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Rotation of Olefins in Dithiocarbamatobis(isocyanide)(olefin)rhodium Complexes

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The π-olefinic complexes, Rh(dtc)(RNC)$_2$(olefin) (dtc = $(CH_3)_2NCS_2^-$; R = p-$CH_3C_6H_4$, 2,4,6-$(CH_3)_3C_6H_2$; olefin = tetracyanoethylene, fumaronitrile, maleonitrile, maleic anhydride), have been synthesized. Variable temperature ^1H nmr spectra suggest that the olefin rotates around the metal–olefin bond accompanying Berry pseudorotation in a trigonal bipyramid. The ν(NC) frequency due to the isocyanide and the free energy of activation ($\Delta G_{Tc}^{\ddagger}$) for the intramolecular rearrangement are discussed in terms of the π-interactions between the rhodium atom and the olefin ligands.

Introduction

Since the rotation of olefins bound to transition metals was first reported for $(C_5H_5)Rh(C_2H_4)_2$ by Cramer,[1a] systematic studies of the olefin rotation have been carried out on square-planar rhodium(I)[1] and platinum(II)[2] olefin complexes. We have previously reported that some five-coordinate rhodium isocyanide complexes containing cyanoolefins show an intramolecular rearrangement in solution.[3] This rearrangement has been interpreted as due to the rotation of the cyanoolefin around the rhodium–olefin bond accompanying the Berry pseudorotation in a trigonal bipyramid, as is shown in Figure 1.[3c] The rotation of olefins in a trigonal bipyramid was also reported for $Fe(CO)_4$(olefin)[4,5] and for $[Os(CO)NO(C_2H_4)(PPh_3)_2][PF_6]$.[6] The mechanism proposed for the former complex, which was based on ^{13}C nmr spectra of carbonyl ligands, is similar to ours.

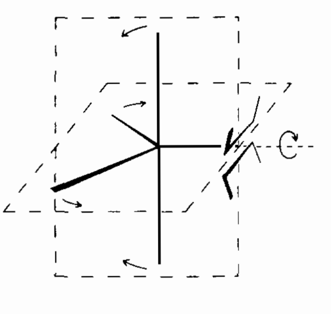

Figure 1. Intramolecular rearrangement.

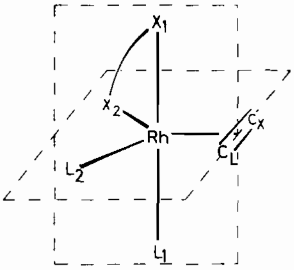

Figure 2. The configuration of Rh(X X)L_2(olefin) (L = isocyanide ligand, X X = chelate ligand, C=C = olefin ligand).

The similar intramolecular rearrangement was found in $Rh(acac)(RNC)_2(TCNE)$ (acac = acetylacetonato ligand, TCNE = tetracyanoethylene), which have a ground state configuration illustrated in Figure 2.[3c] Complexes of this type seem to be favorable in detecting this rearrangement by the nmr technique, because the axial and equatorial positions (L_1 and L_2, X_1 and X_2) or the two ends of the olefin (C_L and C_X), which are in different chemical environments in this configuration, must become equivalent if the rearrangement occurs rapidly ($L_1 \rightleftarrows L_2$, $X_1 \rightleftarrows X_2$, $C_L \rightleftarrows C_X$). Accordingly, the present work was undertaken to extend the scope of non-rigid olefin complexes by using a dimethyldithiocarbamato (dtc, $(CH_3)_2NCS_2^-$) group in place of the acac group as the chelating ligand.

Experimental

Materials

Commercial TCNE and maleic anhydride (MA) were purified by sublimation. Maleonitrile (*cis*-1,2-dicyanoethylene, MN) was kindly supplied by Mr. Koichi Matsumura of Takeda Chemical Industries Co. Ltd. and was purified by sublimation. Fumaronitrile (*trans*-1,2-dicyanoethylene, FN) was of reagent grade and used as supplied. Isocyanides were prepared and purified by the literature method.[7] $[Rh(COD)Cl]_2$ was

TABLE I. Properties and Analytical Data of New Complexes.

Complexes[a]	Dec. Temp. (°C)	Yield (%)	% Carbon		% Hydrogen		% Nitrogen		Mol. wt.[b]	
			Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found
$Rh(dtc)(COD)$	188–190	94	39.88	39.60	5.48	5.56	4.23	4.07	331	343
$Rh(dtc)(2,4,6\text{-}(CH_3)_3C_6H_2NC)_2$	186–188	97	53.80	53.29	5.50	5.42	8.18	8.43	514	520
$Rh(dtc)(2,4,6\text{-}(CH_3)_3C_6H_2NC)_2(TCNE)$	210–212	80	54.29	54.48	4.40	4.19	15.28	15.45	642	635
$Rh(dtc)(2,4,6\text{-}(CH_3)_3C_6H_2NC)_2(FN)$	170–172	86	54.82	54.97	5.11	4.78	11.84	11.77	592	528
$Rh(dtc)(2,4,6\text{-}(CH_3)_3C_6H_2NC)_2(MN)$	162–164	82	54.82	54.80	5.11	5.26	11.84	11.76	592	530
$Rh(dtc)(2,4,6\text{-}(CH_3)_3C_6H_2NC)_2(MA)$	142–144	68	53.03	52.71	4.94	4.85	6.87	6.91	612	536
$Rh(dtc)(p\text{-}CH_3C_6H_4NC)_2$	198–200	98	49.89	49.56	4.41	4.46	9.19	9.18	457	452
$Rh(dtc)(p\text{-}CH_3C_6H_4NC)_2(TCNE)\cdot 1/3CH_2Cl_2$	179–183	75	49.57	49.48	3.39	3.25	15.97	16.13	614	589
$Rh(dtc)(p\text{-}CH_3C_6H_4NC)_2(FN)$	156–160	80	51.59	51.95	4.14	4.13	13.08	12.93	535	490
$Rh(dtc)(p\text{-}CH_3C_6H_4NC)_2(MN)\cdot 1/6C_6H_6$	126–130	90	52.24	52.55	4.23	4.10	12.77	12.87	549	485
$Rh(dtc)(p\text{-}CH_3C_6H_4NC)_2(MA)$	129–132	72	49.73	49.65	3.99	4.03	7.56	7.55	555	486

[a] Abbreviations for ligands: dtc = dimethyldithiocarbamato, COD = cycloocta-1,5-diene, TCNE = tetracyanoethylene, FN = fumaronitrile, MN = maleonitrile, MA = maleic anhydride. [b] Measured in $CHCl_3$ at 37 °C by vapor pressure osmometry.

obtained according to the literature.[8] Preparations of new complexes were performed under dry nitrogen using deaerated solvents at room temperature. Recrystallizations of olefin adducts were usually done in air.

Cycloocta-1,5-diene–dimethyldithiocarbamatorhodium(I), Rh(dtc)(COD)

$[Rh(COD)Cl]_2$ (2.1 mmol) and $Na(dtc)\cdot 2H_2O$ (4.2 mmol) were stirred in CH_2Cl_2 (40 ml) for 2 hr to give a yellow solution. Sodium chloride precipitated was filtered off and the filtrate was evaporated to dryness under reduced pressure. The resulting product was washed with oxygen-free ethanol and dried *in vacuo*.

Dimethyldithiocarbamatobis(2,4,6-trimethylphenyl isocyanide)rhodium(I), $Rh(dtc)(2,4,6\text{-}(CH_3)_3C_6H_2NC)_2$ and a Related Complex

To a stirred solution of $Rh(dtc)(COD)$ (1.5 mmol) in benzene (30 ml) was added dropwise a solution of $2,4,6\text{-}(CH_3)_3C_6H_2NC$ (3.0 mmol) in the same solvent (10 ml). The resulting suspension was stirred for 6 hr. The concentrated suspension was filtered and a yellow product obtained was washed with ether and dried *in vacuo*.

$Rh(dtc)(p\text{-}CH_3C_6H_4NC)_2$ was similarly prepared by the reaction of $Rh(dtc)(COD)$ with $p\text{-}CH_3C_6H_4NC$.

Dimethyldithiocarbamatobis(2,4,6-trimethylphenyl isocyanide)(olefin)rhodium, $Rh(dtc)(2,4,6\text{-}(CH_3)_3C_6H_2NC)_2(olefin)$ (olefin = TCNE, FN, MN, MA) and Related Complexes

To a suspension of $Rh(dtc)(2,4,6\text{-}(CH_3)_3C_6H_2NC)_2$ (0.40 mmol) in benzene (20 ml) was added the appropriate olefin (TCNE: 0.40 mmol, FN: 0.55 mmol, MN: 0.55 mmol, MA: 0.60 mmol). The suspension immediately turned to a clear solution. After two hours' stirring, petroleum ether (b.p. 40–60 °C) was added to the solution, yielding the crystalline product. The TCNE adduct was recrystallized from CH_2Cl_2-petroleum ether and the others from benzene–petroleum ether in the presence of 0.2–0.3 molar amount of additional olefin.

$Rh(dtc)(p\text{-}CH_3C_6H_4NC)_2(olefin)$ (olefin = TCNE, FN, MN, MA) were similarly obtained by the reactions of $Rh(dtc)(p\text{-}CH_3C_6H_4NC)_2$ with the appropriate olefin. These adducts contain residual solvents which could not be removed even under high vacuum, as shown by ^1H nmr.

The properties and analytical data of the new complexes are summarized in Table I.

Physical Measurements

Molecular weights, infrared, and ^1H nmr spectra were measured as described elsewhere.[3a]

Results and Discussion

Characterization

The yellow square-planar complexes, $Rh(dtc)(RNC)_2$, are stable in the solid state but sensitive to air in solution. These parent complexes smoothly reacted with TCNE, FN, MN, and MA to give 1 : 1 adducts. This is in contrast to the previous results that $[Rh(RNC)_4]X$[3a] and $Rh(acac)(RNC)_2$[3c] yielded the adduct only with TCNE. Thus, the transition metal basicity[9] of $Rh(dtc)(RNC)_2$ is thought to be stronger than those of $[Rh(RNC)_4]X$ and $Rh(acac)(RNC)_2$. This difference may arise from the stronger donor property of the dtc group.

The new adducts are yellow crystals, fairly soluble in polar organic solvents, and stable in the solid state. Molecular weight determinations indicate that the

TCNE adduct is essentially monomeric in $CHCl_3$, while the other olefin adducts dissociate to some extent. Infrared spectra of the FN, MN, and MA adducts in solution show a weak ν(NC) band due to the isocyanides of the parent complex (see Table II). It is therefore suggested that these adducts dissociate into Rh(dtc)(RNC)$_2$ and olefin. In the series of Rh(dtc)(2,4,6-$(CH_3)_3C_6H_2NC)_2$(olefin), the temperature of thermal decomposition rises in the order of olefin: MA$<$MN$\sim$FN$<$TCNE. Thus, the dissociative tendency in solution and the decomposition temperature are correlated with the π-acceptor capacity of the olefin.

Infrared Spectra

Infrared frequencies of the parent complexes and the olefin adducts in CH_2Cl_2 are summarized in Table II. All the compounds exhibit an absorption due to the carbamate C–N bond in the 1520–1530 cm^{-1} range, which is characteristic of a sulfur-bonded chelating dtc group.[10] In metal–isocyanide complexes the ν(NC) frequency reflects electron densities on the metal, just as the ν(CO) frequency in metal carbonyls does. Thus, low ν(NC) frequencies of Rh(dtc)(RNC)$_2$ compared with the other square-planar rhodium(I) isocyanide complexes imply relatively high electron densities on the rhodium, which correspond to the high reactivity of this complex. On the other hand, two ν(NC) bands are shifted to higher frequencies on adduct formation, suggesting an electronic charge transfer from the rhodium atom to the olefin ligands. Indeed, the stronger the π-acceptor capacity of olefin, the higher the ν(NC) frequencies. Moreover, a somewhat larger shift is observed for the lower frequency

TABLE II. Ir Data[a] of Rh(dtc)(RNC)$_2$ and Rh(dtc)(RNC)$_2$(olefin) in CH_2Cl_2 (cm^{-1}).

R	Olefin	ν(NC)[b]	$\Delta\nu(a\text{–}b)$[c]	Olefinic Band
p-$CH_3C_6H_4$	–	2128s, 2070s, 2036sh	58	
p-$CH_3C_6H_4$	MA	2169s, 2135s, 2070w*	34	ν(CO); 1798s, 1730s
p-$CH_3C_6H_4$	MN	2175s, 2141s, 2070w*	34	ν(CN); 2207m
p-$CH_3C_6H_4$	FN	2176s, 2142s, 2070w*	34	ν(CN); 2205m
p-$CH_3C_6H_4$	TCNE	2199s, 2179s	20	ν(CN); 2222m
2,4,6-$(CH_3)_3C_6H_2$	–	2120s, 2057s	63	
2,4,6-$(CH_3)_3C_6H_2$	MA	2162s, 2128s, 2057w*	34	ν(CO); 1797s, 1729s
2,4,6-$(CH_3)_3C_6H_2$	MN	2167s, 2133s, 2057w*	34	ν(CN); 2207m
2,4,6-$(CH_3)_3C_6H_2$	FN	2167s, 2134s, 2057w*	33	ν(CN); 2206m
2,4,6-$(CH_3)_3C_6H_2$	TCNE	2190s, 2173s	17	ν(CN); 2223m

[a] Abbreviations: s = strong, m = medium, w = weak, sh = shoulder. [b] Isocyanide vibration. The band with asterisk was not observed in Nujol mulls and, therefore, is assigned to the lower frequency due to the parent complex. [c] Difference between the two strong ν(NC) frequencies.

TABLE III. ^{1}H Nmr Data of Rh(dtc)(RNC)$_2$ and Rh(dtc)(RNC)$_2$(olefin) in CH_2Cl_2 or $CDCl_3$ (asterisk) at 25°C (δ(ppm)).

R	Olefin	Isocyanide		Dtc	Olefinic	$\Delta\delta$[c]
		Phenyl[a]	Methyl[a]	Methyl		
p-$CH_3C_6H_4$	–	7.19, 7.15	2.31	3.29		
p-$CH_3C_6H_4$	MA	7.32, 7.21	2.38	3.24	4.39	2.66
p-$CH_3C_6H_4$	MN	7.39, 7.21	2.37	3.23	3.04	3.19
p-$CH_3C_6H_4$	FN	7.36, 7.21	2.39	3.29	3.22	3.14
p-$CH_3C_6H_4$	TCNE	7.41, 7.23	2.37	3.26		
		7.46, 7.28	2.41	3.34		
2,4,6-$(CH_3)_3C_6H_2$	–	6.85	2.30o; 2.23p	3.31		
2,4,6-$(CH_3)_3C_6H_2$*	MA*	6.87	2.37o; 2.28p	3.25	4.37	2.68
2,4,6-$(CH_3)_3C_6H_2$	MN	6.91	2.40o; 2.28p	3.24	3.08	3.15
2,4,6-$(CH_3)_3C_6H_2$	FN	6.91	2.39o; 2.28p	3.28	3.22	3.14
2,4,6-$(CH_3)_3C_6H_2$	TCNE	6.94	2.42o; 2.30p	3.28		
		6.98	2.43o; 2.33p	3.36		

[a] Approximated as an AB type quartet with the coupling constant of 8 or 9 Hz for the p-$CH_3C_6H_4NC$ derivatives.
[b] o = *ortho*-CH_3, p = *para*-CH_3. [c] Up-field shift of the olefinic proton signal due to adduct formation.

band than for the higher one. Providing that two isocyanide ligands *cis* to each other are placed in a local C_2 symmetry, the higher and lower frequency bands would be assignable to the *a* and *b* modes, respectively. Otsuka *et al.* have suggested that in M(*tert*-BuNC)$_2$ (olefin) (M = Ni, Pd) the difference in frequencies between the *a* and *b* modes, $\Delta\nu(a\text{–}b)$, serves as a measure of the effective π back-bonding to the olefin ligands.[11] As expected, the $\Delta\nu(a\text{–}b)$ of the TCNE adduct is the smallest in our system.

^{1}H *Nmr Spectra*

The ^{1}H nmr data at 25°C are given in Table III, which shows a distinct down-field shift of the isocyanide proton signals and a considerable up-field shift of the olefinic proton signals upon adduct formation. These observations confirm the occurrence of the charge transfer from the rhodium atom to the olefin ligands, as we mentioned for the infrared spectra.

All olefin adducts examined in this study display temperature dependence of ^{1}H nmr spectra. Discussions of the spectra are here limited to the p-$CH_3C_6H_4$ NC derivatives, since essentially similar spectral changes with temperature were observed in the 2,4,6-$(CH_3)_3$ C_6H_2NC analogs.

The variable temperature ^{1}H nmr spectra of the TCNE adduct in $Cl_2CHCHCl_2$ are depicted in Figure 3. The spectrum at 25°C shows a doublet of the dtc-CH_3 signals, a doublet of the isocyanide-CH_3 signals, and two sets of an approximate AB type quartet due to the phenyl ring protons of the isocyanides. On raising the temperature, each of these signals coalesces and finally at 92°C two singlets and only one set of phenyl ring proton signals are observed. These spectral behaviors are independent on both the concentration and the free TCNE added. In view of this result, the mechanism to explain the magnetic equivalence of each proton at high temperatures would be the TCNE rotation around the coordination bond accompanying a Berry pseudorotation with TCNE as pivot in a trigonal bipyramid, as presented in the previous papers[3] (Figure 1).*

Figure 4 shows the spectra of the MN adduct in the olefinic and dtc-CH_3 regions in CH_2Cl_2 at various temperatures. The spectrum at 25°C shows a singlet due to dtc-CH_3 protons and a somewhat broad singlet attributable to the olefinic protons. The spin–spin coupling between the olefinic protons and the ^{103}Rh nucleus was not observed at 25°C. Furthermore, the olefinic proton signal slightly moves up-field with decreasing temperature. These observations suggest the occurrence of a dissociative exchange of the olefin molecule around 25°C. As the temperature is lowered below 1°C, both the dtc-CH_3 and olefinic proton signals are split but the chemical shift of the latter remains unchanged, indicating little olefin dissocia-

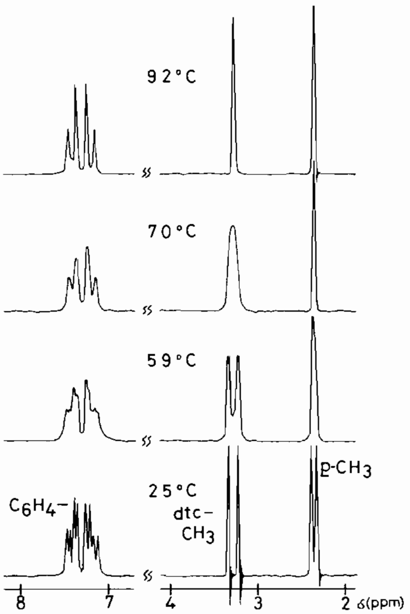

Figure 3. Variable temperature ^{1}H nmr spectra of Rh(dtc)(p-$CH_3C_6H_4NC)_2$(TCNE) in $Cl_2CHCHCl_2$; intensities of the phenyl signals are exaggerated.

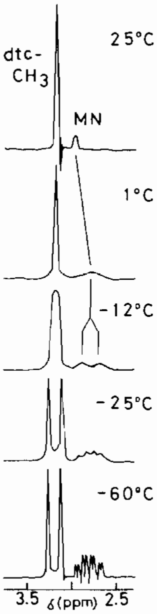

Figure 4. Variable temperature ^{1}H nmr spectra (δ2.5–3.5) of Rh(dtc)(p-$CH_3C_6H_4NC)_2$(MN) in CH_2Cl_2.

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* It is not clear whether the rotation around the carbamate C–N bond in the dtc ligand occurs or not at high temperatures. The magnetic equivalence of two isocyanide ligands, however, cannot be explained by this rotation alone.

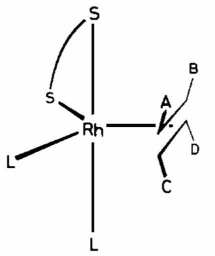

Figure 5. Two possible stereoisomers (L = RNC, S S = dtc) for the MN or MA adducts (A, B = H or C, D = H) and the FN adduct (A, D = H or B, C = H).

tion.* The olefinic proton signal is split into an AB type quartet at $-25\,^\circ$C and finally each peak of the quartet is further split into a doublet due to the coupling with the ^{103}Rh nucleus (J(Rh–H) = 2 Hz) at $-60\,^\circ$C.** The spectral features below $\sim 1\,^\circ$C, where the olefin dissociative process is negligible on the nmr time scale, would also be rationalized in terms of the coupled olefin rotation–Berry pseudorotation. There are two possible stereoisomers (Figure 5) in the ground state configuration, each of which has two enantiomers indistinguishable by the nmr technique. The spectrum at $-60\,^\circ$C, however, shows the presence of either isomer only. A choice between the two isomers cannot definitely be made by the present data.

Similar variable temperature ^{1}H nmr spectra were observed in the FN and MA adducts, except that the spectrum of the MA adduct at $-80\,^\circ$C indicated the presence of two isomers with different populations. The fully resolved limiting spectrum of the MA adduct was not obtained because of a small difference in the chemical shifts between the two isomers. This fact has prevented the determination of the isomer ratio.

Rearrangement Barriers

The free energies of activation for the rearrangement in the olefin adducts were evaluated using the approximate equation

$$\Delta G_{Tc}^{\ddagger} = -RT\ln\frac{\pi\Delta\nu h}{\sqrt{2}kT}$$

where Tc is the coalescence temperature, $\Delta\nu$ is the separation of two dtc-CH$_3$ signals in the absence of exchange, R is the gas constant, h is Planck's constant, and k is Boltzmann's constant. It was reported by Raban *et al.* that this equation gave reliable estimation of $\Delta G_{Tc}^{\ddagger}$ for coalescing uncoupled singlets when $\Delta\nu > 3$ Hz.[12] The Tc and $\Delta G_{Tc}^{\ddagger}$ values obtained are given in Table IV, which also contains those of a related complex, Rh(acac)(RNC)$_2$(TCNE), for comparison. It is to be noted that the $\Delta G_{Tc}^{\ddagger}$ values in the present complexes are high relative to the barriers to the rearrangement which involves only the Berry pseudorotation; Jesson and Meakin have demonstrated that the barriers lie within the range of 6–12 Kcal/mol even in ML$_5$ complexes containing sterically bulky ligands.[13] This result seems to support that the olefin rotation makes a considerable contribution to our rearrangement barrier, as the rotation of NH$_2$ groups does for PF$_3$(NH$_2$)$_2$.[14] Thus, the non-cylindrical π back-bonding from the rhodium atom to the olefin ligand is thought to play an important role for this barrier, since the σ-component of the metal–olefin bonding would little contribute to the barrier by virtue of its cylindrical symmetry. The observed barrier may also involve the steric contribution. Although it is not possible in this study to differentiate between electronic and steric effects, Table IV suggests that the strength of the π back-bonding is remarkably associated with the height of the barrier. Indeed, the height of the barrier increases in the order of π-acceptor capacity of the olefin, MA < MN ~ FN < TCNE. Furthermore, the barrier for Rh(dtc)(RNC)$_2$(TCNE) is somewhat higher than that of Rh(acac)(RNC)$_2$(TCNE). This is consistent with the stronger π-interaction in the former complex, owing to the stronger transition metal basicity of Rh(dtc)(RNC)$_2$.

TABLE IV. Barriers to Intramolecular Rearrangement in Rh(dtc)(RNC)$_2$(olefin).[a]

Olefin	R	Tc[b] (°K)	$\Delta G_{Tc}^{\ddagger}$ [c] (Kcal/mol)
MA	p-CH$_3$C$_6$H$_4$	213	10.9
MN	p-CH$_3$C$_6$H$_4$	261	13.4
MN	2,4,6-(CH$_3$)$_3$C$_6$H$_2$	258	13.3
FN	p-CH$_3$C$_6$H$_4$	270	14.1
FN	2,4,6-(CH$_3$)$_3$C$_6$H$_2$	271	14.1
TCNE*	p-CH$_3$C$_6$H$_4$*	343	18.2
TCNE*	2,4,6-(CH$_3$)$_3$C$_6$H$_2$*	347	18.4
TCNE[d]	p-CH$_3$C$_6$H$_4$[d]	283	14.8
TCNE[d]	2,4,6-(CH$_3$)$_3$C$_6$H$_2$[d]	277	14.6

[a] Measured in CH$_2$Cl$_2$ or Cl$_2$CHCHCl$_2$ (asterisk). [b] ±5 °C. [c] ±0.3 Kcal/mol. [d] Rh(acac)(RNC)$_2$(TCNE).

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* This is also supported by the spectra below 1 °C in the presence of free olefin; the signal due to the free olefin added appears as a sharp singlet at δ6.23 and the coordinated olefinic proton signal shows the same temperature dependence as in the absence of free olefin.

** The isocyanide proton signals at this temperature indicate that two isocyanide ligands are in different chemical environments.

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