Inorganica Chimica Acta, 15 (1975) 161–166
© Elsevier Sequoia S.A., Lausanne – Printed in Switzerland

Acetylacetonatobis(isocyanide)(tetracyanoethylene)rhodium and Related Complexes. Rotation of Tetracyanoethylene

T. KANESHIMA, K. KAWAKAMI and T. TANAKA
Department of Applied Chemistry, Faculty of Engineering, Osaka University, Yamada-kami, Suita, Osaka 565, Japan

Received February 27, 1975

Two types of square-planar rhodium(I) isocyanide complexes, Rh(acac)(RNC)$_2$ (acac = $CH_3COCHCOCH_3^-$; R = t-Bu, p-$CH_3OC_6H_4$, p-$CH_3C_6H_4$, p-ClC_6H_4, 2,4,6-$(CH_3)_3C_6H_2$) and Rh(acac)(R'NC)(PPh$_3$) (R' = p-$CH_3OC_6H_4$, p-$CH_3C_6H_4$, p-ClC_6H_4), have been synthesized. They react with tetracyanoethylene (TCNE) to give the 1:1 adducts, Rh(acac)(RNC)$_2$(TCNE) and Rh(acac)(R'NC)(PPh$_3$)(TCNE). Configurational behaviors of these complexes in solution are described from ir and pmr spectra. Rh(acac)(RNC)$_2$(TCNE) gives temperature-dependent pmr spectra which are interpreted in terms of the TCNE rotation around the rhodium–TCNE bond accompanying Berry pseudorotation in a trigonal bipyramid.

Introduction

Low-valent transition metal complexes containing phosphine and/or carbonyl are widely known to react with cyanoolefins to form adducts with the olefins coordinated rigidly.[1] In contrast, we have recently reported that the cyanoolefins such as tetracyanoethylene (TCNE) and fumaronitrile are rotating around the coordination bond in their adducts with some rhodium(I) isocyanide complexes in solution.[2] This novel metal–cyanoolefin bonding is considered to be associated with the unique transition metal basicity[3] of rhodium(I) complexes containing isocyanide ligands which are moderate σ-donors and are intermediate in π-acceptor capacity between tertiary phosphines and carbon monoxide.[4] Thus, it will be of interest to extend the scope of the cyanoolefin adducts with rhodium(I) isocyanide complexes. This paper reports the preparative and ir and variable-temperature pmr spectral studies of the new type rhodium(I) isocyanide complexes, Rh(acac)(RNC)$_2$ and Rh(acac)(RNC)(PPh$_3$) (acac = $CH_3COCHCOCH_3^-$), and their TCNE adducts.

Experimental

Materials

Commercial TCNE was purified by sublimation; m.p. 201–202° C. Isocyanides were prepared and purified by literature methods.[5] The complexes, Rh(acac)(COD),[6] Rh(acac)(PPh$_3$)$_2$,[7] and Rh(acac)(CO)$_2$,[8] were also obtained by literature methods. Unless otherwise stated, preparations were carried out under nitrogen using deaerated solvents and recrystallizations were done in air.

Preparation of Parent Complexes

Acetylacetonatobis(t-butyl isocyanide)rhodium(I), Rh(acac)(t-BuNC)$_2$ (1a)

A solution of Rh(acac)(COD) (310 mg, 1 mmol) in petroleum ether (b.p. 40–60° C, 15 ml) was treated with *t*-BuNC (167 mg, 2 mmol) at ambient temperature. After stirring for 30 min, the solvent was evaporated *in vacuo*. The resulting oily residue was dissolved in a small volume of CH_2Cl_2 under nitrogen and then slow addition of petroleum ether to the solution gave yellow crystals of *1a* with 1/4 CH_2Cl_2 (311 mg, 80%).

Acetylacetonatobis(p-methoxyphenyl isocyanide) rhodium(I), Rh(acac)(p-$CH_3OC_6H_4NC$)$_2$ (1b)

A solution of *p*-$CH_3OC_6H_4NC$ (267 mg, 2 mmol) in petroleum ether (15 ml) was added dropwise to a stirred solution of Rh(acac)(COD) (310 mg, 1 mmol) in the same solvent (15 ml) at ambient temperature. The resulting suspension was refluxed for 30 min, when greenish yellow crystals of *1b* (435 mg, 93%) were deposited.

The following were similarly obtained by reactions of Rh(acac)(COD) with the appropriate isocyanides: *Rh(acac)(p-$CH_3C_6H_4NC$)$_2$ (1c)* (95%); *Rh(acac)(p-ClC_6H_4NC)$_2$ (1d)* (83%); *Rh(acac)(2,4,6-$(CH_3)_3C_6H_2NC$)$_2$ (1e)* (95%).

Acetylacetonato(p-methoxyphenyl isocyanide)(triphenylphosphine)rhodium(I), Rh(acac)(p-$CH_3OC_6H_4NC$)(PPh$_3$) (2a)

To a stirred orange suspension of Rh(acac)(PPh$_3$)$_2$ (363 mg, 0.5 mmol) in ether (20 ml) was added dropwise a solution of *p*-$CH_3OC_6H_4NC$ (84 mg, 0.63 mmol) in ether (10 ml) at 10° C. The resulting red solution was refluxed for 1 hr. Concentration of the solution *in vacuo* to *ca.* one-third volume gave the yellow product, which was filtered under nitrogen, washed with petroleum ether, and dried *in vacuo* (284 mg, 95%).

The following were prepared in the same way as the p-$CH_3OC_6H_4NC$ analog: *Rh(acac)(p-$CH_3C_6H_4NC$)(PPh_3) (2b)* (93%); *Rh(acac)(p-ClC_6H_4NC)(PPh_3) (2c)* (90%).

Preparation of TCNE Adducts

Acetylacetonatobis(t-butyl isocyanide)(tetracyanoethylene)rhodium, Rh(acac)(t-BuNC)$_2$(TCNE) (3a)

A mixture of Rh(acac)(t-BuNC)$_2$ · 1/4CH_2Cl_2 (194 mg, 0.5 mmol) and TCNE (65 mg, 0.5 mmol) in ether (15 ml) was stirred for 1 hr at ambient temperature. The resulting yellow solution was evaporated to dryness, and the solid obtained was recrystallized from ether to afford yellow crystals of *3a* (387 mg, 78%).

Acetylacetonatobis(p-methoxyphenyl isocyanide)(tetracyanoethylene)rhodium, Rh(acac)(p-$CH_3OC_6H_4NC$)$_2$(TCNE) (3b)

To a suspension of Rh(acac)(p-$CH_3OC_6H_4NC$)$_2$ (234 mg, 0.5 mmol) in ether (15 ml) was added TCNE (65 mg, 0.5 mmol) at ambient temperature to give a colorless solution. A pale yellow precipitate began to form after a few minutes. After about 1 hr the precipitate was collected and recrystallized from CH_2Cl_2–petroleum ether to afford a pale yellow crystalline *3b* (230 mg, 77%).

Similarly prepared were *Rh(acac)(p-$CH_3C_6H_4NC$)$_2$(TCNE) (3c)* (78%), *Rh(acac)(p-ClC_6H_4NC)$_2$(TCNE) (3d)* (78%), and *Rh(acac)(2,4,6-(CH_3)$_3C_6H_2NC$)$_2$(TCNE) (3e)* (77%).

Acetylacetonato(p-methoxyphenyl isocyanide)(triphenylphosphine)(tetracyanoethylene)rhodium, Rh(acac)(p-$CH_3OC_6H_4NC$)(PPh_3)(TCNE) (4a)

To a stirred solution of Rh(acac)(p-$CH_3OC_6H_4NC$)(PPh_3) (299 mg, 0.5 mmol) in benzene (10 ml) was added a solution of TCNE (65 mg, 0.5 mmol) in benzene (15 ml) at ambient temperature. After being stirred for 30 min, the solution was concentrated *in vacuo*. Slow addition of petroleum ether to the solution gave a precipitate, which was recrystallized from benzene–petroleum ether to afford yellow crystals of *4a* (254 mg, 70%).

Rh(acac)(p-$CH_3C_6H_4NC$)(PPh_3)(TCNE) (4b) (72%) and *Rh(acac)(p-ClC_6H_4NC)(PPh_3)(TCNE) (4c)* (69%) were similarly obtained.

Acetylacetonato(triphenylphosphine)(tetracyanoethylene)rhodium, Rh(acac)(PPh_3)(TCNE) (5a)

TCNE (26 mg, 0.2 mmol) was added to a solution of Rh(acac)(PPh_3)$_2$ (145 mg, 0.2 mmol) in benzene (15 ml). A bright yellow product formed was washed with benzene and dried *in vacuo* (81 mg, 68%); ir spectrum (Nujol): ν(CN) due to TCNE, 2253m, 2230w.

Acetylacetonato(p-tolyl isocyanide)(tetracyanoethylene)rhodium, Rh(acac)(p-$CH_3C_6H_4NC$)(TCNE) (5b)

A solution of p-$CH_3C_6H_4NC$ (59 mg, 0.5 mmol) in benzene (10 ml) was slowly added to a solution of Rh(acac)(CO)$_2$ (129 mg, 0.5 mmol) in benzene (10 ml) to evolve carbon monoxide. To the resulting yellow solution was added TCNE (65 mg, 0.5 mmol). The solid obtained upon concentration of the solution was recrystallized from hot CH_2Cl_2 to give yellow crystals (158 mg, 71%); ir spectrum (Nujol): ν(NC) due to isocyanide, 2214s; ν(CN) due to TCNE, 2243m.

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

Physical measurements were performed as described elsewhere.[2]

Results and Discussion

Preparation and Characterization

Rh(acac)(RNC)$_2$ was prepared by reaction of Rh(acac)(COD)[6] with two molar equivalents of the appropriate isocyanide and Rh(acac)(RNC)(PPh_3) by reaction of Rh(acac)(PPh_3)$_2$[7] with a 20–30% excess of the appropriate isocyanide. These rhodium(I) complexes are yellow or greenish yellow in color, diamagnetic, soluble in common organic solvents, and do not show dichroism such as reported for Rh(acac)(CO)$_2$.[8] They are relatively stable in the solid state but not very stable in solution. These parent complexes reacted smoothly with TCNE to give 1 : 1 adducts. These adducts are pale yellow or yellow crystals, diamagnetic, soluble in polar organic solvents, and stable to air. Molecular weight determinations showed the essentially monomeric nature of these new complexes in $CHCl_3$ (Table I). The ir spectra of all complexes exhibit strong bands due to ν(C═O) and ν(C═C) in the range 1500–1600 cm^{-1} and hence indicate the presence of an oxygen-bonded chelating acac group.[9]

The pmr signals of the isocyanides are shifted to a low field upon adduct formation and in the ir spectra the isocyanide ν(NC) bands are always higher in the adducts than in the parent complexes. These two features reveal a charge transfer from the rhodium atom to the TCNE ligands. Ir and pmr data of the parent complexes and their TCNE adducts are summarized in Table II.

Attempts to prepare Rh(acac)(PPh_3)$_2$(TCNE) and Rh(acac)(RNC)(CO)(TCNE) for comparison were hampered by the elimination of PPh_3 and CO, respectively. Instead, complexes of the composition Rh(acac)(PPh_3)(TCNE) and Rh(acac)(RNC)(TCNE) were obtained. Unfortunately, it was not possible to investigate the behavior of these adducts in solution because of their poor solubility in common organic solvents.

TABLE I. Melting Points, Analytical Data, and Molecular Weights of the Complexes.

No.	Complexes[a]	M.p. (° C)[b]	% Carbon		% Hydrogen		% Nitrogen		Mol. Wt.	
			Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found
1a	Rh(acac)(t-BuNC)$_2$ · 1/4CH$_2$Cl$_2$	127–129	47.02	47.29	6.60	6.73	7.19	7.49	390	c
1b	Rh(acac)(p-CH$_3$OC$_6$H$_4$NC)$_2$	132–134	53.86	53.86	4.52	4.72	5.98	5.85	468	468
1c	Rh(acac)(p-CH$_3$C$_6$H$_4$NC)$_2$	143–145	57.81	58.00	4.85	5.07	6.42	6.45	436	451
1d	Rh(acac)(p-ClC$_6$H$_4$NC)$_2$	128–130	47.83	47.79	3.17	3.03	5.87	5.86	477	495
1e	Rh(acac)(2,4,6-(CH$_3$)$_3$C$_6$H$_2$NC)$_2$	193–195	60.98	60.96	5.94	5.96	5.69	5.73	492	476
2a	Rh(acac)(p-CH$_3$OC$_6$H$_4$NC)(PPh$_3$)	145–148	62.32	61.82	4.89	4.74	2.34	2.56	597	619
2b	Rh(acac)(p-CH$_3$C$_6$H$_4$NC)(PPh$_3$)	177–179	64.04	63.83	5.03	5.05	2.41	2.44	581	587
2c	Rh(acac)(p-ClC$_6$H$_4$NC)(PPh$_3$)	176–180	59.87	59.02	4.35	4.23	2.33	2.47	602	c
3a	Rh(acac)(t-BuNC)$_2$(TCNE)	130–132	50.81	50.51	5.08	5.06	16.93	17.00	496	492
3b	Rh(acac)(p-CH$_3$OC$_6$H$_4$NC)$_2$(TCNE)	151–153	54.38	54.71	3.55	3.56	14.09	14.02	596	590
3c	Rh(acac)(p-CH$_3$C$_6$H$_4$NC)$_2$(TCNE)	156–158	57.46	57.22	3.75	3.81	14.89	14.92	564	557
3d	Rh(acac)(p-ClC$_6$H$_4$NC)$_2$(TCNE)	149–151	49.61	49.61	2.50	2.44	13.89	14.13	605	586
3e	Rh(acac)(2,4,6-(CH$_3$)$_3$C$_6$H$_2$NC)$_2$(TCNE)	183–186	60.00	60.21	4.71	4.84	13.54	13.62	621	608
4a	Rh(acac)(p-CH$_3$OC$_6$H$_4$NC)(PPh$_3$)(TCNE)	170–172	61.25	61.06	4.03	4.11	9.65	10.14	726	704
4b	Rh(acac)(p-CH$_3$C$_6$H$_4$NC)(PPh$_3$)(TCNE)	178–180	62.63	63.14	4.12	4.26	9.87	10.01	710	695
4c	Rh(acac)(p-ClC$_6$H$_4$NC)(PPh$_3$)(TCNE)	196–200	59.23	59.32	3.59	3.87	9.59	9.23	730	743
5a	Rh(acac)(PPh$_3$)(TCNE)	>240	58.80	58.35	3.74	3.89	9.46	9.53	592	d
5b	Rh(acac)(p-CH$_3$C$_6$H$_4$NC)(TCNE)	192–194	51.02	51.05	3.16	3.26	15.66	15.68	447	d

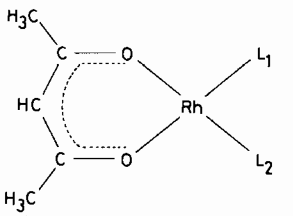
[a] Abbreviations for ligands: acac = acetylacetonato, TCNE = tetracyanoethylene, PPh$_3$ = triphenylphosphine. [b] All complexes melt with decomposition. [c] Decomposition in solution precluded mol. wt. measurements. [d] Poor solubility in common solvents precluded mol. wt. measurements.

TABLE II. Ir and Pmr Data of the Parent Complexes and the TCNE Adducts.

No.	Complexes[a]	Ir,[b] cm^{-1}				Pmr,[f] δ (ppm)					
						Isocyanide			Acac		
		ν(NC)[c]			ν(CN)[d]	$-C_6H_4-$[g]		CH_3-	CH_3-		$-CH-$
1a	Rh(acac)(t-BuNC)$_2$ · 1/4CH$_2$Cl$_2$	2168	2116	2082sh	–	–		1.46	1.94		5.41
1b	Rh(acac)(p-CH$_3$OC$_6$H$_4$NC)$_2$	2162	2101	2056sh	–	7.25	6.80	3.80	2.02		5.49
1c	Rh(acac)(p-CH$_3$C$_6$H$_4$NC)$_2$	2159	2096	2054sh	–	7.19	7.09	2.31	2.02		5.49
1d	Rh(acac)(p-ClC$_6$H$_4$NC)$_2$	2158	2092	2040sh	–	7.28		–	2.02		5.51
1e	Rh(acac)(2,4,6-(CH$_3$)$_3$C$_6$H$_2$NC)$_2$	2147	2082		–	6.77		2.35*o*, 2.24*p*[h]	2.00		5.42
2a	Rh(acac)(p-CH$_3$OC$_6$H$_4$NC)(PPh$_3$)	2090*	2053sh*		–	6.55	6.45	3.70	2.08	1.66	5.41
2b	Rh(acac)(p-CH$_3$C$_6$H$_4$NC)(PPh$_3$)	2089*	2051sh*		–	6.78	6.35	2.16	2.04	1.63	5.37
2c	Rh(acac)(p-ClC$_6$H$_4$NC)(PPh$_3$)[i]	2084*	2041sh*		–	–		–	–		–
3a	Rh(acac)(t-BuNC)$_2$(TCNE)	2232	2210		e	–		1.58	2.07		5.40
3b	Rh(acac)(p-CH$_3$OC$_6$H$_4$NC)$_2$(TCNE)	2223	2202		2239	7.50	6.90	3.83	2.12		5.46
3c	Rh(acac)(p-CH$_3$C$_6$H$_4$NC)$_2$(TCNE)	2221	2200		2239	7.43	7.23	2.40	2.13		5.46
3d	Rh(acac)(p-ClC$_6$H$_4$NC)$_2$(TCNE)	2216	2197		2240	7.59	7.51	–	2.15		5.52
3e	Rh(acac)(2,4,6-(CH$_3$)$_3$C$_6$H$_2$NC)$_2$(TCNE)	2212	2192		2241	6.94		2.42*o*, 2.32*p*[h]	2.12		5.48
4a	Rh(acac)(p-CH$_3$OC$_6$H$_4$NC)(PPh$_3$)(TCNE)	2209			2233	6.92	6.73	3.74	1.92	1.80	4.92
4b	Rh(acac)(p-CH$_3$C$_6$H$_4$NC)(PPh$_3$)(TCNE)	2205			2230	7.04	6.86	2.31	1.92	1.78	4.92
4c	Rh(acac)(p-ClC$_6$H$_4$NC)(PPh$_3$)(TCNE)	2203			2234	7.23	6.90	–	1.93	1.81	4.92

[a] See footnote in Table I for abbreviations of ligands. [b] Measured in CHCl$_3$ or as Nujol mulls (asterisks). [c] Isocyanide vibration. Absorptions are strong except when designated as shoulder (sh). [d] TCNE vibration. [e] Masked by the strong ν(NC) of the isocyanides. [f] Measured in CDCl$_3$ at 25° C. [g] Approximated as an AB type quartet with the coupling constant of about 9 Hz except *1d*, *1e*, and *3e*. *1d*: a sharp singlet. *1e* and *3e*: *meta* proton signals were observed as a sharp singlet. [h] *o* = *ortho*-CH$_3$, *p* = *para*-CH$_3$. [i] Extensive decomposition in solution precluded pmr measurement.

Rh(acac)(RNC)$_2$ (1) and Rh(acac)(RNC)(PPh$_3$) (2)



(1a–1e : $L_1 = L_2 = RNC$
2a–2c : $L_1 = RNC$ $L_2 = PPh_3$)

Ir spectra of *1a–1e* in solution show two strong ν(NC) bands in the region 2160–2080 cm^{-1}, which can be attributed to the symmetrical and antisymmetrical stretching vibrations of the two isocyanide ligands *cis* to each other. Pmr spectra of *1a–1e* show only one acac-methyl resonance and one kind of isocyanide proton resonance, which indicates that two acac-methyl groups and two isocyanides are equivalent, respectively. On the other hand, two acac-methyl groups in *2* exhibit the separate resonances in agreement with the non-equivalence of them.

In the pmr spectra of complexes containing aromatic isocyanide, the phenyl ring proton absorptions are observed as only one set of an approximate AB type quartet except *1e*, whose *meta* protons give a singlet signal. Moreover, these signals show little change in the –70 to +60° C range. Therefore, in this temperature range the phenyl ring would either rotate around the coordination bond or C–N single bond* or remain fixed vertically to the coordination plane.

Rh(acac)(RNC)$_2$(TCNE) (3)

The ir spectra of *3a–3e* both in solution and in the solid state show two strong ν(NC) bands of the isocyanides (Table II). The variable-temperature pmr spectra of *3a* in CH_2Cl_2 are depicted in Figure 1. This adduct exhibits two doublets (relative intensity 3 : 1) arising from *t*-BuNC ligands and acac-methyl groups at –50° C. The separations of the doublets are 3.8 and 11.5 Hz at the 100 MHz instrument, respectively. As the temperature is ascended, these doublets become broad without changing their chemical shifts, and the former coalesces at –12° C and the latter at +15° C. Finally each signal becomes a sharp singlet at δ1.58 and 2.06 at +30° C, respectively. On the other hand, the acac-methine proton resonance in $CDCl_3$ is little dependent on temperature. The pmr spectrum of *3e* in CH_2Cl_2 at –50° C shows four doublets arising from 2,4,6-$(CH_3)_3C_6H_2NC$ ligands and acac-methyl groups. On raising the temperature, each of these doublets coalesces in the order of *para* methyl protons, *meta* protons, *ortho* methyl protons, and acac-methyl protons.

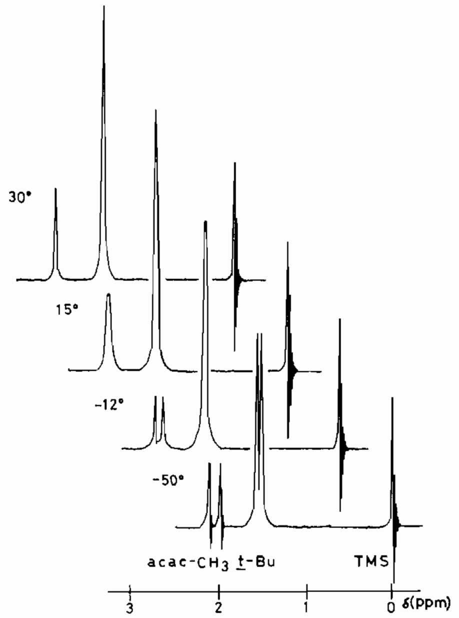


Figure 1. Variable-temperature pmr spectra of Rh(acac)(*t*-BuNC)$_2$(TCNE) (*3a*) in CH_2Cl_2.

The appearance of two kinds of isocyanides and of acac-methyl groups at lower temperatures and their magnetic equivalence at higher temperatures are also observed in *3b, 3c,* and *3d.* In addition, these spectral behaviors are reversible with temperature and not detectively altered by variation of concentration or of solvent, or by the addition of free TCNE. Addition of free isocyanide, however, causes decomposition, which is evidenced by the appearance of a complicated pmr spectrum.

On the basis of these ir and low temperature pmr spectra, *3a–3e* in solution are suggested to have a configuration with both two isocyanides and two acac-methyl groups in different environments, as illustrated in Figure 2. Depending on the RNC–Rh–O angle in Figure 2, this configuration may be considered as either a trigonal bipyramid with TCNE occupying the equatorial position or a square pyramid with TCNE occupying the apical position. We, however, prefer to use the tri-

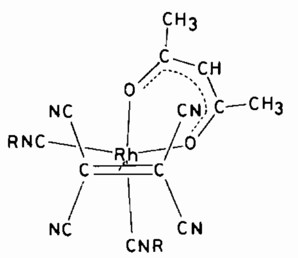


Figure 2. The configuration of Rh(acac)(RNC)$_2$(TCNE) (*3*) in solution (viewed from the TCNE side).

---

* Such isocyanide rotation has also been reported by Orio *et al.*[10]

gonal bipyramid for the configuration of these adducts in solution, since a configuration of this kind is well established for the TCNE adducts of square-planar transition metal complexes by X-ray crystallographic analyses.[11] Moreover, the molecular structure of Rh $(p\text{-}CH_3OC_6H_4NC)_2(P(OPh)_3)$(fumaronitrile)I, which indicates an intramolecular phenomenon[12] similar to those of the present TCNE adducts in solution, has now been found to be a trigonal bipyramid with equatorial fumaronitrile by an X-ray analysis.[13] The pmr spectra of *3a–3e* at higher temperatures would, therefore, be explained in terms of the intramolecular phenomenon which leads to averaging of axial and equatorial positions in the trigonal bipyramid. The physically meaningful mechanism would be the scheme illustrated in Figure 3. This scheme represents the TCNE rotation around the rhodium–TCNE bond which accompanies the Berry pseudorotation[14] with TCNE as pivot.* Similar scheme has been proposed to interpret the variable-temperature pmr spectra of [Rh $(RNC)_4$(TCNE)]X and related complexes in the previous paper.[2] Furthermore, during the course of the present study, similar rotational mode has also been reported for $Fe(CO)_4$(olefin) by Takats *et al.*[15] and Osborn *et al.*[16]

Previously we have suggested that the greater the π-bonding interaction between metal and olefin, the higher the energy barrier of this intramolecular rearrangement.[2] The variation of substituents in isocyanide ligands shows no drastic change in this work. The coalescence temperatures of the acac-methyl resonance in CH_2Cl_2 are measured as follows; *3a* (15°C)**, *3b* (11°C), *3c* (10°C), *3d* (7°C), and *3e* (4°C). Thus the temperature of *3a* is slightly higher than those of other adducts. This fact seems to be qualitatively explained by considering that *t*-BuNC is better σ-donor and poorer π-acceptor than other isocyanides, as evidenced from a comparison of ν(NC) frequencies of the TCNE adducts (Table II).

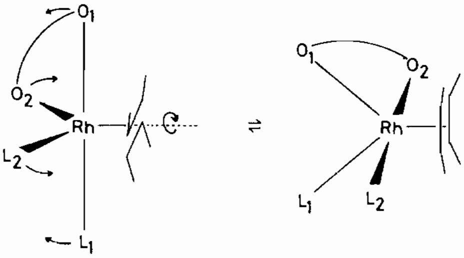


Figure 3. The TCNE rotation accompanying Berry pseudorotation in $Rh(acac)(RNC)_2(TCNE)$ (*3*). ≻═≺ = TCNE, L = RNC, O⌒O = acac.

Rh(acac)(RNC)(PPh$_3$)(TCNE) (4)

The ir spectra of *4a–4c* in $CHCl_3$ display one band due to ν(NC) of isocyanide. The pmr spectra of these adducts in $CDCl_3$ at 25°C shows a sharp singlet of the CH_3O or CH_3 protons of the isocyanide, only one set of an approximate AB type quartet due to the phenyl ring protons of the isocyanide, and a sharp doublet of the acac-methyl protons. These signals are little temperature dependent in the range −70° to +60°C. These data suggest that TCNE is coordinated rigidly in a trigonal bipyramid with the chelating acac ligand occupying an axial and an equatorial position. It is not possible to decide definitely the coordination site of the isocyanide and phosphine ligand.

A comparison of *3* with *4* reveals that the replacement of one isocyanide by triphenylphosphine converts a nonrigid TCNE adduct into a rigid one. This fact may be consistent with the view that *4* has the stronger metal–TCNE π-interaction than *3* because of the stronger σ-donor capacity of the phosphine than the isocyanide.

References

1 W.H. Baddley, *Inorg. Chim. Acta Rev.*, *2*, 7 (1968); J.H. Nelson and H.B. Jonassen, *Coord. Chem. Rev.*, *6*, 27 (1971), and references therein.
2 T. Kaneshima, K. Kawakami and T. Tanaka, *Inorg. Chem.*, *13*, 2198 (1974).
3 D.F. Shriver, *Accounts Chem. Res.*, *3*, 231 (1970); L. Vaska, *Accounts Chem. Res.*, *1*, 335 (1968).
4 L. Malatesta and F. Bonati, "Isocyanide Complexes of Metals", Wiley, New York, N.Y., p. 27.
5 I. Ugi and R. Meyr, *Chem. Ber.*, *93*, 239 (1960).
6 J. Chatt and L.M. Venanzi, *J. Chem. Soc.*, 4735 (1957).
7 A.J. Mukhedkar, V.A. Mukhedkar, M. Green and F.G.A. Stone, *J. Chem. Soc. A*, 3166 (1970).
8 F. Bonati and G. Wilkinson, *J. Chem. Soc.*, 3156 (1964).
9 K. Nakamoto, "Infrared Spectra of Inorganic and Coordination Compounds", 2nd ed, Wiley, New York, N.Y., p. 247.
10 E. Bordignon, U. Croatto, U. Mazzi and A.A. Orio, *Inorg. Chem.*, *13*, 935 (1974).
11 L.M. Muir, K.W. Muir and J.A. Ibers, *Discuss. Faraday Soc.*, *47*, 84 (1969); J.B.R. Dunn, R. Jacobs and C.J. Fritchie, Jr., *J. Chem. Soc. Dalton Trans.*, 2007 (1972).
12 K. Kawakami, K. Take-uchi and T. Tanaka, *Inorg. Chem.*, *14*, 877 (1975).
13 J.A. Ibers, private communication.
14 R.S. Berry, *J. Chem. Phys.*, *32*, 933 (1960).
15 L. Kruczynski, L.K.K. LiShingMan and J. Takats, *J. Am. Chem. Soc.*, *96*, 4006 (1974).
16 S.T. Wilson, N.J. Coville, J.R. Shapely and J.A. Osborn, *J. Am. Chem. Soc.*, *96*, 4038 (1974).
17 D. Kost, E.H. Carlson and M. Raban, *Chem. Commun.*, 656 (1971).

---

* If the configuration in solution is a square pyramid, two magnetically nonequivalent isocyanides and acac-methyl groups would be placed in an identical environment by the TCNE rotation alone.

** The free energy of activation in *3a* at the coalescence temperature is calculated as 15.0 ± 0.2 Kcal/mol using the approximate equation.[17]