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Studies on Interactions of Isocyanides with Transition Metal Complexes. IV.[*1] Dicarbonyl(isocyanide)-π-cyclopentadienylacylmolybdenum[*2]

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Isocyanides were treated with π-$C_5H_5Mo(CO)_3R$ ($R=CH_3$, CH_2Ph) in benzene at room temperature to give π-C_5H_5Mo $(CO)_2$ (isocyanide)COR (A), which exist as a *trans*-isomer in the solid state and as a mixture of *trans*- and *cis*-isomers in solutions, based on the NMR spectra. The structures of the compounds (A) are discussed on the basis of the spectroscopic studies. Studies on *trans* to *cis* isomerization were also carried out kinetically.

In the previous paper, we have reported that isocyanides insert into the alkylnickel sigma bonds of triphenylphosphine-π-cyclopentadienylalkylnickel to give π-cyclopentadienyl(isocyanide) alkylalkyliminomethylnickel.[1] In the course of our studies on this series,[2,3] we obtained dicarbonyl(isocyanide)-π-cyclopentadienylacylmolybdenum as a mixture of *cis*- and *trans*- isomers in solutions by the reactions of isocyanides with tricarbonyl-π-cyclopentadienylalkylmolybdenum.

Reactions of tricarbonyl-π-cyclopentadienylalkylmolybdenum with phosphorus ligands have been studied under a variety of conditions to give dicarbonyl(phosphorus ligand)-π-cyclopentadienylacylmolybdenum.[4,5] These monosubstituted compounds, π-$C_5H_5Mo(CO)_2(PR_3)COR$, can be expected to exist as *cis*- and *trans*- isomers. However, the structures of the resultant complexes have consisted solely of the *trans*-isomer, and existence of a *cis*-isomer has not been known as yet.

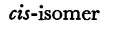
We wish to report the isomerism between *cis*- and *trans*-dicarbonyl (isocyanide)-π-cyclopentadienylacylmolybdenum, and their temperature- and time-dependent phenomena.

Results and Discussion

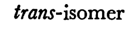
Preparation and Identification of π-$C_5H_5Mo(CO)_2(CNR')COR$. Treatment of *t*-butyl isocyanide with tricarbonyl-π-cyclopentadienylmethylmolybdenum, π-$C_5H_5Mo(CO)_3CH_3$, in benzene at room temperature gave yellow crystals **1**, which were soluble in most organic solvents and stable to air in the solid state. Compound **1** was formulated as π-$C_5H_5Mo(CO)_3(CNC(CH_3)_3)CH_3$, based on the elementary analysis. The structure was characterized by spectroscopic study and chemical reaction. The infrared spectrum showed four bands at 2140, 1962, 1880 and 1615 cm^{-1}; the first band was attributable to a terminal isocyanide group, the last band to a ketonic carbonyl group and the other two bands to the terminal carbonyl groups. The reaction of *t*-butyl isocyanide with π-$C_5H_5Mo(CO)_2(PPh_3)COCH_3$ also gave compound **1**. It was concluded from the results that compound **1** was π-$C_5H_5Mo(CO)_2(CNC(CH_3)_3)COCH_3$. The NMR spectrum showed two signals for each of cyclopentadienyl, isocyanide and acyl protons, suggesting the existence of two isomers, *cis*- and *trans*-isomers, which were depicted as follows.

The reaction with 2,6-dimethylphenyl isocyanide gave a similar complex, π-$C_5H_5Mo(CO)_2(C_9H_9N)COCH_3$ **2**. π-$C_5H_5Mo(CO)_3CH_2Ph$ was allowed to react with *t*-butyl isocyanide to give π-$C_5H_5Mo(CO)_2(CNC(CH_3)_3)COCH_2Ph$ **3** which were shown to exist as a mixture of *cis*- and *trans*-isomers in solutions by NMR spectrum. The complexes prepared here are summarized in Tables 1 and 2.

It should be noted that the benzylic methylene



cis-isomer



trans-isomer

[*1] Part I: Y. Yamamoto and N. Hagihara, This Bulletin, **39**, 1085 (1966). Part II: Y. Yamamoto and N. Hagihara, *ibid.*, **42**, 2077 (1969). Part III: Y. Yamamoto, H. Yamazaki and N. Hagihara, *J. Organometal. Chem.*, **18**, 189 (1969).

[*2] Presented at the 22nd Annual Meeting of the Chemical Society of Japan, Tokyo, April, 1969.

1) Y. Yamamoto, H. Yamazaki and N. Hagihara, This Bulletin, **41**, 532 (1968); *J. Organometal. Chem.*, **18**, 189 (1969).

2) Y. Yamamoto and N. Hagihara, This Bulletin, **39**, 1085 (1966).

3) Y. Yamamoto and N. Hagihara, *ibid.*, **42**, 2077 (1969).

4) K. W. Barnett and P. M. Treichel, *Inorg. Chem.*, **6**, 294 (1967).

5) P. J. Craig and M. Green, *J. Chem. Soc.*, *A*, **1968**, 1978; *ibid.*, **1969**, 157.

TABLE 1. PRODUCTS OF THE REACTIONS OF TRICARBONYL-π-CYCLOPENTADIENYLALKYLMOLYBDENUM WITH ISOCYANIDES: π-$C_5H_5Mo(CO)_2(CNR')COR$

R	R′	Mp (°C)	Yield (%)	Analyses Found (Calcd)			IR (cm^{-1})*3		
				C	H	N	N≡C	C≡O	>C=O
CH_2Ph	$C(CH_3)_3$	115.5—116.5	73	60.14 (60.16)	5.23 (5.30)	3.54 (3.54)	2140	1958 1880	1615
CH_3	$C(CH_3)_3$	104—105	56	49.07 (48.91)	4.88 (4.99)	4.12 (4.06)	2140	1962 1880	1615
CH_3	C_8H_9*2	91.5—92.5	42	57.44 (57.61)	4.78 (4.57)	3.58 (3.73)	2119	1948 1878	1623

*1 All melting points were measured in the nitrogen filled capillaries.
*2 2,6-dimethylphenyl.
*3 KBr disk.

TABLE 2. NMR SPECTRA OF π-$C_5H_5Mo(CO)_2(CNR')COR$

R	R′	Solvent		(τ)				
				$(CH_3)_3$	$COCH_3$	$COCH_2$	C_5H_5	C_6H_5 *2
CH_2Ph	$C(CH_3)_3$	C_6D_6	*cis*	9.1*2		5.70, 5.63	5.02	2.55—3.05
			trans			5.43	5.10	
		CS_2	*cis*	8.62		6.09*3	4.87	2.7 —3.2
			trans	8.54		5.93	5.01	
		$CDCl_3$	*cis*	8.52*2		5.85, 5.92	4.75	2.6 —3.2
			trans			5.76	4.88	
CH_3	$C(CH_3)_3$	CS_2	*cis*	8.53	7.73		4.85	
			trans	8.50	7.65		4.99	
		$CDCl_3$	*cis*	8.50	7.54		4.66	
			trans	8.48	7.43		4.81	
CH_3	C_8H_9*1	CS_2	*cis*		7.58		4.72	3.85—3.0
			trans		7.53		4.83	8.66*4

*1 1,2-Dimethylphenyl.
*2 The chemical shift difference between *cis*- and *trans*-isomer was too small to be analyzed.
*3 This signal was broad.
*4 This signal was attributable to *ortho*- and *meta*-methyl groups.

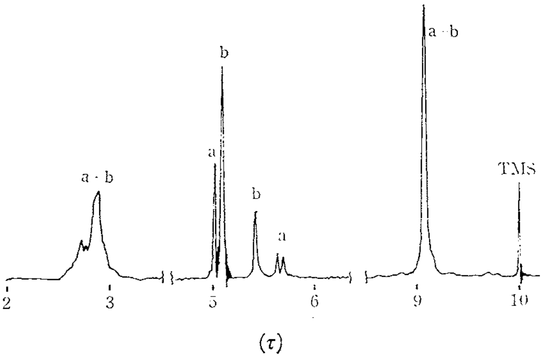


Fig. 1. NMR spectrum of π-$C_5H_5Mo(CO)_2(CNC(CH_3)_3)COCH_2Ph$ in C_6D_6 at 23°C.

protons of the isomer (a) in C_6D_6, as shown in Fig. 1, consist of two relatively sharp resonances of equal intensity separated by 4.2 cps, suggesting the magnetic nonequivalence of methylene protons of the isomer (a).

The origin of the magnetic nonequivalence has been the subject of several investigations.[6,7] Two reasons may be generally considered for the origin of magnetic nonequivalence of the methylene protons: (1) the restricted rotation of the methylene and (2) the existence of an asymmetric moiety adjacent to the methylene. In both cases, the protons of a methylene group display AB-type nuclear magnetic resonance spectra.[6]

Thus, if the phenylacetyl group is in *cis* position to a *t*-butyl isocyanide ligand in the complex **3**, the *cis*-isomer will be more sterically inhibited than the *trans*-isomer. Furthermore, there is no plane of symmetry in the *cis*-isomer.

It is reasonable to conclude that the isomer (a) is assigned to a *cis*-isomer and the isomer (b) to a *trans*-isomer.

The only two central peaks of the AB quartet were

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6) For example, E. I. Snyder, *J. Amer. Chem. Soc.*, **85**, 2624 (1963).

7) H. S. Gutowsky, *J. Chem. Phys.*, **37**, 2196 (1962); H. S. Gutowsky, G. G. Beiford and P. E. McMahon, *ibid.*, **36**, 3353 (1962).

Tadle 3. *cis*- and *trans*-Isomer ratio of π-C_5H_5-$Mo(CO)_2(CNR')COR$ in a variety of solvents at 23°C

R	R′	Solvent	Dielectric constant*1	*trans* (%)	*cis* (%)
CH_2Ph	$C(CH_3)_3$	C_6D_6	2.24	64	36
		CS_2	2.59	73	27
		$CDCl_3$	3.73	66	34
		CH_3COCH_3	19.6	63	37
CH_3	$C(CH_3)_3$	CS_2	2.59	69	31
		$CDCl_3$	3.73	64	39
CH_3	C_8H_9*2	$CDCl_3$	3.73	67	33

*1 R. J. Angelici and F. Basolo, *J. Amer. Chem. Soc.*, **84**, 2495 (1962). C_6D_6 = value of C_6H_6. $CDCl_3$ = Value of $CHCl_3$.

*2 2,6-Dimethylphenyl.

Table 4. Temperature-dependence of the isomer ratio of π-$C_5H_5Mo(CO)_2(CNC(CH_3)_3)COR$ in $CDCl_3$

Temp. (°C)	R = CH_2Ph		R = CH_3	
	trans (%)	*cis* (%)	*trans* (%)	*cis* (%)
23	66	34	64	36
− 3	75	25	67	33
−10	77	23	68	32

observed in the NMR spectrum of the benzyl protons of the *cis*-isomer, because of large $J_{AB}/\delta_B-\delta_A$ value and also of low concentration of the *cis*-isomer. In this assignment the cyclopentadienyl proton resonance of a *cis*-isomer exists in the lower field than that of a *trans*-isomer.

In an attempt to examine the structures of the complexes **1**, **2**, and **3** in the solid state, the crystalline samples of the complexes are dissolved in deuteriochloroform at −50°C and NMR spectra were recorded at this temperature. Only the *trans*-isomer was present in the solutions. When the solutions were allowed to reach room temperature, the growth of the cyclopentadienyl resonance due to the *cis*-isomer could be observed. It seems reasonable to assume that in the crystalline state these complexes exist only as the *trans*-isomer.

Trans-structures of the complexes **1**, **2**, and **3** in the solid state were also supported by infrared spectra. It is known that stereochemistry of the monosubstituted compounds π-$C_5H_5Mo(CO)_2LX$ (L = phosphorus ligands, X = alkyl, acyl, halogen) is assigned from the optical densities, D_a and D_s, of the asymmetric and symmetric CO stretching vibrations.[8,9] The application of this rule to the complexes **1**, **2**, and **3** suggests that they are *trans*-forms.

Temperature- and Time-dependent Phenomena in the Isomerism of Dicarbonyl(isocyanide)-π-cyclopentadienylacylmolybdenum. The compounds **1**, **2**, and **3** were found to exist as the *trans*-isomer in the solid state, and as a mixture of *cis*- and *trans*-isomers in solutions. The final equilibrium position scarcely depends on solvents, and the equiliblium mixtures of *cis*- and *trans*-π-$C_5H_5Mo(CO)_2(CNR')COR$ in a variety of solvents contained *ca.* 65% of the *trans*-isomer, as shown in Table 3.

The temperature-dependence of equilibrium positions was also observed. Thus, the concentration of the *trans*-isomer increased with lowering temperature, as shown in Table 4.

The *trans* to *cis* isomerization was briefly studied kinetically and found to proceed at a conveniently measurable rate of −3——10°C in $CDCl_3$, although it was impossible to measure the isomerization rate at room temperature.

Kinetic study showed that the reactions were first-order in the *trans*-isomer, because there was a very small change in the rate constant accompanying an almost fivefold change in concentration, as shown in Table 5. Added *t*-butyl isocyanide did not depress the rate, and this may suggest that isomerization was not responsible for the dissociative mechanism, such as had been observed in the *cis* to *trans* isomerization of $Mn(CO)_3(P(OPh)_3)_2Br$.[10] Detailed kinetic studies will be reported later.

Table 5. Rates of isomerization of *trans* to *cis*-π-$C_5H_5Mo(CO)_2(CNC(CH_3)_3)COR$ in $CDCl_3$

R	°C	mol/m*l*(10^4)	*k*(10^3)
CH_2Ph	−3	1.67	37.7
CH_2Ph	−10	1.70	15.0
CH_3	−3	1.97	40.6
CH_3	−3	9.30	39.8
CH_3	−10	1.49	16.9
CH_3	−10	7.47	16.7

Origin of Magnetic Nonequivalence of Methylene Protons in π-$C_5H_5Mo(CO)_2(CNC(CH_3)_3)COCH_2Ph$. In an attempt to resolve whether the restricted rotation or the existence of a molecular asymmetric center is responsible for the magnetic nonequivalence of the methylene protons in the *cis*-isomer, studies on the temperature dependence of complex **3** were carried out in various solvents.

At 23°C the *cis*-isomer has a relatively broad peak at 6.09τ in the proton NMR spectrum in CS_2, which is attributable to the methylene protons. On lowering of temperature this became a little broad band and was split into doublet at −9°C. When the solution was chilled to −50°C, the absorption

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8) W. Beck, A. Melnikoff and R. Stahl, *Chem. Ber.*, **99**, 3721 (1966).

9) A. R. Manning, *J. Chem. Soc.*, *A*, **1967**, 1984.

10) R. J. Angelici, F. Basolo and A. J. Poe, *J. Amer. Chem. Soc.*, **85**, 2215 (1963).

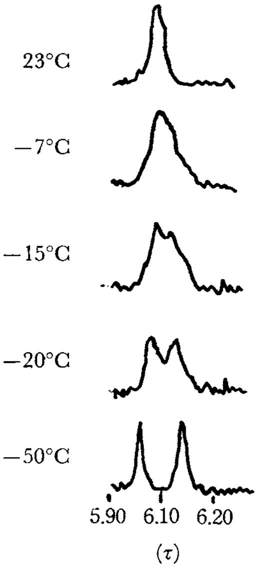

Fig. 2. Temperature dependence of the methylene protons of *cis*-π-$C_5H_5Mo(CO)_2(CNC(CH_3)_3)CO$-$CH_2Ph$ in CS_2.

at 6.09τ was split into two relatively sharp signals at 6.06 and 6.14τ, in an approximate relative intensity 1:1, as shown in Fig. 2.

The average position of two new peaks at −50°C is found quite near the original peak at 23°C.

In the proton NMR spectrum in C_6D_6, the methylene proton resonance of the *cis*-isomer at room temperature appeared as two peaks at 5.70 and 5.62τ. They became relatively broad with rise of temperature, and at 65°C the spectrum consisted of one single broad peak, as shown in Fig. 3. An attempt to measure the spectra at higher temperatures was unsuccessful, because of decomposition of complex **3**. Accordingly, we could not observe a sharp singlet resonance which might be derived from rapid rotation of the phenyl acetyl group.

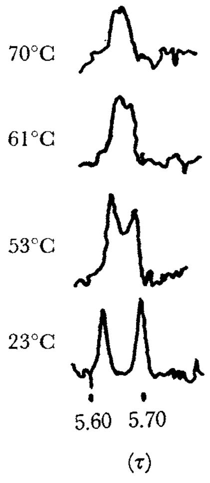

Fig. 3. Temperature dependence of the methylene protons of *cis*-π-$C_5H_5Mo(CO)_2(CNC(CH_3)_3)CO$-$CH_2Ph$ in C_6D_6.

Although we cannot rule out response for the magnetic nonequivalence arising from the existence of the asymmetric center, it seems more reasonable to assume that the steric inhibition of free rotation of the phenyl acetyl group causes the methylene group to be magnetically nonequivalent.

Decarbonylation of π-$C_5H_5Mo(CO)_2(CNC(CH_3)_3)COCH_2Ph$ (3). Decarbonylation of complex **3** was briefly studied. With ultraviolet irradiation in benzene, evolution of carbon monoxide occurred to give complex **4**, π-$C_5H_5Mo(CO)_2(CNC(CH_3)_3)$-$CH_2Ph$ characterized by the absence of an acyl carbonyl band from the infrared spectrum. Contrary to expectation, there was no evidence for the existence of the isomers. Thus, the NMR spectrum in CS_2 showed four signals at 8.51 (singlet, 9H, $(CH_3)_3C$) 7.16 (singlet, 2H, CH_2), 4.91 (singlet, 5H, C_5H_5) and 3.00τ (singlet, 5H, C_6H_5).

In an attempt to confirm the structure of complex **4**, the NMR spectrum in lower temperatures was studied.

The spectrum at −60°C gave rise to only a minor change as compared to the room-temperature spectrum. Difference in each chemical shift was observed.

If complex **4** is a *cis*-isomer, the benzylic methylene protons are expected to be magnetically nonequivalent as has been observed in complex **3**. No line splitting suggests that **4** is a *trans*-isomer. The relative intensities of the terminal carbonyl bands in the infrared spectrum also suggests *trans*-forms for **4**.

In the decarbonylation mechanism of acylmanganese carbonyl derivatives, it is known that the acyl CO becomes coordinated and a coordinated CO is eliminated.[11] If decarbonylation reaction of π-$C_5H_5Mo(CO)_2(CNC(CH_3)_3)COCH_2Ph$ proceeds through a similar mechanism, decarbonylation from the *cis*-isomer will preferentially proceed. However, there is no evidence that the *cis*-isomer is the first decarbonylation product, and since it is not isomerized subsequently to the *trans*-isomer, its mechanism remains undecided at present.

Experimental

Reactions were carried out under a nitrogen atmosphere. All melting points are uncorrected. The infrared spectra were obtained by a Perkin-Elmer 521 spectrometer. The NMR spectra were recorded by a Varian Model A-60 instrument, using tetramethylsilane as an internal standard.

Materials. Various isocyanides[12] and tricarbonyl-

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11) For example: R. J. Mawby, F. Basolo and R. G. Pearson, *J. Amer. Chem. Soc.*, **86**, 5043 (1964).

12) I. Ugi and R. Meyer, *Chem. Ber.*, **93**, 239 (1960).

π-cyclopentadienylalkylmolybdenum[13] were prepared according to the procedures in literatures.

Reaction of Tricarbonyl-π-cyclopentadienylbenzylmolybdenum with *t*-Butyl Isocyanide. *t*-Butyl isocyanide (0.26 g) in benzene (5 m*l*) was added dropwise to a stirred solution of tricarbonyl-π-cyclopentadienylbenzylmolybdenum (1.0 g) in benzene (15 m*l*). After 9 hr at room temperature, the reaction mixture was evaporated to about 5 m*l* under reduced pressure and chromatographed on alumina, benzene being used as eluant. The orange yellow fraction was collected, and the solvent was evaporated almost to dryness. Recrystallization from THF - *n*-hexane gave π-$C_5H_5Mo(CO)_2(CNC(CH_3)_3)COCH_2Ph$ (0.69 g, 57.5%).

The reactions of tricarbonyl-π-cyclopentadienylalkylmolybdenum with isocyanides were also carried out by the same procedures described above to give the corresponding dicarbonyl-π-cyclopentadienyl(isocyanide)acylmolybdenum.

Reaction of Dicarbonyl-π-cyclopentadienyl(triphenylphosphine)acetylmolybdenum with *t*-Butyl Isocyanide. *t*-Butyl isocyanide (0.3 g) in benzene (5 m*l*) was added dropwise to a solution of π-$C_5H_5Mo(CO)_2(PPh_3)COCH_3$ (0.52 g) in benzene (15 m*l*). After 9 hr, the reaction mixture was evaporated to about 5 m*l* under reduced pressure and chromatographed on alumina, benzene being used as eluant. The yellow fraction was collected and solvent was evaporated almost to dryness. Recrystallization from benzene - *n*-hexane gave π-$C_5H_5Mo(CO)_2(CNC(CH_3)_3)COCH_3$ (0.16 g 48%).

Decarbonylation of π-$C_5H_5Mo(CO)_2(CNC(CH_3)_3)COCH_2Ph$(3). Compound **1**(1.6 g) in THF (25 m*l*) was irradiated with ultraviolet light at room temperature. After 30 hr, the reaction mixture was evaporated to about 10 m*l* under reduced pressure and chromatographed on alumina, using benzene as eluant. Evaporation of the yellow fraction and recrystallization of the residue from *n*-hexane - benzene gave π-$C_5H_5Mo(CO)_2(CNC(CH_3)_3)CH_2Ph$ (0.43 g, 25%, mp 68—72°C). Found: C, 58.46; H, 5.56; N, 3.85%. Calcd for $C_{19}H_{21}NO_2Mo$: C, 58.32; H, 5.54; N, 3.58%.

Determination of Rates of Isomerization. *trans* to *cis* isomerization was determined by following the appearance of cyclopentadienyl protons resonance of the *cis*-isomer. For rate studies of the isomerization of *trans*-π-$C_5H_5Mo(CO)_2$(isocyanide)COR, the solid complex was dissolved in $CDCl_3$ at −50°C and its rate of isomerization was followed in the desired temperature. Approximately 2 min was allowed for the system to attain the measured temperature. Typical changes in spectra with time are shown in Fig. 4. The spectrum at $t=0$ min is that of *trans*-π-$C_5H_5Mo(CO)_2$(isocyanide)COR, and at $t=\infty$ that of the equilibrium position. First-order rate constants were obtained from the slope of plots of $\ln(A-A_\infty)$ *vs.* t, time, where A is a magnitude of the *trans*-complex at time t. A_∞ is *trans*-content in the equilibrium position.

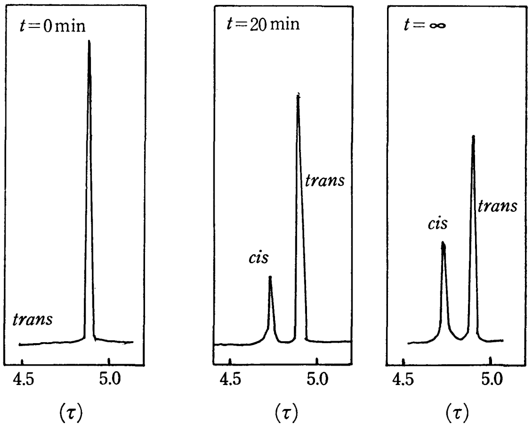

Fig. 4. NMR spectra during the isomerization of *trans*-π-$C_5H_5Mo(CO)_2(CNC(CH_3)_3)COCH_2Ph$ in $CDCl_3$ at −10°C.

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[13] P. J. Craig and M. Green, *Chem. Commun.*, **1967** 1246.