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Preparations and Characterization of Some Carbonyl(1-cyanoethyl)ruthenium(II) Complexes

Katsuma Hiraki,* Naoyuki Ochi, Tsuneyuki Kitamura, Yoko Sasada, and Sumio Shinoda†
Department of Industrial Chemistry, Faculty of Engineering, Nagasaki University, Bunkyo-machi, Nagasaki 852
†*Institute of Industrial Science, The University of Tokyo, Roppongi-7, Minato-ku, Tokyo 106*

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A hydridoruthenium(II) complex [RuClH(CO)(PPh$_3$)$_3$] reacted easily with acrylonitrile and fumaronitrile to give chloro-bridged binuclear (1-cyanoethyl)ruthenium(II) complexes, [{Ru(MeCHCN)Cl(CO)(PPh$_3$)$_2$}$_2$] (**2**) and [{Ru(NCCH$_2$CHCN)Cl(CO)(PPh$_3$)$_2$}$_2$], respectively. Complex **2** reacted with 4-picoline (pic), Na[BHPz$_3$] (Pz=1-pyrazolyl), Na[BPz$_4$], and Na[Et$_2$NCS$_2$]·3H$_2$O to afford the corresponding (1-cyanoethyl)ruthenium(II) complexes, [{Ru(MeCHCN)Cl(CO)(pic)(PPh$_3$)}$_2$] (**3**), [Ru(MeCHCN)(BHPz$_3$)(CO)(PPh$_3$)] (accompanied by a small amount of [Ru$_2$(MeCHCN)$_2$Cl(BHPz$_3$)(CO)$_2$(PPh$_3$)$_4$]), [Ru$_2$(MeCHCN)$_2$Cl(BPz$_4$)(CO)$_2$(PPh$_3$)$_2$], and Na[Ru(MeCHCN)Cl(Et$_2$NCS$_2$)(CO)(PPh$_3$)], respectively. Complex **3** reacted with thallium(I) acetylacetonate [Tl(acac)], resulting in the formation of [{Ru(MeCHCN)(acac)(CO)(PPh$_3$)}$_2$] and [Ru(MeCHCN)(acac)(CO)(pic)(PPh$_3$)]. These new complexes were characterized by means of elemental analysis and spectroscopic data. The diastereoisomerism was also discussed as regards these (1-cyanoethyl)ruthenium(II) complexes.

It is interesting to investigate the coordination behavior of (1- and 2-cyanoalkyl)ruthenium(II) complexes, in connection with catalytic hydrodimerization[1–3] and polymerization[4] of acrylonitrile with ruthenium complexes. However, little has been known about the (cyanoalkyl)ruthenium(II) complexes,[5] whereas only a few papers have been reported concerning the coordination behavior of octahedral alkylruthenium(II) complexes.[6–9]

It has been recently reported from our laboratory that some substituted olefins insert into the hydridoruthenium (H–Ru) bond of (carbonyl)chlorohydridotris(triphenylphosphine)ruthenium(II) (**1**) to give stable organoruthenium(II) complexes.[5] Since [{Ru(MeCHCN)Cl(CO)(PPh$_3$)$_2$}$_2$] (**2**), prepared from the reaction of **1** with acrylonitrile, was insoluble in usual organic solvents, its 4-picoline (pic) derivative [{Ru(MeCHCN)Cl(CO)(pic)(PPh$_3$)}$_2$] (**3**) was prepared. Complex **3** had also a binuclear structure and was assumed to consist of a few diastereoisomers.[5] In this paper, reactions of **2** and **3** with several anionic chelating ligands were carried out, in order to prepare mononuclear (1-cyanoethyl)ruthenium(II) complexes and to confirm whether the isomers in **3** were caused by asymmetric 1-carbon and ruthenium atoms or not. In addition, the resulting complexes were isolated and characterized on the basis of elemental analysis and spectroscopic data.

Experimental

General Procedures and Materials. Melting points, IR spectra, and ^{1}H and ^{31}P-NMR spectra were obtained according to the previous paper.[10] The molecular weight of a complex was determined in benzene using a Corona model 114 vapour pressure osmometer.

Solvents were dried and distilled by the usual methods, and all preparative operations were performed in an atmosphere of dry nitrogen. Complex **1**,[11] sodium poly(1-pyrazolyl)borates Na[BPz$_3$H] (Pz=1-pyrazolyl) and Na[BPz$_4$],[12] and thallium(I) acetylacetonate[13] were prepared according to the literature methods. The other reagents were commercial samples, and were used without further purification.

Reaction of 1 with Acrylonitrile. A THF suspension (60 ml) containing **1** (1 mmol) and acrylonitrile (7.5 mmol) was stirred at room temperature for 23 h to give a pale yellowish green precipitate. The precipitate was collected and washed with hexane and diethyl ether to yield a greenish gray solid [{Ru(MeCHCN)Cl(CO)(PPh$_3$)$_2$}$_2$] (**2**).

Reaction of 2 with 4-Picoline. A THF suspension (35 ml) involving **2** (0.24 mmol) and 4-picoline (1.4 mmol) was stirred at room temperature for 20 h to yield a yellow solution. After concentration, the yellow solution was diluted with diethyl ether to give a pale green powder, [{Ru(MeCHCN)Cl(CO)(pic)(PPh$_3$)}$_2$] (**3**).

Reaction of 1 with Fumaronitrile. A THF suspension (30 ml) containing **1** (1 mmol) and fumaronitrile (3.75 mmol) was stirred at room temperature for 20 h to result in an orange-brown solution. After concentration under a reduced pressure, the orange-brown solution was diluted with 80 ml of hexane to yield an orange-brown powder. The powder was collected and washed with diethyl ether to give a yellow-brown powder, [{Ru(NCCH$_2$CHCN)Cl(CO)(PPh$_3$)$_2$}$_2$] (**4**).

Reaction of 2 with Na[BHPz$_3$]. A THF suspension (20 ml) involving **2** (0.27 mmol) and Na[BHPz$_3$] (0.55 mmol) was stirred at 40 °C for 4 h. After filtration, the resulting filtrate was evacuated under a reduced pressure, and chromatographed over silica-gel column (Wako gel, 200 mesh, 150×12ϕ mm). A yellow fraction was eluted with benzene, and concentration of this afforded yellow solids, [Ru(MeCHCN)(BHPz$_3$)(CO)(PPh$_3$)] (**5**). Moreover, a pale yellow fraction was eluted with acetone, and evaporation of this gave a small amount of pale yellow solids, [Ru$_2$(MeCHCN)$_2$Cl(BHPz$_3$)(CO)$_2$(PPh$_3$)$_4$] (**6**).

Reaction of 2 with Na[BPz$_4$]. A benzene suspension (40 ml) containing **2** (0.25 mmol) and Na[BPz$_4$] (0.55 mmol) was refluxed for 9 h. After filtration, the filtrate was concentrated and diluted with hexane to yield cream-yellow precipitates. The precipitates were recrystallized from dichloromethane-hexane to give a cream-yellow powder, [Ru$_2$(MeCHCN)$_2$Cl(BPz$_4$)(CO)$_2$(PPh$_3$)$_2$] (**7**).

Reaction of 2 with Na[Et$_2$NCS$_2$]·3H$_2$O. A THF suspension (60 ml) of **2** (0.2 mmol) and Na[Et$_2$NCS$_2$]·3H$_2$O (0.48 mmol) was stirred at room temperature for 91 h to yield greenish white precipitates. The precipitates were washed with diethyl ether and hexane, successively, to afford greenish white solids, Na[Ru(MeCHCN)Cl(Et$_2$NCS$_2$)(CO)(PPh$_3$)] (**8**).

Reaction of 3 with Thallium(I) Acetylacetonate. A dichloromethane suspension (30 ml) containing **3** (0.52 mmol) and Tl(acac) (1.05 mmol) was stirred at room temperature for 72 h.

After filtration, the resulting solution was chromatographed upon the silica-gel column. A yellow fraction was eluted with benzene, concentrated under a reduced pressure, and diluted with hexane to give a light yellow powder, $[\{Ru(MeCHCN)(acac)(CO)(PPh_3)\}_2]$ (**9**). The second yellow fraction was eluted with dichloromethane, and evacuated to dryness *in vacuo*. The resulting residue was washed with hexane to afford a pale yellow powder, $[Ru(MeCHCN)(acac)(CO)(pic)(PPh_3)]$ (**10**).

Results and Discussion

Preparation. The hidridoruthenium(II) complex **1** reacted smoothly with acrylonitrile and fumaronitrile in THF at room temperature to give sparingly soluble binuclear complexes $[\{Ru(MeCHCN)Cl(CO)(PPh_3)_2\}_2]$ (**2**)[5] and $[\{Ru(NCCH_2CHCN)Cl(CO)(PPh_3)_2\}_2]$ (**4**), respectively. Complex **2** was treated with 4-picoline (in THF at room temperature), with $Na[BPz_4]$ (in refluxing benzene), and with $Na[Et_2NCS_2]\cdot 3H_2O$ (in THF at room temperature) to yield $[\{Ru(MeCHCN)Cl(CO)(pic)(PPh_3)\}_2]$ (**3**), $[Ru_2(MeCHCN)_2Cl(BPz_4)(CO)_2(PPh_3)_2]$ (**7**), and $Na[Ru(MeCHCN)Cl(Et_2NCS_2)(CO)(PPh_3)]$ (**8**), respectively. Complexes **3** and **7** have also binuclear structures, whereas **8** has an ionic structure and is actually insoluble in usual organic solvents.

In order to obtain neutral mononuclear-type complexes, reactions between **2** and $Na[BHPz_3]$ and between **3** and Tl(acac) were examined. The former reaction produced two complexes, which were separated by column chromatography and formulated as $[Ru(MeCHCN)(BHPz_3)(CO)(PPh_3)]$ (**5**) and $[Ru_2(MeCHCN)_2Cl(BHPz_3)(CO)_2(PPh_3)_4]$ (**6**). From the latter reaction, two complexes were formed, separated similarly, and formulated as $[\{Ru(MeCHCN)(acac)(CO)(PPh_3)\}_2]$ (**9**) and $[Ru(MeCHCN)(acac)(CO)(pic)(PPh_3)]$ (**10**). The yields and elemental analyses of **2**—**10** are summarized in Table 1.

General Properties. The IR spectra of **2**—**10** lacked a ν(Ru–H) band near 2000 cm^{-1}, which had been observed in the starting complex, **1**, and showed one strong band in the range of 1905—1945 cm^{-1}, assignable to a terminal carbonyl group, whereas **4**, **5**, and **7** exhibited one or two additional shoulders near 1910 and 1950 cm^{-1} (Table 2). Furthermore, **2**, **3**, **5**—**8**, and **10** exhibited a medium band near 2200 cm^{-1}, characteristic of an uncoordinated cyano group. The ^{1}H-NMR spectra of **3**, **5**—**7**, and **10** each exhibited two, three or four doublets in the region of δ 0.2—1.4, ascribable to methyl group adjacent to methine group. On the basis of these data and the elemental analyses, **2**, **3**, **5**—**8**, and **10** were attributed to carbonyl(1-cyanoethyl)ruthenium(II) complexes. Complex **4** showed two ν(C≡N) bands at 2205 and 2230 cm^{-1}, implying that **4** contained a 1,2-dicyanoethyl group.

Complexes **2**—**10** are stable in a solid state in the air and considerably stable in solution under a nitrogen stream. Their stability is possibly associated with electron-delocalization effect due both to the coordination of appropriately σ-donating and π-accepting carbonyl group and PPh_3 ligand and to the electron-accepting cyano group adjacent to the 1-carbon.

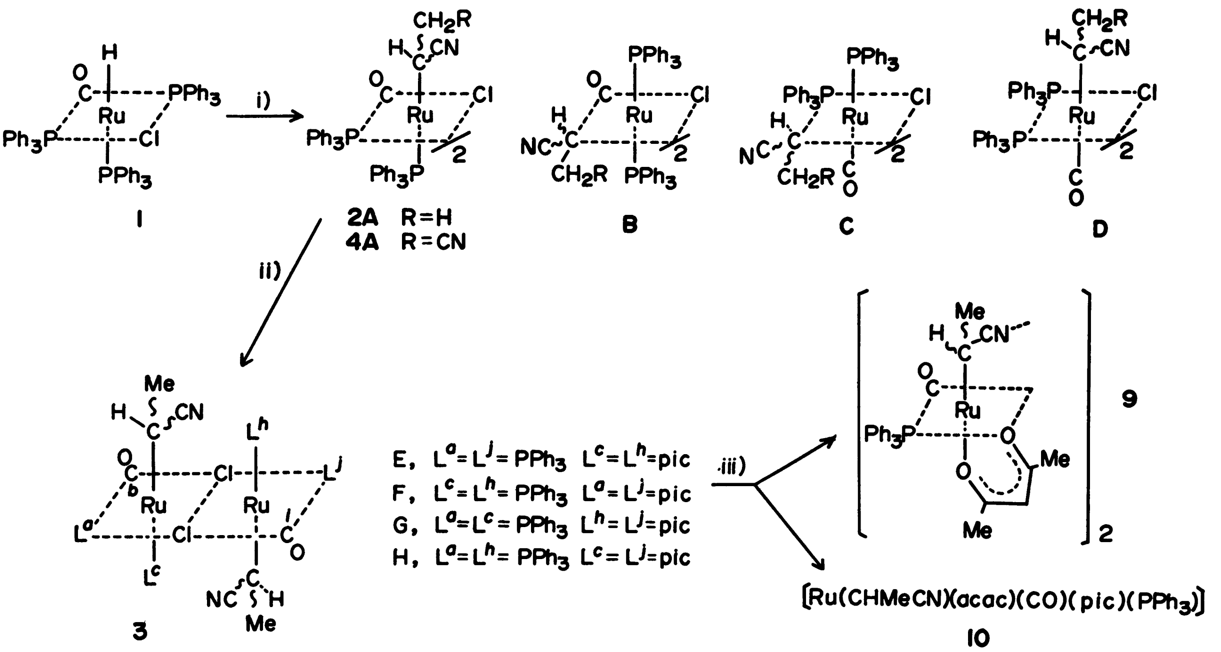
TABLE 1. YIELDS AND ELEMENTAL ANALYSES OF THE RUTHENIUM COMPLEXES

Complex		Yield/%	Mp θ_m/°C	Found(Calcd)(%) C	H	N
$[\{Ru(MeCHCN)Cl(CO)(PPh_3)_2\}_2]$	**2**	83	151—157	64.99(64.65)	4.85(4.61)	1.58(1.88)
$[\{Ru(MeCHCN)Cl(CO)(pic)(PPh_3)\}_2]$	**3**	58	165—171	59.23(58.59)	4.51(4.57)	4.66(4.88)
$[\{Ru(NCCH_2CHCN)Cl(CO)(PPh_3)_2\}_2]$	**4**	75	165—175	64.62(64.11)	4.42(4.33)	3.46(3.65)
$[Ru(MeCHCN)(BHPz_3)(CO)(PPh_3)]$	**5**	31	158—160	56.60(56.55)	4.60(4.44)	14.50(14.89)
$[Ru_2(MeCHCN)_2Cl(BHPz_3)(CO)_2(PPh_3)_4]$	**6**	9	130—131	65.52(64.24)	5.06(4.72)	5.73(6.73)
$[Ru_2(MeCHCN)_2Cl(BPz_4)(CO)_2(PPh_3)_2]$	**7**	41	224	55.88(55.73)	4.24(4.18)	10 83(11.61)
$Na[Ru(MeCHCN)Cl(Et_2NCS_2)(CO)(PPh_3)]$	**8**	38	210	49.12(49.73)	4.65(4.48)	4.18(4.30)
$[\{Ru(MeCHCN)(acac)(CO)(PPh_3)\}_2]$	**9**	26	162—168	59.88(59.55)	5.06(4.18)	2.41(2.57)
$[Ru(MeCHCN)(acac)(CO)(pic)(PPh_3)]$	**10**	29	174—175	62.31(62.16)	5.29(5.22)	3.99(4.39)

TABLE 2. CHARACTERISTIC IR BANDS OF THE COMPLEXES[a)]

Complex	ν_{CO}/cm^{-1}	$\nu_{C\equiv N}$/cm^{-1}	Others
2	1925 s	2215 m	
3	1930 s	2200 m	1620 m, 1502 w[(C=N)+(C=C)]
4	1910 sh, 1932 s 1960 sh	2230 m, 2205 w	
5	1943 s, 1950 sh	2200 m	2487 m[ν(BH)]
6	1943 s,	2200 m, 2238 w	2488 m[ν(BH)]
7	1919 s, 1942 sh	2182 m, 2217 sh	
8	1907 s	2195 m	1482 s[ν(C⋯N)], 1262 s[(C=S)]
9	1932 s	2200 sh, 2240 m	1591 s, 1520 s[ν(C=O)+ν(C=C)]
10	1924 s	2200 m	1589 s, 1520 s[ν(C=O)+ν(C=C)] 1622 m[ν(C=N)]

a) Measured in KBr disk, values in cm^{-1}.



Scheme 1. i) Acrylonitrile (for **2**) or fumaronitrile (for **4**). ii) 4-Picoline (pic) with **2**. iii) Tl (acac). See Fig. 2 as regards the diasteroisomers of **3** and **4** and Fig. 4 as regards those of **9** and **10**.

Chloro-bridged Binuclear Complexes 2—4. The elemental analyses of **2**—**4** imply that each of these three complexes has one chlorine atom and four other coordination sites per ruthenium atom, indicating a chloro-bridged binuclear structure (Scheme 1).[10] Indeed, chlorine atoms have been reported to serve as bridge-forming ligands in many chlororuthenium(II) complexes.[10,14,15] It is noteworthy that **2** and **3** showed the single intensive $\nu(C\equiv O)$ band, although they have the binuclear structures and consist of a few diastereoisomers (*vide infra*).[5] This indicates that the diastereoisomerism for **2** and **3** has actually little influence on the $\nu(C\equiv O)$ band and that the two carbonyl groups in the binuclear structure are coordinated in an inversion symmetry (a *b,i*-CO type in Scheme 1) rather than in a C_2 rotational one around the Cl-Cl axis (a *b,j*-CO type) and in a C_1 one (a *b,g*- or a *b,h*-CO type). A binuclear dicarbonyl complex in the C_2 or the C_1 symmetry would show two $\nu(C\equiv O)$ bands, according to group theory. As concerns mononuclear moiety in **2** or **4**, four types A-D are possible, as shown in Scheme 1. However, types C and D are ruled out, because relatively bulky ligands, two PPh_3 ones and one 1-cyanoethyl group are located at facial positions in these types, and because both carbonyl ligand and chloro one in **1** must remain unmoved at trans positions to each other in the mild reaction conditions from **1** to **2** and **4**, as elucidated in the cases of the reactions of **1** with carbon disulfide[16] and with 2-formylpyridine.[17]

The mononuclear moiety in **2** and **4** is diastereomeric, owing to both asymmetric 1-carbon and ruthenium atoms (Fig. 1). Accordingly, **4**, which consists of two $\{Ru(NCCH_2CHCN)Cl(CO)(PPh_3)_2\}$ moieties, has two, three, or four diastereoisomers. Indeed, the $^{31}P\{^1H\}$-NMR spectrum of **4** in CH_2Cl_2[18] showed six fairly sharp signals at 20.5, 28.1, 35.1, 45.9, 47.0, and 47.9 ppm to the lower field from 85% H_3PO_4 as an external reference (virtually equal intensity, each *ca.* 0.45P; without clearly detectable coupling), two fairly broad ones at 23.0 and 30.1 ppm (each intensity, *ca.* 0.25P), and complicated ones in the range of 37.3—43.7 ppm (total intensity, *ca.* 0.8P).[19] Furthermore, it is clearly demonstrated by **10** that each of the $^{31}P\{^1H\}$-NMR signals corresponds to coordinated PPh_3 ligand in each diastereoisomer, unless the signals overlap with each other (*vide infra*). Therefore, the eight signals of **4**, *i.e.*, the six fairly sharp ones and the two fairly broad ones correspond to eight kinds of coordinated PPh_3 ligands due to three diastereoisomers of **4** (Fig. 2)[20] and are inconsistent with types B and D as regards the major components of **4**, since each of these two types would produce two diastereoisomers, and show only four ^{31}P-NMR signals. Accordingly, type A, where two PPh_3 ligands are situated at *cis* positions to each other, is most probable as the mononuclear moiety of the major components of **4** and possibly as that of **2**.[21] This conclusion is strongly supported both by the fact that $[\{Ru(MeCHCN)Cl(CO)(PPh_3)[P(OMe)_3]\}_2]$, derived from **2** and $P(OMe)_3$ at room temperature, exhibited relatively small $^2J(PP)$ values (26—32 Hz), which were

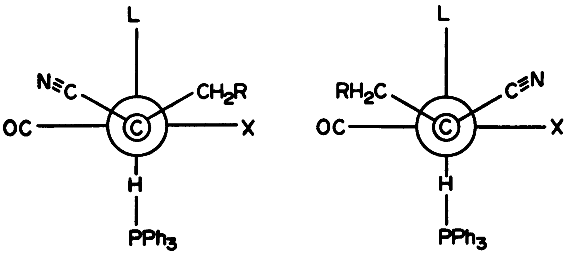


Fig. 1. Diastereoisomerism of $\{Ru(RCH_2CHCN)X(CO)L(PPh_3)\}$ moiety. The ruthenium atom is represented as an outer circle.

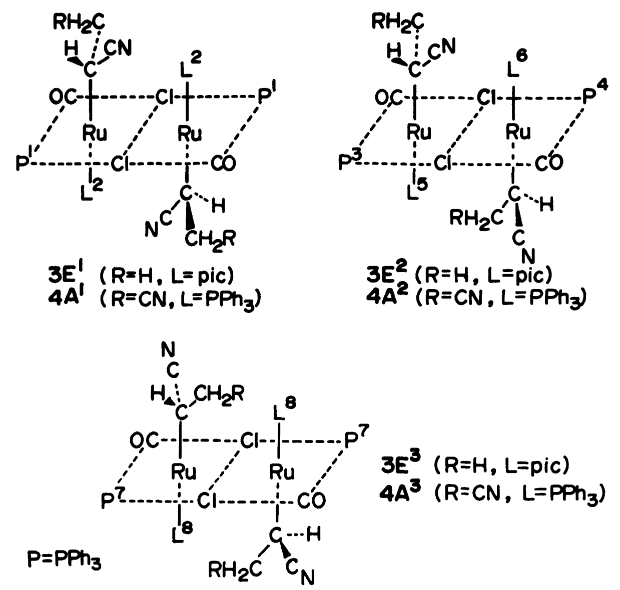


Fig. 2. Proposed structures for the diastereoisomers of **3** or **4**. See Ref. 19 as regards the minor components of **4**.

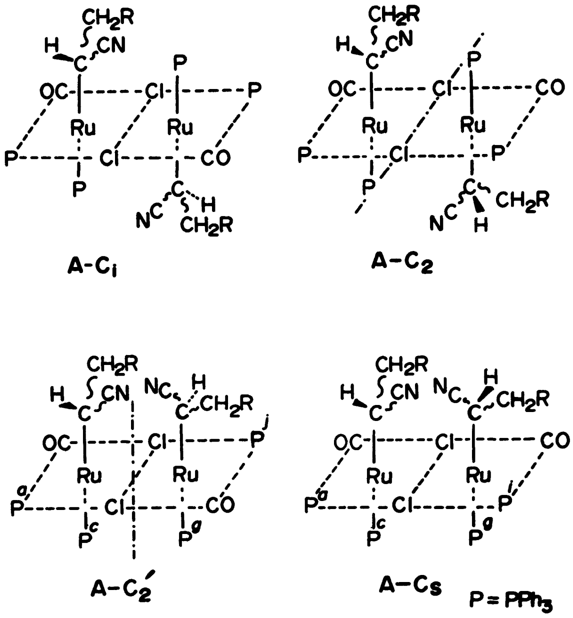


Fig. 3. Possible binuclear structures for **2A** and **4A**. See Ref. 23.

ascribable to *cis*-couplings between two nonequivalent phosphorus nuclei,[22] and by the *cis*-coordination of the two PPh$_3$ ligands confirmed for the analogous insertion products obtained from **1** and CS$_2$[16] or 2-formylpyridine[17] at mild conditions.

As for the binuclear structure of **2** or **4**, which consists of two A-typed {Ru(RCH$_2$CHCN)Cl(CO)(PPh$_3$)$_2$} moieties, four structures A-C$_1$, -C$_2$, -C$_2'$, and -C$_S$ are possible in consideration of their symmetry groups,[23] as shown in Fig. 3. However, structures A-C$_2'$ and -C$_S$

Table 3. ^{1}H-NMR data of the ruthenium(II) complexes[a]

Complex	1-Cyanoethyl Me[b]	1-Cyanoethyl CH[c]	Other ligand[d]			
3[e]	0.23(3H)	—[f]	2.26(3H,s,Me)[g]			
	0.36(3H)	—[f]	2.37(3H,s,Me)[g]			
5	0.52(1.8H)[h]	1.77(0.6H,q)[h]	6.06(0.6H,t,4-H)[h,i]	6.73(0.6H,d,3-H)[h,i]		8.00(0.6H,b,5-H)[h]
			6.16(0.6H,b,4-H)[h]	6.96(0.6H,d,3-H)[h,i]		
			5.84(1H,t,4-H)[j]	7.64(1.6H,b,3- and 5-H's)		7.80(1H,d,5-H)[i]
	1.36(1.2H)[h]	2.05(0.4H,q)[h]	6.03(0.4H,t,4-H)[h,i]	6.69(0.4H,d,3-H)[h,i]		7.77(0.4H,d,5-H)[h,i]
			6.25(0.4H,t,4-H)[h,i]	7.07(0.4H,d,3-H)[h,i]		7.88(0.4H,b,5-H)[h]
6	1.36(3.6H)	1.64(1.2H,b)	5.92(1H,t,4-H)[i]	6.69(1H,b,3-H)		7.86(0.6H,b,5-H)[j]
	1.24(1.2H)	—[f]	6.03(1H,b,4-H)	6.96(0.6H,b,3-H)		2.60(1H,b,B<u>H</u>)
	0.94(1.2H)	—[f]	6.23(1H,b,4-H)	7.11(0.6H,b,3-H)[j]		
7	0.84(3H)[k]	1.1—1.4(2H,c)	6.00—6.4(4H,c,4-H)[i]			
	0.92(3H)[k]					
9	0.95(4.2H)[k]	—[f]	1.68(4.2H,s,Me)	1.71(4.2H,s,Me)		4.74(1.2H,s,CH)
						4.70(0.2H,s,CH)
	0.93(1.8H)[k]	—[f]	1.62(1.8H,s,Me)	1.64(1.8H,s,Me)		4.76(0.4H,s,CH)
						4.80(0.2H,s,CH)
10	1.00(1.5H)	—[f]	2.34(2.1H,s,Me)[g]	1.56(3H,s,Me)		4.73(0.4H,s,CH)
	0.77(0.6H)	—[f]	2.05(0.6H,s,Me)[g]	1.63(0.6H,s,Me)	1.83(0.6H,s,Me)	5.07(0.2H,s,CH)
	1.16(0.6H)	—[f]		1.68(0.6H,s,Me)	1.89(0.6H,s,Me)	5.13(0.2H,s,CH)
	0.98(0.3H)	—[f]	2.31(0.3H,s,Me)[g]	1.94(0.3H,s,Me)	2.01(0.3H,s,Me)	4.64(0.1H,s,CH)
						5.31(0.05H,s,CH)
						5.52(0.05H,s,CH)

a) Value (ppm). In CDCl$_3$, except **3**. Proton number is given in parentheses. Phenyl protons and pyridine-ring protons are omitted. b) Doublet with ^3J(HH)=*ca.* 8 Hz, unless noted elsewhere. c) Signal shape is also given in parentheses. d) Signal shape and assignment are also given in parentheses. 3-, 4-, and 5-H's belong to the 1-pyrazolyl groups. e) In CD$_2$Cl$_2$. f) Methine proton resonance was obscured by the other signals. g) Methyl group of 4-picoline. h) Resonances in two neighboring lines correspond to one isomer. i) ^3J(HH)=2—2.3 Hz. j) The other signal was obscured by the phenyl protons. k) Doublet with ^3J(HH)=*ca.* 7 Hz.

are unfavorable, because these two structures would give rise to considerable steric repulsion between four relatively bulky PPh_3 ligands coordinated together at near positions, *i.e.*, at *a*, *c*, *g*, and *i* or *j* sites. Both structures A-C_2 and -C_S seem unlikely in consideration of the single $\nu(C\equiv O)$ band (*vide ante*).[24] On the basis of these discussions, both **2** and the major components of **4** are attributable to structure A-C_1.

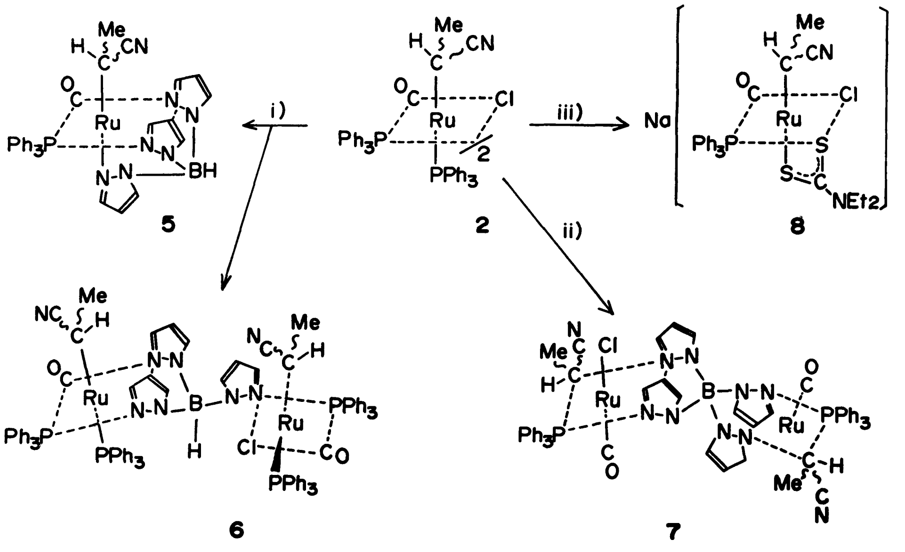
It is noteworthy that 4-picoline gave rise to the replacement of two PPh_3 ligands in **2** instead of the splitting of the chloro-bridge,[10] to afford **3** with **E**-, **F**-, **G**-, and/or **H**-type structures due to geometrical isomerism and coordination position one (Scheme 1).[25] This replacement was facilitated both by strong trans influence of the 1-cyanoethyl groups located at *trans* positions to the leaving PPh_3 ligands and somewhat by steric interaction between the two *cis*-located PPh_3 ligands in **2**.[16,17] In addition, types **G** and **H** are unfavorable, since each of them is composed of two nonequivalent {Ru(MeCHCN)Cl(CO)LL'} moieties (where L and L' are PPh_3 and/or pic) which would show two $\nu(C\equiv O)$ bands (*vide ante*). Moreover, type **G** is also inadequate, because the second PPh_3 ligand coordinated to the ruthenium atom is insusceptible to the replacement by 4-picoline, owing to the considerably strong *trans* influence of PPh_3. On the basis of these considerations, **3** was assignable to type **E**.

The ^{1}H-NMR spectrum of **3** exhibited both two picoline-methyl resonances at δ 2.26 (3H) and 2.37 (3H) and two doublets at δ 0.23 (3H) and 0.36 (3H), assignable to the methyl protons of the 1-cyanoethyl moieties (Table 3). These data indicate that **3**, which consists of two {Ru(MeCHCN)Cl(CO)(pic)(PPh_3)} moieties, has three diastereoisomers, **3E**^{1}, **3E**^{2}, and **3E**^{3} similar to the cases of **4** (Fig. 2). Indeed, the ^{31}P-{^{1}H}-NMR spectrum in CH_2Cl_2 showed four singlets of a virtually equal intensity at 89.13, 89.25, 95.82, and 95.91 ppm from trimethyl phosphite as an external reference,[5] corresponding to four kinds of PPh_3 ligand in **3E**^{1}, **3E**^{2}, and **3E**^{3}. The population ratio of **3E**^{1}, **3E**^{2}, and **3E**^{3} is virtually 1 : 2 : 1 on the basis of the ^{31}P nuclear resonances, indicating an actually statistical isomer ratio. This implies that acrylonitrile was inserted into the H-Ru bond in **1** in a non-stereoselective fashion.

$BHPz_3$ and BPz_4 Complexes 5—7. The ^{1}H-NMR spectrum of the mononuclear $BHPz_3$ complex **5** exhibited both two sets of doublets at δ 0.52 (1.8H, Me) and 1.36 (1.2H, Me) and two sets of quartets at δ 1.77 (0.6H, C$\underline{H}$) and 2.05 (0.4H, C$\underline{H}$) (Table 3). These data indicate that **5** consists of two diastereoisomers, with a population ratio of about 6 : 4. Furthermore, **5** showed four triplets in the range of δ 5.8—6.3 and a broad signal at δ 6.16, assignable to 4-H's of the 1-pyrazolyl groups, supporting the existence of the two diastereoisomers.

Thus, the two diastereoisomers were detected for the mononuclear complex, **5**, which contains the C_3-symmetric $BHPz_3$ ligand. This is quite consistent with the three diastereoisomers, proposed for **3**. The two diastereoisomers of **5** could not be separated by the silica gel column chromatography. Similar [hydrotris(1-pyrazolyl)borato]ruthenium(II) complexes, [Ru(C_6H_4–N=NPh-*o*)($BHPz_3$)$(CO)_2$] and [Ru(C_6H_4–N=NPh-*o*,1-*C*,*N'*)($BHPz_3$)(CO)] have been reported by Bruce *et al.*[15]

The reaction of **2** with Na[$BHPz_3$] produced a small amount of the binuclear complex, **6**, in which one tridentate [$BHPz_3$] group possibly serves as a bridging ligand. Since **6** contains two PPh_3 ligands per ruthenium atom, similarly to **2**, the relative positions of the two PPh_3 ligands are assumed to remain unchanged during the reaction. Two 1-pyrazolyl groups in the $BHPz_3$ ligand form a six-membered boat-typed ring[26–28] with one of the two ruthenium atoms. The third 1-pyrazolyl group is coordinated to the other ruthenium atom at the *cis* or *trans* position to the 1-carbonyl group. Accordingly, two {Ru(MeCHCN)(CO)$(PPh_3)_2$} moieties in **6** are nonequivalent. It looks unlikely that the third 1-pyrazolyl group is located at the axial site of the six-membered boat-formed Ru-$(N\text{-}N)_2$-B ring, because this configuration would give rise to a serious steric interaction between the Pz-Ru(MeCHCN)Cl(CO)$(PPh_3)_2$ moiety and the PPh_3 ligand coordinated



Scheme 2. i) Na[$BHPz_3$] at 40 °C. ii) Na[BPz_4] in refluxing benzene. iii) Na[Et_2NCS_2]·$3H_2O$.

to the first ruthenium atom. Since **6** is associated both with two kinds of diastereoisomerism due to the two nonequivalent [Ru(MeCHCN)(CO)$(PPh_3)_2$] moieties and with one *cis-trans* geometrical isomerism, there are at least eight possible isomers for **6**. However, **6** showed only three doublets at δ 1.36, 1.24, and 0.94 attributable to the methyl protons of the 1-cyanoethyl groups with about 3 : 1 : 1 of intensity ratio. While it is difficult to assign the three doublets to the isomers of **6**, probable configurations for **6** are tentatively shown in Scheme 2.[29] Complex **6** might be an intermediate in the reaction from **2** to **5**.

The binuclear complex, **7** involves one PPh_3 ligand per ruthenium atom in sharp contrast with **6**, and has one quadridentate $[BPz_4]^-$ ligand, which acts as two sets of bidentate chelates, bridging both a {Ru(MeCHCN)-Cl(CO)(PPh_3)} moiety and a {Ru(MeCHCN)(CO)-(PPh_3)} one. Trofimenko[30] has reported on similar bridging $[BPz_4]$-typed complexes, $[(\eta^3\text{-}CH_2CRCH_2)\text{-}Pd(Pz_2BPz_2)Pd(\eta^3\text{-}CH_2CRCH_2)]^+$.
Then, the two ruthenium atoms in **7** are six- and five coordinate, and nonequivalent. The latter five coordination of the ruthenium(II) complexes is unusual and probably associated with a steric interaction between fairly bulky PPh_3 ligand and BPz_4 one. Analogous five-coordinate ruthenium(II) complex has been reported as regards [Ru(dtim)Cl$(PPh_3)_2$] (dtim=1,3-di-*p*-tolyl-2-imidazolidinylidenato-2-*C*,2′-*C*).[31] On the basis of these discussions, there are many possible isomers for **7**. However, **7** exhibited only two doublets at δ 0.84 and 0.93 for the methyl protons of the 1-cyanoethyl moieties with a vertually equal intensity. Probable configurations for **7** are tentatively shown in Scheme 2,[32] like the case of **6**.

Acac Complexes **9** *and* **10**. The binuclear acac-type complex **9** was obtained together with the mononuclear complex, **10**. These two complexes showed two bands near 1590 and 1510 cm^{-1}, characteristic of the *O*,*O*′-chelating acac ligand. Complex **9** exhibited a ν(C≡N) band at 2240 cm^{-1}, which is about 20—40 cm^{-1} higher than those of the other (1-cyanoethyl)ruthenium-(II) complexes. The molecular weight of **9** was 1091; Calcd for [{Ru(MeCHCN)(acac)(CO)(PPh_3)}$_2$], 1089. These data indicate that **9** has a binuclear structure, and that two 1-cyanoethyl groups bridge two ruthenium atoms. A bridge structure with the acac-oxygen atoms is unfavorable in **9**. In a non-bridging state, bond angles Ru–C–C(≡N) and C–Ru←N(≡C) in a *cis*-form are expected to be approximately 109°28′ and 90°, respectively, and a bonding chain, C–C≡N→Ru is virtually straight. Then, the bridging {Ru–CHMe–C≡N→}$_2$ moiety forms a rhombus or an octagon, and presumably holds more or less strain.

The ^1H-NMR spectrum of **9** exhibited four acac-methine proton resonances in an intensity ratio of nearly 6 : 2 : 1 : 1, whereas only two doublets (<u>Me</u>CHCN–) and four acac-methyl proton resonances were distinguished (Table 3). The ^{31}P-{H}-NMR spectrum in CH_2Cl_2 also showed four singlets at 34.6, 54.6, 31.6, and 53.0 ppm to the lower field from 85% H_3PO_4 in the similar intensity ratio to the acac-methine protons. It is noteworthy that the four ^{31}P-NMR signals appeared in unequal intensities as well as the four methine-proton ones did. Furthermore, the Ru–Ru

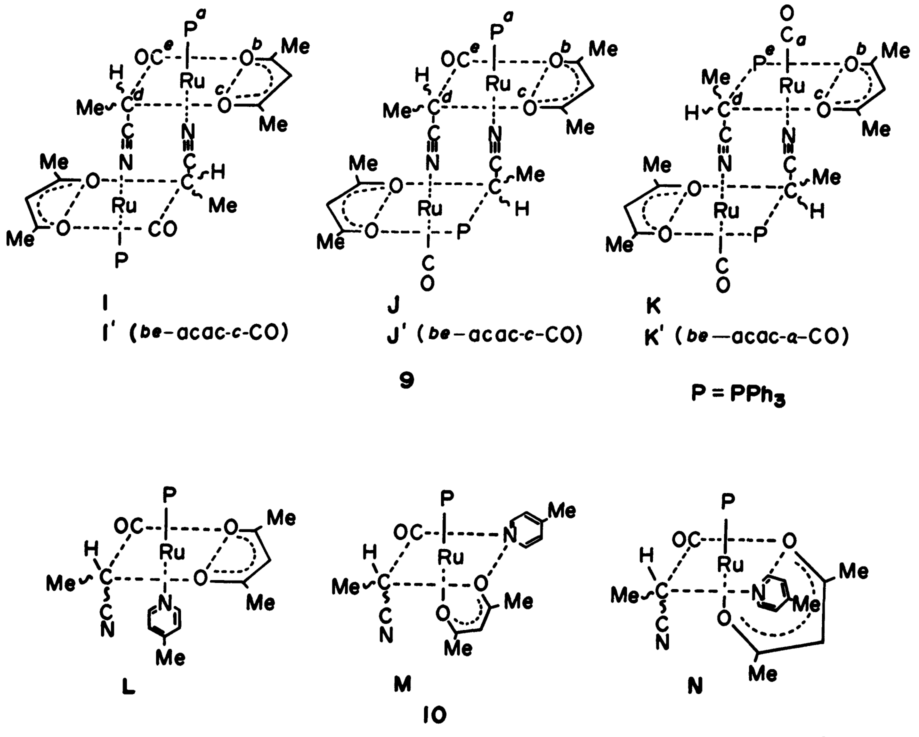


Fig. 4. Proposed structures for the isomers of **9** and **10**. The visual angles for **9** are changed from that in Scheme 1. See Ref. 33 as regards I′, J′, and K′, the geometrical isomers of I, J, and K, respectively.

distance in **9** is so long that the two {Ru(MeCHCN)(acac)(CO)(PPh_3)} moieties have little influence on each other except the bridge formation through the two cyano groups. These facts indicate that the four ^{31}P-NMR signals are not caused by the diastereoisomerism of the binuclear structure of **9**, in contrast with the chloro-bridged binuclear complexes, **3** and **4**, but correspond to four kinds of PPh_3 ligand in the mononuclear {Ru(MeCHCN)(acac)(CO)(PPh_3)} moiety. It is certain that **9** retains PPh_3 and carbonyl and 1-cyanoethyl groups at facial positions together as well as **3** does, since these three ligands show the comparatively strong *trans* influence. Accordingly, the four kinds of PPh_3 ligand are assignable both to the diastereoisomerism due to the asymmetric 1-carbon and ruthenium atoms and to geometrical isomerism exemplified by PPh_3 ligand at *a*- or *e*-site, as shown in Fig. 4. Since the two {Ru(MeCHCN)(acac)(CO)(PPh_3)} moieties are combined in the binuclear structure with fairly free fashion, another geometrical isomerism in the binuclear structure probably takes place to produce new pairs, *e.g.*, I and I′.[33] Thus, **9** was associated with many isomers, as shown in Fig. 4.

Complex **10** contains 4-picoline ligand and is monomeric. Its ^1H-NMR spectrum showed six acac-methine proton resonances in an intensity ratio of approximately 4 : 2 : 2 : 1 : 0.5 : 0.5, together with four doublets ($\underline{Me}$CHCN–), seven singlets for acac methyl protons and three singlets for picoline-methyl protons (Table 3). The ^{31}P-{^1H}-NMR spectrum in CH_2Cl_2 exhibited six singlets, overlapping with each other, at 52.6, 53.8, 54.6, 57.1, 58.2, and 58.9 ppm to the lower field from 85% H_3PO_4. These facts indicate that **10** consists of three geometrical isomers, L, M, and N, each of which contains two diastereoisomers with respect to {Ru(MeCHCN)(CO)(pic)(PPh_3)} moiety. The three ligands, PPh_3 and carbonyl and 1-cyanoethyl groups, which had been coordinated at facial positions in **3**, remain unmoved after the reaction with Tl(acac), by the same reason as the case of **9**. Then, it is certain that no other geometrical isomers than L, M, and N were formed. It is noted that the six isomers for **10** correspond to the ^{31}P-NMR signals very well as well as to the acac-methine proton ones (*vide ante*). Replacement of 4-picoline must take place during the reaction from **3** to two isomers, L and N.

Attempts to separate these isomers were unsuccessful, because chromatographic treatment of **10** yielded a mixture of **9** and **10**. The former complex was produced by liberating 4-picoline from **10** on the silica gel column with adsorbing ability.

Concluding Remarks. The binuclear 1-cyanoethyl complex **2** reacted fairly easily with 4-picoline and some uni-negative chelating ligands to give **3** and **5**—**8**. It is noteworthy that one of the two PPh_3 ligands per ruthenium atom in **2** is easily replaced, except for **6** produced in a low yield. The reaction of **3** with Tl(acac) gave rise both to the detachment of 4-picoline yielding **9** and to the rearrangement of 4-picoline yielding **10**-L and -N, in addition to the normal bridge-cleavage yielding **10**-M. The strong *trans* influence of the 1-cyanoethyl group is responsible for the substitution of the ligand located *trans* to the 1-cyanoethyl group.

The {Ru(RCH_2CHCN)(CO)(PPh_4)} moiety in **3**—**10** contains the asymmetric 1-carbon and ruthenium atoms, and gives rise to the diastereoisomerism. Accordingly, the mononuclear complex **5** involving the C_3-symmetric $BHPz_3$ ligand consists of two isomers, whereas the binuclear complex **3** is composed of three isomers. On the other hand, **6**, **7**, **9**, and **10** consist of several isomers, owing to the nonequivalent {Ru(MeCHCN)(CO)(PPh_3)$_n$} moieties and/or the geometrical isomerism, in addition to the diastereoisomerism.

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18) Owing to the poor solubility of **4**, its ^{31}P-{^1H}-NMR spectrum in CH_2Cl_2 was recorded after 17300 pulses for 14.4 h by the FT-NMR spectrometer.

19) The complicated signals were associated with a few minor components. However, these signals could not be analyzed clearly owing to overlapping with noise.

20) See the next section, with respect to the binuclear structure. The two smaller signals at 23.0 and 30.1 ppm may be attributable to a diastereoisomer with a small population ratio, presumably owing to stereochemical requirement.

21) It was erroneous that [{Ru(MeCHCN)Cl(CO)(PPh_3)$_2$}$_2$] had two sets of two *trans*-located PPh_3 ligands in Ref. 5.

22) K. Hiraki and N. Ochi, Unpublished data.

23) Both substituents upon the 1-carbon atom of the 1-cyanoethyl groups and those upon phosphorus atoms are ignored as for the symmetry.

24) Hypotetical structures for the diastereoisomers of **2** belonging to the C_2 or the C_s symmetry group and for their 4-picoline-substitution products are able to be drawn in similar manners as described for **4A** and **3E**, respectively (Fig. 2).

25) It was erroneous that the 4-picoline ligands in [{Ru(MeCHCN)Cl(CO)(pic)(PPh_3)}$_2$] were situated at *trans* positions to the remaining PPh_3 ligands in Ref. 5.

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32) There are also the other possible configurations for **7**.

33) As for I′, J′, and K′, the geometrical isomers of I, J, and K, respectively, the coordination sites only for the acac ligand and carbonyl group are given in parentheses in Fig. 4 for simplification.