Ru_2(\mu\text{-}OC_5H_4N)_2(CO)_2L_2]$.[7]

In our previous study on the reaction of $[Ru_3(CO)_{12}]$ with 2-(chloromethyl)pyridine the first isolated insoluble product $[\{RuCl[C(O)CH_2C_5H_4N](CO)_2\}_2]$ reacted with PPh_3 to give the organic-soluble mononuclear acyl complex $[RuCl\{C(O)CH_2C_5H_4N\}(CO)(PPh_3)_2]$.[10] We report here details on the reaction of $[Ru_3(CO)_{12}]$ with 2,6-bis(chloromethyl)pyridine followed by MeOH and PPh_3 to give new dinuclear ruthenium(II) complexes of type **VI**. Some of this work has been described in a preliminary fashion.[11]



Scheme 1 R = CH_2Cl

Experimental

All synthetic reactions were carried out in an atmosphere of nitrogen, using solvents which were redistilled under argon. Commercially available 2,6-bis(chloromethyl)pyridine and $[Ru_3(CO)_{12}]$ were used without further purification. The numbering scheme in the pyridine ring for NMR spectral assignment is illustrated in Scheme 1.

Syntheses

$[Ru_2Cl_2\{C(O)CH_2C_5H_3NCH_2\}(CO)_4]$ 1. The compound $[Ru_3(CO)_{12}]$ (0.31 g, 0.48 mmol) and $ClCH_2C_5H_3NCH_2Cl$ (0.76 g, 4.3 mmol) were suspended in toluene (12 cm^3) and the mixture was refluxed for 8 h with stirring. As the reaction proceeded, the solution obtained at 90 °C turned from wine red to pale yellow, then orange, gradually depositing a bright yellow product which was collected, washed with Et_2O and then dried *in vacuo*. Yield: 0.31 g (84%) (Found: C, 27.92; H, 1.29; N, 2.71. Calc. for $C_{12}H_7Cl_2NO_5Ru_2$: C, 27.81; H, 1.36; N, 2.70%).

$[Ru_2(\mu\text{-}Cl)\{\mu\text{-}C(O)CH_2C_5H_3NCH_2\text{-}C,N,C'\}Cl(CO)_4(MeOH)_2]$ 2. A suspension of complex **1** (0.10 g, 0.19 mmol) in MeOH (10 cm^3) was refluxed for a few minutes, and the resulting clear and still hot solution was filtered. The filtrate was concentrated to half of the original volume under reduced pressure and stored at 0 °C. The resulting off-white precipitate was collected and dried *in vacuo*. Yield: 0.070 g (62%) (Found: C, 28.98; H, 2.51; N, 2.52. Calc. for $C_{14}H_{15}Cl_2NO_7Ru_2$: C, 28.88; H, 2.60; N, 2.40%). From the concentrated methanol solution, yellow prismatic crystals suitable for an X-ray crystallographic analysis were obtained on standing at room temperature.

$[Ru_2(\mu\text{-}Cl)\{\mu\text{-}C(O)CH_2C_5H_3NCH_2\text{-}C,N,C'\}Cl(CO)_4(PPh_3)]$ 3. A suspension of complex **1** (0.10 g, 0.20 mmol) in MeOH (8 cm^3) was heated at 65 °C and carbon monoxide gas was bubbled through the solution obtained for 1 h. To the resulting mixture was added dropwise a solution of PPh_3 (0.051 g, 0.19 mmol) in CH_2Cl_2 (2 cm^3). When the solution became turbid, bubbling of CO was stopped and again the mixture was refluxed for 0.5 h under an atmosphere of CO. The precipitate formed was collected, washed with Et_2O, then dried *in vacuo*. Yield: 0.10 g (68%) (Found: C, 45.54; H, 2.80; N, 1.83. Calc. for $C_{30}H_{22}Cl_2NO_5PRu_2$: C, 46.16; H, 2.84; N, 1.79%). Yellow prismatic crystals suitable for an X-ray crystallographic analysis were obtained by recrystallization from $CHCl_3$–Et_2O.

$[Ru_2(\mu\text{-}Cl)\{\mu\text{-}C(O)CH_2C_5H_3NCH_2\text{-}C,N,C'\}Cl(CO)_3(PPh_3)_2]$ 4. A mixture of complex **1** (0.15 g, 0.29 mmol) and PPh_3 (0.20 g, 0.76 mmol) in benzene (10 cm^3) was refluxed for 5 h. After cooling, the precipitate formed was collected, washed with Et_2O, then dried *in vacuo*. The complex was recrystallized from $CHCl_3$–Et_2O in air. Yield 0.27 g (92%) (Found: C, 54.53; H, 3.41; N, 1.38. Calc. for $C_{47}H_{37}Cl_2NO_4P_2Ru_2$: C, 55.63; H, 3.67; N, 1.38%). Yellow plates suitable for an X-ray crystallographic analysis were obtained by recrystallization from $CHCl_3$–hexane.

Crystallography

All measurements were carried out at room temperature on a Rigaku AFC7S diffractometer for complex **2**, and on a AFC7R diffractometer for **3** and **4**. Crystallographic data are given in Table 4. Periodic remeasurement of three standard reflections revealed no significant crystal decay or electronic instability in each case. Intensities were measured from continuous ω–2θ scans. All intensity data were corrected for Lorentz-polarization effects and absorption corrections by the ψ-scan method[12] were also applied to **2** and **3** and for **4** were made using the program DIFABS.[13] The structures of **2** and **3** were solved by heavy-atom methods (DIRDIF 94,[14] PATTY[15] and SAPI 91[16]) and that of **4** by direct methods (SIR 92[17]); all three structures were refined by full-matrix least-squares analysis on *F*. All the full-occupancy non-hydrogen atoms were refined anisotropically. The crystal of **4** included one hexane molecule per complex as solvent of crystallization. It was disordered heavily and was refined isotropically. The highest residual peak for **4** (Table 4) resulted from this disorder. Hydrogen atoms of the three structures were introduced in their calculated positions, except for those of the disordered hexane molecules. Then hydrogen atoms of **2** and **3** were refined isotropically but those of the hydroxyl group of the two co-ordinated methanol molecules were not refined. Computations were carried out using TEXSAN[18] program systems.

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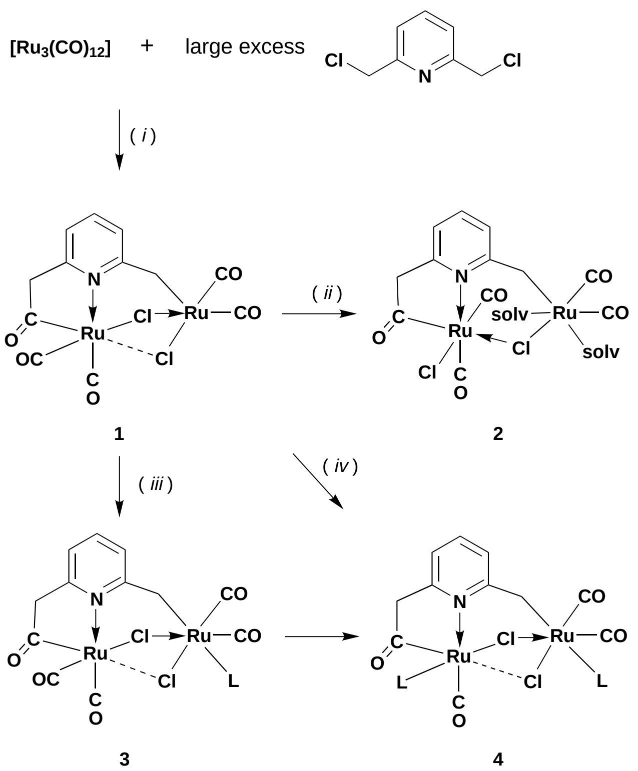


Scheme 2 solv = MeOH, L = PPh_3. Reagents and conditions: (*i*) toluene, reflux for 8 h; (*ii*) MeOH, reflux for a few minutes; (*iii*) MeOH–CH_2Cl_2, L, reflux for 0.5 h under CO; (*iv*) benzene, 2.6L, −CO, reflux for 5 h. Dashed lines represent the secondary bonding interactions. The structure of **1** is tentative

Other measurements

Infrared spectra were obtained in Nujol mulls with a JASCO DS-701G spectrometer, NMR spectra on JEOL JNM GX-400 (in the case of ^1H and ^{13}C) and α-400 (for ^{31}P) instruments. Tetramethylsilane and H_3PO_4 were used as internal (for ^1H and ^{13}C) and external (for ^{31}P) standards, respectively. The FAB mass spectra were obtained with a JEOL JMS AX-500 spectrometer in the positive mode using 3-nitrobenzyl alcohol as a matrix, dichloromethane as solvent and xenon as bombardment gas.

Results and Discussion

Syntheses and spectral characterization

As shown in Scheme 2, the cluster $[Ru_3(CO)_{12}]$ reacted with a large excess of $ClCH_2C_5H_3NCH_2Cl$ in refluxing toluene to give a bright yellow precipitate **1** which gave satisfactory analysis as $[Ru_2Cl_2\{C(O)CH_2C_5H_3NCH_2\}(CO)_4]$. The IR spectrum (Table 1) of **1** showed a sharp ν(C=O) band at 1680 cm^{-1} in addition to several ν(C≡O) bands around 2000 cm^{-1}, indicating that an acyl complex has been formed *via* oxidative addition of the C–Cl bond followed by migratory insertion of CO. Complex **1** was scarcely soluble in non-co-ordinating solvents but readily dissolved in acetonitrile at room temperature giving a clear solution, from which it could not be recovered. When a methanol suspension of **1** was heated at 65 °C for a few minutes the complex reacted with solvent molecules giving a clear yellow solution, from which the methanol adduct $[Ru_2(\mu\text{-}Cl)\{\mu\text{-}C(O)CH_2C_5H_3NCH_2\text{-}C,N,C'\}Cl(CO)_4(MeOH)_2]$ **2** was isolated, after working up, in 62% yield (Scheme 2). The solubilities of **2** in non-co-ordinating solvents were also poor. Similarly to **1**, the IR spectrum (Table 1) showed ν(C=O) at 1630 cm^{-1} as a rather broad, medium band. Owing to the very weak bonding ability of the added solvent molecules, the FAB mass spectrum (Table 1) did not show the parent peak, although there were many fragment peaks (M − 2solv) (solv = MeOH), (M − 2solv − CO), (M − 2solv − CO − Cl) and so on.

Table 1 Infrared and FAB mass spectroscopic data for the complexes

Complex	IR[a]/cm^{-1}		
	ν(C$\equiv$O)	ν(C=O)	Mass, *m*/*z*[b]
1 [$Ru_2Cl_2\{C(O)CH_2C_5H_3NCH_2\}(CO)_4$]	2060, 2040, 2000, 1980, 1970 (sh)	1680	
2 [$Ru_2(\mu$-$Cl)\{\mu$-$C(O)CH_2C_5H_3NCH_2$-*C*,*N*,*C*′}-$Cl(CO)_4(MeOH)_2$]	2050, 1970	1630	519 (*M* − 2solv), 490 (*M* − 2solv − CO), 455 (*M* − 2solv − CO − Cl), 427 (*M* − 2solv − 2CO − Cl), 399 (*M* − 2solv − 3CO − Cl), 371 (*M* − 2solv − 4CO − Cl)
3 [$Ru_2(\mu$-$Cl)\{\mu$-$C(O)CH_2C_5H_3NCH_2$-*C*,*N*,*C*′}-$Cl(CO)_4(PPh_3)$]	2050, 2020, 1975, 1950 (sh)	1675	780 (M^+), 753 (*M* − CO), 745 (*M* − Cl), 724 (*M* − 2CO), 717 (*M* − Cl − CO), 689 (*M* − Cl − 2CO), 662 (*M* − Cl − 3CO), 633 (*M* − Cl − 4CO)
4 [$Ru_2(\mu$-$Cl)\{\mu$-$C(O)CH_2C_5H_3NCH_2$-*C*,*N*,*C*′}-$Cl(CO)_3(PPh_3)_2$]	2040, 1970	1630	1015 (M^+), 986 (*M* − CO), 979 (*M* − Cl), 958 (*M* − 2CO), 922 (*M* − 2CO − Cl), 881 (*M* − L − CO), 754 (*M* − L − 3CO − 2Cl), 689 (*M* − PPh_3 − CO − Cl), 633 (*M* − PPh_3 − 3CO − Cl)

[a] In Nujol. [b] solv = MeOH, L = $C(O)CH_2C_5H_3NCH_2$.

Table 2 Proton and ^{31}P-{^1H} NMR data for the complexes[a]

Complex (Solvent)	^1H					^{31}P
			C_5H_3N			
	$RuCH_2$	$RuC(O)CH_2$	H^3, H^5	H^4	Others	
$ClCH_2C_5H_3NCH_2Cl$ ($CDCl_3$)			7.4 (d) [7.9]	7.73 (t) [7.9]	4.64 (CH_2Cl)	
1 (CD_3CN)						
Major	2.80, 3.18 (ABq, br) [9.2]	3.72, 4.67 (ABq, br) [20.3]	7.14 (d), 7.31 (d) [7.9] [7.9]	7.67 (t) [7.9]		
Minor	2.73, 3.27 (ABq) [8.5]	3.70, 4.59 (ABq) [19.5]	7.12 (d), 7.27 (d) [7.9] [7.9]	7.65 (t) [7.9]		
2 (CD_3CN)						
Major	2.79, 3.18 (ABq, br) [9.2]	3.72, 4.66 (ABq, br) [20.1]	7.14 (d), 7.30 (d) [6.7] [7.9]	7.67 (t) [7.9]	3.28 (d) [5.5] (Me), 2.17 (d) [5.5] (OH)	
Minor	2.72[b] (ABq)	3.69, 4.59 (ABq) [19.5]	7.12 (d), 7.27 (d) [5.5] [7.9]	7.65 (t) [7.9]		
3 ($CDCl_3$)	3.60, 3.93 (ABX) [9.7] {9.5, 7.9}	3.76, 3.98 (ABq) [19.5]	6.92 (d), 7.28 (d) [7.3] [7.9]	*c*	7.23–7.65 (Ph)	19.4
4 ($CDCl_3$)	3.25, 3.27 (ABX) [9.0] {13.0}	2.96, 3.34 (ABq) [19.5]	6.52 (d), 7.01 (d) [7.3] [7.9]	*c*	7.25–7.73 (Ph)	17.2, 52.0

[a] Measured at 400 MHz, *J*(H–H) and *J*(H–P) values in square brackets and braces respectively in Hz. [b] Overlapped with the methyl resonances. [c] Overlapped with phenyl resonance.

The ^1H NMR spectra (Table 2) of complexes **1** and **2** in CD_3CN showed a marked resemblance to one another, except that the methyl and hydroxyl resonances assignable to the methanol molecules appeared in the spectrum of **2**. Both spectra showed two sets of resonances corresponding to the major and minor species (approximately 6 : 4 in intensity) in the respective regions of the $RuCH_2$ and $RuC(O)CH_2$ protons and of the pyridine-ring protons, indicating that both **1** and **2** exist in solution as a mixture of at least two diastereoisomers. The geminal coupling constants (*ca.* 20 Hz) observed for the $RuC(O)CH_2$ protons are appreciably larger than those (*ca.* 9 Hz) for the $RuCH_2$ protons. Large coupling constants of the $RuC(O)CH_2$ protons were also observed for the analogous acyl complex [$\{RuCl[C(O)CH_2C_5H_4N](CO)_2\}_2$][10] and seem to be characteristic of the cyclometallated pyridin-2-ylmethylcarbonyl moiety having a diastereotopic methylene group. The pyridine-ring protons gave three resonances consisting of two doublets and one triplet, indicating the asymmetric structures of the complexes. Similarly to the ^1H NMR spectra, the ^{13}C-{^1H} NMR spectra of **1** and **2** in CD_3CN (Table 3) also showed two sets of resonances for the major and minor isomeric species in the regions of the $RuCH_2$ and $RuC(O)CH_2$ carbons and of the pyridine-ring carbons. Two separate resonances assignable to the Ru*C*(O)CH_2 carbons appeared at δ 240.8 and 241.6 for **1** and δ 241.0 and 241.9 for **2**. In spite of measurement in a co-ordinating solvent, complex **2** retained the methanol molecules, because two methyl carbon resonances corresponding to the major and minor isomeric species appeared at δ 49.7 and 49.9 in the relative intensity of *ca.* 7.5 : 2.5. As described later, a pair of carbonyl ligands is co-ordinated to each ruthenium atom in a diastereoisomer of **2** with the *cis* arrangement. Therefore, four resonances for the respective isomer, *i.e.* a total of eight, are expected for the carbonyl carbons. In practice, however, the spectra showed only six resonances in the region of δ 194–199. The remainder probably overlaps with two of the six carbonyl resonances. The similarity of the NMR spectral pattern of **1** in CD_3CN with that of **2** in the same solvent strongly suggests that complex **1** dissolves in CD_3CN with adduct formation analogous to that of **2**.

In order to solubilize complex **1** we examined its reaction with PPh_3. When **1** was allowed to react with PPh_3 in the mole ratio of 1 : 2.6 in refluxing benzene we obtained the organic-soluble bis(phosphine) derivative [$Ru_2(\mu$-$Cl)\{\mu$-$C(O)CH_2C_5H_3NCH_2$-*C*,*N*,*C*′}$Cl(CO)_3(PPh_3)_2$] **4** in 92% yield (Scheme 2). While this paper was in preparation, we found that the same complex can be more easily synthesized in a dichloromethane suspension at room temperature. As revealed by X-ray crystal analysis of **4** (see later), one CO ligand is extruded from **1** during the reaction to form **4**. Under conditions of varying reactant mole ratios, solvents, reaction temperatures and times, we examined the reaction of **1** with PPh_3 to prepare the monophosphine derivative. Although the best result was obtained when using one-fifth mol of PPh_3 per complex in refluxing methanol for 0.5 h, the isolated product still was a 13 : 1 mixture

Table 3 Carbon-13 NMR data for the complexes[a]

Complex (Solvent)	$RuCH_2$	$RuC(O)CH_2$	C_5H_3N C^2	C^3	C^4	C^5	C^6	PPh_3 C^i	C^o	C^m	C^p	Others
$ClCH_2C_5H_3NCH_2Cl$ ($CDCl_3$)			156.2	121.9	137.9	121.9	156.2					46.4 (CH_2Cl)
1 (CD_3CN)												
Major	17.1	63.7	162.0	117.7	138.8	123.3	175.9					194.6, 195,0, 195.6, 196.6, 197.9, 198.0 (CO); 240.8, 241.6 [$C(O)CH_2$]
Minor	20.1	63.5	162.1	*b*	139.2	121.6	175.3					
2 (CD_3CN)												
Major	17.2	63.8	162.2	*b*	138.9	123.4	175.5					49.7, 49.9 (Me); 194.7, 195.1, 195.8, 196.7, 198.0, 198.2 (CO); 241.0, 241.9 [$C(O)CH_2$]
Minor	20.1	63.6	162.2	121.7	139.3	123.7	176.0					
3 ($CDCl_3$)	26.3 (d) [63.1]	62.7	158.6	116.1	138.9	121.2 (d) [2.7]	173.6 (d) [4.4]	132.7 (d) [38.1]	133.7 (d) [10.3]	128.5 (d) [10.3]	130.4	193.4, 193.6, 195.7 (d) [5.9], 196.3 (d) [5.9] (CO); 236.4 [$C(O)CH_2$]
4 ($CDCl_3$)	24.9 (d) [64.6]	60.0	158.8	115.2	137.4	119.8	171.6 (d) [4.4]	*c*	133.9 (d) [10.3]	128.3 (d) [8.8]	130.3	196.2 (d) [5.9], 196.3 (d) [5.9], 201.4 (d) [19.1] (CO); 250.8 (d) [11.3] [$C(O)CH_2$]
								132.0 (d) [49.9]	133.8 (d) [10.3]	128.2 (d) [10.2]	130.0	

[a] Measured at 100 MHz, *J*(C–P) values in square brackets in Hz. [b] Overlapped with resonances of the solvent. [c] Partially overlapped with the phenyl *o*-carbon resonances.

Table 4 Crystallographic data for complexes **2**–**4**

	2	**3**	**4**·C_6H_{14}
Formula	$C_{14}H_{15}Cl_2NO_7Ru_2$	$C_{30}H_{22}Cl_2NO_5PRu_2$	$C_{53}H_{51}Cl_2NO_4P_2Ru_2$
M	582.32	780.53	1100.98
Space group	$P2_1$	$P\bar{1}$	$C2/c$
Crystal system	Monoclinic	Triclinic	Monoclinic
a/Å	9.771(1)	10.219(1)	19.265(4)
b/Å	9.183(2)	16.785(1)	9.729(3)
c/Å	11.7297(9)	9.343(1)	48.814(3)
α/°		105.760(8)	
β/°	108.317(7)	90.168(10)	102.03(1)
γ/°		105.521(8)	
U/Å^3	999.1(2)	1481.2(3)	8947(3)
Z	2	2	8
D_c/g cm^{-3}	1.936	1.750	1.634
F(000)	568	772	4480
μ(Mo-Kα)/cm^{-1}	18.13		
μ(Cu-Kα)/cm^{-1}		107.81	76.45
Scan rate/° min^{-1}	8.0	8.0	8.0
ω-Scan angle/°	1.84 + 0.50 tan θ	1.37 + 0.30 tan θ	0.94 + 0.30 tan θ
$2\theta_{max}$/°	60.0	113.6	113.7
Crystal size/mm	0.25 × 0.25 × 0.60	0.06 × 0.06 × 0.29	0.20 × 0.30 × 0.03
Maximum, minimum transmission factors	0.876, 0.998	0.713, 0.998	0.835, 1.000
No. data collected	3241	4235	6659
No. unique data	3083	3966	6422
No. data in refinement [$I > 3.00\sigma(I)$]	2902	3636	5134
No. refined parameters	263	459	540
Final R (R')	0.022 (0.031)	0.036 (0.065)	0.043 (0.078)
Goodness of fit, S	1.57	1.88	1.38
Maximum, minimum peaks in final difference map/e Å^{-3}	0.68, −0.44	0.67, −1.06	1.42, −0.47
Shift/e.s.d. in last cycle	0.27	0.01	0.59

Table 5 Selected bond lengths (Å) and angles (°) for complexes **3** and **4**·C_6H_{14}

	3	**4**·C_6H_{14}		**3**	**4**·C_6H_{14}
Ru(1)–Cl(1)	2.434(1)	2.466(1)	Ru(2)–C(6)	2.201(6)	2.218(6)
Ru(1)···Cl(2)*	2.855(2)	2.941(2)	O(1)–C(8)	1.201(8)	1.233(7)
Ru(1)–P(2)		2.315(2)	N–C(1)	1.366(8)	1.342(8)
Ru(1)–N	2.126(5)	2.145(5)	N–C(5)	1.357(7)	1.357(8)
Ru(1)–C(8)	2.002(7)	1.958(6)	C(1)–C(7)	1.492(9)	1.473(9)
Ru(2)–Cl(1)	2.496(1)	2.489(1)	C(5)–C(6)	1.482(9)	1.455(9)
Ru(2)–Cl(2)	2.445(1)	2.419(2)	C(7)–C(8)	1.51(1)	1.530(8)
Ru(2)–P(1)	2.464(2)	2.460(2)			
Cl(1)–Ru(1)–N	80.9(1)	77.3(1)	Cl(2)–Ru(2)–C(12)	89.0(2)	91.0(2)
Cl(1)–Ru(1)–C(8)	96.3(2)	94.1(2)	P(1)–Ru(2)–C(11)	93.8(2)	93.5(2)
Cl(1)–Ru(1)–C(10)	95.0(2)	95.2(2)	P(2)–Ru(2)–C(12)	96.5(2)	96.8(2)
P(2)–Ru(1)–N		96.2(1)	C(6)–Ru(2)–C(11)	87.4(3)	87.4(3)
P(2)–Ru(1)–C(8)		88.4(2)	C(6)–Ru(2)–C(12)	83.2(2)	84.7(3)
P(2)–Ru(1)–C(10)		91.6(2)	C(11)–Ru(2)–C(12)	91.1(2)	88.7(3)
N–Ru(1)–C(8)	81.1(2)	82.2(2)	Ru(1)–Cl(1)–Ru(2)	91.97(4)	93.43(5)
N–Ru(1)–C(9)	95.8(2)		Ru(1)–N–C(1)	114.7(4)	113.6(4)
C(8)–Ru(1)–C(9)	87.5(3)		Ru(1)–N–C(5)	126.0(4)	123.8(4)
C(8)–Ru(1)–C(10)	92.0(3)	93.0(2)	N–C(1)–C(7)	114.6(5)	116.1(5)
C(9)–Ru(1)–C(10)	89.3(3)		N–C(5)–C(6)	116.8(5)	117.4(5)
Cl(1)–Ru(2)–Cl(2)	85.40(5)	83.77(5)	Ru(2)–C(6)–C(5)	114.4(4)	111.5(4)
Cl(1)–Ru(2)–P(1)	84.28(5)	84.31(5)	C(1)–C(7)–C(8)	112.7(6)	114.0(5)
Cl(1)–Ru(2)–C(6)	95.8(2)	94.1(2)	Ru(1)–C(8)–O(1)	126.4(6)	127.6(4)
Cl(1)–Ru(2)–C(11)	94.4(2)	96.4(2)	Ru(1)–C(8)–C(7)	113.2(5)	113.6(4)
Cl(2)–Ru(2)–P(1)	95.95(5)	94.93(5)	O(1)–C(8)–C(7)	120.4(6)	118.8(5)
Cl(2)–Ru(2)–C(6)	82.9(2)	84.2(2)			

* Ru–Cl Secondary bonding,[19,20] (see text).

of the mono- and bis-phosphine derivatives on the basis of the relative intensities of the corresponding ^{1}H NMR resonances. This difficulty to isolate the monophosphine derivative as a pure product probably comes from the ready elimination of CO from the monophosphine derivative so as to accept the second phosphine molecule. Therefore, we tried the 1 : 1 reaction under an atmosphere of CO in a refluxing mixture of MeOH–CH_2Cl_2 and succeeded in isolating the pure monophosphine derivative $[Ru_2(\mu\text{-}Cl)\{\mu\text{-}C(O)CH_2C_5H_3NCH_2\text{-}C,N,C'\}Cl(CO)_4(PPh_3)]$ **3** in 68% yield (Scheme 2). Although we have not tried to prepare **4** by the reaction of **3** with PPh_3, **4** appears to be formed through **3**. The monophosphine derivative **3** showed a sharp ν(C=O) band at 1675 cm^{-1}, while the bis(phosphine) derivative **4** had a broad one at 1630 cm^{-1} (Table 1), indicating that both the complexes retain the acyl structure of **1**. Contrary to the methanol adduct **2**, the FAB mass spectra (Table 1) of complexes **3** and **4** showed their parent peaks. When the fragmentation patterns are compared, fragment peaks such as (M − L − CO) [L = $C(O)CH_2C_5H_3NCH_2$], (M − L − 3CO − 2Cl), (M − PPh_3 − CO − Cl) and (M − PPh_3 − 3CO − Cl) were observed only for the bis(phosphine) derivative **4** and hence the replacement of one CO ligand by the second PPh_3

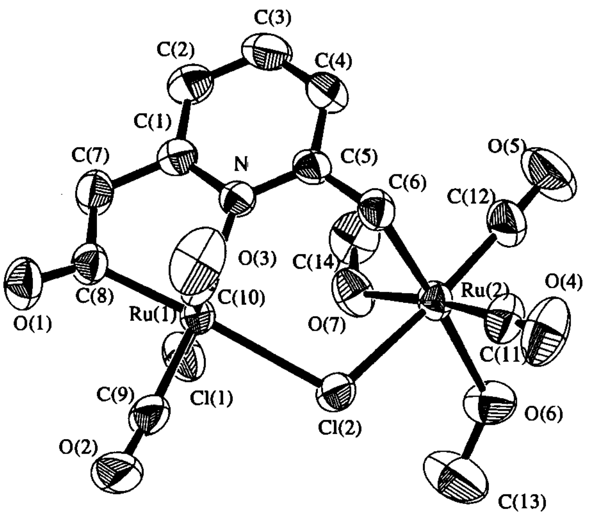


Fig. 1 Molecular structure of a diastereoisomer of complex **2**. Hydrogen and phenyl carbon atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): Ru(1)–Cl(1) 2.446(1), Ru(1)–Cl(2) 2.623(1), Ru(1)–N 2.153(4), Ru(1)–C(8) 1.987(4), Ru(2)–Cl(2) 2.413(1), Ru(2)–O(6) 2.266(4), Ru(2)–O(7) 2.143(3), Ru(2)–C(6) 2.120(4), O(1)–C(8) 1.216(5), C(1)–C(7) 1.489(6), C(5)–O(6) 1.478(6) and C(7)–C(8) 1.520(7); Ru(1)–Cl(2)–Ru(2) 108.29(4), Ru(2)–C(6)–C(5) 113.3(3), Ru(1)–C(8)–O(1) 129.5(4), Ru(1)–C(8)–C(7) 110.9(3) and O(1)–C(8)–C(7) 119,4(4)

molecule seems to destabilize the basic framework of the complex toward electron impact.

As is seen in Table 2, the ^{1}H NMR spectra of the mono- and bis-phosphine derivatives, **3** and **4**, in $CDCl_3$ consist of one set of resonances for the $RuCH_2$ and $RuC(O)CH_2$ protons and for the pyridine ring protons, in addition to those of the PPh_3 ligand(s). In contrast to the cases of **1** and **2**, the $RuCH_2$ proton resonances of **3** appear at lower fields as an ABX pattern by coupling with geminal proton and ^{31}P nuclei, their coupling constants being calculated by a computer simulation as shown in Table 2. Thus the first attack of the PPh_3 molecule occurs at the methylene-co-ordinated ruthenium center of **1**. The same conclusion can be drawn from the ^{13}C NMR data for **3** in $CDCl_3$, because the $RuCH_2$ carbon resonance appeared at δ 26.3 as a doublet with $^2J_{CP} = 63.1$ Hz (Table 3). The large $^2J_{CP}$ value suggests that the phosphine ligand attaches to the position *trans* to the methylene carbon. This is consistent with the result of the X-ray analysis. In the carbonyl region the ^{13}C NMR spectrum of **3** showed two singlets and two doublets with the same values of $^2J_{CP} = 5.9$ Hz, indicating that a pair of carbonyl ligands is present on each metal atom. The ^{31}P-{^{1}H} NMR spectrum of **4** in $CDCl_3$ (Table 2) showed two resonances at δ 17.2 and 52.0 as separate singlets without ^{31}P–^{31}P coupling. This means that the second phosphine molecule in **4** is ligated to the acylruthenium atom. The result is in contrast to that for **2** in which the two methanol molecules are co-ordinated to the same ruthenium atom (see later). In the case of **4** the co-ordination of two PPh_3 ligands to the same metal atom may be hindered owing to their bulkiness and/or the strong *trans* lability of the carbonyl ligand. The ^{1}H NMR spectrum of **4** showed the $RuCH_2$ and $RuC(O)CH_2$ resonances at higher fields compared to those of **3**, respectively, as ABX and AB quartet patterns. The values of the coupling constants, J_{gem} and $^3J_{HP}$, for the former resonances were also calculated by a computer simulation as shown in Table 2. As the AB quartet pattern shows, the $RuC(O)CH_2$ protons do not couple with the ^{31}P nucleus on the acyl-co-ordinated metal atom. As shown in Table 3, the resonances assignable to the carbonyl carbons appeared as three doublets in the range of δ 196.2–201.4. Of these, two exhibited the same $^2J_{CP}$ value of 5.9 Hz as that of **3** and the other the larger value of 19.1 Hz. The result can be understood as one of the two CO ligands on the acyl-co-ordinated ruthenium atom in **3** was replaced by the second PPh_3 molecule. The larger $^2J_{CP}$ value for the latter doublet probably reflects the shorter bond length of (acyl)Ru–P than that of (methylene)Ru–P.

Structures of complexes 2–4

The molecular structure of a diastereoisomer of complex **2** is shown in Fig. 1. Selected bond lengths and angles are given in the caption. The complex is dinuclear and each Ru atom has a distorted octahedral geometry. The Ru(1) atom is co-ordinated by N, Cl(1) and two carbons, C(9) and C(10) (*cis*-CO), in an equatorial plane and axially situated C(8) (acyl) and Cl(2) (bridging). On the other hand, Ru(2) is ligated to two carbons, C(6) (methylene) and C(11) (carbonyl), and two oxygens, O(6) and O(7) (*cis*-MeOH), in an equatorial plane with *trans*-axial C(12) (carbonyl) and Cl(2) (bridging). A five-membered ring including Ru(1) is formed by using the N(1), C(1) and C(7) atoms from the $CH_2C_5H_3NCH_2$ group together with the migratory inserted carbonyl carbon, C(8). One more terminal carbon, C(6), of the $CH_2C_5H_3NCH_2$ group is directly σ bonded to Ru(2). Thus the Ru(1) and Ru(2) atoms are doubly connected by a chlorine atom and a $C(O)CH_2C_5H_3NCH_2$ group. The cyclometallated ring is not planar and the maximum deviation from the plane defined by the five atoms is 0.21 Å for C(8). This is in contrast to the case of the mononuclear complex $[RuCl\{C(O)CH_2C_5H_4N\}(CO)(PPh_3)_2]$.[10] Dinucleation possibly forces the ring to adopt the distorted structure.

The molecular structures of the mono- and bis-phosphine derivatives, **3** and **4**, are compared with each other in Fig. 2. Selected bond lengths and angles are listed in Table 5. In analogy with **2**, complexes **3** and **4** are dinuclear and two Ru atoms are doubly connected by a chlorine atom and a $C(O)CH_2C_5H_3NCH_2$ group. In either **3** or **4**, the $C(O)CH_2C_5H_3NCH_2$ group is again cyclometallated to Ru(1) with the donor atom, N, of the pyridine ring and the acyl carbon, C(8), and σ bonded to Ru(2) with the methylene carbon, C(6). However, the structures of **3** and **4** are somewhat different from that of **2** in the configuration around one of two Ru atoms. For example, in **3** Ru(2) has a distorted octahedral arrangement with six donor atoms, P(1), C(6) (methylene), C(11) and C(12) (*cis*-CO), and Cl(1) (bridging) and Cl(2) (terminal), but Ru(1) is co-ordinated by five donor atoms, N, Cl(1) (bridging) and C(9) and C(10) (*cis*-CO), in a basal plane, and the axially situated C(8) (acyl). The co-ordination around the Ru atoms in **4** is the same as that in **3**, except that the carbonyl carbon, C(9), in **3** has been replaced by the donor atom, P(2), of the added PPh_3 molecule. The chlorine atom, Cl(2), that is attached to Ru(2) is in the vicinity of the vacant site on the Ru(1) atom and a pseudo-octahedral geometry around Ru(1) is completed by unusually close Ru(1) · · · Cl(2) contacts of 2.855(2) Å in **3** and 2.941(2) Å in **4**. These Ru · · · Cl distances are longer than not only the usual octahedral Ru–Cl (terminal) bond length (2.409 Å),[21] but that [2.623(1) Å] of Ru(1)–Cl(2) (bridging) in **2**, which is elongated by the *trans* influence of the acyl ligand. The secondary bonding concept has been used to describe inter-[19] and intra-molecular[20] interactions showing distances much longer than normal single bonds and much shorter than the sum of the van der Waals radii. When the elongation of the M–Cl separation relative to the normal single-bond distance is observed, excesses under 1.0 Å are considered to be indicative of the existence of M–Cl secondary bonding.[22] If applied to our structures, this criterion would establish a maximum Ru–Cl distance of 3.41 Å. The above-mentioned Ru · · · Cl distances are within the value, thus indicating the existence of the secondary bonding interactions between Ru(1) and Cl(2) in **3** and **4**. Such a M–Cl secondary bonding interaction is also observed for *o*-chlorine atoms in mononuclear (pentachlorophenyl)rhodium(II) complexes.[23] We add here that the existence of such a Ru · · · Cl secondary bonding in **4** was not considered in our preliminary report.[11]

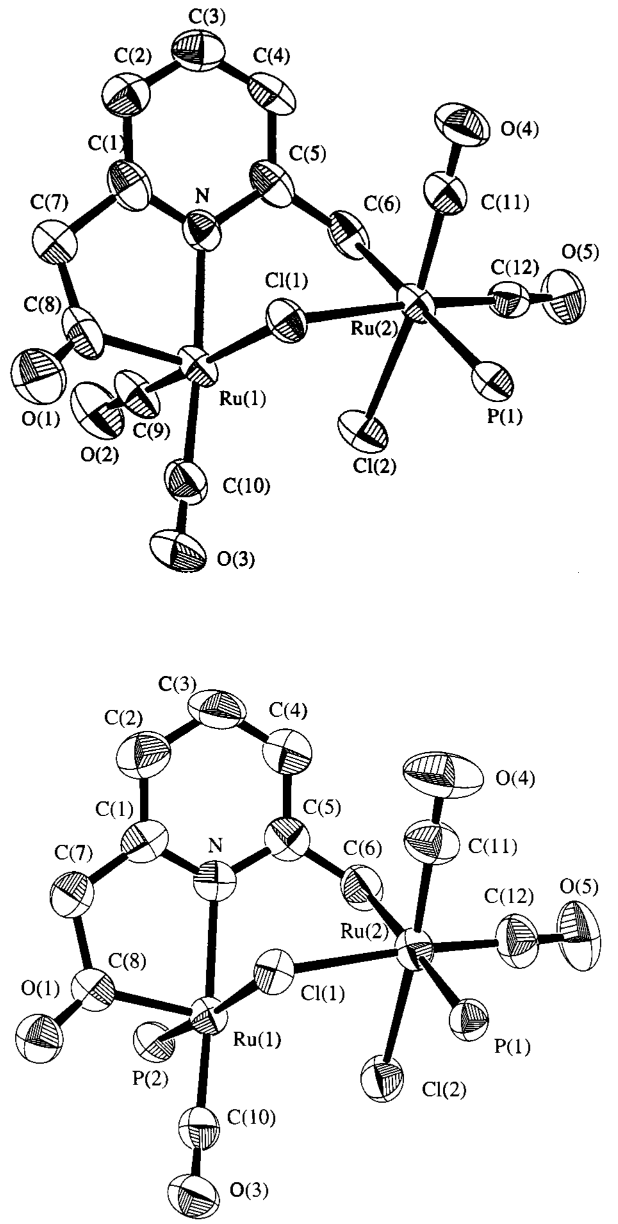
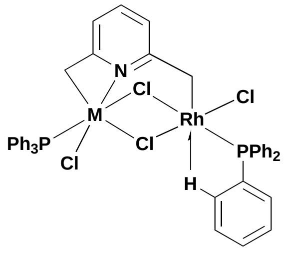


Fig. 2 The molecular structures of complexes **3** (upper) and **4** (lower). Hydrogen and phenyl carbon atoms are omitted for clarity. The solvent of crystallization is also omitted

The cyclometallated ring of complex **3** is not planar. In this case, the C(7) and C(8) atoms deviate by −0.16 and 0.12 Å, respectively, from the plane defined by the five atoms. On the other hand, the cyclometallated ring of **4** is nearly planar and the O(1) atom is also within 0.09 Å below the plane. The plane, however, is not coplanar to the pyridine ring. The dihedral angle between the two planes is 10.3°. The bond lengths Ru(1)–Cl(1) and Ru(2)–Cl(1) in **3** are comparable and the corresponding bond lengths in **4** are also comparable, because of the equivalent or approximately equivalent *trans* influences of the *trans* ligands. The Ru–C (carbonyl) bond lengths are in the normal ranges of 1.835(6)–1.902(7) [average 1.863(28)] in **3** and 1.842(7)–1.859(6) Å [average 1.852(9) Å] in **4**. The Ru(2)–P(1) bond length [2.460(2) Å] in **4**, which is comparable to that [2.464(2) Å] in **3**, is 0.145 Å longer than the Ru(1)–P(2) bond length, reflecting the *trans* influence of the methylene carbon, C(6).

The structures of complexes **3** and **4** are of interest in connection with those of dirhodium(III) homo- and iridium(III)-rhodium(III) hetero-dinuclear complexes shown, which have been revealed by X-ray analyses to have a pseudo-octahedral structure with weak Rh···HC (aryl) interactions for one of the two metal centers.[1d] When we compare the structure of **4** with these it is particularly intriguing that the existence of the Ru···Cl secondary bonding interaction in **4** prevents a Ru···HC (aryl) interaction.



M = Rh, Ir

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