Journal of Organometallic Chemistry
Elsevier Sequoia S.A., Lausanne
Printed in The Netherlands

STUDIES ON INTERACTIONS OF ISOCYANIDES WITH TRANSITION METAL COMPLEXES

VI*. DIRECT INSERTION OF CYCLOHEXYL ISOCYANIDE INTO THE BENZYL–MOLYBDENUM σ BOND**

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(Received April 16th, 1970)

SUMMARY

Reactions of tricarbonyl-π-cyclopentadienylalkylmolybdenum compounds with cyclohexyl isocyanide were carried out. Reaction of cyclohexyl isocyanide with the methylmolybdenum derivative resulted in carbonyl insertion, affording an acyl complex, π-$C_5H_5Mo(CO)_2(CNC_6H_{11})COCH_3$. No reaction occurred with the cyano- or chloromethyl derivatives. On the other hand, treatment with several *p*-substituted benzyl derivatives gave the imino complex, π-$C_5H_5Mo(CO)_3[C(CH_2$-C_6H_4X-*p*$)$=$NC_6H_{11}]$ ($X=Cl, H, OCH_3$), as a main product and a small amount of the acyl complex. The yield of the imino complex increased and that of the acyl complex decreased with the increase of electron-attracting power of the *para*-substituent. The mechanism of isocyanide insertion reaction is discussed.

It is well-known that the reactions of carbon monoxide and phosphorus ligands with cyclopentadienylmetal carbonyl alkyls undergo the so-called carbonyl insertion to give the acyl complexes[1–5].

$$\pi\text{-}C_5H_5M(CO)_nR + L \rightarrow \pi\text{-}C_5H_5M(CO)_{n-1}(L)COR$$

In the previous paper, we reported that isocyanides (which have an electronic structure similar to that of carbon monoxide) can also undergo the carbonyl insertion reaction, affording an acyl complex. For example, the methyl and benzyl derivatives of tricarbonyl-π-cyclopentadienylmolybdenum react with tert-butyl and 2,6-dimethylphenyl isocyanide to give dicarbonyl-π-cyclopentadienyl(isocyanide)acylmolybdenum π-$C_5H_5Mo(CO)_2(CNR')COR$ ($R=CH_3$, CH_2Ph; $R'=C(CH_3)_3$, 2,6-dimethylphenyl), which existed in an equilibrium mixture of *cis*- and *trans*-isomers in solutions, and as *trans*-isomers in the solid state[6]. On the other hand, we also reported that isocyanide was inserted into a carbon–nickel σ bond to give an imino complex π-$C_5H_5Ni(CNR')(C(R)$=$NR')$ in the reaction of (triphenylphosphine)-π-cyclopentadienylalkylnickel with isocyanides[7].

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* For Part V see ref. 22.

** Presented at the Symposium of Organometallic Chemistry, Osaka, October, 1969.

In our extensive studies concerning the interaction of isocyanides with alkyl transition metal complexes, we found that the reactions of benzyl derivatives of tricarbonyl-π-cyclopentadienylmolybdenum with cyclohexyl isocyanide underwent isocyanide insertion to produce the imino complexes, in addition to carbon monoxide insertion reaction.

We report on this subject and about the mechanism of the isocyanide insertion.

RESULTS AND DISCUSSION

Treatment of tricarbonyl-π-cyclopentadienylmethylmolybdenum with cyclohexyl isocyanide in benzene at room temperature resulted in a carbonyl insertion reaction to afford dicarbonyl-π-cyclopentadienyl(cyclohexyl isocyanide)acetylmolybdenum, π-$C_5H_5Mo(CO)_2(CNC_6H_{11})COCH_3$, which existed as a mixture of *cis*- and *trans*-isomers in solution* .

In the reaction of the (cyanomethyl)- or (chloromethyl)molybdenum analogues with cyclohexyl isocyanide, unconverted starting material was recovered.

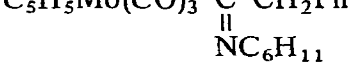
On the other hand, the reaction of tricarbonyl-π-cyclopentadienylbenzylmolybdenum with cyclohexyl isocyanide in benzene at room temperature gave yellow (I) and yellow orange crystals (II). The complex (I) was identified as π-$C_5H_5Mo(CO)_2$-$(CNC_6H_{11})COCH_2Ph$, characterized by the presence of a coordinated isocyanide band at 2139 cm^{-1} and an acyl carbonyl band at 1614 cm^{-1} in its IR spectrum, which existed as a mixture of *cis*- and *trans*-isomers in solution*.

The complex (II), being very stable in the solid state, was formulated as π-$C_5H_5Mo(CO)_3(CNC_6H_{11})CH_2Ph$ on the basis of its elemental analysis and its molecular weight determination.

Evidence concerning the structure was obtained from its IR and NMR spectrum and from its decomposition with hydrogen peroxide. The IR spectrum showed three characteristic bands at 1954, 1880 and 1594 cm^{-1}. The C–N stretching frequency of the coordinated isocyanide has been known to appear higher than 2000 cm^{-1}. Thus, the band at 1594 cm^{-1} is assigned to a carbon–nitrogen double bond, suggesting the insertion of isocyanide into a benzyl–molybdenum σ bond. Two other bands are attributable to the terminal carbonyl groups. The oxidative degradation of compound (II) with H_2O_2 gave *N*-cyclohexylphenylacetamide:

$$\text{(II)} \xrightarrow{H_2O_2} \mathrm{PhCH_2CONHC_6H_{11}}$$

It was concluded from these results that the compound (II) was tricarbonyl-π-cyclopentadienyl[benzyl(cyclohexylimino)methyl]molybdenum.



$$\mathrm{C_5H_5Mo(CO)_3{-}\underset{\underset{\textstyle NC_6H_{11}}{\|}}{C}{-}CH_2Ph}$$

(II)

The NMR spectrum of compound (II) measured in $(CD_3)_2SO$ showed a sharp singlet at τ 4.46 attributable to the cyclopentadienyl group, two broad resonances at ca. 8.0 and 2.5 due to the cyclohexyl and phenyl groups, respectively, and furthermore,

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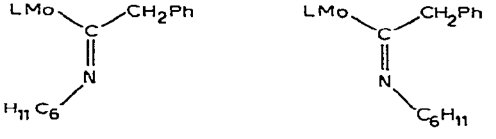
* Existence of *cis*- and *trans*-isomers was confirmed by the NMR spectrum. For assignment of two isomers, see ref. 6. Similar assignment has been reported by others[8-10].

two singlets at 4.70 and 4.28 assignable to the benzylic methylene protons. Observation of two methylene resonances is of interest, indicating the presence of two isomers.

We assigned two isomers to *syn-* and *anti*-forms, as shown in the following:



anti-form *syn*-form

L = $(\pi\text{-}C_5H_5)(CO)_3$

It is known that both *syn-* and *anti*-forms exist in some Schiff's bases and the α-proton resonance in *cis*-position to the *N*-substituent appears in lower field than that in *trans*-position to the *N*-substituent[11–12]. According to this, we tentatively assigned the signal at τ 4.70 to the methylene group of *anti*-isomers and that at τ 4.28 to the methylene group of *syn*-isomers.

Similar imino complexes were also obtained from the reactions of *p*-chloro- and (*p*-methoxybenzyl)molybdenum derivatives with cyclohexyl isocyanide. The complexes prepared here are summarized in Tables 1 and 2.

TABLE 1

$\pi\text{-}C_5H_5Mo(CO)_3[C(CH_2C_6H_4X\text{-}p){=}NC_6H_{11}]$

X	Yield[a] (%)	M.p.[b] (°C)	Analyses, found (calcd.) (%) C	H	N	Mol. wt.[c]
Cl	72	210	54.81 (55.07)	4.61 (4.53)	2.93 (2.92)	
H	51	170	59.34 (59.33)	5.89 (5.21)	3.21 (3.15)	453 (445)
OCH_3	40	157–159	58.35 (58.11)	4.67 (4.38)	2.93 (3.15)	

[a] Isolated yield. [b] All compounds decomposed without melting. [c] By the vapour pressure osmometric method in $CHCl_3$.

The benzylmolybdenum derivatives (ex. $PhCH_2$, σ^* 0.22)[13] in which the benzyl radical is more electron-attracting than the methyl group ($\sigma^* = 0.00$) and less electron-attracting than the chloromethyl ($\sigma^* = 1.05$)[13] and the cyanomethyl group ($\sigma^* > 1.05$)[*], underwent isocyanide insertion. The methylmolybdenum derivative afforded the carbonyl insertion product.

On the other hand, alkylmolybdenum derivatives having high electron-attracting groups, such as chloromethyl and cyanomethyl did not undergo the insertion reaction, probably because of the strength of a carbon–molybdenum σ bond. The

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[*] From comparison of σ_p(CN) with σ_p(Cl).

same trend was noted in the reaction of (cyanomethyl)cobalt tetracarbonyl with triphenylphosphine[14].

This suggests presence of delicate electronic effects in the choice of direction of the insertion reaction, the carbonyl or the isocyanide insertion.

TABLE 2

IR AND NMR SPECTRA OF π-$C_5H_5Mo(CO)_3[C(CH_2C_6H_4X$-$p)$=$NC_6H_{11}]$

X	IR (cm^{-1})[a]		NMR, τ (ppm)				
	C≡O	C=N	C_6H_{10}[b]	CH_2[c]		C_5H_5[c]	Phenyl and other groups
				syn	*anti*		
Cl	1954 1892	1593	7.9–9.2	4.69	4.26	4.43	2.52[d]
H	1954 1880	1594	7.9–9.2	4.70	4.28	4.46	2.2–3.0[e]
OCH_3	1948 1886	1598	8.2–9.2	4.61	4.31	4.49	2.80[f] 6.29[g]

[a] KBr method. [b] Broad signal. [c] Singlet. [d] AB type, center value, J_{AB} 8.4 Hz. δ_{AB} 32.1 Hz, [e] Complex signal. [f] AB type, center value, J_{AB} 8.7 Hz, δ_{AB} 54.3 Hz. [g] Singlet, CH_3O.

In an attempt to resolve the characteristic reactivity of benzylmolybdenum derivatives, the NMR spectra of the starting materials, π-$C_5H_5Mo(CO)_3CH_2C_6H_4X$-$p$, were measured (Tables 3 and 4.).

TABLE 3

NMR SPECTRA OF π-$C_5H_5Mo(CO)_3CH_2C_6H_4X$-$p$ IN $CDCl_3$

X	NMR, τ (ppm)[a]			
	C_5H_5	CH_2	C_6H_4	OCH_3
Cl	4.81 (s)	7.16 (s)	2.89 (s)	
H	4.83 (s)	7.12 (s)	2.6–3.1 (c)	
OCH_3	4.85 (s)	7.06 (s)	3.09 (q)	6.25 (s)

[a] s = singlet; c = complex signal; q = AB type, center value, J_{AB} 9.0 Hz, δ_{AB} 24.6 Hz.

The tendency to shielding of the benzylic methylene protons increased with the electron-attracting power in the order OCH_3, H, Cl, suggesting a transfer of an electron from molybdenum metal to the methylene group by means of an inductive effect of the *para*-substituent, although the chemical shift differences of the benzylic methylene proton resonances are not significant.

In the series of *para*-substituted benzylmolybdenum derivatives, the yield of an imino complex increased and that of an acyl complex decreased with the increase of electron-attracting power of the *para*-substituent. These indicate that the more polarizable benzyl group favours more formation of an imino complex than that of an acyl one. Restated, the high anionic character of the methylene group facilitated a

TABLE 4

PRODUCTS OF THE REACTIONS OF Na[π-$C_5H_5Mo(CO)_3$] WITH ALKYL HALIDES: π-$C_5H_5Mo(CO)_3CH_2X$

X	M.p.[a] (°C)	Yield (%)	Analyses found (calcd.) (%) C	H	IR (cm^{-1})[b] C=O
C_6H_4Cl-*p*	97.5–99.5	75	49.11 (48.61)	2.99 (2.99)	2002, 1930, 1899
C_6H_5	86–87[c]	65	53.41 (53.59)	3.58 (3.60)	1999, 1933, 1910
$C_6H_4OCH_3$-*p*	101–103	63	50.98 (51.02)	3.73 (3.75)	2002, 1925, 1895
CN[d]	140–145	52	42.05 (42.13)	2.30 (2.47)	2190[e], 2010, 1924
Cl[f]	105–107	43	36.47 (36.70)	2.56 (2.40)	2013, 1945, 1920

[a] All compounds decomposed with melting. [b] KBr method. [c] Lit.[21] 87–88°. [d] N, 4.90% (4.91); NMR ($CDCl_3$, τ): 8.58 (s, CH_2), 4.50 (s, C_5H_5). [e] $\nu(C{\equiv}N)$. [f] NMR ($CDCl_3$, τ): 5.82 (s, CH_2), 4.53 (s, C_5H_5).

transfer of the alkyl group to the isocyanide ligand. One reason for this may be correlated with higher contribution of resonance form (A) than that of (B), being realized in the coordination of isocyanide to the transition metal[15];

$$\text{R}-\overset{\oplus}{\overset{\frown}{\text{N}\equiv\text{C}}}-\overset{\ominus}{\text{M}} \leftrightarrow \text{R}-\overline{\text{N}}=\text{C}=\text{M}$$

(A)* (B)

Steric effects are also important in the isocyanide insertion reaction. The reaction of tricarbonyl-π-cyclopentadienylbenzylmolybdenum with a hindered isocyanide, such as tert-butyl isocyanide led to carbonyl insertion rather than isocyanide one[6]. A similar effect has been observed in the reaction of (triphenylphosphine)-π-cyclopentadienylalkylnickel with tert-butyl isocyanide[7].

The mechanism on the insertion reaction of cyclohexyl isocyanide into a carbon–molybdenum bond has been now considered. It is well known that the reactions of nucleophiles with alkylmetal carbonyl complexes afford an acyl complex through the ligand replacement, accompanied by a transfer of the alkyl group to a coordinated CO ligand. On the other hand, there are several studies in which an entering nucleophile was directly inserted into the carbon–transition metal bond.

It was established by Wojcicki *et al.* that the reactions of sulfur dioxide with alkylmetal carbonyl complexes, such as iron[16], manganese[17], and molybdenum[18] underwent direct insertion of sulfur dioxide into a carbon–metal bond, affording the corresponding sulfinate complexes.

Formation of the imino complex in the present study indicates formally a direct insertion reaction of isocyanide into a carbon–molybdenum bond.

Two simple routes concerning the isocyanide insertion reaction may be considered on the basis of Bibler and Wojcicki's mechanism of the sulfur dioxide insertion[16]. The first results from an initial formation of the acyl complex π-$C_5H_5Mo(CO)_2$-

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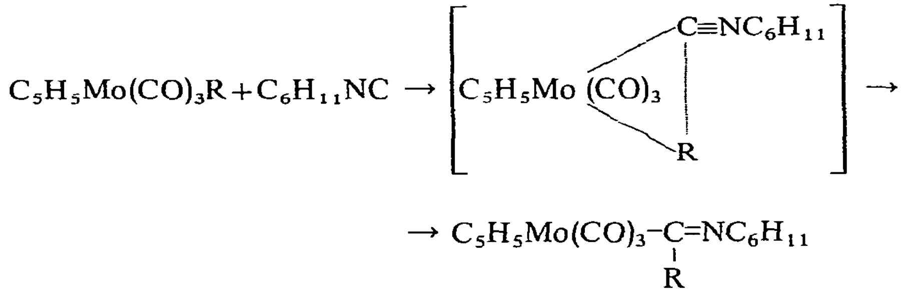
* The resonance form (A) was postulated as an analogue of the nitrilium ion[19].

$(CNC_6H_{11})COCH_2Ph$, followed by a rapid migration of the benzyl group to the coordinated isocyanide ligand. The second path involves direct attack of isocyanide on molybdenum, accompanied by a transfer of the alkyl group to the isocyanide ligand.

Experiments to possibly resolve between the two suggested mechanisms were conducted. The attempts to rearrange the acyl complex to the imino complex (II) were unsuccessful. This suggests ruling out the first path, and speaks in favor of direct isocyanide insertion (the second route), presumably through an activated complex resulting from simultaneous $Mo–CNC_6H_{11}$ bond formation and Mo–R bond breaking:



$$C_5H_5Mo(CO)_3R + C_6H_{11}NC \rightarrow [C_5H_5Mo(CO)_3 \cdots C{\equiv}NC_6H_{11} \cdots R] \rightarrow C_5H_5Mo(CO)_3{-}\underset{\displaystyle R}{\underset{|}{C}}{=}NC_6H_{11}$$

EXPERIMENTAL

All reactions were carried out under a nitrogen atmosphere. The IR spectra were obtained by a Perkin–Elmer 521 spectrometer. The NMR spectra were recorded by a JEOL C-60 instrument, using tetramethylsilane as an internal standard.

Isocyanides were prepared according to the procedures in the literature[20]. *para*-Substituted benzyl and monosubstituted methyl derivatives of tricarbonyl-π-cyclopentadienylmolybdenum were prepared by a modification of King's method[21].

Analyses and IR spectra of alkylmolybdenum complexes prepared are summarized in Table 4.

Reaction of tricarbonyl-π-cyclopentadienylmethylmolybdenum with cyclohexyl isocyanide.

Cyclohexyl isocyanide (0.44 g, 4.0 mmole) in benzene (5 ml) was added dropwise to a solution of π-$C_5H_5Mo(CO)_3CH_3$ (0.78 g, 3.0 mmole) in benzene (20 ml). After 6h, the reaction mixture was evaporated to about 5 ml under reduced pressure and chromatographed on alumina, benzene being used as eluant. The yellow orange fraction was collected and evaporated almost to dryness. Recrystallization from hexane/benzene gave π-$C_5H_5Mo(CO)_2(CNC_6H_{11})COCH_3$ (0.53 g, 48%); m.p. 80–82° (decomposing with melting). (Found: C, 52.30; H, 5.20; N, 3.67. $C_{16}H_{19}MoNO_3$ calcd.: C, 52.04; H, 5.19; N, 3.79%.) IR (KBr, cm^{-1}): 2150 (N≡C), 1950, 1856 (C≡N), 1604 (C=O). NMR (CS_2, τ)*: 7.6–8.6 (b, C_6H_{10}), 7.45 (s, CH_3, *cis*), 7.37 (s, CH_3, *trans*), 5.55–5.95 (b, CH), 4.85 (s, C_5H_5, *trans*), 4.72 (s, C_5H_5, *cis*). *trans*-Isomer 71%, *cis*-isomer 39%.

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* b = broad signal. s = singlet.

Reaction of tricarbonyl-π-cyclopentadienylbenzylmolybdenum with cyclohexyl isocyanide

To a solution of $\pi\text{-}C_5H_5Mo(CO)_3CH_2Ph$ (1.0 g, 3 mmole) in benzene (25 ml) was added 0.4 g (3.7 mmole) of cyclohexyl isocyanide at room temperature and then stirred for 8h. The mixture was evaporated to about 10 ml under reduced pressure to precipitate yellow orange solid. The resulting solid was removed by filtration and recrystallized from CH_2Cl_2/hexane and identified as $\pi\text{-}C_5H_5Mo(CO)_3[C(CH_2Ph){=}NC_6H_{11}]$ (0.68 g). The filtrate was chromatographed on alumina. The yellow band was eluted with benzene and collected. Evaporation of the eluate gave $\pi\text{-}C_5H_5Mo(CO)_2(CNC_6H_{11})COCH_2Ph$ (0.06 g, 4%); m.p. 93–95° (decomposing with melting). (Found: C, 59.35; H, 5.33; N, 3.23. $C_{22}H_{23}MoNO_3$ calcd.: C, 59.33; H, 5.21; N, 3.15%.) IR (KBr, cm^{-1}): 2139 (N≡C), 1952, 1880 (C≡O), 1614 (C=O). NMR (CS_2, τ): 7.9–9.0 (b, C_6H_{10}), 7.0–7.4 (b, CH), 6.06 (s, CH_2, *cis*), 5.96 (s, CH_2, *trans*), 4.95 (s, C_5H_5, *trans*), 4.80 (s, C_5H_5, *cis*), 2.8–3.3 (b, C_6H_5). *trans*-Isomer 64%, *cis*-isomer 36%.

Reaction of tricarbonyl-π-cyclopentadienyl(p-methoxybenzyl)molybdenum with cyclohexyl isocyanide

By procedures similar to those described above, $\pi\text{-}C_5H_5Mo(CO)_2(CNC_6H_{11})COCH_2C_6H_4OCH_3\text{-}p$ (0.144 g, 13%), m.p. 116–119° (decomposing with melting), and $\pi\text{-}C_5H_5Mo(CO)_3[C(CH_2C_6H_4OCH_3\text{-}p){=}NC_6H_{11}]$ (0.40 g, 40%) were obtained from 0.80 g (2.2 mmole) of $\pi\text{-}C_5H_5Mo(CO)_3CH_2C_6H_4OCH_3\text{-}p$ and 0.44 g (4.0 mmole) of cyclohexyl isocyanide. (Found: C, 58.40; H, 4.53; N, 2.94. $C_{23}H_{25}MoNO_4$ calcd.: C, 58.11; H, 4.38; N, 2.95%.) IR (KBr cm^{-1}): 2130 (N≡C), 1952, 1880 (C≡O), 1599 (C=O).

Oxidative reaction of tricarbonyl-π-cyclopentadienyl[benzyl(cyclohexylimino)methyl]-molybdenum with hydrogen peroxide

A mixture of $\pi\text{-}C_5H_5Mo(CO)_3(C(CH_2Ph){=}NC_6H_{11})$(0.8 g) and 3% H_2O_2 (10 ml) was stirred for 3 h at room temperature. The brown-colored organic layer was washed by aquous $NaHCO_3$ and then dried with sodium sulfate. Evaporation of solvent and sublimation of the residue gave $C_6H_5CH_2CONHC_6H_{11}$ (213 mg, 75%). The infrared spectrum and the melting point of this compound were identical with those of the authentic *N*-cyclohexylphenylacetamide.

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