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Contribution from the Facoltà di Chimica Industriale, Università di Venezia, Venezia, Italy, Istituto Chimico, Università di Ferrara, Ferrara, Italy, Department of Chemistry, Louisiana State University, Baton Rouge, Louisiana 70803, and Istituto di Chimica, Università di Trieste, Trieste, Italy

Reactions of Tetracyanoethylene Oxide with Some Noble Metal Complexes

M. LENARDA,*^{1a} R. ROS,^{1a} O. TRAVERSO,^{1b} W. D. PITTS,^{1c} W. H. BADDLEY,^{1c} and M. GRAZIANI*^{1d}

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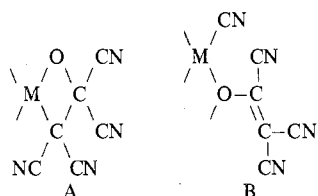
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Reactions of tetracyanoethylene oxide with some noble metal complexes of platinum, palladium, rhodium, and iridium have been investigated, and a number of compounds have been isolated and characterized. The new complexes include both four-member metalocycles and the opened isomers, tricyanoethenolato complexes. The latter are formed via a thermal isomerization of the metalocycles. Photochemical isomerization of the metalocycles has also been observed and studied.

Introduction

Reactions involving the transformations of epoxides to various other organic compounds via catalysis by transition metal complexes have been described by a number of investigators.² These studies have dealt primarily with the organic products, with less attention having been given to organometallic intermediates that may have been formed. With a view toward isolating and characterizing organometallic intermediates, we have studied the reactions of 2,2,3,3-tetracyanooxacyclopropane (tetracyanoethylene oxide, TCNEO) with a number of noble metal complexes.

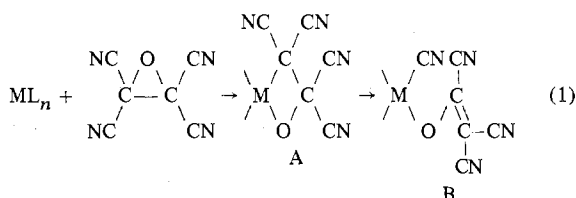
Previously we reported the preparation³ of complexes of the type [PtL₂(TCNEO)] (L = tertiary phosphines and arsines) and the structure⁴ of [Pt(AsPh₃)₂(TCNEO)]. We describe herein products of two types — cyclic complexes A and tri-



cianoethenolato complexes B—which have been obtained from reactions of TCNEO with low-valent transition metal complexes of rhodium, iridium, palladium, and platinum. Also described are the thermal and photochemical rearrangements of type A to type B complexes.

Results and Discussion

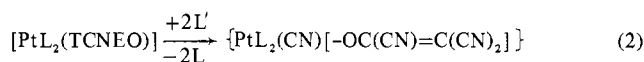
(1) Preparation of Complexes. Tetracyanoethylene oxide has been found to react readily with a number of low-valent noble metal substrates to give cyclic complexes (A) via insertion of the metallic moiety into the C—O bond, tricyanoethenolato complexes (B), presumably formed by subsequent isomerization of the initially formed cyclic complexes, or mixtures of A and B, eq 1. Data for the new complexes are



given in Table I. Thus, as already reported^{3b,4} for the Pt(0) substrates [Pt(AsPh₃)₄], [Pt(PPh₃)_{3 or 4}], and {Pt[P(*p*-

CH₃C₆H₄)₃]₃}, reactions occur immediately with TCNEO in benzene, THF, or CH₂Cl₂ at room temperature to give type A cyclic compounds (1A, 2A, 3A of Table II). Also, in the case of [Pt(CO)₂(PPh₃)₂], reaction with TCNEO in benzene at room temperature proceeds with gas evolution to give cyclic [Pt(PPh₃)₂(TCNEO)] (2A).

While most of the Pt(0) complexes which were studied gave metalocycles as described above, one compound gave a different product. From the reaction of [Pt(PPh₂Me)₄] and TCNEO in THF at room temperature, a compound believing to contain a tricyanoethenolato group, type B, was obtained, 4B. Apparently the presence of more basic phosphines in the coordination sphere is conducive to the type A → type B transformation. In fact, it was found that type B complexes were obtained on workup of ligand-exchange reactions according to eq 2. Type A isomers are easily distinguished from



1A, L = AsPh₃

2A, L = PPh₃

4B, L' = PPh₂Me

5B, L' = PEt₃

the type B isomers by infrared spectroscopy. The latter complexes show several absorption bands (see Table II) in the range 2140–2220 cm⁻¹ ascribable to cyano groups and an olefinic absorption at ca. 1590 cm⁻¹. In the type A cyclic compounds there is no olefinic band and there is only one C≡N stretching frequency at ca. 2220 cm⁻¹.

The palladium(0) complexes [Pd(PPh₃)₄] and {Pd[P(*p*-CH₃C₆H₄)₃]₃} reacted with TCNEO in THF at room temperature to give the type B complexes on workup, 7B and 8B. When the reaction was carried out at 0 °C, mixtures of type A and type B isomers were obtained. Attempts to isolate a pure type A isomer of palladium were not successful. The A → B rearrangement is very facile for palladium, but considerably more difficult for platinum, where in the case of cyclic [Pt(PPh₃)₂(TCNEO)] and the *p*-tolylphosphine analogue, temperatures of 170 and 140 °C, respectively, were required for the isomerization. Also, the isomerization was found to be sensitive to the nature of the solvent, going to completion only in protic solvents such as ethanol.

Reactions of TCNEO with complexes of nickel(0), rhodium(I), and iridium(I) did not always proceed as cleanly to give well-defined products as in the above-described reactions of palladium(0) and platinum(0) complexes.

When TCNEO and [Ir(PPh₃)₂(CO)Cl] were mixed in benzene at room temperature a darkening of the solution was

Table I. Analytical Data and Physical Properties

No.	Compd	Mp, °C dec	Mol wt ^a found (calcd)	Anal. found (calcd)		
				C	H	N
1A	Pt(AsPh ₃) ₂ (TCNEO) ^b					
2A	Pt(PPh ₃) ₂ (TCNEO) ^b					
2B	Pt(PPh ₃) ₂ (CN)[OC(CN)= C(CN) ₂]	265-268		58.3 (58.40)	3.55 (3.50)	6.3 (6.48)
3A	Pt[P(<i>p</i> -tolyl) ₃] ₂ (TCNEO) ^b					
3B	Pt[P(<i>p</i> -tolyl) ₃] ₂ (CN)[OC(CN)= C(CN) ₂]	265-267	961 (948)	60.4 (60.82)	4.7 (4.46)	5.85 (5.91)
4B	Pt(PPh ₃ Me) ₂ (CN)[OC(CN)= C(CN) ₂]	86-89	764 (739)	52.15 (51.96)	3.5 (3.54)	7.55 (7.57)
5B	Pt(PEt ₃) ₂ (CN)[OC(CN)= C(CN) ₂]	65-75		38.05 (37.57)	5.0 (5.25)	9.6 (9.73)
6B	Pt(PPh ₃) ₂ (CH ₂ C ₆ H ₅)[OC- (CN)=C(CN) ₂]	180-182	923 (929)	61.65 (62.07)	4.05 (4.01)	4.5 (4.52)
7B	Pd(PPh ₃) ₂ (CN)[OC(CN)= C(CN) ₂]	235-239	754 (775)	64.90 (65.08)	4.05 (3.90)	6.95 (7.23)
8B	Pd[P(<i>p</i> -tolyl) ₃] ₂ (CN)[OC- (CN)=C(CN) ₂]	262-265		66.9 (67.07)	4.95 (4.93)	6.3 (6.52)
9B	Pd(PPh ₃) ₂ (CH ₃)[OC(CN)= C(CN) ₂]	145-149	751 (764)	65.70 (66.02)	4.45 (4.35)	5.75 (5.50)
10A	Ir(PPh ₃) ₂ (CO)Cl(TCNEO)	235-237	908 (924)	55.4 (55.87)	3.25 (3.27)	6.10 (6.06)
11A	Ir(PPh ₃) ₂ (CO)Br(TCNEO)	223-224		53.4 (53.31)	2.85 (3.12)	5.6 (5.78)
12B	Ir(PPh ₃) ₂ (CO)[OC(CN)= C(CN) ₂]	203-205		58.9 (58.46)	3.55 (3.50)	4.9 (4.87)
13A	Rh(PPh ₃) ₂ (CO)Cl(TCNEO)	210-215	823	61.9 (61.85)	3.75 (3.62)	6.45 (6.71)

^a Dichloroethane solution, ca. 5.10⁻³ M. ^b Complexes 1A, 2A, and 3A from ref 4.

Table II. Selected Infrared Bands^a

No.	Compd ^b	$\nu(\text{C}\equiv\text{N})$		$\nu(\text{C}=\text{C})$	$\nu(\text{C}-\text{O})$ [$\nu(\text{C}\equiv\text{O})$]
		CC≡N	MC≡N		
1A	Pt(AsPh ₃) ₂ (TCNEO)	2220 m			1070 m
2A	Pt(PPh ₃) ₂ (TCNEO)	2220 m			1070 m
2B	Pt(PPh ₃) ₂ (CN)[OC(CN)= C(CN) ₂]	2220 m	2140 m	1595 s	
		2185 m			
3A	Pt[P(<i>p</i> -tolyl) ₃] ₂ (TCNEO)	2220 m			1075 m
3B	Pt[P(<i>p</i> -tolyl) ₃] ₂ (CN)[O- C(CN)=C(CN) ₂]	2200 m	2140 m	1600 s	
		2180 m			
4B	Pt(PPh ₃ Me) ₂ (CN)[OC(CN)= C(CN) ₂]	2200 m	2140 w-m	1590 s	
		2180 m			
5B	Pt(PEt ₃) ₂ (CN)[OC(CN)= C(CN) ₂]	2200 m	2140 w-m	1600 s	
		2180 m			
6B	Pt(PPh ₃) ₂ (CH ₂ C ₆ H ₅)[OC(CN)= (CN) ₂]	2230 m		1610 s	
		2190 m			
7B	Pd(PPh ₃) ₂ (CN)[OC(CN)= C(CN) ₂]	2200 m	2140 w-m	1600 s	
		2180 m			
8B	Pd[P(<i>p</i> -tolyl) ₃] ₂ (CN)[OC(CN)= C(CN) ₂]	2200 m	2140 w-m	1600 s	
		2190 m		1590 s	
		2180 m			
9B	Pd(PPh ₃) ₂ (CH ₃)[OC(CN)= C(CN) ₂]	2220 m		1600 s	
		2190 m			
10A	Ir(PPh ₃) ₂ (CO)Cl(TCNEO)	2220 m			1080 m
					[2050 s]
11A	Ir(PPh ₃) ₂ (CO)Br(TCNEO)	2218 m			1075 m
					[2050 s]
12B	Ir(PPh ₃) ₂ (CO)[OC(CN)= C(CN) ₂]	2230 m		1610 s	[2000 s]
		2200 m			
13A	Rh(PPh ₃) ₂ (CO)Cl(TCNEO)	2200 m			1080 m
					[2080 s]
	[NEt ₄] ⁺ [OC(CN)=C(CN) ₂] ⁻	2220 m		1600 s	
		2190 m			
	[AsPh ₄] ⁺ [OC(CN)=C(CN) ₂] ⁻	2215 m		1595 s	
		2195 m			

^a Nujol or hexachlorobutadiene mull-NaCl or -KBr, cm⁻¹ (±5). ^b Complexes 1A, 2A, and 3A from ref 4.

observed after 15 min, and eventually a black tar appeared. Analogous behavior occurred for [Ir(PPh₃)₂(CO)Br] and [Rh(PPh₃)₂(CO)Cl]. With boiling benzene as the solvent, in

contrast, it was possible to isolate the cyclic type A complexes [Ir(PPh₃)₂(CO)X(TCNEO)] (X = Cl, Br) (10A, 11A) and [Rh(PPh₃)₂(CO)Cl(TCNEO)] (13A).

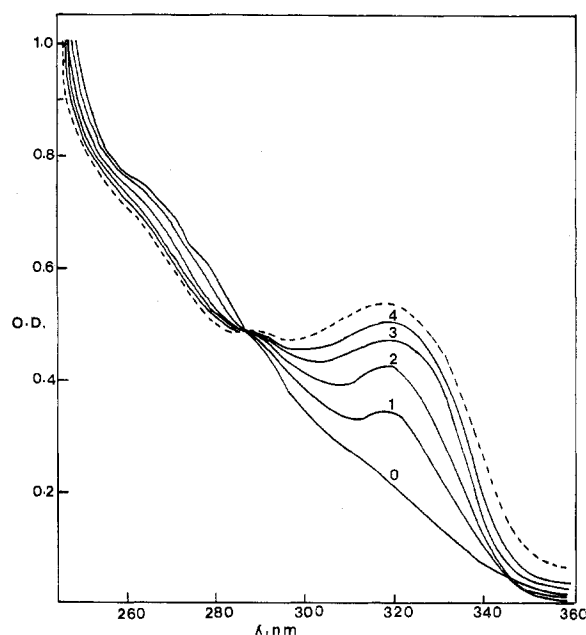
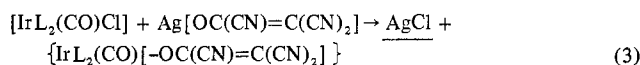


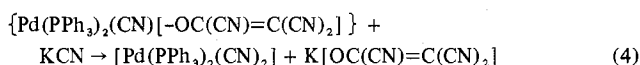
Figure 1. Spectra changes for a 1×10^{-4} M solution of $[\text{Pt}(\text{PPh}_3)_2(\text{TCNEO})]$ irradiated at 280 nm in CH_2Cl_2 . Curves 0, 1, 2, 3, and 4 were recorded after 0, 10, 20, 30, and 40 minutes, respectively. Dashed line = $\text{Ag}[\text{OC}(\text{CN})=\text{C}(\text{CN})_2]$.

Reactions of TCNEO with several other iridium and rhodium substrates gave materials which we were not able to purify.

While in a mechanistic sense tricyanoethenolato complexes are obtained indirectly from reactions of noble metal substrates and tetracyanoethylene oxide, they may be prepared directly via metathesis wherein a halide ligand is displaced by the tricyanoethenolato anion. Vaska's complex, $[\text{Ir}(\text{PPh}_3)_2(\text{CO})\text{Cl}]$, reacted with the silver salt of tricyanoethenol (eq 3) in dichloroethane and gave a 70% yield cyanoethenola-



toiridium(I) complex, **12B**. Tricyanoethenolato complexes **6B** and **9B** were also obtained by metathesis manner from $[\text{Pd}(\text{PPh}_3)_2(\text{CH}_3)\text{I}]$ and $[\text{Pt}(\text{PPh}_3)_2(\text{benzyl})\text{Cl}]$. Spectral comparisons of these directly obtained tricyanoethenolato complexes with those which were obtained from thermal isomerization of the cyclic type A complexes corroborated the idea that the isomerization products contain the tricyanoethenolato moiety. Evidence that the type B complexes prepared from TCNEO contain the coordinated tricyanoethenolato anion was obtained by the displacement reaction shown in eq 4. The displaced tricyanoethenolato anion was



precipitated with the Ph_4As^+ cation and the salt was identified by comparison with an authentic sample.

Reactivity of the cyclic type A compounds was briefly examined. Thus, $[\text{Pt}(\text{PPh}_3)_2(\text{TCNEO})]$ reacted with cyanide ion to give $[\text{Pt}(\text{PPh}_3)_2(\text{CN})_2]$. Electrophilic agents such as HCl and HCN also cleaved the ring to give $[\text{Pt}(\text{PPh}_3)_2\text{X}_2]$ ($\text{X} = \text{Cl}, \text{CN}$).

(2) Photochemistry of Cyclic $[\text{Pt}(\text{PPh}_3)_2(\text{TCNEO})]$. Irradiation at 280 nm of a deoxygenated solution of $[\text{Pt}(\text{PPh}_3)_2(\text{TCNEO})]$ (cyclic isomer **2A**) in CH_2Cl_2 induced the spectral change shown in Figures 1 and 2. Removal of the solvent, followed by crystallization of the crude product gave a yellow-brown solid. The infrared spectrum in Nujol mull showed bands in the region $1550\text{--}2250 \text{ cm}^{-1}$ at 1600, 2160,

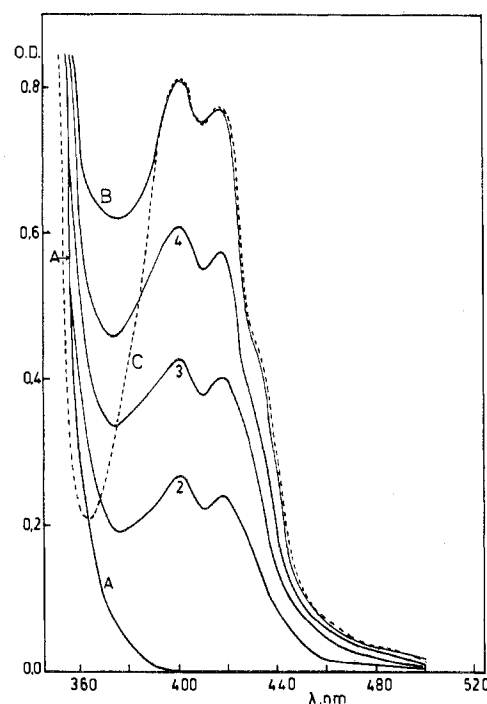


Figure 2. Spectra of 4.5×10^{-3} M solutions in CH_2Cl_2 of: A, $[\text{Pt}(\text{PPh}_3)_2(\text{TCNEO})]$; B, $[\text{Pt}(\text{PPh}_3)_2(\text{CN})[\text{OC}(\text{CN})=\text{C}(\text{CN})_2]]$; C, $\text{Ag}[\text{OC}(\text{CN})=\text{C}(\text{CN})_2]$. Curves 2, 3, and 4: spectra of a 4.5×10^{-3} solution in CH_2Cl_2 of $[\text{Pt}(\text{PPh}_3)_2(\text{TCNEO})]$ after 2, 3, and 4 h, respectively, of irradiation at 280 nm.

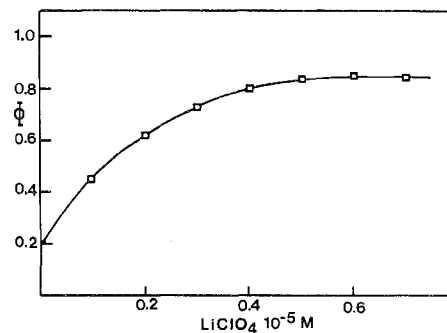


Figure 3. Effect of LiClO_4 on the quantum yield of $[\text{Pt}(\text{PPh}_3)_2(\text{CN})[\text{OC}(\text{CN})=\text{C}(\text{CN})_2]]$ formation in CH_2Cl_2 . Irradiation wavelength was 280 nm.

2200, and 2220 cm^{-1} . This product, which was identified by comparison with an authentic sample as the open isomer $[\text{Pt}(\text{PPh}_3)_2(\text{CN})[\text{OC}(\text{CN})=\text{C}(\text{CN})_2]]$ (**2B**), had been formed by photochemical isomerization in one step as indicated by the maintenance of the isobestic point during the photolysis (Figure 1). When $[\text{Pt}(\text{AsPh}_3)_2(\text{TCNEO})]$ or $[\text{Pt}[\text{P}(p\text{-tolyl})_3]_2(\text{TCNEO})]$ were used, the same type of products were obtained indicating that the same photochemical pattern was operative and it is unaffected by the basicity of the coordinated ligands. The quantum yield, at variance, was found to be solvent dependent, and the values are 0.14, 0.20, and 0.85 for CHCl_3 , CH_2Cl_2 , and $\text{C}_2\text{H}_5\text{OH}$. This result, associated to the effect of ionic strength on the quantum yield (Figure 3), could indicate that the isomerization reaction proceeds through a polar transition state.

Experimental Section

(1) Materials and Instrumentation. The complexes $[\text{Pt}(\text{AsPh}_3)_4]$,⁵ $[\text{Pt}(\text{PPh}_3)_4]$,⁶ $[\text{Pt}[\text{P}(p\text{-tolyl})_3]_3]$,⁷ $[\text{Pt}(\text{PPh}_2\text{Me})_4]$,⁸ $[\text{Pt}(\text{CO})_2(\text{PPh}_3)_2]$,⁸ $[\text{Pd}(\text{PPh}_3)_4]$,⁹ $[\text{Pd}[\text{P}(p\text{-tolyl})_3]_4]$,⁷ $[\text{Ir}(\text{PPh}_3)_2(\text{CO})\text{Cl}]$,¹⁰ $[\text{Pd}(\text{PPh}_3)_2(\text{CH}_3)\text{I}]$,¹¹ $[\text{Pt}(\text{PPh}_3)_3(\text{CH}_2\text{C}_6\text{H}_5)\text{Cl}]$,¹² $[\text{Pt}(\text{PPh}_3)_2(\text{TCNEO})]$ (cyclic isomer, type A),⁴ and $[\text{Pt}(\text{AsPh}_3)_2(\text{TCNEO})]$ (cyclic isomer, type A)⁴ were prepared as reported in literature. The silver salt of

percyanoethenolate anion, $\text{Ag}[\text{OC}(\text{CN})=\text{C}(\text{CN})_2]$, was synthesized as previously reported,¹³ as was tetracyanooxirane.¹⁴

Infrared spectra were recorded on Perkin-Elmer 457 or 323 spectrophotometers using Nujol and hexachlorobutadiene mulls. Ultraviolet spectra were monitored using a Perkin-Elmer 157 P spectrometer. Molecular weights were determined on a Mecrolab 302 vapor pressure osmometer.

Irradiation Procedure. Radiation of 280 nm was obtained using a Hanau Q400 lamp associated with an interference double filter. The reaction was carried out in a standard cell (1-cm thickness, about 3 mL of volume) thermostated at 20 °C. The solutions were deoxygenated either by nitrogen bubbling or by the freeze-pump-thaw technique and handled under a nitrogen atmosphere. The quantum yields were calculated from the linear plot of DA (difference in absorbance between irradiated and not irradiated solutions) vs. irradiation time. The intensities of the incident light were measured using a ferricoxalate actinometer before and after each photochemical run.

For all the new complexes synthesized, elemental analysis, molecular weight, melting point, and significant infrared bands are reported in Tables I and II. All the reactions were carried out in nitrogen atmosphere.

(II) Preparations. (A) Reactions of TCNEO with Pt(0), Pd(0), Rh(I), and Ir(I) Substrates. (1) $\{\text{Pt}(\text{PPh}_3)_2(\text{TCNEO})\}$ (2A). Dicarboxylbis(triphenylphosphine)platinum(0) (0.38 g, 0.5 mmol) was dissolved at room temperature in 50 mL of CH_2Cl_2 . A slight excess of tetracyanoethylene oxide (0.1 g, 0.7 mmol) was added and the mixture was stirred for 0.5 h. Methanol (20 mL) was added and then CH_2Cl_2 was removed under reduced pressure until the complex precipitated. Recrystallization of the yellow solid from $\text{CH}_2\text{Cl}_2/\text{CH}_3\text{OH}$ afforded 0.4 g (90%) of 2A.

(2) $\{\text{Pt}(\text{PPh}_2\text{Me})_2(\text{CN})[\text{OC}(\text{CN})=\text{C}(\text{CN})_2]\}$ (4B). $\{\text{Pt}(\text{PPh}_2\text{Me})_4\}$ (2.25 g, 3.0 mmol) and TCNEO (0.432 g, 3.0 mmol) were dissolved in 20 mL of anhydrous THF. The solution was stirred at room temperature for 30 min. After removal of the solvent, the residue was dissolved in methanol and precipitated with water. The yellow solid, which was filtered and dried under vacuum, was obtained in 65% yield.

(3) $\{\text{Pd}(\text{PPh}_3)_2(\text{CN})[\text{OC}(\text{CN})=\text{C}(\text{CN})_2]\}$ (7B). $\{\text{Pd}(\text{PPh}_3)_4\}$ (3.46 g, 3.0 mmol) was dissolved in 50 mL of anhydrous THF. TCNEO (0.57 g, 4.0 mmol) was added and the solution was stirred for 30 min to give a yellow precipitate in a brown solution. Addition of hexane gave a yellow solid which was filtered, dried under vacuum, and crystallized from $\text{CHCl}_3/\text{hexane}$ (80%).

(4) $\{\text{Pd}[\text{P}(p\text{-tolyl})_3]_2(\text{CN})[\text{OC}(\text{CN})=\text{C}(\text{CN})_2]\}$ (8B). $\{\text{Pd}[\text{P}(p\text{-tolyl})_3]_3\}$ (3.05 g, 3.0 mmol) was dissolved in dry benzene and TCNEO (0.57 g, 4.0 mmol) was added to the solution. The mixture was stirred for 30 min at room temperature, the solvent was evaporated to small volume, and ethanol was added. The yellow solid collected by filtration and washed with ethanol and petroleum ether (60%).

(5) $\{\text{Ir}(\text{PPh}_3)_2(\text{CO})\text{Cl}(\text{TCNEO})\}$ (Cyclic Isomer, 10A). TCNEO (0.216 g, 1.5 mmol) was added to a solution of $\{\text{Ir}(\text{PPh}_3)_2(\text{CO})\text{Cl}\}$ (0.781 g, 1 mmol) in 50 mL of boiling benzene. On cooling, a pale yellow solid precipitated. Methanol was added, and the precipitate was filtered and crystallized from $\text{CHCl}_3/\text{MeOH}$ (60%).

(6) $\{\text{Ir}(\text{PPh}_3)_2(\text{CO})\text{Br}(\text{TCNEO})\}$ (Cyclic Isomer, 11A). The compound $\{\text{Ir}(\text{PPh}_3)_2(\text{CO})\text{Br}\}$ (0.41 g, 0.5 mmol) was dissolved in 80 mL of boiling benzene. To this solution was added 10 mL of boiling benzene containing 0.072 g (0.5 mmol) of TCNEO. The solution was stirred at reflux for 1 h. A brown precipitate which formed was removed by filtration (0.2 g, 35%) and recrystallized from dichloromethane/hexane.

(7) $\{\text{Rh}(\text{PPh}_3)_2(\text{CO})\text{Cl}(\text{TCNEO})\}$ (Cyclic Isomer, 13A). To a 50-mL solution of $\{\text{Rh}(\text{PPh}_3)_2(\text{CO})\text{Cl}\}$ (0.35 g, 0.50 mmol) in benzene at reflux was added 10 mL of benzene containing TCNEO (0.072 g, 0.50 mmol). The orange precipitate, which formed as the solution was stirred, was collected by filtration (0.34 g, 75%).

(B) Exchange Reactions. (1) $\{\text{Pt}(\text{PEt}_3)_2(\text{CN})[\text{OC}(\text{CN})=\text{C}(\text{CN})_2]\}$ (5B). An excess of PEt_3 (0.4 mL) was added to a $\text{CH}_2\text{Cl}_2/\text{Et}_2\text{O}$ solution of $\{\text{Pt}(\text{PPh}_3)_2(\text{TCNEO})\}$ (2A) (0.867 g, 1.0 mmol) at room temperature. A yellow solution was immediately obtained. This was evaporated to dryness, and the residue was washed several times with Et_2O to give a yellow solid (75%).

(2) $\{\text{Pt}(\text{PPh}_2\text{Me})_2(\text{CN})[\text{OC}(\text{CN})=\text{C}(\text{CN})_2]\}$ (4B). Excess of PPh_2Me (0.9 mL) was added to a suspension of $\{\text{Pt}(\text{AsPh}_3)_2(\text{TCNEO})\}$ (1A) (1.902 g, 2.0 mmol) in benzene at room temperature.

From the solution an oil separated. After several washings with hexane to eliminate the excess PPh_2Me , an off-white solid was obtained. This was washed with hexane and ethyl ether and dried under vacuum (90%). This complex was found to be identical with the compound obtained by direct reaction of $\{\text{Pt}(\text{PPh}_2\text{Me})_4\}$ and TCNEO, as above described.

(C) Thermal Rearrangements. (1) $\{\text{Pt}[\text{P}(p\text{-tolyl})_3]_2(\text{TCNEO})\}$, $\{\text{Pt}[\text{P}(p\text{-tolyl})_3]_2(\text{TCNEO})\}$ (3A) (0.20 g) was suspended in 5 mL of ethanol. The suspension was heated in a sealed tube with stirring. At 150 °C the solid dissolved to give a yellow solution. On cooling a yellow solid separated in almost quantitative yield. This compound was identified as the open isomer $\{\text{Pt}[\text{P}(p\text{-tolyl})_3]_2(\text{CN})[\text{OC}(\text{CN})=\text{C}(\text{CN})_2]\}$ (3B) (90%). Use of less polar solvents gave a mixture of the two isomers.

(2) $\{\text{Pt}(\text{PPh}_3)_2(\text{TCNEO})\}$. A suspension of the complex (0.2 g) in 3 mL of ethanol was heated for 2 h at 170 °C in a sealed tube. When the solution was allowed to cool to room temperature a yellow solid separated. This was identified as $\{\text{Pt}(\text{PPh}_3)_2(\text{CN})[\text{OC}(\text{CN})=\text{C}(\text{CN})_2]\}$.

(D) Tricyanoethenolate Complexes via Metathesis. (1) $\{\text{Ir}(\text{PPh}_3)_2(\text{CO})[\text{OC}(\text{CN})=\text{C}(\text{CN})_2]\}$ (12B). To a solution of $\{\text{Ir}(\text{PPh}_3)_2(\text{CO})\text{Cl}\}$ (1.56 g, 2.0 mmol) in 50 mL of 1,2-dichloroethane was added silver tricyanoethenolate $\text{Ag}[\text{OC}(\text{CN})=\text{C}(\text{CN})_2]$ (0.451 g, 2.0 mmol). The solution was stirred for 15 min at 60 °C and AgCl precipitated. After cooling, AgCl was filtered, and addition of hexane to the solution gave a bright yellow solid, which was recrystallized from benzene/ethanol (70%).

(2) $\{\text{Pd}(\text{PPh}_3)_2(\text{CH}_3)[\text{OC}(\text{CN})=\text{C}(\text{CN})_2]\}$ (9B). To a solution of $\{\text{Pd}(\text{PPh}_3)_2(\text{CH}_3)\text{I}\}$ (0.772 g, 1.0 mmol) in 50 mL of 1,2-dichloroethane was added $\text{Ag}[\text{OC}(\text{CN})=\text{C}(\text{CN})_2]$ (0.226 g, 1.0 mmol). The resulting suspension was refluxed for 15 min. Silver iodide was removed from the cooled solution. Addition of *n*-hexane to the filtrate caused a yellow solid to precipitate. It was filtered and washed with methanol and diethyl ether (95%).

(3) $\{\text{Pt}(\text{PPh}_3)_2(\text{CH}_2\text{C}_6\text{H}_5)[\text{OC}(\text{CN})=\text{C}(\text{CN})_2]\}$ (6B). To $\{\text{Pt}(\text{PPh}_3)_2(\text{CH}_2\text{C}_6\text{H}_5)\text{Cl}\}$ (0.845 g, 1.0 mmol) dissolved in 100 mL of 1,2-dichloroethane was added $\text{Ag}[\text{OC}(\text{CN})=\text{C}(\text{CN})_2]$ (0.266 g, 1 mmol). The solution was refluxed for 15 min and allowed to cool, and AgCl was removed. From the filtrate a yellow solid was obtained after addition of *n*-hexane. The product was filtered, washed with ethanol, and dried (85%).

(E) Reactivity of $\{\text{Pd}(\text{PPh}_3)_2(\text{CN})[\text{OC}(\text{CN})=\text{C}(\text{CN})_2]\}$ and $\{\text{Pt}(\text{PPh}_3)_2(\text{TCNEO})\}$. (1) $\{\text{Pd}(\text{PPh}_3)_2(\text{CN})[\text{OC}(\text{CN})=\text{C}(\text{CN})_2]\}$ + KCN . To a solution of $\{\text{Pd}(\text{PPh}_3)_2(\text{CN})[\text{OC}(\text{CN})=\text{C}(\text{CN})_2]\}$ (1.552 g, 2.0 mmol) in 75 mL of CH_2Cl_2 was added potassium cyanide (0.13 g, 2.0 mmol) dissolved in 75 mL of $\text{C}_2\text{H}_5\text{OH}$ containing 10 mL of H_2O . The clear solution became turbid. After 0.5 h CH_2Cl_2 was evaporated, and the solution was filtered, leaving a solid which was identified as $\{\text{Pd}(\text{PPh}_3)_2(\text{CN})_2\}$ (1.2 g) for comparison with an authentic sample. To the filtrate was added $[\text{AsPh}_4]\text{Cl}$ (2.0 mmol) in 25 mL of $\text{C}_2\text{H}_5\text{OH}$. After partial evaporation of the solvent a white solid was obtained (0.32 g) which was identified as $[\text{AsPh}_4][\text{OC}(\text{CN})=\text{C}(\text{CN})_2]$ by comparison with authentic sample.

(2) $\text{Pt}(\text{PPh}_3)_2(\text{TCNEO}) + \text{HX}$ (X = Cl, CN). The ring isomer $\{\text{Pt}(\text{PPh}_3)_2(\text{TCNEO})\}$ (2A) was dissolved in THF or benzene and HCN or HCl, respectively, was bubbled through the solution. *cis*- $\{\text{Pt}(\text{PPh}_3)_2\text{X}_2\}$ (X = Cl or CN) in almost quantitative yield was obtained, but no attempts to identify the organic moiety were made.

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Registry No. 1A, 53675-47-1; 2A, 53675-48-2; 2B, 63848-68-0; 3A, 53675-49-3; 3B, 63848-67-9; 4B, 63848-66-8; 5B, 63848-65-7; 6B, 63848-64-6; 7B, 63848-63-5; 8B, 63848-62-4; 9B, 63848-61-3; 10A, 63848-60-2; 11A, 63848-59-9; 12B, 63866-32-0; 13A, 63848-58-8; $\text{Pt}(\text{CO})_2(\text{PPh}_3)_2$, 15377-00-1; $\text{Pt}(\text{PPh}_2\text{Me})_4$, 27121-53-5; $\text{Pd}(\text{PPh}_3)_4$, 14221-01-3; $\text{Pd}[\text{P}(p\text{-tolyl})_3]_3$, 27903-26-0; $\text{Ir}(\text{PPh}_3)_2(\text{CO})\text{Cl}$, 15318-31-7; $\text{Ir}(\text{PPh}_3)_2(\text{CO})\text{Br}$, 15842-08-7; $\text{Rh}(\text{PPh}_3)_2(\text{CO})\text{Cl}$, 15318-33-9; $\text{Pd}(\text{PPh}_3)_2(\text{CH}_3)\text{I}$, 53228-65-2; $\text{Pt}(\text{PPh}_3)_2(\text{CH}_2\text{C}_6\text{H}_5)\text{Cl}$, 63902-72-7; $\text{Ag}[\text{OC}(\text{CN})=\text{C}(\text{CN})_2]$, 63848-57-7; $[\text{NEt}_4]^+[\text{OC}(\text{CN})=\text{C}(\text{CN})_2]^-$, 63833-71-6; $[\text{AsPh}_4]^+[\text{OC}(\text{CN})=\text{C}(\text{CN})_2]^-$, 63848-56-6.

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Contribution from the Institute of Physical and Chemical Research, Wako-shi, Saitama, 351 Japan

Studies on the Interaction of Isocyanide with Transition-Metal Complexes. 15.¹ New Type of Insertion Reactions of Isocyanide into Alkyliron Complexes

YASUHIRO YAMAMOTO* and HIROSHI YAMAZAKI

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Reactions of $\eta\text{-C}_5\text{H}_5\text{Fe}(\text{CO})(\text{CNC}_6\text{H}_{11})\text{CH}_2\text{R}$ ($\text{R} = \text{H}$, Ph , or $p\text{-ClC}_6\text{H}_4$) with $\text{C}_6\text{H}_{11}\text{NC}$ in THF or benzene at reflux produced the cyclic carbene complexes $\eta\text{-C}_5\text{H}_5\text{Fe}(\text{CO})[-\text{C}(=\text{NC}_6\text{H}_{11})\text{C}(\text{NHC}_6\text{H}_{11})=\text{C}(\text{R})\text{C}(\text{NHC}_6\text{H}_{11})-]$. The complexes having two different N substituents such as $\eta\text{-C}_5\text{H}_5\text{Fe}(\text{CO})[-\text{C}(=\text{NR}^1)\text{C}(\text{NHR}^2)=\text{C}(\text{R})\text{C}(\text{NHR}^1)-]$ ($\text{R} = \text{H}$ or Ph ; $\text{R}^1 = \text{C}_6\text{H}_{11}$; $\text{R}^2 = (\text{CH}_3)_3\text{C}$ or PhCH_2) and $\eta\text{-C}_5\text{H}_5\text{Fe}(\text{CO})[-\text{C}(=\text{NR}^1)\text{C}(\text{NHR}^1)=\text{C}(\text{R})\text{C}(\text{NHR}^2)-]$ ($\text{R} = \text{H}$; $\text{R}^1 = \text{C}_6\text{H}_{11}$; $\text{R}^2 = (\text{CH}_3)_3\text{C}$) were obtained from the reactions between $\eta\text{-C}_5\text{H}_5\text{Fe}(\text{CO})(\text{CNR}^2)\text{R}$ and R^1NC or between $\eta\text{-C}_5\text{H}_5\text{Fe}(\text{CO})[-\text{C}(=\text{NR}^1)\text{C}(\text{R})=\text{NR}^1]$ and R^2NC , respectively. Reaction of $\eta\text{-C}_5\text{H}_5\text{Fe}(\text{CO})[\text{CNC}(\text{CH}_3)_3]\text{CH}_3$ with *tert*-butyl isocyanide gave $\eta\text{-C}_5\text{H}_5\text{Fe}(\text{CO})[\text{CNC}(\text{CH}_3)_3][\text{C}(\text{CH}_3)=\text{NC}(\text{CH}_3)_3]$. $\eta\text{-C}_5\text{H}_5\text{Fe}(\text{CO})(\text{CNR})\text{C}_6\text{H}_4\text{X-}p$ ($\text{R} = \text{C}_6\text{H}_{11}$ or $(\text{CH}_3)_3\text{C}$; $\text{X} = \text{H}$ or Cl) reacted with $\text{C}_6\text{H}_{11}\text{NC}$ to give the trisimino complex $\eta\text{-C}_5\text{H}_5\text{Fe}(\text{CO})(\text{CNC}_6\text{H}_{11})[-\text{C}(=\text{NC}_6\text{H}_{11})\text{C}(=\text{NC}_6\text{H}_{11})\text{C}(\text{C}_6\text{H}_4\text{X-}p)=\text{NR}]$. This compound catalyzed polymerization of cyclohexyl isocyanide. The mechanism for the formation of cyclic carbene and trisimino complexes was discussed.

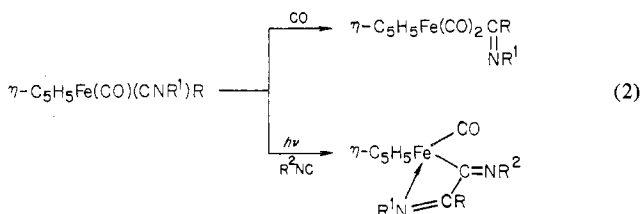
Introduction

It is well known that isocyanide coordinates to a variety of transition metals.² One of the current interests in the coordination chemistry of isocyanide has been focused on the insertion reaction.^{3,4} The reactions between isocyanides and transition metal alkyl complexes proceed with formation of the imino complexes (eq 1). Palladium⁵ and nickel⁶ alkyl



complexes underwent successive insertion of isocyanides to give the polyimino complexes. These multiple insertions are considered as an intermediate process of the coordinated polymerization of isocyanides catalyzed by transition metal complexes.⁷

Recently we have reported that $\eta\text{-C}_5\text{H}_5\text{Fe}(\text{CO})(\text{CNR}^1)\text{R}$ reacted with carbon monoxide to give an iminoacyl complex.⁸ When irradiated with a mercury lamp in the presence of isocyanide, this complex led to an insertion of two isocyanide molecules into an iron-carbon σ bond (eq 2). During our



extensive studies on these subjects we found that the thermal reactions of $\eta\text{-C}_5\text{H}_5\text{Fe}(\text{CO})(\text{CNR}^1)\text{CH}_2\text{R}$ with isocyanide gave the new bidentate carbene complexes which resulted from an insertion of two isocyanide molecules into a metal-carbon σ bond and from an unexpected insertion of the third isocyanide molecule into the C-H bond of an alkyl group rather

than into the iron-carbon σ bond. These reactions proceed with activation of the C-H bond induced by an insertion of isocyanide.

We wish to report the new type of insertion reactions of isocyanides. A preliminary account has appeared previously.¹⁰

Experimental Section

The preparation and handling of organoiron complexes were carried out in an atmosphere of nitrogen. Melting points were taken on a Mitamura melting point apparatus and are uncorrected. Infrared spectra were recorded on a Shimadzu IR-27G spectrometer. Proton NMR spectra were obtained on Varian HA-100B or JEOL C-60HL spectrometers, using tetramethylsilane as an internal reference. The mass spectra were measured on Nippondenshi Type JPS-1S mass spectrometer with a direct inlet system.

Materials. Isocyanides¹¹ were prepared by procedures described in the literature. The organoiron complexes $\eta\text{-C}_5\text{H}_5\text{Fe}(\text{CO})(\text{CNR})\text{CH}_2\text{C}_6\text{H}_4\text{X-}p$ ($\text{R} = \text{C}_6\text{H}_{11}$ or PhCH_2 ; $\text{X} = \text{H}$ or Cl),⁸ $\eta\text{-C}_5\text{H}_5\text{Fe}(\text{CO})[\text{CNC}(\text{CH}_3)_3]\text{R}$ ($\text{R} = \text{CH}_3$ ⁹ or Ph ¹²), $\eta\text{-C}_5\text{H}_5\text{Fe}(\text{CO})(\text{CNC}_6\text{H}_{11})\text{C}_6\text{H}_4\text{Cl-}p$,¹² $\eta\text{-C}_5\text{H}_5\text{Fe}(\text{CO})(\text{PPh}_3)\text{CH}_3$,¹³ $\eta\text{-C}_5\text{H}_5\text{Fe}(\text{CO})[-\text{C}(=\text{NC}_6\text{H}_{11})\text{C}(\text{CH}_3)=\text{NC}_6\text{H}_{11}]$,⁹ and $\eta\text{-C}_5\text{H}_5\text{Fe}(\text{CO})[-\text{C}(=\text{NC}_6\text{H}_{11})\text{C}(\text{CH}_3)=\text{NC}(\text{CH}_3)_3]$ ⁹ were prepared according to the literature methods.

Preparation of Cyclic Carbene Complexes. The representative examples are described below. Analytical data and physical properties of the carbene complexes are given in Tables I and II.

(a) $\eta\text{-C}_5\text{H}_5\text{Fe}(\text{CO})[-\text{C}(=\text{NC}_6\text{H}_{11})\text{C}(\text{NHC}_6\text{H}_{11})=\text{C}(\text{Ph})\text{C}(\text{NHC}_6\text{H}_{11})-]$ (**1**). A solution of $\eta\text{-C}_5\text{H}_5\text{Fe}(\text{CO})(\text{CNC}_6\text{H}_{11})\text{CH}_2\text{Ph}$ (0.35 g, 1.0 mmol) and $\text{C}_6\text{H}_{11}\text{NC}$ (0.44 g, 4 mmol) in benzene (30 mL) was refluxed for 25 h and the solvent was removed under reduced pressure. The residue was purified by chromatography on alumina. Elution with *n*-hexane gave a pale yellow solution. Workup of the solution gave the unreacted starting material (trace). Elution with $\text{CH}_2\text{Cl}_2\text{-THF}$ (10:1) gave a brown solution. Removal of the solvent and crystallization of the residue from $\text{CH}_2\text{Cl}_2\text{-}n\text{-hexane}$ at -30°C gave the title complex **1** (0.34 g, 60%).

(b) $\eta\text{-C}_5\text{H}_5\text{Fe}[-\text{C}(=\text{NC}_6\text{H}_{11})\text{C}(\text{NHC}_6\text{H}_{11})=\text{C}(\text{H})\text{C}(\text{NHC}_6\text{H}_{11})-]$ (**3**). From $\eta\text{-C}_5\text{H}_5\text{Fe}(\text{CO})(\text{PPh}_3)\text{CH}_3$. A mixture of $\eta\text{-C}_5\text{H}_5\text{Fe}$ -