BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 52 (5), 1372—1376 (1979)

Preparations and Characterization of Cycloruthenated Complexes Derived from 1-Phenylpyrazole, 2-Phenylpyridine, and Benzo[*h*]quinoline

Katsuma Hiraki,* Yayoi Obayashi,† and Yoko Oki

Department of Industrial Chemistry, Faculty of Engineering,
Nagasaki University, Bunkyo-machi, Nagasaki, 852

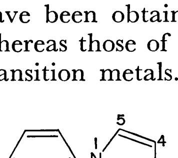
(Received September, 1, 1978)

A pale yellow solution, prepared from $\mathrm{RuCl_3 \cdot 3H_2O}$ and carbon monoxide in 2-methoxyethanol, reacted with 1-phenylpyrazole (Hphpz), 2-phenylpyridine (Hphpy), and benzo[*h*]quinoline (Hbzqn) to give new chloro-bridging dinuclear cycloruthenated complexes, $[\{\mathrm{RuCl(C{\sim}N)(CO)_2}\}_2]$ ($\mathrm{C{\sim}N}$=cycloruthenated moiety). These complexes reacted with Tl(acac) (acac=acetylacetonato ligand), γ-picoline (pic), and triphenylphosphine resulting in the break-down of the chloro-bridging bond of the complexes, and afforded new mononuclear cycloruthenated complexes, $[\mathrm{Ru(acac)(C{\sim}N)(CO)_2}]$, $[\mathrm{RuCl(C{\sim}N)(CO)_2(pic)}]$, and $[\mathrm{RuCl(C{\sim}N)(CO)_{\mathit{n}}(PPh_3)_{3-\mathit{n}}}]$ (n=2 for phpz, and n=1 for phpy and bzqn), respectively. The complexes prepared in this study were characterized by IR, ^{1}H-NMR, and mass spectroscopies.

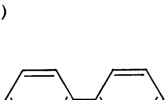
Recently, cyclometallation reactions have become of interest in view of the stabilization of transition metal–carbon σ bonds[1–3] and of availabilities for the syntheses of heterocycles.[3] Several investigations have been reported concerning cycloruthenation reactions of azobenzene,[2,4–7] polyhaloazobenzene,[2,6] benzo[*h*]quinoline,[8] Schiff bases derived from benzaldehyde,[9] triphenylphosphite,[2,7,10] triphenylphosphine[2,7] and 1,3-di-*p*-tolylimidazolidin-2-ylidene group.[11] These cycloruthenation reactions in most cases were carried out using activated ruthenium species, such as $[\{\mathrm{RuCl_2(CO)_3}\}_2]$,[4,9] or alkyl-,[6,7] hydrido-,[10] or zerovalent[5,8,9] ruthenium complexes.

This paper deals with direct and convenient cycloruthenation reactions of 1-phenylpyrazole (Hphpz), 2-phenylpyridine (Hphpy), and benzo[*h*]quinoline (Hbzqn) yielding new chloro-bridging dinuclear cycloruthenated complexes, and with some mononuclear complexes prepared by the bridge-splitting reactions of the dinuclear complexes with thallium acetylacetonate [Tl(acac)], γ-picoline (pic), and triphenylphosphine ($\mathrm{PPh_3}$).

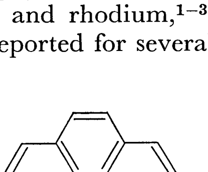
Cyclometallated complexes of Hphpz and Hphpy have been obtained with palladium and rhodium,[1–3] whereas those of Hbzqn have been reported for several transition metals.[1,2]



phpz



phpy



bzqn

Experimental

Materials. Commercial grade ruthenium(III) chloride trihydrate ($\mathrm{RuCl_3 \cdot 3H_2O}$), benzo[*h*]quinoline, and γ-picoline were used without further purification. 1-Phenylpyrazole,[12] 2-phenylpyridine,[13] and Tl(acac)[14] were prepared according to the methods described in the literature. Solvents were dried by usual procedures and distilled.

General Procedures. IR spectra were obtained using a Hitachi 285 grating spectrometer. ^{1}H- and ^{31}P-NMR spectra were run on JEOL model-JNM-MH-100 and -FX-100 spectrometers, respectively. Molecular weights were determined using a JEOL model MS-01SG double-focussing mass spectrometer, referring to parent ion peaks. Melting points were determined on a Yanagimoto MP-S3 microstage apparatus and are uncorrected. All preparative operations were performed in an atmosphere of dry dinitrogen.

Cycloruthenation Reactions of Hphpz, Hphpy, and Hbzqn. Carbon monoxide was bubbled into a 2-methoxyethanol solution (30 ml) of $\mathrm{RuCl_3 \cdot 3H_2O}$ (1 g) under refluxing for 6 h to give a yellow solution. An excess amount of Hphpz (2.6 g) was added to the yellow solution, and the mixture was refluxed for 3.5 h. A yellow precipitate was separated and washed with diethyl ether and benzene to afford di-μ-chloro-tetracarbonylbis{2-(1′-pyrazolyl)phenyl-1-*C*,2′-*N*}-diruthenium(II) (**1**) in 60% yield. 2-Phenylpyridine and benzo[*h*]quinoline reacted similarly with the yellow solution to yield $[\{\mathrm{RuCl(phpy)(CO)_2}\}_2]$ (**2**) and $[\{\mathrm{RuCl(bzqn)(CO)_2}\}_2]$ (**3**), respectively.

*Reactions of **1**, **2**, and **3** with Tl(acac).* Thallium acetylacetonate (0.6 mmol) and **1** (0.3 mmol) in 40 ml of dichloromethane were stirred under refluxing for 7 h and then at ambient temperature for 98 h. After the reaction mixture was filtered and concentrated, hexane was added to the resulting solution. A pale reddish gray solid precipitated and was washed with hexane to give mononuclear acetylacetonatodicarbonyl{2-(1′-pyrazolyl)phenyl(1-*C*,2′-*N*)}ruthenium(II) (**4**) in 45.9% yield.

Complexes **2** and **3** also reacted similarly with Tl(acac) to afford $[\mathrm{Ru(acac)(phpy)(CO)_2}]$ (**5**) and $[\mathrm{Ru(acac)(bzqn)(CO)_2}]$ (**6**), respectively.

*Reactions of **1**, **2**, and **3** with Triphenylphosphine.* A dichloromethane suspension containing **1** (0.4 mmol) and triphenylphosphine (2.0 mmol) was stirred at room temperature for 22 h. The resulting solution was concentrated, and diethyl ether was added. On standing overnight at 5—6 °C, the mixture yielded a white crystal, which was separated and washed with diethyl ether to give mononuclear dicarbonylchloro{2-(1′-pyrazolyl)phenyl(1-*C*,2′-*N*)}triphenylphosphineruthenium(II)-diethyl ether(2/1) (**7**) in 87.4% yield.

Complexes **2** and **3** also reacted analogously with triphenylphosphine to yield $[\mathrm{RuCl(phpy)(CO)(PPh_3)_2}]$ (**8**) and $[\mathrm{RuCl(bzqn)(CO)(PPh_3)_2}]$ (**9**), respectively.

*Reactions of **1**, **2**, and **3** with γ-Picoline.* A dichloromethane suspension (40 ml) involving **1** (0.4 mmol) and γ-picoline (2.4 mmol) was stirred at room temperature for 3.5 h. After the concentration of the resultant solution, followed by addition of hexane, an off-white powder precipitated. Recrystallization of the off-white powder from dichloromethane gave a mother liquor and a white granule,

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† Present address: Sagamidai-jutaku 3-101, Iwase 531, Matsudo 271.

The evaporation to dryness of the mother liquor, followed by recrystallization from dichloromethane-hexane, afforded a pale gray solid, dicarbonylchloro(γ-picoline){2-(1′-pyrazolyl)phenyl-1-*C*,2′-*N*}ruthenium(II) (**10a**) in 46.9% yield. Three times recrystallizations of the white granule from dichloromethane yielded **10b** (2.9% yield), which was ascribed to an isomer of **10a** by elemental analysis, IR, and ^{1}H-NMR data.

Complex **2** reacted similarly with 4-picoline and gave [RuCl(phpy)$(CO)_2$(pic)] (**11a**) and a slight amount of a mixture consisting of **11a** and a by-product. Attempts to separate the mixture into the components were unsuccessful.

A dichloromethane suspension (25 ml) containing **3** (0.27 mmol) and γ-picoline (0.73 mmol) was refluxed for 4 h and stirred at ambient temperature for 14 h. After the concentration of the resulting solution, addition of hexane yielded a dark yellow microcrystal and a mother liquor. A silica-gel chromatography of a dichloromethane solution of the microcrystal afforded a yellow solid [RuCl(bzqn)$(CO)_2$(pic)] (**12a**). An orange-yellow powder, formed gradually from the mother liquor on cooling, produced an orange yellow solid [{RuCl(bzqn)(CO)(pic)}$_2$] (**12b**) with recrystallization from dichloromethane-hexane.

Results and Discussion

Cycloruthenation Reactions of Hphpz, Hphpy, and Hbzqn. Chatt *et al.*[15)] reported that the 2-methoxyethanol solution of $RuCl_3 \cdot 3H_2O$ was refluxed under bubbling carbon monoxide to yield the yellow solution, in which a main ruthenium species was represented by $[RuCl_m(CO)_n]$.[16)] This solution reacted easily with tertiary phosphine or arsine resulting in the formation of complexes, $[RuCl_2(CO)_2L_2]$ (L=a neutral donor ligand).[15)] In the present study, the yellow solution reacted also with Hphpz, Hphpy, and Hbzqn under reflux to give the cycloruthenated dinuclear complexes, $[\{RuCl(C{\frown}N)(CO)_2\}_2]$ ($C{\frown}N$=cycloruthenated moiety), **1**, **2**, and **3**, respectively (*vide infra* as for configurations). On the other hand, the preparation of a more carbonylated ruthenium complex, $[\{RuCl_2(CO)_3\}_2]$, needs higher pressure of carbon monoxide than 10 atm.[17)] In consideration of these facts, it seems certain that the main ruthenium species in the yellow solution bears two carbonyl groups, and has a divalent state, not the initial trivalent one, judging from the π-back bonding character of the carbonyl groups. Accordingly, the main ruthenium species is represented by $[RuCl_2(CO)_2S_2]$, where S means a solvent molecule or a chloro ligand. The cycloruthenation reactions are shown by the following equation:

$$[RuCl_2(CO)_2S_2] + 2H(C{\frown}N) \longrightarrow$$
$$1/2[\{RuCl(C{\frown}N)(CO)_2\}_2] + H_2(C{\frown}N)\cdot Cl + 2S.$$

These reactions proceed fairly smoothly, and seem to provide a convenient route for the syntheses of the cycloruthenated complexes of the aryl-substituted heterocycles. Driving forces for these reactions are possibly associated both with a basicity of the heterocycles and with a structural factor of the aryl-substituted heterocycles susceptible to the cyclometallation.[1—3,8)] Tables 1—3 summarize yields, elemental analyses, and some properties of **1**, **2**, and **3** and their derivatives.

Complexes **1**, **2**, and **3** are stable and insoluble in common organic solvents. Each of these complexes contains terminal carbonyls as shown by IR spectra (Table 2), and has one chlorine atom and four other coordination sites per ruthenium atom, as indicated clearly by the elemental analyses (Table 1). It has been well known that most of divalent ruthenium complexes have a six-coordinated structure,[4,8,9,15,17)] and that chlorine atoms serve as bridging ligands to form a dinuclear structure in chlororuthenium(II) complexes.[4,17)] On the basis of these considerations, of the high insolubilities, and of reactivities towards a few reagents as stated later, each of **1**, **2**, and **3** was assigned to the dinuclear structure having the chlorine bridges, similarly to $[\{RuCl(azb)(CO)_2\}_2]$, (Hazb=azobenzene).[4)]

Acetylacetonato and Triphenylphosphine Complexes. The dinuclear complexes **1**, **2**, and **3** reacted with Tl(acac) to afford the mononuclear acetylacetonatoruthenium(II) complexes **4**, **5**, and **6**, respectively.

TABLE 1. YIELDS AND PROPERTIES OF THE RUTHENIUM COMPLEXES

Complex		Yield (%)	Mp[a)] (°C)	Color	C (%)		H (%)		N (%)	
					Calcd	Found	Calcd	Found	Calcd	Found
$\{RuCl(phpz)(CO)_2\}_2$	**1**	60.0	243	Off white	39.36	39.79	2.10	2.09	8.35	8.24
$\{RuCl(phpy)(CO)_2\}_2$	**2**	61.5	262—263	Pale yellow	45.35	45.60	2.31	2.59	4.02	3.99
$\{RuCl(bzqn)(CO)_2\}_2$	**3**	64.8	278—280	Yellow	48.59	49.26	2.17	2.47	3.78	3.78
$Ru(acac)(phpz)(CO)_2$	**4**	45.9	176—178	Pale reddish gray	48.12	47.68	3.53	3.31	7.01	7.06
$Ru(acac)(bzpn)(CO)_2$	**5**	68.6	140—164	Pale brown	52.68	52.53	3.68	3.82	3.41	3.40
$Ru(acac)(bzqn)(CO)_2$	**6**	72.6	213—219	Pale yellowish brown	55.30	56.18	3.48	3.58	3.22	3.34
$RuCl(phpz)(CO)_2(PPh_3)$[b)]	**7**	87.4	190	White	58.64	58.17	4.29	4.12	4.41	4.43
$RuCl(phpy)(CO)(PPh_3)_2$	**8**	47.9	277—231	Yellow	68.39	68.51	4.51	4.49	1.66	1.57
$RuCl(bzqn)(CO)(PPh_3)_2$	**9**	57.7	270	Yellow	68.90	69.27	4.42	4.42	1.62	1.61
$RuCl(phpz)(CO)_2(pic)$	**10a**	46.9	187—190	Pale gray	47.61	48.23	3.29	3.24	9.80	9.89
	10b	2.9	164—167	White	47.61	47.53	3.29	3.22	9.80	9.65
$RuCl(phpy)(CO)_2(pic)$	**11a**	40.0	183—188	Dark yellow	51.88	51.58	3.44	3.37	6.37	6.31
$RuCl(bzqn)(CO)_2(pic)$	**12a**	25.2	204—210	Yellow	54.37	54.20	3.26	3.24	6.04	6.00
$\{RuCl(bzqn)(CO)(pic)\}_2$	**12b**	10.0	270	Orange yellow	55.11	55.14	3.47	3.82	6.48	6.59

a) With decomposition. b) Containing a half mole of diethyl ether as solvent of crystallization.

Table 2. Characteristic IR bands and molecular weights of the complexes

Complex	ν(C=O) (cm^{-1})$^{a)}$	M. W.$^{c)}$
1	2038, 1987, 1962, 1941(sh) 1928(w)$^{b)}$	—
2	2020, 1975, 1946, 1928(w) 1908(sh)$^{b)}$	—
3	2015, 1978, 1960, 1930(w)$^{b)}$	—
4	2040, 1978	400(400)
5	2040, 1974	411(411)
6	2030, 1970	—
7	2040, 1985	—
8	1910$^{b)}$	—
9	1920$^{b)}$	—
10a	2050, 1987	—
10b	2020, 1940$^{b)}$	—
11a	2050, 1987	—
12a	2045, 1984	—
12b	1923, 1950(sh), 1975(w), 2040(w)	—

a) In chloroform solution, unless noted elsewhere. b) In KBr disc. c) Calculated value corresponding to ^{102}Ru is given in parentheses.

Triphenylphosphine also cleaved the chloro-bridging bonds of the dinuclear complexes, giving mononuclear complexes **7**, **8**, and **9**. These complexes are stable in a solid state and soluble in dichloromethane and chloroform. The acetylacetonato complexes decompose slowly in the solution, whereas the triphenylphosphine complexes are stable in the solution, too.

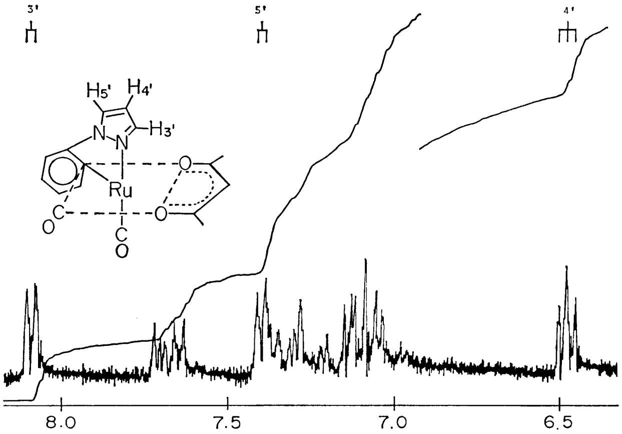


Fig. 1. ^{1}H-NMR spectrum of **4** in CD_2Cl_2 solution (δ-value from TMS).

^{1}H-NMR spectrum of **4** (Table 3 and Fig. 1) shows two doublets at δ 7.41 (1H, 5'-H, J=2.5 Hz) and 8.09 (1H, 3'-H, J=2.5 Hz), one triplet at δ 6.49 (1H, 4'-H) and two multiplets at δ 7.6—7.75 (1H) and 6.9—7.4 (3H), in addition to signals characteristic of the acac group. The multiplets differ completely from that of Hphpz, and are due to an *o*-phenylene group of the phpz moiety. As for mass spectrum of **4**, peaks of *m*/*e* corresponding to ^{102}Ru appeared at 400, 372, 344, 301, 273 and 245, which were ascribable to a parent peak [Ru(acac)(phpz)(CO)$_2$]$^+$, and fragment peaks [Ru(acac)(phpz)(CO)]$^+$, [Ru(acac)(phpz)]$^+$, [Ru(phpz)(CO)$_2$]$^+$, [Ru(phpz)(CO)]$^+$, and [Ru(phpz)]$^+$, respectively. These evidences elucidated unambiguously the cycloruthenated structure of the phpz moiety in **4**. Mass spectrum of **5** gave also a very similar pattern to that of **4**, to which the phpy moiety corresponded in place of the phpz one. This fact and the aromatic proton resonances[18] in ^{1}H-NMR spectrum of **5** indicate analogously the cycloruthenated structure of the phpy moiety in **5**. Complex **6** was similarly ascribed to the cycloruthenated structure on the basis of the ^{1}H-NMR spectrum.[19]

It is noted that **8** and **9** bear two triphenylphosphine ligands and one carbonyl group, while **7** has one triphenylphosphine ligand and two carbonyl groups, similarly to [RuCl(azb)(CO)$_2$(PPh$_3$)].[4] It is certain that both the phpy and bzqn moieties have a more conjugated skeleton than the phpz and azb moieties. The difference of the skeletal conjugation is probably responsible for that of the substitution of the carbonyl group with triphenylphosphine in these complexes. A proton-decoupled ^{31}P-NMR spectrum of **9** in dichloromethane showed a sharp singlet at 105.20 ppm to upper field from trimethyl phosphite (external standard). This fact proves undoubtedly that two triphenyl-

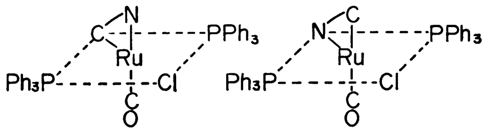
Table 3. ^{1}H-NMR data of the ruthenium complexes$^{a)}$

Complex	Pyrazolyl group				acac or pic			
	3'-H	4'-H	5'-H	$J_{4,3 \text{ or } 5}$	C$_\gamma$H$^{b)}$ or H$_\alpha$$^{c)}$	H$_\beta$	$J_{\alpha\beta}$	CH$_3$
	δ, ppm	δ, ppm	δ, ppm	Hz	δ, ppm	δ, ppm	Hz	δ, ppm
4$^{d)}$	8.09(d)	6.49(t)	7.41(d)	2.5	b) 5·26(s)$^{e)}$	—	—	1.69(s), 2.09(s)
5$^{f)}$	—	—	—	—	b) 5.26(s)$^{e)}$	—	—	1.68(s), 2.12(s)
6$^{f)}$	—	—	—	—	b) 5.47(s)	—	—	1.62(s), 2.23(s)
7$^{g,h)}$	8.31(d)	6.47(t)	7.23(d)	2.5	—	—	—	—
10a$^{d)}$	8.29(d)	6.55(t)	8.09(d)	2.5	c) 8.37(d)	6.97(d)	6.5	2.24(s)
10b$^{f)}$	8.18(d)	6.51(t)	7.2 (d)$^{i)}$	2.5	c) 8.97(d)	7.4 (d)$^{i)}$	6.0	2.48(s)
11a	—	—	—	—	c) 8.32(d)	6.93(d)	6.5	2.20(s)
12a$^{g)}$	—	—	—	—	c) 8.33(d)	6.76(d)	6.3	2.11(s)

a) In CD_2Cl_2, unless noted elsewhere. Abbreviations used: s=singlet, d=doublet, t=triplet, q=quartet. b) Acac group. c) Pic group. d) See the text about the *o*-phenylene protons. e) Confirmed by a measurement in $CDCl_3$ solution. f) See the notes 18, 19, and 21 about the aromatic protons of **5**, **6**, and **10b**, respectively. g) In $CDCl_3$. h) Containing CH$_2$[δ 3.58(q, J=7.0 Hz, 2H)] and CH$_3$[δ 1.25(t, 3H)] resonances of diethyl ether. i) Overlapping with the *o*-phenylene protons.

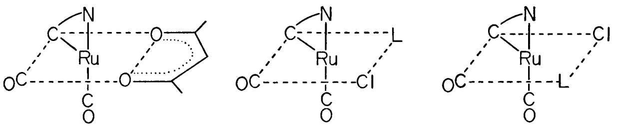
phosphine ligands in **9** are located at *trans* positions to each other, but not at *cis* positions, because the two triphenylphosphine ligands at the latter positions would be magnetically unequivalent and result in two ^{31}P resonances. The *trans* configuration of the ligands is presumably due to a steric interaction among the two triphenylphosphine ligands and the chelating bzqn moiety.

Accordingly, two isomers A and B are possible for **9**, as demonstrated in Fig. 2. IR spectrum of this complex exhibits a comparatively low frequency of ν(CO) band. Low stretching frequencies of carbonyl group have been observed for [RuCl$_2$(CO)(pyridine)$_3$]$^{20)}$ and [Ru(azb)(pz$_3$BH)(CO)] (pz=1-pyrazolyl),$^{4)}$ possessing the carbonyl group *trans* to a nitrogen donor ligand. In consideration of these facts, **9** was ascribed to configuration A, in which the nitrogen donor site was situated at a *trans* position to the carbonyl group. Complex **8** was also associated with the configuration A, from the similarity of the composition and the ν(CO) frequency.



A B

Fig. 2. Possible configurations of the bis(triphenylphosphine) complexes. C⌒N=the cycloruthenated moiety.



C D E

Fig. 3. Possible configurations of the dicarbonyl complexes. L=triphenylphosphine or γ-picoline.

Complexes **4**, **5**, **6**, and **7** show two strong ν(CO) bands near 1978 and 2040 cm^{-1}, revealing a *cis* coordination of the two carbonyl groups. One of the two carbonyl groups is presumably situated at a *trans* position to the nitrogen donor site, analogously to the cases of **8** and **9**, since the coordinations of these ligands are likely to be unaffected by the splitting reactions of the chlorobridging bonds of **1**, **2**, and **3** with Tl(acac) or triphenylphosphine. These discussions lead to proposals that **4**, **5**, and **6** are assignable to configuration C, and that **7** is to configuration D or E (Fig. 3).

γ-Picoline Complexes. γ-Picoline also reacted with **1**, **2**, and **3** to yield corresponding derivatives **10**, **11**, and **12**, respectively. Each of **10** and **12** was separated into a major product **a** and a minor one **b** by means of the repeated recrystallizations. These complexes are stable in a solid state and soluble in dichloromethane and chloroform.

Mononuclear complexes **10a**, **11a**, and **12a** showed very similar ν(CO) bands to those of **4**, **5**, **6**, and **7**, suggesting a similarity among the configurations of these complexes. ^{1}H-NMR spectrum of **10a** contains two multiplets at δ 7.0—7.4 (3H) and 7.7—7.9 (1H) assignable to the *o*-phenylene protons, in addition to γ-picoline and pyrazolyl proton resonances (Table 3), indicating the cycloruthenated structure of the phpz moiety in **10a**. Moreover, ^{1}H-NMR spectrum of **10b**$^{21)}$ showed lower field γ-picoline proton resonances than that of **10a** did. It is expected that all the protons of γ-picoline *trans* to a carbonyl group are deshielded more strongly owing to a π-back bonding character of the carbonyl group than those of γ-picoline *trans* to the aryl carbon. On the basis of these discussions, **10b** was assigned to configuration D, whereas **10a**, **11a**, and **12a** to configuration E.

Complex **12b** exhibited a medium ν(CO) band at 1923 cm^{-1}, accompanied by very weak bands at 1950, 1975, and 2040 cm^{-1}. Elemental analysis of **12b** reveals that this complex is not an isomer of the main product **12a**, but has one chlorine atom and four other coordination sites per ruthenium atom, similarly to **3**. These data are consistent with a dimeric structure of **12b**, retained even during the reaction of **3** with γ-picoline, although γ-picoline has been regarded as a typical bridge-splitting reagent. Complex **12b** was probably formed by a substitution of two carbonyl groups in **3** with two γ-picoline ligands, in place of the chlorine-bridge splitting reaction. However, further characterization of **12b** was impossible, since its yield was low and irreproducible.

Dinuclear Complexes. All the mononuclear complexes derived from the dinuclear ones **1**, **2**, and **3** had one or two carbonyl ligands, but not more than three. In addition, all the mononuclear dicarbonyl complexes exhibited two strong ν(CO) bands. These facts indicate that each ruthenium atom in the dinuclear complexes is coordinated with two carbonyl groups in a *cis* form, but not in a *trans* form. Accordingly, one of the two carbonyl groups is necessarily located at a *cis* position to the two bridging chlorine atoms. On the basis of these discussions and the conclusion that the nitrogen donor site of the cycloruthenated moiety was situated at the *trans* position to one of the carbonyl groups, as stated above, four isomers are

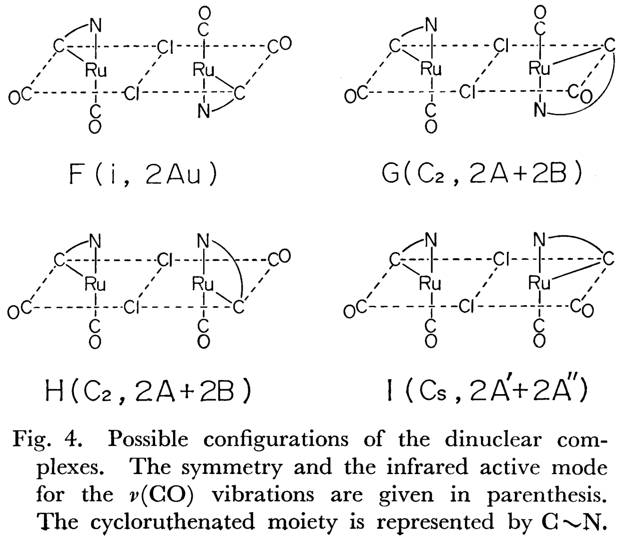


Fig. 4. Possible configurations of the dinuclear complexes. The symmetry and the infrared active mode for the ν(CO) vibrations are given in parenthesis. The cycloruthenated moiety is represented by C⌒N.

possible for each of **1**, **2**, and **3**, as depicted in Fig. 4. In Fig. 4, symmetry and an infrared active mode for the carbonyl stretching vibrations are given for each somer.

IR spectrum of **1**, **2**, or **3** shows three strong ν(CO) bands and a few weak ones. In consideration of the steric interaction between the two cycloruthenated moieties, it appears that each of these dinuclear complexes consists of two isomers, F and G. This proposal is reasonable, since all the mononuclear complexes investigated in the present study can be derived by a substitution of the bridging chlorine atoms, and by an additional substitution of one carbonyl group only in the cases of **8** and **9**, from F or G without any rearrangement of the other ligands.

We wish to express our gratitude to Mrs. Hisako Mazume and Miss Yumi Kojima of Nagasaki University for their technical assistances and also to Mr. Toru Hinomoto of Japan Electron Optics Laboratory for the ^{31}P-NMR measurement.

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