

Dicarbonylbis(triphenylphosphine)(fumaronitrile)ruthenium(0) and Related Complexes. Preparation and Configuration in Solution

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Reactions of $Ru(CO)X(PPh_3)_3$ ($X = CO, p-CH_3C_6H_4NC, p-CH_3OC_6H_4NC$) with fumaronitrile (FN), maleonitrile (MN), dimethyl fumarate (DF), and maleic anhydride (MA) yielded a series of olefin complexes of ruthenium(0), $Ru(CO)X(PPh_3)_2Y$ ($Y = FN, MN, DF, MA$). $Ru(CO)_2(PPh_3)_2(FN)$ and the MN analog are suggested to exist as two geometrical isomers in solution, which are interconvertible possibly through the olefin rotation accompanied by the Berry pseudorotation. The remaining olefin complexes were found to adopt rigid configurations. $Ru(CO)_2(PPh_3)_3$ also reacted with tetrafluoroethylene to give $Ru(CO)_2(PPh_3)_2[(CF_2)_4]$, which contains a ruthenacyclopentane ring.

Introduction

Low-valent transition metal complexes with electron-withdrawing olefins have been extensively studied not only as model compounds in catalytic reactions [1] but also from interest in their structures and bonding properties [2, 3]. Recently, the authors reported that some Rh(I) isocyanide complexes react with cyanoolefins to give a series of adducts with a stereochemically nonrigid property in solution. This may arise both from the relatively weak transition metal basicity and small steric hindrance of the Rh(I) substrates [4–8]. The transition metal basicity of Ru(0) complexes may be somewhat greater than that of Rh(I) counterparts [9]. It is therefore anticipated that the reaction of Ru(0) complexes with electron-withdrawing olefins would give a new class of stereochemically nonrigid compounds.

Here we report the preparations of Ru(0) or Ru(II) complexes containing electrophilic olefins such as fumaronitrile (FN), maleonitrile (MN), dimethylfumarate (DF), maleic anhydride (MA), and tetrafluoroethylene, and their configuration in solution on the basis of variable temperature 1H nmr spectra.

Experimental

Materials and General Procedures

$RuCl_3 \cdot xH_2O$ was of reagent grade purity and used as supplied. Commercial FN, DF, and MA were purified by sublimation. MN was kindly supplied by Mr. Koichi Matsumura, Takeda Chemical Industries Co. Ltd., and was purified by sublimation. Preparations and reactions of Ru(0) complexes were carried out under dry nitrogen. $Ru(CO)_2(PPh_3)_3$ was obtained according to the literature [10]. $Ru(CO)(RNC)(PPh_3)_3$ ($R = p-ClC_6H_4, p-CH_3OC_6H_4$) were prepared in a more convenient manner than that described in the literature [11] as follows; a CH_3OH (30 ml) suspension of $RuHCl(CO)(RNC)(PPh_3)_2$ [11] ($R = p-CH_3C_6H_4$ or $p-CH_3OC_6H_4$, 1.6 mmol), PPh_3 (6.5 mmol), and CH_3ONa (23 mmol) was refluxed for 24 hr. The resulting precipitate was collected and recrystallized from $CH_2Cl_2-CH_3OH$ in the presence of PPh_3 (3.3 mmol) to give orange-red crystals (55% for both complexes). The *p*-tolyl isocyanide complex involved a half molecule of CH_2Cl_2 .

Dicarbonylbis(triphenylphosphine)(fumaronitrile)ruthenium(0), $Ru(CO)_2(PPh_3)_2(FN)$ (1a) and Related Compounds

A solution of $Ru(CO)_2(PPh_3)_3$ (0.38 mmol) and FN (0.44 mmol) in CH_2Cl_2 (10 ml) was stirred for 2 hr at room temperature, followed by evaporation to dryness under reduced pressure. The product obtained was recrystallized from $CH_2Cl_2-C_2H_5OH$ to afford pale yellow crystals of **1a** (58%).

Analogous olefin complexes, $Ru(CO)_2(PPh_3)_2Y$ ($Y = MN$ (**1b**), **DF** (**1c**)), $Ru(CO)(p-CH_3C_6H_4NC)(PPh_3)_2Y$ ($Y = FN$ (**2a**), **MN** (**2b**), **DF** (**2c**), **MA** (**2d**)), and $Ru(CO)(p-CH_3OC_6H_4NC)(PPh_3)_2Y$ ($Y = FN$ (**3a**), **MN** (**3b**)) were similarly prepared by reactions of the Ru(0) substrates with the appropriate olefin. **3b** was solvated by one-third molecule of CH_2Cl_2 . **1b** and **2b** were successfully recrystallized under dry nitrogen.

TABLE I. Analytical Data and Molecular Weights of Ru(CO)X(PPh₃)₂Y.^a

| X | Y | %C | %H | %N | Mol. wt. |
|---|---------------------------------|------------------|----------------|----------------|---------------------------|
| CO | FN | 66.20 (66.40) | 4.21 (4.25) | 3.77 (3.69) | 771 (760) |
| CO | MN | 66.01 (66.40) | 4.09 (4.25) | 3.45 (3.69) | — (760) |
| CO | DF | 63.99 (64.00) | 4.44 (4.64) | | 803 (826) |
| <i>p</i> -CH ₃ C ₆ H ₄ NC | FN | 69.13 (69.33) | 4.43 (4.63) | 4.92 (4.95) | 893 (849) |
| <i>p</i> -CH ₃ C ₆ H ₄ NC | MN | 69.38 (69.33) | 4.54 (4.63) | 4.68 (4.95) | — (849) |
| <i>p</i> -CH ₃ C ₆ H ₄ NC | DF | 66.88 (66.95) | 4.90 (4.96) | 1.72 (1.53) | 864 ^b (915) |
| <i>p</i> -CH ₃ C ₆ H ₄ NC | MA | 67.32 (67.74) | 4.53 (4.52) | 1.67 (1.61) | 894 (869) |
| <i>p</i> -CH ₃ OC ₆ H ₄ NC | FN | 67.88 (68.05) | 4.36 (4.55) | 5.01 (4.86) | 837 (865) |
| <i>p</i> -CH ₃ OC ₆ H ₄ NC | MN | 66.70 (66.33) | 4.49 (4.48) | 4.73 (4.70) | 869 (865) |
| CO | (CF ₂) ₄ | 53.30 (53.43) | 3.56 (3.34) | | 851 (882) |

^a Calculated values in parentheses. others in CHCl₃ at 37 °C.

^b In CH₂Cl₂ at 25 °C;

Dicarbonylbis(triphenylphosphine)tetrakis(difluoromethylene)ruthenium(II) Dichloromethane Solvate, Ru(CO)₂(PPh₃)₂[(CF₂)₄]·CH₂Cl₂ (4)

An C₂H₅OH (30 ml) solution of CF₂BrCF₂Br (60 mmol) was added to Zn powder (120 mg atom) in refluxing C₂H₅OH (30 ml) to generate CF₂=CF₂, which was bubbled into a stirred solution of Ru(CO)₂(PPh₃)₃ (0.6 mmol) in CH₂Cl₂ (30 ml) for 30 min at room temperature. The resulting solution was handled as described above to yield off-white crystals (26%).

Analytical data and molecular weights of the complexes obtained are summarized in Table I.

Physical Measurements

Ir and ¹H nmr spectra were measured as described elsewhere [5]. Molecular weights were determined using a Mechrolab 302 or a Knauer Vapor Pressure Osmometer.

Results and Discussion

Properties and Characterization

The Ru(CO)X(PPh₃)₂Y complexes are all air-stable both in the solid state and in solution, except Ru(CO)X(PPh₃)₂(MN) (X = CO and *p*-CH₃C₆H₄NC) which gradually decompose in solution in air. Mole-

cular weight determinations indicate that Ru(CO)X(PPh₃)₂Y other than the two complexes mentioned above are essentially monomeric in solution (Table I). As shown in Table II, the ν(C=O) and ν(N=C) frequencies of Ru(CO)X(PPh₃)₂Y are higher by 48–152 and 65–79 cm⁻¹ than those of the corresponding parent complexes, respectively.* In addition, the olefinic proton signals move upfield by 3.56–4.96 ppm on coordination. These results indicate the occurrence of a charge transfer from the metal to olefins.

Ru(CO)₂(PPh₃)₂Y (Y = FN(1a), MN(1b))

The FN protons of 1a in CDCl₃ at -61 °C occur as a doublet and a triplet signal, as seen in Fig. 1. The appearance of these signals is markedly dependent on the temperature; with ascending temperature, the doublet signal is intensified at the expense of the triplet. On further warming, both signals broaden, followed by coalescence into a broad singlet at 24 °C. Finally, the signal appears as a sharp singlet at 56 °C. These signal patterns hardly change by the addition of an equimolar amount of FN or excess PPh₃. Moreover, the doublet and triplet observed at low temperatures are both converted into a singlet by irradiation of the ³¹P nucleus. These results suggest that two geometrical isomers coexist in solution at low temperatures and they are interconvertible *via* an intramolecular process. This is compatible with the essentially monomeric nature of the complexes (Table I). By analogy with some cyanoolefin adducts of Rh(I) reported previously [4–8], the process would involve the interconversion between two isomers A and B *via* a coupled olefin rotation–Berry pseudorotation, as illustrated in Fig. 2. The coexistence of A and B is supported by the ir spectrum of 1a in CHCl₃, which shows one strong and two weak ν(C=O) bands (Table II).

The doublet and triplet signals are assigned to the FN protons of A and B, respectively. Thus, the apparent triplet can be ascribed to an AA'XX' spin system composed of the two FN protons (A and A') and the two mutually *trans* ³¹P nuclei (X and X'). An approximate calculation [12] by assuming that J_{AA'} = 8, J_{XX'} = 400, J_{AX} = J_{A'X'} = 3, and J_{AX'} = J_{A'X} = 10 Hz in B affords a virtual triplet ¹H nmr pattern which is in agreement with the observed one. The two FN protons and two ³¹P nuclei in A also constitute an AA'XX' spin system. However, the J_{XX'} value would be small owing to a *cis*-coupling of the two ³¹P nuclei (X and X') to give the limiting doublet. At higher temperatures, the fast dissociative exchange of FN or PPh₃ may occur on the nmr time

*The ν(C=C) of the olefin complexes has not been assigned with confidence, because of the occurrence of several absorptions due to PPh₃ or RNC near 1300 cm⁻¹ where the ν(C=C) band is expected to appear.

TABLE II. Ir Frequencies^a (cm⁻¹) in CHCl₃ and Proton Chemical Shifts^b (ppm) in CDCl₃ of Ru(CO)X(PPh₃)₂Y.

| X | Y | $\nu(\text{C}\equiv\text{O})$ | $\nu(\text{N}\equiv\text{C})$ | $\delta(\text{CH})^c$ | $\delta(p\text{-CH}_3)$ | $\delta(\text{C}_6\text{H}_4)$ |
|---|---------------------------------|-------------------------------|-------------------------------|-----------------------|-------------------------|--------------------------------|
| CO | FN | 2016w, 1981s, 1953w | | (1.32t, 2.18d) | | |
| CO | MN | 2031w, 1979s, 1956w | | (1.24t, 2.12d) | | |
| CO | DF | 1971s | | 3.28d | | |
| <i>p</i> -CH ₃ C ₆ H ₄ NC | FN | 1978s | 2149s | 1.95dd, 2.16dd | 2.28s | 6.39d, 6.92d |
| <i>p</i> -CH ₃ C ₆ H ₄ NC | MN | 1966s | 2155m | 2.08d | 2.24s | 6.56d, 6.88d |
| <i>p</i> -CH ₃ C ₆ H ₄ NC | DF | 1971s | 2143s | 3.37dd,d | 2.23s | 6.26d, 6.83d |
| <i>p</i> -CH ₃ C ₆ H ₄ NC | MA | 1974s | 2151s | 3.18d | 2.21s | 6.27d, 6.81d |
| <i>p</i> -CH ₃ OC ₆ H ₄ NC | FN | 1978s | 2154s | 1.93dd, 2.16dd | 3.74s | 6.43d, 6.61d |
| <i>p</i> -CH ₃ OC ₆ H ₄ NC | MN | 1966s | 2158s | 2.06d | 3.70s | 6.63s |
| CO | (CF ₂) ₄ | 2057s, 1999s | | | | |

^a s = strong, m = medium, w = weak. $\nu(\text{C}\equiv\text{O}) = 1905$ for Ru(CO)₂(PPh₃)₃; $\nu(\text{C}\equiv\text{O}) = 1899$, $\nu(\text{N}\equiv\text{C}) = 2078$ for Ru(CO)(*p*-CH₃C₆H₄NC)(PPh₃)₃; $\nu(\text{C}\equiv\text{O}) = 1896$, $\nu(\text{N}\equiv\text{C}) = 2079$ for Ru(CO)(*p*-CH₃OC₆H₄NC)(PPh₃)₃ in Nujol mulls. ^b At room temperature or at -61 °C in parentheses. s = singlet, d = doublet, t = triplet, dd = doublet of doublets. ^c Olefinic proton signals. $\delta(\text{CH})$ of free FN, MN, DF and MA in CDCl₃ are 6.28, 6.20, 6.84 and 7.01, respectively. ^d Signal of the other olefinic proton is masked by the DF methyl proton signal at δ 3.13.

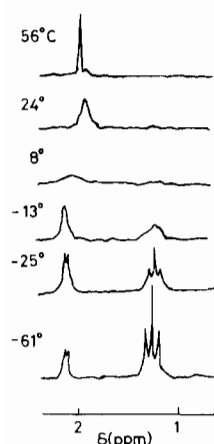


Fig. 1. Variable temperature nmr spectra of the Ru(CO)₂(PPh₃)₂(FN) (**1a**) in CDCl₃.

scale, since the spin-spin couplings could not be found at 56 °C. A similar behavior was observed in the ¹H nmr spectra of **1b**.

Equilibrium constants, $K = [\text{B}]/[\text{A}]$, were determined by integrating the proton signals of **1a** and **1b** in CDCl₃ at several temperatures. Thermodynamic parameters obtained by plotting $\log K$ vs. T^{-1} are: $\Delta H^\circ = -17.7 \pm 0.5$ kJ/mol, $\Delta S^\circ = -72.0 \pm 2.1$ J/deg mol for **1a**; $\Delta H^\circ = -14.4 \pm 2.1$ kJ/mol, $\Delta S^\circ = -72.0 \pm 8.8$ J/deg mol for **1b**. Thus, the enthalpy term favors the structure **B**, while the entropy one favors **A**. On the other hand, all five-coordinate transition metal-cyanoolefin complexes studied by X-ray analysis are known to adopt the configuration analogous to **A** in the solid state [13–16].

Ru(CO)₂(PPh₃)₂(DF) (**1c**)

Olefinic protons of **1c** in CDCl₃ appear as a filled-in doublet signal [17] which shows little temperature

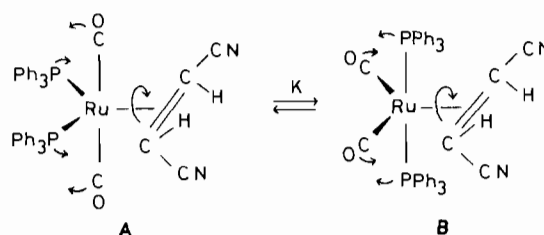


Fig. 2. Two isomers of Ru(CO)₂(PPh₃)₂(FN) (**1a**).

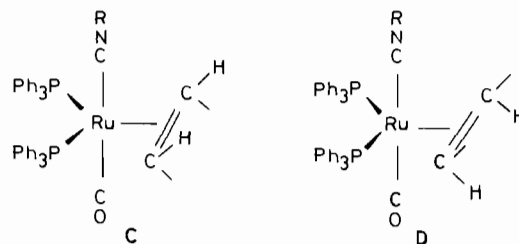


Fig. 3. Two possible configurations of Ru(CO)(RNC)(PPh₃)₂Y: R = *p*-CH₃C₆H₄, Y = MN (**2b**) and MA (**2d**); R = *p*-CH₃OC₆H₄, Y = MN (**3b**).

dependence in the range of -57° to 55 °C. The signal can also be attributed to an AA'XX' spin system composed of two olefinic protons and two ³¹P nuclei. An analogous nmr pattern was previously reported for the FN proton signals of [Ir(*p*-CH₃C₆H₄NC)₂(PPh₃)₂(FN)]ClO₄ [18]. In view of this result and the appearance of only one $\nu(\text{C}\equiv\text{O})$ in the ir spectrum (Table II), **1c** assumes a rigid configuration similar to **A** (Fig. 2). The stereochemical rigidity of **1c** is possibly due to the bulkiness of the methoxycarbonyl group of DF, since the electron affinity of olefins (DF < FN ~ MN) predicts that the DF complex may be more labile than the FN or MN analog.

$Ru(CO)(RNC)(PPh_3)_2Y$ ($R = p\text{-}CH_3C_6H_4$, $Y = FN$ (**2a**), MN (**2b**), DF (**2c**), MA (**2d**); $R = p\text{-}CH_3OC_6H_4$, $Y = FN$ (**3a**), MN (**3b**))

FN proton signals of **2a** in $CDCl_3$ appear as a quartet of doublets, which also shows little temperature dependence in the range of -41° to $55^\circ C$. The spectrum is well explained by assuming a trigonal bipyramidal configuration, in which two PPh_3 and FN are located in equatorial positions. This configuration predicts the nonequivalence of two FN protons, giving an AB type quartet signal ($J(H-H) = 8$ Hz). Each signal further splits into a doublet by coupling only with the ^{31}P nucleus *trans* to each proton ($J(H-P) = 4$ Hz). **2c** and **3a** may adopt a similar rigid configuration. On the other hand, **2b**, **2d**, and **3b** exhibit only one doublet signal of MN or MA ($J(H-P) = 3-4$ Hz). This observation can be explained by assuming that the two magnetically equivalent olefinic protons are coupled only with the ^{31}P nucleus *trans* to each proton. There are two possible configurations, **C** and **D** (Fig. 3), in these complexes.

In view of the lower steric repulsion between RNC and H, the configuration **C** may be preferred to **D**.

All the complexes described in this section are rigid in solution. This result may partly be ascribed to the fact that RNC is a stronger σ -donor and weaker π -acceptor than CO; substitution of RNC for CO in **1a** or **1b** increases metal basicity, resulting in stronger metal-olefin bonds. The bulkiness of RNC compared with CO may also be responsible for the rigid configuration.

$Ru(CO)_2(PPh_3)_2[(CF_2)_4] \cdot CH_2Cl_2$ (**4**)

This complex exhibits two strong $\nu(C\equiv O)$ bands in relatively high frequency regions (Table II). This is consistent with an octahedral configuration which involves a ruthenacyclopentane ring, $RuCF_2CF_2CF_2CF_2$, two mutually *cis* CO, two mutually *trans* PPh_3 , and the metal in the formal oxidation state of +2. Similar metallacyclopentane moieties have been reported in $Fe(CO)_4[(CF_2)_4]$ [19], $Co(\pi\text{-}Cp)(CO)[(CF_2)_4]$ [20],

$NiL_2[(CF_2)_4]$ [21], and $Rh(acac)L_2[(CF_2)_4]$ [22] ($L =$ tertiary phosphine or phosphite).

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