lar isomers 3 and 4 as well as the other complexes studied are tabulated in Table III. There is only one peak in the T_{1g} region of the spectrum, and absolute configuration assignments are easily made. Isomers 1 and 3 of *uns-cis*-[Co(EDDA)(*R*-pn)]$^+$ which have negative peaks are assigned as net Δ isomers[27] (Δ, Δ, Δ, Λ)[29] and isomers 2 and 4 with positive peaks are assigned as net Λ isomers (Λ, Λ, Λ, Δ). Comparison of the *uns-cis*-[Co(EDDA)(*R*-pn)]$^+$ CD spectrum with those obtained for the closely related optical isomers of *uns-cis*-[Co(EDDA)(en)]$^+$, Figure 8, permits the assignment of absolute configuration to these isomers. Table IV presents the complete assignments for the *uns-cis*-[Co(EDDA)(en)]$^+$ and *uns-cis*-[Co(EDDA)(*R*-pn)]$^+$ isomers. These assignments have been recently confirmed by a crystal and molecular structure determination of the Δ-cis,trans(N-O) isomer of *uns-cis*-[Co(EDDA)(*R*-pn)]$^+$.[30]

Table IV. Summary of Assignments of *uns-cis*-[Co(EDDA)(en)]$^+$ and [Co(EDDA)(*R*-pn)]$^+$ Isomers

Isomer	Methyl position in pmr	Geometrical isomer	Absolute confign
(+)-[Co(EDDA)(en)]$^+$			Λ
(−)-[Co(EDDA)(en)]$^+$			Δ
[Co(EDDA)(*R*-pn)]$^+$			
1[a]	Downfield	Cis,cis(N–O)	Δ
2	Downfield	Cis,cis(N–O)	Λ
3	Upfield	Cis,trans(N–O)	Δ
4	Upfield	Cis,trans(N–O)	Λ

[a] Order of elution from Dowex 50W-X8 cation-exchange column.

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Registry No. Na[Co(EDDA)(CO_3)], 50306-68-8; (−)-*uns-cis*-[Co(EDDA)(en)]BCS, 51921-55-2; (+)-*uns-cis*-[Co(EDDA)(en)]BCS, 51920-86-6; (−)-*uns-cis*-[Co(EDDA)(en)]Cl, 51897-56-4; (+)-*uns-cis*-[Co(EDDA)(en)]Cl, 51897-57-5; Δ-*cis,cis*(N–O)-[Co(EDDA)(*R*-pn)]-Cl, 51920-87-7; Λ-*cis,cis*(N–O)-[Co(EDDA)(*R*-pn)]Cl, 51920-88-8; Δ-*cis,trans*(N–O)-[Co(EDDA)(*R*-pn)]Cl, 51920-89-9; Λ-*cis,trans*(N–O)-[Co(EDDA)(*R*-pn)]Cl, 51922-19-1; meridional *uns-cis*-[Co(EDDA)-(L-ala)], 51922-20-4; facial *uns-cis*-[Co(EDDA)(L-ala)], 51920-90-2.

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Contribution from the Department of Applied Chemistry,
Faculty of Engineering, Osaka University, Yamada-kami, Suita, Osaka 565, Japan

Rotation of Coordinated Cyanoolefins in Their Adducts with Some Rhodium(I) Isocyanide Complexes

TOKITAKA KANESHIMA, KATSUHIKO KAWAKAMI, and TOSHIO TANAKA*

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The three types of rhodium(I) isocyanide complexes [Rh($RNC)_4$]X, [Rh($RNC)_2(PPh_3)_2$]X, and Rh(RNC)($PPh_3)_2$Cl react with tetracyanoethylene (TCNE) and fumaronitrile (FN) to give the complexes [Rh($RNC)_4$(TCNE)]X (X = BPh_4, R = CH_3; X = ClO_4, R = *p*-$CH_3OC_6H_4$, *o*- and *p*-$CH_3C_6H_4$, *p*-ClC_6H_4), Rh($RNC)_2$(PPh_3)(olefin)I and [Rh($RNC)_2(PPh_3)_2$(olefin)]ClO_4 (R = CH_3, *p*-$CH_3OC_6H_4$, olefin = TCNE, FN), and Rh(*p*-$CH_3OC_6H_4$NC)($PPh_3)_2$(TCNE)Cl. Their ir and pmr spectra suggest configurations of these complexes in solution. The TCNE adducts except [Rh($RNC)_4$(TCNE)]X show little temperature dependence in their pmr spectra and may have the TCNE coordinated rigidly perhaps in a trigonal-bipyramidal configuration. On the other hand, [Rh($RNC)_4$(TCNE)]X and each of the FN adducts give temperature-dependent pmr spectra, which may be interpreted in terms of the cyanoolefin rotation in time-averaged square-pyramidal configurations. The difference in the bonding is discussed qualitatively in terms of the basicity of the metal substrates and the acidity of the cyanoolefins.

Introduction

The coordination compounds formed between basic transition metal complexes and various π acids have been extensively investigated in recent years.[1] This can be attributed to the profound relation of these compounds to homogeneous catalysis,[2] as well as to the still controversial aspects of the chemical bonding involved in the system,[3] although the problem seems to be settled qualitatively.[4] Most studies have dealt with the combination of phosphine and/or carbonyl complexes of Rh(I), Ir(I), Ni(0), and Pt(0) and activated olefins and acetylenes. Especially, cyanoolefins are widely used as π acids,[5] and the adducts isolated generally contain the cyanoolefins coordinated rigidly to the metal atoms.[1]

It is anticipated that if the transition metal basicity[6] of a certain square-planar complex is only moderate or weak, then its interaction with cyanoolefins will be different from those of other complexes described so far, possibly leading to some novel type of bonding. Isocyanides are known to be moderate σ donors and are probably intermediate in π-acceptor capacity between tertiary phosphines and carbon monoxide.[7] In this respect it is of interest to examine the behavior of some square-planar isocyanide complexes of Rh(I) toward various cyanoolefins.

Here we report the preparative and ir and variable-temperature pmr spectral studies on the reactions of tetracyanoethylene (TCNE) and fumaronitrile (FN) with the following

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three types of Rh(I) isocyanide complexes: $[Rh(RNC)_4]X$,[8,9] $[Rh(RNC)_2(PPh_3)_2]X$,[10] and $Rh(p\text{-}CH_3OC_6H_4NC)(PPh_3)_2Cl$.[9] Some of the results described herein have been communicated.[11]

Experimental Section

Materials. Rhodium trichloride trihydrate and FN were of reagent grade and used as supplied. Commercial TCNE was purified by sublimation; mp 201-202°. Isocyanides were prepared and purified by literature methods.[12] $[Rh(CH_3NC)_4]BPh_4$,[9] $[Rh(RNC)_4]ClO_4$ (R = *p*-$CH_3OC_6H_4$, *o*- and *p*-$CH_3C_6H_4$, *p*-ClC_6H_4),[8] and $[Rh(p\text{-}CH_3OC_6H_4NC)_2(PPh_3)_2]X$ (X = I, ClO_4)[10,13] were also obtained by literature methods. Procedures similar to those described in the literature[9,13] were used to synthesize $[Rh(CH_3NC)_2(PPh_3)_2]X$ (X = I, ClO_4) and $Rh(p\text{-}CH_3OC_6H_4NC)(PPh_3)_2Cl$, except that methyl isocyanide was substituted for *p*-methoxyphenyl isocyanide and *vice versa.* Preparations of the adducts were carried out in a nitrogen atmosphere at ambient temperature, unless otherwise noted. Recrystallizations could be done in open air.

Preparation of the TCNE Adducts. Tetrakis(methyl isocyanide)(tetracyanoethylene)rhodium Tetraphenylborate, $[Rh(CH_3NC)_4(TCNE)]BPh_4$ (1a). A solution of TCNE (105 mg, 0.80 mmol) in benzene (15 ml) was added dropwise to a stirred suspension of $[Rh(CH_3NC)_4]BPh_4$ (470 mg, 0.80 mmol) in CH_2Cl_2 (50 ml) to give a pale yellow solution. White precipitate began to form after a few minutes. After 1 hr the precipitate was collected on a filter, washed with ether, dried *in vacuo,* and recrystallized from acetone to give a white crystalline **1a** (453 mg, 79%), mp 183-185° dec.

Tetrakis(*p*-methoxyphenyl isocyanide)(tetracyanoethylene)rhodium Perchlorate, $[Rh(p\text{-}CH_3OC_6H_4NC)_4(TCNE)]ClO_4$ (1b). To a solution of $[Rh(p\text{-}CH_3OC_6H_4NC)_4]ClO_4$ (440 mg, 0.60 mmol) in CH_2Cl_2 (50 ml) was added TCNE (80 mg, 0.60 mmol), and the colorless solution was stirred for 1 hr. Petroleum ether (bp 40-60°) was added slowly to the solution to give the product which was recrystallized from CH_2Cl_2-petroleum ether to afford pale yellow crystals of **1b** (412 mg, 80%).

The following were similarly obtained by the reactions of the appropriate rhodium substrates with TCNE: **tetrakis(*p*-tolyl isocyanide)(tetracyanoethylene)rhodium perchlorate, $[Rh(p\text{-}CH_3C_6H_4NC)_4(TCNE)]ClO_4$ (1c)** (81%); **tetrakis(*o*-tolyl isocyanide)(tetracyanoethylene)rhodium perchlorate, $[Rh(o\text{-}CH_3C_6H_4NC)_4(TCNE)]ClO_4$ (1d)** (77%); **tetrakis(*p*-chlorophenyl isocyanide)(tetracyanoethylene)rhodium perchlorate, $[Rh(p\text{-}ClC_6H_4NC)_4(TCNE)]ClO_4$ (1e) (69%).**

Iodobis(methyl isocyanide)(triphenylphosphine)(tetracyanoethylene)rhodium, $Rh(CH_3NC)_2(PPh_3)(TCNE)I$ (2a). To a stirred suspension of $[Rh(CH_3NC)_2(PPh_3)_2]I$ (415 mg, 0.50 mmol) in benzene (40 ml) was added a solution of TCNE (65 mg, 0.50 mmol) in benzene (10 ml) at 40°. The suspension turned to a red solution. After being stirred for 1 hr at 40°, the solution was concentrated *in vacuo* to give the product. Recrystallization from CH_2Cl_2-ether gave orange-red crystals of **2a** (159 mg, 46%), mp 204-206° dec.

Iodobis(*p*-methoxyphenyl isocyanide)(triphenylphosphine)(tetracyanoethylene)rhodium, $Rh(p\text{-}CH_3OC_6H_4NC)_2(PPh_3)(TCNE)I$ (2b). TCNE (65 mg, 0.50 mmol) was added to an orange solution of $[Rh(p\text{-}CH_3OC_6H_4NC)_2(PPh_3)_2]I$ (510 mg, 0.50 mmol) in CH_2Cl_2 (50 ml). After being stirred for 1 hr, the solution was concentrated *in vacuo*. Slow addition of petroleum ether to the solution precipitated the product, which was recrystallized from CH_2Cl_2-petroleum ether to give golden yellow crystals of **2b** (366 mg, 83%), mp 230° dec.

Similarly prepared were **bis(methyl isocyanide)bis(triphenylphosphine)(tetracyanoethylene)rhodium perchlorate, $[Rh(CH_3NC)_2(PPh_3)_2(TCNE)]ClO_4$ (3a),** recrystallized from CH_2Cl_2-ether (80%) and **bis(*p*-methoxyphenyl isocyanide)bis(triphenylphosphine)(tetracyanoethylene)rhodium perchlorate, $[Rh(p\text{-}CH_3OC_6H_4NC)_2(PPh_3)_2(TCNE)]ClO_4$ (3b)** (84%).

Chloro(*p*-methoxyphenyl isocyanide)bis(triphenylphosphine)(tetracyanoethylene)rhodium, $Rh(p\text{-}CH_3OC_6H_4NC)(PPh_3)_2(TCNE)Cl$ (4). To a solution of $Rh(p\text{-}CH_3OC_6H_4NC)(PPh_3)_2Cl$ (475 mg, 0.60 mmol) in CH_2Cl_2 (30 ml) was added TCNE (80 mg, 0.60 mmol). After being stirred for 3 hr, the soltuion was concentrated *in vacuo.* Slow addition of petroleum ether precipitated the product, which was recrystallized from CH_2Cl_2-petroleum ether to give yellow crystals of **4** (372 mg, 67%), mp 215-217° dec.

Preparation of the FN Adducts. Iodobis(methyl isocyanide)(triphenylphosphine)(fumaronitrile)rhodium, $Rh(CH_3NC)_2(PPh_3)(NCCH{=}CHCN)I$ (5a). To a stirred suspension of $[Rh(CH_3NC)_2(PPh_3)_2]I$ (420 mg, 0.50 mmol) in benzene (30 ml) was added a solution of FN (120 mg, 1.50 mmol) in benzene (15 ml) at 45°. The suspension gradually turned to an orange solution. After being stirred for 5 hr at 45°, concentration of the solution *in vacuo* gave the product, which was recrystallized from CH_2Cl_2-petroleum ether to give orange crystals of **5a** (198 mg, 61%), mp 181-183° dec.

Iodobis(*p*-methoxyphenyl isocyanide)(triphenylphosphine)(fumaronitrile)rhodium, $Rh(p\text{-}CH_3OC_6H_4NC)_2(PPh_3)(NCCH{=}CHCN)I$ (5b), was similarly prepared (70%), mp 170-172° dec.

Bis(methyl isocyanide)bis(triphenylphosphine)(fumaronitrile)rhodium Perchlorate, $Rh(CH_3NC)_2(PPh_3)_2(NCCH{=}CHCN)]ClO_4$ (6a). To a solution of $[Rh(CH_3NC)_2(PPh_3)_2]ClO_4$ (403 mg, 0.50 mmol) in CH_2Cl_2 (30 ml) was added FN (45 mg, 0.55 mmol). The yellow solution was stirred for 10 hr and concentrated *in vacuo.* Slow addition of petroleum ether to the solution gave the product, which was recrystallized from CH_2Cl_2-petroleum ether to afford yellow crystals of **6a** (323 mg, 73%).

Bis(*p*-methoxyphenyl isocyanide)bis(triphenylphosphine)(fumaronitrile)rhodium perchlorate, $[Rh(p\text{-}CH_3OC_6H_4NC)_2(PPh_3)_2(NCCH{=}CHCN)]ClO_4$ (6b), was similarly obtained (71%).

The analytical data, conductivity, and molecular weights of the complexes are summarized in Table I.

Physical Measurements. The electric conductivity was measured in 10^{-4} *M* CH_3CN solution by using a Yokogawa F-255A universal bridge and a cell with the cell constant of 0.322 cm^{-1}. CH_3CN was distilled over P_2O_5 five times to give $\kappa = 1.6 \times 10^{-7}$ ohm^{-1} cm^{-1}. Molecular weights were determined in $CHCl_3$, using a Hitachi Perkin-Elmer 115 vapor pressure osmometer. The ir spectra were recorded on Hitachi Perkin-Elmer 225 (4000-400 cm^{-1}) and Hitachi EPI-L (700-200 cm^{-1}) spectrophotometers in Nujol mulls and in 3.5-6.5 wt % CH_2Cl_2 or $CHCl_3$ solution. The pmr spectra were recorded on a Japan Electron Optics JNM-PS-100 spectrometer equipped with a JNM-VT-3B variable-temperature controller in 3.5-6.5 wt % CH_2Cl_2, $CDCl_3$, or C_6H_5CN solution. Tetramethylsilane was used as internal reference.

Results and Discussion

Preparation. Three types of rhodium(I) isocyanide complexes, $[Rh(RNC)_4]X$, $[Rh(RNC)_2(PPh_3)_2]ClO_4$, and $Rh(p\text{-}CH_3OC_6H_4NC)(PPh_3)_2Cl$, reacted smoothly with TCNE to give 1:1 adducts. $[Rh(RNC)_2(PPh_3)_2]ClO_4$, furthermore, formed 1:1 adducts with FN. $[Rh(RNC)_2(PPh_3)_2]I$, however, upon reaction with the cyanoolefins, dissociated one molecule of PPh_3 and took the iodide into the coordination sphere to produce the neutral adducts $Rh(RNC)_2(PPh_3)(olefin)I$ (olefin = TCNE and FN). This result is similar to that reported by Boshi, *et al.*,[14] who found that $[Rh(PhNC)_2(PPh_3)_2]Cl$ and $[Rh(PhNC)_4]Cl$ reacted with TCNE to give neutral adducts, $Rh(PhNC)_2(PPh_3)(TCNE)Cl$ and $Rh(PhNC)_3(TCNE)Cl$, respectively. However, reactions of $[Rh(p\text{-}CH_3C_6H_4NC)_4]ClO_4$ with other π acids such as tetrafluoroethylene, FN, maleic anhydride, dimethyl and diethyl maleate, and diphenylacetylene led only to recovery of the starting materials.

The adducts isolated are orange, yellow, or off-white and are indefinitely stable to air in the solid state. In the ir spectra the isocyanide $\nu(N{\equiv}C)$ bands in the adducts are always higher than in the parent four-coordinate compounds. Moreover, the pmr signals of the isocyanides are shifted to the lower field upon adduct formation. These two features reveal a charge transfer from the rhodium atom to the cyano-

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Table I. Analytical Data, Conductivity, and Molecular Weights of the Complexes

		% carbon		% hydrogen		% nitrogen			Mol wt	
No.	Complexes[a]	Calcd	Found	Calcd	Found	Calcd	Found	Λ[b]	Calcd	Found
1a	$[Rh(CH_3NC)_4(TCNE)]BPh_4$	63.88	63.87	4.49	4.52	15.79	15.69	109		
1b	$[Rh(p\text{-}CH_3OC_6H_4NC)_4(TCNE)]ClO_4$	52.88	52.23	3.27	2.99	12.98	13.11	139		
1c	$[Rh(p\text{-}CH_3C_6H_4NC)_4(TCNE)]ClO_4$	57.12	56.49	3.53	2.94	14.02	14.03	137		
1d	$[Rh(o\text{-}CH_3C_6H_4NC)_4(TCNE)]ClO_4$	57.12	56.83	3.53	3.42	14.02	14.16	147		
1e	$[Rh(p\text{-}ClC_6H_4NC)_4(TCNE)]ClO_4$	46.36	45.74	1.83	1.87	12.73	12.67			
2a	$Rh(CH_3NC)_2(PPh_3)(TCNE)I$	47.89	47.55	3.01	3.22	11.97	11.61		702	696
2b	$Rh(p\text{-}CH_3OC_6H_4NC)_2(PPh_3)(TCNE)I$	54.20	54.20	3.32	3.30	9.26	9.48		885	880
3a	$[Rh(CH_3NC)_2(PPh_3)_2(TCNE)]ClO_4$	58.96	58.83	3.87	3.95	8.97	8.79	141		
3b	$[Rh(p\text{-}CH_3OC_6H_4NC)_2(PPh_3)_2(TCNE)]ClO_4$	61.83	62.13	3.78	3.96	7.72	7.49	142		
4	$Rh(p\text{-}CH_3OC_6H_4NC)(PPh_3)_2(TCNE)Cl$	65.00	64.99	4.19	4.04	7.97	7.58		924	906
5a	$Rh(CH_3NC)_2(PPh_3)(FN)I$	47.88	47.53	3.55	3.54	8.59	8.39		652	608
5b	$Rh(p\text{-}CH_3OC_6H_4NC)_2(PPh_3)(FN)I$	54.25	54.26	3.77	3.74	6.40	6.70		836	825
6a	$[Rh(CH_3NC)_2(PPh_3)_2(FN)]ClO_4$	59.57	59.24	4.32	4.25	6.32	6.62	162		
6b	$[Rh(p\text{-}CH_3OC_6H_4NC)_2(PPh_3)_2(FN)]ClO_4$	62.68	62.78	4.33	4.33	5.45	5.23	143		

[a] Abbreviations for ligands: TCNE, tetracyanoethylene; FN, fumaronitrile; PPh_3, triphenylphosphine. [b] Molar conductivity in ohm^{-1} cm^2 mol^{-1}.

Table II. Ir and Pmr Data of the Parent Complexes and the Cyanoolefin Adducts

		Ir,[b] cm^{-1}		Pmr,[f] τ, ppm		
No.	Complex[a]	$\nu(N{\equiv}C)$[c]	$\nu(C{\equiv}N)$[d]	$-C_6H_4-$[g]	CH_3-	Solvent (temp)
	$[Rh(CH_3NC)_4]BPh_4$	2197*			6.71	C_6H_5CN (24°)
1a	$[Rh(CH_3NC)_4(TCNE)]BPh_4$	2265	2230		6.43	C_6H_5CN (46°)
	$[Rh(p\text{-}CH_3OC_6H_4NC)_4]ClO_4$	2150*		2.48, 2.97	6.23	
1b	$[Rh(p\text{-}CH_3OC_6H_4NC)_4(TCNE)]ClO_4$	2221	*e*	2.28, 2.68	6.20	CH_2Cl_2 (45°)
	$[Rh(p\text{-}CH_3C_6H_4NC)_4]ClO_4$	2153*		2.67, 2.80	7.68	
1c	$[Rh(p\text{-}CH_3C_6H_4NC)_4(TCNE)]ClO_4$	2228	*e*	2.29, 2.70	7.58	CH_2Cl_2 (45°)
	$[Rh(o\text{-}CH_3C_6H_4NC)_4]ClO_4$	2145*		Multiplet	7.51	
1d	$[Rh(o\text{-}CH_3C_6H_4NC)_4(TCNE)]ClO_4$	2208	*e*	Multiplet	7.45	CH_2Cl_2 (24°)
	$[Rh(CH_3NC)_2(PPh_3)_2]I$	2181*			7.51	
2a	$Rh(CH_3NC)_2(PPh_3)(TCNE)I$	2251	2219		6.73	
5a	$Rh(CH_3NC)_2(PPh_3)(FN)I^h$	2227	2207		6.93	$CDCl_3$ (55°)
	$[Rh(p\text{-}CH_3OC_6H_4NC)_2(PPh_3)_2]I$	2080*		3.43, 3.99	6.27	
2b	$Rh(p\text{-}CH_3OC_6H_4NC)_2(PPh_3)(TCNE)I$	2205	2230	2.94, 3.24	6.24	
5b	$Rh(p\text{-}CH_3OC_6H_4NC)_2(PPh_3)(FN)I^h$	2173	2213	3.07, 3.31	6.23	$CDCl_3$ (50°)
	$Rh(p\text{-}CH_3OC_6H_4NC)(PPh_3)_2Cl$	2135*		3.43, 4.06	6.24	
4	$Rh(p\text{-}CH_3OC_6H_4NC)(PPh_3)_2(TCNE)Cl$	2184	2223	3.31, 3.43	6.22	
	$[Rh(CH_3NC)_2(PPh_3)_2]ClO_4$	2177*			7.49	
3a	$[Rh(CH_3NC)_2(PPh_3)_2(TCNE)]ClO_4$	2247	2224		6.81	
6a	$[Rh(CH_3NC)_2(PPh_3)_2(FN)]ClO_4{}^h$	2232, 2177	2217		7.41	$CDCl_3$ (50°)
	$[Rh(p\text{-}CH_3OC_6H_4NC)_2(PPh_3)_2]ClO_4$	2124*		3.41, 3.82	6.25	
3b	$[Rh(p\text{-}CH_3OC_6H_4NC)_2(PPh_3)_2(TCNE)]ClO_4$	2195	2225	3.10, 3.43	6.15	
6b	$[Rh(p\text{-}CH_3OC_6H_4NC)_2(PPh_3)_2(FN)]ClO_4{}^h$	2175, 2124	2213	3.29, 3.77	6.23	$CDCl_3$ (57°)

[a] Abbreviations for ligands: TCNE, tetracyanoethylene; FN, fumaronitrile; PPh_3, triphenylphosphine. [b] Measured in $CHCl_3$ or as Nujol mulls (asterisks). [c] Isocyanide vibration. [d] Cyanoolefin vibration. [e] Masked by the strong and broad $\nu(N{\equiv}C)$ of the isocyanides. [f] Measured in $CDCl_3$ at 24° unless otherwise noted. [g] Approximated as an AB type quartet with the coupling constant of about 9 Hz. [h] The FN protons were observed as broad singlets at τ 6.86 (**5a**), 6.69 (**5b**), 4.20 (**6a**), and 4.02 (**6b**), respectively.

olefin ligands. Ir and pmr data of the parent compounds and the new cyanoolefin adducts are summarized in Table II.

Bonding. The cyanoolefin adducts isolated in our study can be grouped into two categories with regard to the bonding behavior of the cyanoolefins in solution at room temperature: rigid and nonrigid.

The Rigid Adducts: 2–4. The ir spectra of **2** and **3** in $CHCl_3$ at room temperature show only one $\nu(N{\equiv}C)$ band of the isocyanides (Table II). The pmr spectra of **2a** and **3a** in $CDCl_3$ show a sharp singlet due to the CH_3 protons (Table II). The pmr spectra of **2b** and **3b** in $CDCl_3$ show a sharp singlet due to the CH_3O protons and only one set of an approximate AB type quartet arising from the phenyl ring protons. Little temperature dependence is observed in these signals in the temperature range between +55 and −75°. Stereochemical nonrigidity throughout this temperature range for compounds of this kind will probably be unlikely. Thus these results, together with the X-ray data on closely related compounds, *i.e.*, $IrBr(CO)(PPh_3)_2(TCNE)$,[15] suggest that these adducts have the TCNE coordinated rigidly perhaps in a trigonal-bipyramidal configuration with the two isocyanides trans to each other.

4 is monomeric in $CHCl_3$ (Table I) and the ir and pmr spectra show the presence of a single type of the isocyanides. No temperature dependence in its pmr spectra suggests that **4** also has rigidly bonded TCNE.

The Nonrigid Adducts: 1a-1d.[16] In our preliminary communication,[11] we reported, on the basis of 60-MHz pmr spectra, that in **1b-1d** in solution the TCNE moiety is rotating rapidly at higher temperatures. The 100-MHz variable-temperature pmr spectra of **1c** have now been obtained and shown in Figure 1, which more clearly indicates the magnetic equivalence of the four isocyanides at higher temperatures and the appearance of two kinds of isocyanides at low temperature. The coalescence temperature decreases in the order ortho protons > meta protons > para methyl protons.[17]

Similar temperature-dependent pmr spectra are observed

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(15) L. M. Muir, K. W. Muir, and J. A. Ibers, *Discuss. Faraday Soc.*, 47, 84 (1969).

(16) **1e** is not sufficiently soluble to obtain satisfactory pmr spectra, which prevents further study of this compound.

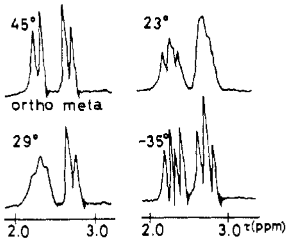

Figure 1. Temperature-dependent pmr spectra of phenyl ring protons of $[Rh(p\text{-}CH_3C_6H_4NC)_4(TCNE)]ClO_4$ (**1c**) in CH_2Cl_2. The para CH_3 signal was observed as a singlet above 20° and as a doublet at −20°.

for the CH_3NC analog **1a**. The methyl proton signal at τ 6.43 is a sharp singlet at 46°, broadens as the temperature is lowered, coalesces at 33.0°, and splits into a doublet with a separation of 10.0 Hz at −8°. The temperature dependence of the pmr spectra is not detectably altered by variation of concentration or of solvent or by the addition of 2 molar equiv of TCNE. On the other hand, addition of 2 molar equiv of methyl isocyanide caused not only a color change but also a complicated spectral change which is completely different from those illustrated above and cannot be explained easily.

Based on these results, this kind of the temperature dependence of the pmr spectra may be interpreted in terms of some intramolecular phenomenon: the partly restricted rotation of the TCNE[18] around the coordination bond in *a time-averaged square-pyramidal configuration*[19] as is illustrated in Figure 2. Another reason that we have suggested a time-averaged *square pyramid* is that the ir spectra of **1a-1d** in solution at room temperature show only one strong and broad $\nu(N{\equiv}C)$ vibration, which is consistent with a local symmetry of C_{4v} for the four isocyanides. In contrast to our results, Kaska and Kimball[20] reported that $[(CH_3NC)_4\text{-}Co(CH_3CO_2C{\equiv}CCO_2CH_3)]^{2+}$ exhibited four $\nu(N{\equiv}C)$ bands and two kinds of CH_3 proton signals due to CH_3NC. To this ion they assigned a trigonal bipyramid with the acetylene coordinated rigidly.

This rotational mode would be equally explained in terms of either a distorted square pyramid or a distorted trigonal bipyramid. The TCNE rotation in a square pyramid is illustrated in Figure 2a and the rhodium atom may deviate out of the basal plane made by the four isocyanide ligands to some extent. The TCNE rotation in a trigonal bipyramid illustrated in Figure 2b will also result in an interchange of axial and equatorial isocyanides, if it is assumed to accompany bending motions of the coordination bonds between the isocyanide ligands and the rhodium atom in the Berry mechanism.[21] The low-temperature limiting configuration may be a distorted square pyramid with the TCNE fixed above the two trans isocyanides which may be bent away from the TCNE to some extent, and depending on the extent of this bending, this configuration may be equally considered as a distorted trigonal bipyramid. Definite choice of the configuration would be possible only after the L-Rh-L angle in Figure 2 is known. The approximate free energy of activation to rotation of TCNE in **1a** at the coalescence temperature is calculated as 16.6 kcal/mol on the bais of the peak separation method and Eyring's equation.[22]

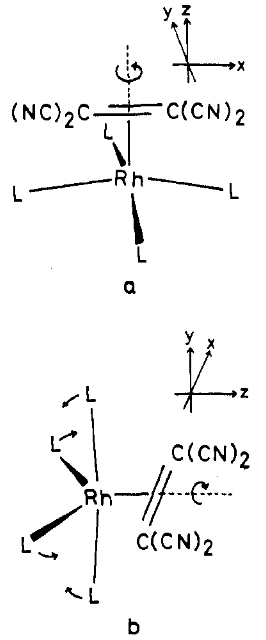

Figure 2. The time-averaged square-pyramidal configuration of the nonrigid $[Rh(RNC)_4(TCNE)]^+$ (**1**) (L = RNC): (a) illustrated as a distorted square pyramid; (b) illustrated as a distorted trigonal bipyramid.

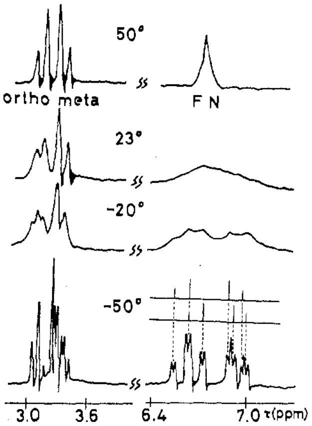

Figure 3. Temperature-dependent pmr spectra of $Rh(p\text{-}CH_3OC_6H_4NC)_2(PPh_3)(FN)I$ (**5b**) in $CDCl_3$. Signals for para CH_3O and PPh_3 are omitted. The para CH_3O signal was observed as a singlet above −30° and as a doublet at −40°. Intensity of the FN signal is exaggerated.

5a and 5b. The ir spectra of **5a** and **5b** at room temperature show only one strong and broad $\nu(N{\equiv}C)$ band due to the isocyanides (Table II), indicating the trans alignment of the two isocyanides. The pmr spectra of **5b** in $CDCl_3$ show a temperature dependence as shown in Figure 3. At

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(17) The lower field component can be safely assigned as due to the ortho protons. The ortho protons are considered to accept the stronger magnetic anisotropic effect due to some intramolecular rearrangement than the meta protons and therefore must coalesce at higher temperatures.

(18) The temperature dependence would equally be interpreted by pseudorotations of four isocyanide ligands in the Ray and Dutt fashion [P. Ray and N. K. Dutt, *J. Indian Chem. Soc.*, **20**, 81 (1943)], if TCNE is assumed to be rigidly bonded to the rhodium atom. However, the rotation of TCNE is more physically meaningful, because the temperature-dependent pmr spectral features of the closely related systems 1-6 can be more consistently explained in terms of the qualitative basicity and acidity of the metal substrates and cyanoolefins (see later).

(19) We are indebted to a referee for his suggestion of this term.

(20) W. C. Kaska and M. E. Kimball, *Inorg. Nucl. Chem. Lett.*, 4, 719 (1968).

(21) E. L. Muetterties, *Accounts Chem. Res.*, 3, 266 (1970).

(22) R. Cramer and J. J. Mrowca, *Inorg. Chim. Acta*, 5, 528 (1971), and references therein.

50° this compound exhibits a sharp singlet at τ 6.23 due to the CH_3O protons, only one set of an approximate AB type quartet at τ 3.07 and 3.31 arising from the phenyl ring protons of the isocyanides, and a rather broad signal at τ 6.69 attributable to the FN protons. No observation of coupling between the FN protons and the ^{103}Rh nucleus at this temperature may be due to a very little dissociative exchange of the FN, although **5b** is essentially monomeric at 25° (Table I). As the temperature is lowered, the FN proton signal becomes broad, but the chemical shift remains almost constant, indicating little olefin dissociation at lower temperature. The lower field component (ortho proton signals) and the higher field one (meta proton signals) of the quartet[23] coalesce around 23 and −10°, respectively. Finally at −50°, the CH_3O proton signal is split into a doublet (separation of 0.02 ppm), the quartet changes to multiplet, and the FN signal is split into two pairs of AB type quartets; each peak of which is further split into a doublet due to coupling with the ^{103}Rh nucleus (J(Rh-H) = 2 Hz). The decrease in coalescence temperature in the order ortho protons > meta protons > para methoxy protons indicates the magnetic nonequivalence of the phenyl ring protons. This can be due to dynamic anisotropy of the FN, which is very similar to that described for the TCNE adduct **1c** (Figure 2), for which rotation of TCNE is deduced. Thus, the features of the ir and temperature-dependent pmr spectra of **5b** can also be explained in terms of the FN rotating in a time-averaged square-pyramidal configuration.

The temperature-dependent pmr spectra of **5a** can also be interpreted by the rotating FN. The pattern of the FN signal at −23°, although partly masked by the CH_3NC signal, is very similar to that of **5b** (Figure 3). The broad isocyanide singlet at higher temperatures is split into four signals at τ 6.90, 6.92, 6.95, and 6.97 at −23°, indicating four different magnetic environments for the isocyanides.

When the rotation of the FN is restricted at low temperature, **5a** and **5b** can have two different configurations as illustrated in Figure 4. The two protons of the FN and the two isocyanides in each isomer are nonequivalent. The pmr spectra at low temperature show four CH_3NC signals in **5a** and two pairs of AB type quartets for the FN protons in **5b**. Therefore, both of the isomers exist in solution.

6a and 6b. The $\nu(N\equiv C)$ frequencies of **6b** and its parent compound (Table II) suggest a dissociative equilibrium of FN in **6b**. The $\nu(C\equiv N)$ band of the coordinated FN is observed at 2213 cm^{-1}. The $\nu(N\equiv C)$ band of 2175 cm^{-1} can be assigned as due to the adduct in view of the magnitude of its frequency shift. Appearance of only one $\nu(N\equiv C)$ band in the undissociated adduct in solution suggests trans isocyanides.

The pmr spectra of **6b** show two phenomena for this compound. As the temperature is lowered, the ring protons of the isocyanides become less shielded and their signals are broadened. On the other hand, the FN signal observed as a slightly broad singlet at τ 4.02 at 57°, which is close to the chemical shift of free FN at τ 3.62, is shifted upfield with broadening and at 23° disappears. A very broad FN signal is observed around τ 4.17 upon addition of 1.3 molar equiv of FN to **5b** in $CDCl_3$ at 24°. These pmr spectra can be rationalized in terms of the following dissociative equilibrium of the FN. This result is also consistent with the ir spectrum.

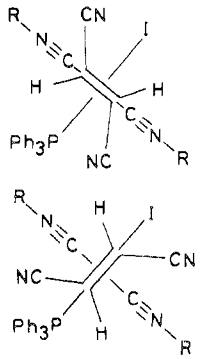

Figure 4. Isomeric forms of $Rh(RNC)_2(PPh_3)(FN)I$ (**5**) (viewed from the FN side). The rhodium atom is omitted for clarity.

$$[Rh(RNC)_2(PPh_3)_2(FN)]ClO_4 \rightleftharpoons [Rh(RNC)_2(PPh_3)_2]ClO_4 + FN$$

With the temperature further descending, the higher field component (ortho proton signal) and the lower field component (meta proton signal) of the quartet[24] coalesce around −2 and −25°, respectively, and finally at −62° there appears an AB type quartet at τ 3.18 and 3.55 for the ring protons. On the other hand, the FN signal appears again as a broad signal around τ 6.62 at −25°, narrows without changing chemical shift, and finally at −62° is split into a doublet due to coupling with the ^{103}Rh nucleus (J(Rh-H) = 2 Hz). The constant chemical shift of the FN protons indicates very little olefin dissociation. Occurrence of rotation of FN is likely, judging from the spectral feature of the AB type quartet below −2° in analogy with those of **1c** (Figure 1) and **5b** (Figure 3). The pmr spectra indicate that when the FN is fixed at low temperature, **6b** exists as a single isomer in contrast to the case of **5**. A similar behavior can be deduced for **6a** from its ir and pmr spectra.

Difference in Bonding. The transition metal basicity of the coordinatively unsaturated d^8 metal complexes $[Rh(RNC)_4]X$ is considered to be relatively weak because of a high π acidity of the isocyanide ligands.[7] This postulate is consistent with the fact that TCNE (electron affinity of 2.89 eV[25]), one of the strongest olefinic π acids, is the only activated olefin that was found to form adducts. In view of the weak transition metal basicity, the metal to olefinic π bonding in **1** may be weaker than in an analogous adduct such as $IrBr(CO)(PPh_3)_2(TCNE)$[15] according to the Dewar-Chatt-Duncanson model of bonding.[4] This postulate would lead to the more facile olefin rotation in **1**, since the barrier to rotation should be a function of π bonding; *i.e.*, the greater the π-bonding interaction, the higher the energy barrier.[26] Actually, TCNE in **1** is found to rotate rapidly in solution at room temperature. In connection with rotation of coordinated olefins, Cramer and his coworkers[22] have reported that the C_2H_4 groups coordinated to the rhodium atoms in the compounds $(\eta^5\text{-}C_5H_5)Rh(C_2H_4)_2$, $(\eta^5\text{-}C_5H_5)Rh(C_2H_4)SO_2$, and $(\eta^5\text{-}C_5H_5)Rh(C_2H_4)(C_2F_4)$ rotate freely at higher temperatures and that in the last compound the C_2F_4 is rigid. Moreover, the X-ray crystallographic analysis of the last compound shows that the distortions of the ole-

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[23] The method of assignment of the ortho and meta protons is similar to the case of $[Rh(RNC)_4(TCNE)]X$.

[24] The method of assignment of the ortho and meta protons is similar to those described for $[Rh(p\text{-}CH_3C_6H_4NC)_4(TCNE)]ClO_4$ (**1c**) and $Rh(p\text{-}CH_3OC_6H_4NC)_2(PPh_3)(FN)I$ (**5b**). The inversion of the chemical shift between the ortho and meta protons is considered to be due to the anisotropic effect of the phenyl rings and/or the electron-donating effect of the two phosphine ligands.

[25] A. C. Farragher and A. M. Page, *Trans. Faraday Soc.*, 63, 2369 (1967).

[26] K. S. Wheelock, J. H. Nelson, L. C. Cusachs, and H. B. Jonassen, *J. Amer. Chem. Soc.*, 92, 5110 (1970).

fin moieties, upon adduct formation, are less striking in the C_2H_4 than in the C_2F_4 unit, which is explained in terms of the weaker metal to olefin π bonding in the Rh-C_2H_4 than in the Rh-C_2F_4 bond.[27] On the other hand, X-ray analyses show that $IrBr(CO)(PPh_3)_2(TCNE)$,[15] $IrH(CO)(PPh_3)_2(FN)$,[28] and $IrCl(CO)(AsPh_3)_2(TCNE)$[29] adopt trigonal-bipyramidal configurations with the cyanoolefins coordinated rigidly and that the degrees of distortion of their geometries, upon adduct formation, indicate strong π-bonding interactions between the iridium atoms and the cyanoolefins. No evidence for the free rotation of the cyanoolefins around the coordination bond is reported for these compounds.[1]

Comparison of **1a** and **1b** with **2a** and **2b**, respectively, shows that the replacement of the two isocyanides with two triphenylphosphines in the parent complexes has produced a change in the bonding behavior of TCNE toward the rhodium atom, from nonrigid to rigid. It is well known that the tertiary phosphines have more σ-donor and less π-acceptor capacity compared with the isocyanides.[30] Thus an expected increase in the transition metal basicity of $[Rh(RNC)_2(PPh_3)_2]ClO_4$ compared with that of $[Rh(RNC)_4]X$, which is evidenced from a comparison of their ν(N≡C) data (Table II), seems to cause formation of the rigid adducts **2a** and **2b**. In addition, $[Rh(RNC)_2(PPh_3)_2]ClO_4$ can react with FN (electron affinity of 0.78 eV[25]), and in the adducts formed (**6a** and **6b**) the FN is rotating. This result suggests that a moderate π-bonding interaction between the more basic Rh(I) substrate and a rather weak π acid FN yields the nonrigid adducts.

Although Raman spectra of some of these compounds were measured, they were unfortunately too complicated to assign the $\nu(\mathrm{C}\overset{\cdots}{-}\mathrm{C})$ of the coordinated olefins with confidence, precluding a quantitative comparison of the π-bonding interaction. In connection with $[Rh(RNC)_2(PPh_3)_2(olefin)]ClO_4$ (olefin = TCNE or FN), it is suggestive that the analogous iridium compounds $[Ir(p\text{-}CH_3C_6H_4NC)_2(PPh_3)_2(olefin)]ClO_4$ (olefin = TCNE, FN, or maleic anhydride) synthesized by us recently[31] are found to have trigonal-bipyramidal configurations with the rigidly bonded olefins. In view of the generally stronger basicity of a certain Ir(I) complex than that of an analogous Rh(I) complex,[2] the stronger π-bonding interactions between the iridium atom and the olefins have probably resulted in the rigid adducts even for the FN and maleic anhydride.

Acknowledgment. We are indebted to Professor H. G. Kuivila, Visiting Professor invited by the Japan Society for the Promotion of Science at Osaka University, for improvement of the text of this paper.

Registry No. **1a**, 51567-54-5; **1b**, 36682-31-2; **1c**, 36620-24-3; **1d**, 51567-56-7; **1e**, 36620-25-4; **2a**, 51567-62-5; **2b**, 51567-63-6; **3a**, 51567-58-9; **3b**, 51567-60-3; **4**, 51567-61-4; **5a**, 51635-58-6; **5b**, 51635-59-7; **6a**, 51635-61-1; **6b**, 51635-63-3; $[Rh(CH_3NC)_4]BPh_4$, 34742-53-5; $[Rh(p\text{-}CH_3OC_6H_4NC)_4]ClO_4$, 14075-09-3; $[Rh(p\text{-}CH_3C_6H_4NC)_4]ClO_4$, 43093-67-0; $[Rh(o\text{-}CH_3C_6H_4NC)_4]ClO_4$, 51567-65-8; $[Rh(CH_3NC)_2(PPh_3)_2]I$, 51743-55-6; $[Rh(p\text{-}CH_3OC_6H_4NC)_2(PPh_3)_2]I$, 51567-66-9; $[Rh(p\text{-}CH_3OC_6H_4NC)(PPh_3)_2]Cl$, 51567-67-0; $[Rh(CH_3NC)_2(PPh_3)_2]ClO_4$, 51703-33-4; $[Rh(p\text{-}CH_3OC_6H_4NC)_2(PPh_3)_2]ClO_4$, 51567-69-2.

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Contribution from the Department of Chemistry,
Northwestern University, Evanston, Illinois 60201

Interaction of Four-Coordinate Rhodium(I) Complexes with Boron-Containing Lewis Acids

D. D. LEHMAN and D. F. SHRIVER*

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The interaction of Lewis acids with $RhCl(PPh_3)_3$, $RhClCO(PPh_3)_2$, $[Rh(diphos)_2]BPh_4$, $RhClC_8H_{12}PPh_3$, and $[RhC_8H_{12}(PPh_3)_2]PF_6$ is reported. The Lewis acid complexes were characterized by stoichiometry, molecular weight, medium- and far-infrared, and ^{11}B, ^{31}P, ^{19}F, ^{1}H, and ^{103}Rh nmr data. Several types of reactions involving metal basicity, halide basicity, and phosphine abstraction were observed.

Of major interest in the study of platinum metal complexes have been their reactions with simple substrates such as O_2, SO_2, C_2H_4, HX, RX, H_2, CO, and C_2H_2.[1] These reactions generally involve synergic bonding between the platinum metal and the substrate, while substrates that can complex solely as σ-electron acceptors, such as group III Lewis acids, have not been as extensively studied. Those platinum metal complexes that have been investigated with Lewis acids have usually led to the formation of metal base-Lewis acid adducts.[1i,2-8] Studies involving Lewis acids with other metal

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(1) For example, among the many papers appearing, are the following: (a) J. P. Collman, *Accounts Chem. Res.*, 1, 136 (1968); (b) L. Vaska, *ibid.*, 1, 335 (1968); (c) D. F. Shriver, *ibid.*, 3, 231 (1970); (d) J. Halpern, *ibid.*, 3, 386 (1970); (e) J. P. Collman and W. R. Roper, *Advan. Organometal. Chem.*, 7, 53 (1968); (f) J. A. Osborn, F. H. Jardine, J. F. Young, and G. Wilkinson, *J. Chem. Soc. A*, 1711 (1966); (g) M. C. Baird and G. Wilkinson, *ibid.*, 865 (1967); (h) T. Blackmore, M. I. Bruce, and F. G. A. Stone, *ibid.*, 2376 (1971); (i) T. E. Nappier, Jr., and D. W. Meek, *J. Amer. Chem. Soc.*, 94, 306 (1972).

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