

**Preparation and Characterization of Dinuclear and Trinuclear
Metal Complexes, [(PPh₃)₂(CO)M(μ-E)M(CO)(PPh₃)₂]X₂
(M=Rh, Ir; E=Pyrazine, 4,4'-Bipyridyl, X=SO₃CF₃;
E=Pd(CN)₄, Pt(CN)₄, X=none)**

Jaejung Ko*, Myunggab Lee, Moonsik Kim, and Sang Ook Kang†

Department of Chemical Education, Korea National University of Education, Chungbuk 363-791

†*Department of Chemistry, College of Natural Sciences, Korea University, Choongnam 339-800*

Received October 30, 1991

Hydrocarbon solution of (PPh₃)₂(CO)MOSO₂CF₃ (M=Rh, Ir) reacts rapidly with pyrazine or 4,4'-bipyridyl to yield dinuclear metal complexes [(PPh₃)₂(CO)M(μ-pyrazine)M(CO)(PPh₃)₂](SO₃CF₃)₂ (I: M=Rh; III: M=Ir) or [(PPh₃)₂(CO)M(μ-4,4'-bipyridyl)M(CO)(PPh₃)₂](SO₃CF₃)₂ (II: M=Rh; IV: M=Ir), respectively. Compounds I, II, III, and IV were characterized by ¹H-NMR, ¹³C-NMR, ³¹P-NMR, and infrared spectrum. Ethanol solution of (PPh₃)₂(CO)MOSO₂CF₃ (M=Rh, Ir) also reacts with (TBA)₂M'(CN)₄ (M'=Pd, Pt) to yield trinuclear metal complexes [(PPh₃)₂(CO)M-NCM'(CN)₂CN-M(CO)(PPh₃)₂] (V: M=Rh, M'=Pd; VI: M=Rh, M'=Pt; VII: M=Ir, M'=Pd; VIII: M=Ir, M'=Pt). The trinuclear metal complexes V, VI, VII, and VIII are bridged by the cyanide groups. The infrared spectrum of V, VI, VII, and VIII supports the presence of the bridged cyanide and terminal cyanide group.

Introduction

The preparation of three-dimensional metal complex hosts able to accommodate aromatic molecules is of great importance in both organic and inorganic chemistry¹. Recently, Robson and coworker² reported the design and construction of a new class of scaffolding-like materials comprising infinite polymer frameworks of 3D-linked molecular rods. Iwamoto and Nishimori³ have developed novel three-dimensional host structure from the Hofman-type Cd(NH₃)₂Ni(CN)₄. Although scaffolding-like materials and Hofman-type clathrate are shape specific, the flexible structural modification is quite difficult. Ogura and coworkers⁴ prepared a macrocyclic polynuclear complex [(en)Pd(4,4'-bpy)]₄(NO₃)₈ by constructing the inorganic host as a molecule. Such an approach is important because the structural design is easily controlled. This idea prompted us to prepare dinuclear metal complexes as a simple model. The dinuclear metal complexes are bridged by pyrazine, 4,4'-bipyridyl, and M(CN)₄ (M=Pd, Pt). The four bridging compounds show interesting features because they are able to control the size.

In this paper, we wish to report the formation of dinuclear and trinuclear metal complexes bridged by pyrazine, 4,4'-bipyridyl, and M(CN)₄.

Experimental Section

All manipulations of air-sensitive materials were carried out under an argon atmosphere with use of standard Schlenk or vacuum line technique or a Mebraun MB150 glovebox. ¹H-NMR, ¹³C-NMR, and ³¹P-NMR spectra were recorded on a Bruker WM-250 spectrometer in CDCl₃. Chemical shifts are given in parts per million relative to tetramethylsilane for ¹H and ¹³C-NMR spectra, 85% H₃PO₄ for ³¹P-NMR spectra. Cyclic voltammetry was carried out with a Potentiostat/Galvanostat Model 273 at a glassy-carbon electrode with an Ag/AgCl couple as a reference electrode and tetra-n-butyl-

ammonium perchlorate (TBAP) as an electrolyte in CH₃CN. IR spectra were obtained by using a Perkin-Elmer 1310 instrument. Conductivity measurement was conducted with an Industrial Instruments Model RC216B2. Elemental analyses were carried out at the Basic Science Research Center. Reagent grade tetrahydrofuran (THF) and benzene were distilled under argon from sodium-benzophenone ketyl. Dichloromethane was distilled under Ar from calcium hydride. (PPh₃)₂(CO)MCl (M=Rh, Ir)⁵. (PPh₃)₂(CO)MOSO₂CF₃ (M=Rh, Ir)⁶, K₂[Pt(CN)₄]·3H₂O⁷, K₂Pd(CN)₄, and (TBA)₂M(CN)₄⁸ (M=Pd, Pt; TBA=tetrabutylammonium) were prepared according to literature methods. Pyrazine and 4,4'-Bipyridyl were purchased from Aldrich. MCl₃·xH₂O (M=Rh, Ir) and K₂M'Cl₄ (M'=Pd, Pt) were purchased from Strem.

Preparation of [(CO)(PPh₃)₂Rh(μ-pyrazine)Rh(PPh₃)₂](SO₃CF₃)₂ (I). To a stirred benzene solution of (CO)(PPh₃)₂RhOSO₂CF₃ (0.44 g, 5.47 mmol) was added pyrazine (0.022 g, 2.73 mmol) in benzene (5 ml) dropwise. Upon addition of pyrazine, yellow product was precipitated out. The solution was stirred at room temperature for additional 1 hr. The yellow precipitate was filtered off and washed with benzene (2×5 ml) and hexane (5 ml). The bright yellow powder was recrystallized from 4 ml: 0.5 ml dichloromethane/hexane. The yield was 0.36 g (77.9%). mp. 256°C. IR (on pellet; cm⁻¹) 3018(w), 2004(s), 1582(w), 1473(s), 1428(s), 1412(s), 1304(m), 1272(s), 1257(s), 1245(sh), 1218(s), 1187(s), 1155(sh), 1146(s), 1132(s), 1092(s), 1070(w), 1022(s), 1008(w), 994(m), 811(s), 796(m), 742(s), 704(s), 692(s), 630(s), 612(w). Anal. Calcd. for C₈₀F₆H₆₄N₂O₈Rh₂S₂: C, 56.88; H, 3.82. Found: C, 57.00; H, 3.70.

Preparation of [(CO)(PPh₃)₂Rh(μ-4,4'-bipyridyl)Rh(PPh₃)₂](SO₃CF₃)₂ (II). To a stirred benzene (20 ml) solution of (CO)(PPh₃)₂RhOSO₂CF₃ (0.41 g, 5 mmol) was added 4,4'-bipyridyl (0.039 g, 2.5 mmol) in benzene (10 ml) dropwise. The yellow product was immediately precipitated out. The solution was stirred at room temperature for 1 hr. The yellow precipitate was filtered off and washed with ben-

zene (2×10 ml) and hexane (10 ml). The yellow powder was recrystallized by dichloromethane/hexane and dried *in vacuo*. The yield of II was 92%. mp. 262°C. IR (on pellet; cm^{-1}) 3018(w), 1995(s), 1600(m), 1474(s), 1429(s), 1409(m), 1302(w), 1268(vs), 1245(sh), 1219(s), 1182(w), 1160(sh), 1145(s), 1092(s), 1071(w), 1024(s), 994(m), 818(s), 746(s), 704(s), 692(vs), 631(s), 612(w). Anal. Calcd. for $\text{C}_{86}\text{F}_6\text{H}_{68}\text{N}_2\text{O}_8\text{Rh}_2\text{S}_2$: C, 58.51; H, 3.88. Found: C, 58.82; H, 3.59.

Preparation of [(CO)(PPh₃)₂Ir(μ-pyrazine)Ir(PPh₃)₂(CO)](SO₃CF₃)₂ (III). To a stirred benzene (25 ml) solution of (CO)(PPh₃)₂IrOSO₂CF₃ (0.5 g, 5.60 mmol) was added pyrazine (0.22 g, 2.7 mmol) in benzene (10 ml). Upon addition of pyrazine, the yellow powder was immediately precipitated out. After stirring the solution for 1 hr, the yellow precipitate was filtered off and washed with benzene (2×15 ml) and hexane (10 ml). The pure product was obtained by recrystallization of the powder with use of a mixture of dichloromethane (5 ml) and hexane (1 ml). The yield of III was 74.7%. mp. 265°C. IR (on pellet; cm^{-1}) 3022(w), 1997(s), 1585(w), 1476(m), 1431(s), 1416(m), 1308(w), 1275(s), 1259(s), 1248(sh), 1220(m), 1190(w), 1151(s), 1138(s), 1097(s), 1070(w), 1028(s), 1012(w), 998(m), 811(w), 805(m), 750(s), 695(s), 635(s), 607(w). Anal. Calcd for $\text{C}_{80}\text{F}_6\text{H}_{68}\text{N}_2\text{O}_8\text{Ir}_2\text{S}_2$: C, 51.44; H, 3.45. Found: C, 50.88; H, 3.55.

Preparation of [(CO)(PPh₃)₂Ir(μ-4,4'-bipyridyl)Ir(PPh₃)₂(CO)](SO₃CF₃)₂ (IV). The same procedure was taken as described in the preparation of [(CO)(PPh₃)₂Ir(μ-pyrazine)Ir(PPh₃)₂(CO)](SO₃CF₃)₂. The isolated yield was 83%. mp. 271°C. IR (on pellet; cm^{-1}) 3023(w), 1985(s), 1608(m), 1477(s), 1430(s), 1411(m), 1305(sh), 1262(vs), 1247(sh), 1221(s), 1182(w), 1162(sh), 1145(s), 1093(s), 1070(w), 1027(s), 996(m), 821(s), 748(s), 704(sh), 694(vs), 638(s), 608(w). Anal. Calcd. for $\text{C}_{86}\text{F}_6\text{H}_{68}\text{N}_2\text{O}_8\text{Ir}_2\text{S}_2$: C, 53.14; H, 3.53. Found: C, 53.12; H, 3.64.

Preparation of [(CO)(PPh₃)₂RhNCPd(CN)₂CNRh(PPh₃)₂(CO)](SO₃CF₃)₂ (V). To a stirred ethanol solution of (CO)(PPh₃)₂RhOSO₂CF₃ (0.30 g, 3.78 mmol) (TBA)₂Pd(CN)₄ (0.13 g, 1.87 mmol) in ethanol (10 ml) was added dropwise. The yellow precipitate was immediately formed. After stirring the solution for 1 hr, the yellow precipitate was filtered off and washed with ethanol (10 ml) and ether (10 ml). The yellow product was dried *in vacuo*. The yield of V was 56%. mp. 245°C. IR (on pellet; cm^{-1}) 3022(m), 2150(s), 2130(sh), 1990(s), 1580(w), 1475(s), 1428(s), 1330(w), 1308(w), 1258(w), 1185(m), 1158(w), 1092(s), 1070(w), 1024(m), 995(m), 804(br, w), 748(s), 703(sh), 692(s), 616(w). Anal. Calcd for $\text{C}_{78}\text{H}_{60}\text{N}_4\text{O}_2\text{P}_4\text{Rh}_2\text{Pd}$: C, 61.58; H, 3.97. Found: C, 61.15; H, 3.60.

Preparation of (CO)(PPh₃)₂RhNCPt(CN)₂CNRh(PPh₃)₂(CO) (VI). The synthetic procedure of VI was same as that of V. The yield of VI was 78%. mp. 120°C. IR (on pellet; cm^{-1}) 3025(m), 2160(s), 2140(st.), 1990(s), 1585(w), 1572(w), 1479(s), 1433(s), 1330(w), 1310(w), 1270(br, m), 1185(m), 1160(m), 1097(s), 1072(w), 1029(w), 1000(m), 850(br, m), 810(br, w), 748(s), 710(sh), 697(s), 640(w), 620(w). Anal. Calcd for $\text{C}_{78}\text{H}_{60}\text{N}_4\text{O}_2\text{PtRh}_2$: C, 58.18; H, 3.76. Found: C, 57.68; H, 3.77.

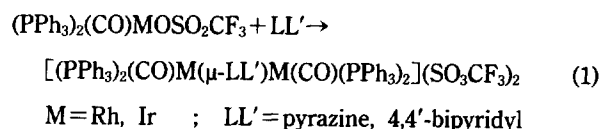
Preparation of (CO)(PPh₃)₂IrNCPd(CN)₂CNIr(PPh₃)₂(CO) (VII). The synthetic procedure of VII was same as that of V. The yield of VII was 61%. mp. 195°C. IR (on pellet; cm^{-1}) 3020(m), 2155(s), 2130(sh), 1972(s), 1580(w), 1564(w), 1473(s), 1427(s), 1328(w), 1305(w), 1255(w), 1180(m), 1155(m), 1092(s), 1070(m), 1025(m), 995(m), 850(br, w), 742(s), 705(s),

692(s), 620(w), 605(w). Anal. Calcd for $\text{C}_{78}\text{H}_{60}\text{N}_4\text{O}_2\text{PdIr}_2$: C, 55.11; H, 3.56. Found: C, 55.06; H, 3.14.

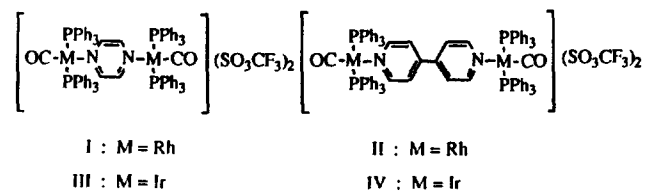
Preparation of (CO)(PPh₃)₂IrNCPt(CN)₂CNIr(PPh₃)₂(CO) (VIII). The synthetic procedure of VIII was same as that of V. The yield of VIII was 88%. mp. 164°C. IR (on pellet; cm^{-1}) 3025(m), 2158(s), 2130(sh), 1977(s), 1585(w), 1570(w), 1480(s), 1433(s), 1332(w), 1308(w), 1280(br, w), 1187(m), 1160(w), 1099(s), 1075(w), 1030(w), 1000(m), 850(br, w), 750(s), 712(s), 695(s), 612(m). Anal. Calcd for $\text{C}_{78}\text{H}_{60}\text{N}_4\text{O}_2\text{PtIr}_2$: C, 52.37; H, 3.38. Found: C, 52.26; H, 3.36.

Results and Discussion

The pyrazine and 4,4'-bipyridyl bridged dinuclear metal complexes have been prepared according to Eq. (1).



The addition of pyrazine or 4,4'-bipyridyl to a stirred benzene solution of (PPh₃)₂(CO)MOSO₂CF₃ (M = Rh, Ir) affords a yellow precipitate. The resulting yellow compounds, [(PPh₃)₂(CO)M(μ-pyrazine)M(CO)(PPh₃)₂](SO₃CF₃)₂ and [(PPh₃)₂(CO)M(μ-4,4'-bipyridyl)M(CO)(PPh₃)₂](SO₃CF₃)₂ were isolated air-stable, crystalline solids in high yield, as shown below.



The four-coordinated rhodium(I) complex Rh(CO)L₂X (L = PPh₃, PCy₃, PMe₂Ph; X = OClO₃, OSO₂CF₃) was known to react with pyridine⁹, 2-methylpyridine⁹, quinine⁹, and imidazoles¹⁰ to give four-coordinate cations of general form [Rh(CO)L₂N]⁺ (N = pyridine, 2-methylpyridine, quinine, imidazoles). In this reaction, the ligands containing nitrogen atom are considered to coordinate a metal center by converting a weak Rh-O bond into anion. It is interesting to note that perchlorate and trifluoromethanesulfonate ligands in Rh(CO)(PPh₃)₂X is so labile that they are readily replaced by various solvent molecules¹¹. Accordingly, it is reasonable to expect that the reaction of pyrazine or 4,4'-bipyridyl containing two nitrogen atoms with Rh(CO)(PPh₃)₂X proceeds to give dinuclear metal complexes bridged by bifunctional ligands.

The structure of compounds I-IV were deduced from their NMR, IR spectra, conductivity measurement, and elemental analyses. The ¹H-NMR spectrum of II taken in CDCl₃ at room temperature exhibits resonance of bipyridyl at δ 7.73 and δ 7.10 (see Figure 1 and Table 1).

It's pattern consists of two doublet due to the spin coupling between the two hydrogens. The values are very close to those of the compound [(en)Pd(4,4'-bpy)]₄(NO₃)₈ reported by Fujita and coworker⁴. The carbonyl and 4,4'-bpy ligands are presumed to be in a *trans* position in order to augment the electronic effect of π bonding¹². The ¹³C-NMR spectrum of II taken in CDCl₃ exhibits three peaks of bipyridyl at

Table 1. ^1H -NMR, ^{13}C -NMR, and ^{31}P -NMR Data^a

Compound	^1H chemical shift, δ		^{13}C chemical shift, δ	^{31}P chemical shift, δ
	H_a^b	H_β^c		
I	7.90		149.72	29.05 (d, $J_{\text{Rh-P}} = 127.58$ Hz)
II	7.73 (d, $J = 5$ Hz)	7.10 (d, $J = 5$ Hz)	151.06 (C_α), 144.52 (C_γ), 123.54 (C_β)	29.27 (d, $J_{\text{Rh-P}} = 128.79$ Hz)
III	7.91		149.63	24.27
IV	7.70 (d, $J = 5$ Hz)	7.19 (d, $J = 5$ Hz)	149.92 (C_α), 144.19 (C_γ), 123.40 (C_β)	24.80

^aThe chemical shifts are measured in CDCl_3 . Doublet is abbreviated as d. The notation for singlet is omitted. ^b4,4'-bipyridyl proton next to nitrogen. ^c4,4'-pyridyl proton next to αH .

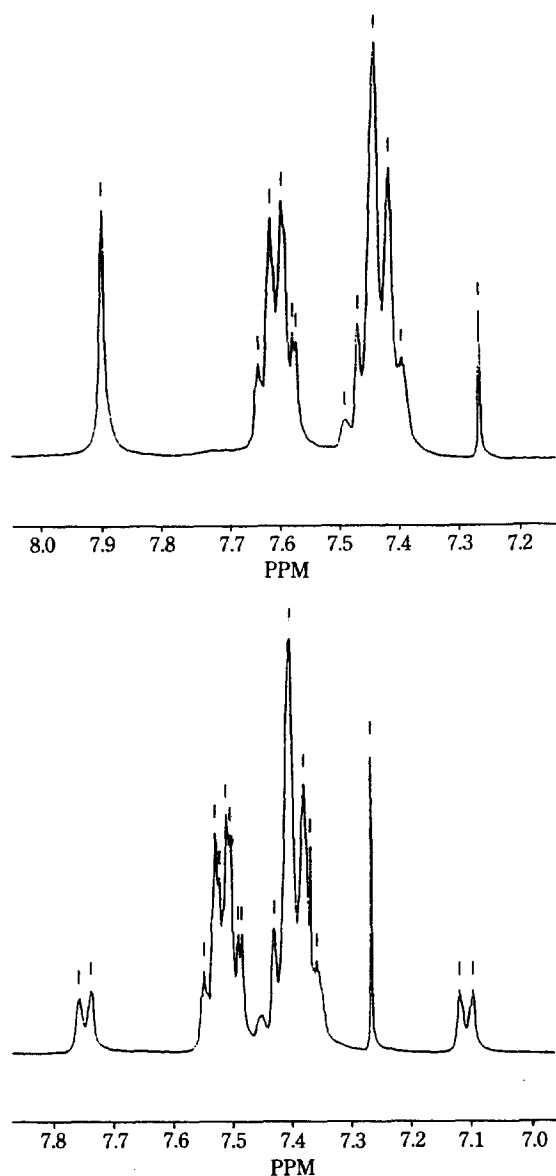


Figure 1. (a) ^1H -NMR spectrum of the complex I is GDCl_3 , (b) ^1H -NMR spectrum of the complex II in CDCl_3 .

δ 151.06, 144.52, and 123.54. The three peaks are assigned to the C_α , C_β and C_γ , respectively. The values are also close to those of the compound $[(\text{en})\text{Pd}(4,4'\text{-bpy})_4(\text{NO}_3)_8]$. In addition, many peaks are found in the region between δ 128 and δ 135, presumably due to the resonances of aromatic

Table 2. IR Data^a, Conductivity Measurement^b, and Cyclic Voltammetric Peak Potentials^c

Compound	IR frequency, cm^{-1}	Conductivity $\Lambda^{-1}\Omega^{-1}\text{mol}^{-1}\text{cm}^2$	CV peak potentials	
			$E_{a, \text{irrev.}}^d$	$E_{a, \text{rev.}}$
I	2004	157.2	1.47	2.12
II	1995	161.3	1.48	1.97
III	1997	155.8	1.45	2.10
IV	1985	159.1	1.46	1.95

^aOn pellet. ^bMeasured at a concentration of 0.001 M in CH_3CN . ^cScan rate = 200 mV/s unless otherwise noted. ^dThe anodic peak corresponds to the irreversible net one-electron reduction of these compounds.

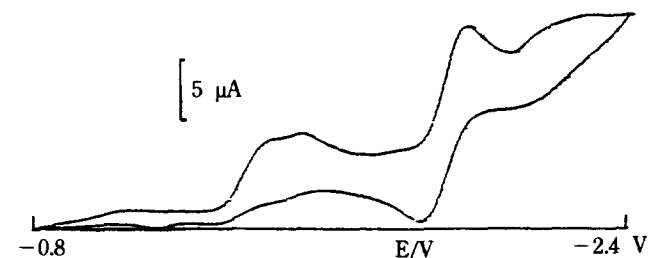


Figure 2. Cyclic voltammogram of II, 1 mM in $\text{CH}_3\text{CN}/0.1$ M $(n\text{-Bu})_4\text{NClO}_4$ at room temperature (scan rate: 50 mV/s; reference electrode: SCE).

carbons of triphenylphosphine. The ^{31}P -NMR spectrum of II exhibits one doublet at 29.27 ($J_{\text{Rh-P}} = 128.79$ Hz), indicating that two chemically equivalent triphenylphosphines are present. Thus, based on the spectroscopic data, the compound adapts highly symmetric geometry. The infrared spectrum of II on pellet (see Table 2) shows a strong absorption at 1995 cm^{-1} , due to the CO stretching mode.

It is interesting to note that the frequency of II is relatively high, in spite of the presence of the 4,4'-bipyridyl containing the nitrogen atom, compared with that of compounds $(\text{PPh}_3)_2(\text{CO})\text{RhCl}$ and $(\text{PPh}_3)_2(\text{CO})\text{RhOSO}_2\text{CF}_3$, which occur at 1960 and 1985 cm^{-1} , respectively. The relatively high value is presumed to be attributable to the dication. The conductivities of I-IV is in the region of 155-165 $\Lambda^{-1}\Omega^{-1}\text{mol}^{-1}\text{cm}^2$. The values show that the compounds are 1 : 2 electrolytes¹³.

The electrochemistry of II exhibits a quasi-reversible one-electron reduction in $\text{CH}_3\text{CN}/\text{TBAP}$ ($E_{1/2} = -1.97$ V; $i_d/i_a = 0.94$; $E_a - E_c = 142$ mV) and an irreversible one-electron reduction ($E_a = -1.48$ V) (see Figure 2). The potentials at which

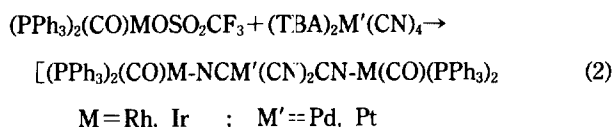
Table 3. IR Data for CN-Bridged Compounds

Compound	$\nu(\text{C}\equiv\text{N}), \text{cm}^{-1}$		$\nu(\text{CO}), \text{cm}^{-1}$
	B_{2u}	B_{3u}	
V	2130	2150	1990
VI	2140	2160	1990
VII	2130	2155	1972
VIII	2130	2158	1977
IX	2098	2112	1962
$[\text{Cp}_2\text{ZrNCPt}(\text{CN})_2\text{CN}]_2$	2144	2165	
$(\text{TBA})_2\text{Pd}(\text{CN})_4$		2108	
$(\text{TBA})_2\text{Pt}(\text{CN})_4$		2108	
$(\text{TBA})_2\text{Pt}(\text{CN}^{15})_4$		2081	

these processes occur are summarized in Table 2. On the other hand, the reduction of $(\text{PPh}_3)_2(\text{CO})\text{IrOSO}_2\text{CF}_3$ occurs at $E_a = -1.37$ V and the reversible reduction of bipyridyl occurs at $E_a = -1.79$ V and acetonitrile. Accordingly, one-electron reduction at $E_a = -1.48$ V may be interpreted to be attributable to the reduction of metal center. The quasireversible reduction at $E_{1/2} = -1.97$ V is interpreted to the reduction of ligand site.

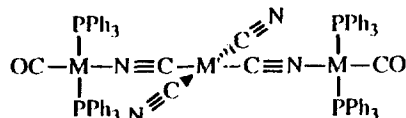
On view of the coordination of the ligands containing nitrogen to the complexes $(\text{PPh}_3)_2(\text{CO})\text{MOSO}_2\text{CF}_3$, it is quite reasonable to predict that the cyano group in the complexes can coordinate the complexes $(\text{PPh}_3)_2(\text{CO})\text{MOSO}_2\text{CF}_3$ ($M = \text{Rh}, \text{Ir}$). Indeed, the cyano group in the complexes $(\text{TBA})_2\text{M}'(\text{CN})_4$ ($M' = \text{Pd}, \text{Pt}$) was shown to coordinate the complexes.

The CN bridged trinuclear metal complexes have been prepared according to the general Eq. (2).



As the CN coordinated metal complexes, there are some examples demonstrating the basicity of transition metal coordinated cyanide ligand toward boron-containing Lewis acids. These compounds involve the formation of ligand-bridged adducts, such as $\text{Fe-CN} \rightarrow \text{BF}_3^{14}$. The cyanide in *trans*- $\text{PtH}(\text{CN})\text{L}_2$ ($L = \text{PEt}_3$) possesses a lone pair of electrons and reacts rapidly with $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ and ZnCl_2 in acetonitrile to give 2:1 adducts $\text{Cl}_2\text{M}(\text{NCNPtL}_2\text{H})_2^{15}$. It is well known that the rhodium(I) complex $\text{Rh}(\text{CO})(\text{PPh}_3)_2\text{OClO}_3$ is replaced by acetonitrile to give cationic complex, $[\text{Rh}(\text{CO})(\text{PPh}_3)_2\text{NCCH}_3]^+\text{ClO}_4^-$. Accordingly, we have decided to investigate the interaction of $(\text{TBA})_2\text{Pt}(\text{CN})_4$ with $(\text{PPh}_3)_2(\text{CO})\text{RhOSO}_2\text{CF}_3$. Indeed, the addition of $(\text{TBA})_2\text{Pd}(\text{CN})_4$ or $(\text{TBA})_2\text{Pt}(\text{CN})_4$ to a stirred ethanol solution of $(\text{PPh}_3)_2(\text{CO})\text{MOSO}_2\text{CF}_3$ affords an yellow powder.

The yellow compound, $(\text{PPh}_3)_2(\text{CO})\text{M}-\text{NCPd}(\text{CN})_2\text{CN}-\text{M}(\text{CO})(\text{PPh}_3)_2$ (V: $M = \text{Rh}$; VII: $M = \text{Ir}$), and $(\text{PPh}_3)_2(\text{CO})\text{M}-\text{NCPt}(\text{CN})_2\text{CN}-\text{M}(\text{CO})(\text{PPh}_3)_2$ (VI: $M = \text{Rh}$; VIII: $M = \text{Ir}$), were iso-



lated as air-stable yellow solid in a relatively high yield (see below).

Infrared spectroscopy was used to investigate a series of trinuclear metal complexes because of the sensitivity of ν (CN) to the nature of the group attached to the cyanide. The infrared spectrum of VI (see Table 3) shows two bands at 2140 and 2160 cm^{-1} in the cyanide region. The modes indicate that both terminal and bridging cyanide are present. In this case, group theory leads us to expect two IR-active bands since the local symmetry about the platinum metal would be D_{2h} and the CN vibrations span the representation $b_{2u} + b_{3u}$. The two C-N stretching modes are assigned to a terminal CN stretching (b_{2u}) mode and a bridged cyanide vibrational model (b_{3u}). The values are very close to those of cyanide-bridgepolymer, $[\text{Cp}_2\text{ZrNCPt}(\text{CN})_2\text{CN}]_n$, reported by Risen and coworker¹⁷. The problem still arises as to why the CN stretching mode is shifted to a higher frequency compared with that of $(\text{TBA})_2\text{Pt}(\text{CN})_4$, which occurs at 2108 cm^{-1} . When the lone pair of nitrogen is coordinated to the rhodium complex, the CN stretching mode tends to shift a higher frequency because the electrons are removed from the antibonding $2p\pi^*$ orbital. The second problem is to demonstrate us as to whether the cyanide group is coordinated to the rhodium complex. In order to clarify the coordination mode, we synthesized the labelled $(\text{TBA})_2\text{Pt}(\text{CN}^*)_4$ with use of KCN^* . Addition of $(\text{TBA})_2\text{Pt}(\text{CN}^*)_4$ to a stirred benzene solution of $(\text{PPh}_3)_2(\text{CO})\text{RhOSO}_2\text{CF}_3$ affords the stable, yellow trinuclear complex $(\text{PPh}_3)_2(\text{CO})\text{Rh}-\text{NCPt}(\text{CN}^*)_2\text{CN}^*-\text{Rh}(\text{CO})(\text{PPh}_3)_2$ IX. The infrared spectra of the labelled trinuclear complexes gave us a more conclusive result. The principal features of the infrared spectrum of IX is similar to that of compounds VI. The single $\nu(\text{CN})$ band of $(\text{TBA})_2\text{Pt}(\text{CN}^*)_4$ at 2081 cm^{-1} is replaced in IX by two bands at 2098 and 2112 cm^{-1} , as expected for D_{2h} local symmetry. The 2112 cm^{-1} band, shifted by nearly +31 cm^{-1} relative to $\text{Pt}(\text{CN}^*)_4^{2-}$, is assigned to a terminal cyanide vibration (b_{3u} in local D_{2h}). The 2112 cm^{-1} band is assigned to a bridging cyanide vibration (b_{3u}) and the 2098 cm^{-1} band is assigned to a terminal cyanide vibration (b_{2u}). The shift to a higher frequency compared with that of $\text{Pt}(\text{CN}^*)_4^{2-}$ is attributable to a slight decrease in the π back-bonding to the CN ligand from the platinum atom.

In summary, these complexes are interesting in that they give some simple structural ideas with regard to the deliberate design and construction of a new series of polymer with infinite framework structure. The oxidation reaction of compounds I-VIII and mechanistic works are in progress.

Acknowledgment. This work was supported by grants from the Korea Science and Engineering Foundation. We thank Professor Ilkyang Kim for measurement of cyclic voltammogram.

References

1. J. L. Atwood, J. E. D. Davies, D. D. MacNicol; Inclusion Compounds, Academic Press: New York, p. 29 (1984).
2. (a) B. F. Hoskins and R. Robson, *J. Am. Chem. Soc.*, **112**, 1546 (1990); (b) B. F. Hoskins and R. Robson, *J. Am. Chem. Soc.*, **111**, 5962 (1989); (c) B. F. Abrahams, B. F. Hoskins and R. Robson, *J. Chem. Soc., Chem Commun.*, **60**, 1549 (1990).

3. (a) S. Nishikiori and T. Iwamoto, *Chem. Lett.*, 319 (1984); (b) S. Nishikiori and T. Iwamoto, *Chem. Lett.*, 1129 (1983); (c) T. Hasegawa, S. Nishikiori, and T. Iwamoto, *Chem. Lett.*, 1659 (1985). (d) S. Nishikiori and T. Iwamoto, *Chem. Lett.*, 1127 (1987).
4. M. Fujita, J. Yazaki, and K. Ogura, *J. Am. Chem. Soc.*, **112**, 5645 (1990).
5. (a) D. Evans, J. A. Osborn and G. Wilkinson, *Inorg. Syn.*, **11**, 99 (1968); (b) K. Vrieze, J. P. Collman, C. T. Sears, and M. Kubota, *Inorg. Syn.*, **11**, 101 (1968).
6. D. J. Liston, Y. J. Jee, W. R. Scheidt, and C. A. Reed, *J. Am. Chem. Soc.*, **111**, 6643 (1989).
7. J. H. Bigelow, *Inorg. Syn.*, **2**, 250 (1946).
8. W. R. Mason and H. B. Gray, *J. Am. Chem. Soc.*, **90**, 5721 (1968).
9. G. K. N. Reddy and B. R. Ramesh, *J. Organomet. Chem.*, **87**, 347 (1975).
10. G. K. N. Reddy and B. R. Ramesh, *Indian J. Chem. Chem. Sect. A.*, **15A**, 621 (1977).
11. J. Peone, Jr. and L. Vaska, *Angew. Chem. Int. Ed. Engl.*, **10**, 511 (1971).
12. (a) J. L. Burmeister and N. J. DeStefano, *Inorg. Chem.*, **8**, 1546 (1969); (b) D. M. L. Goodgame and M. A. Hitchman, *Inorg. Chem.*, **3**, 1389 (1964).
13. D. A. MacInnes, "The Principles of Electrochemistry", Dover, New York, p. 342 (1961).
14. J. S. Kritoff and D. F. Shriver, *Inorg. Chem.*, **12**, 1788 (1975).
15. L. E. Manzer and G. W. Parshall, *Inorg. Chem.*, **15**, 3114 (1976).
16. H. M. Jeong and C. S. Chin, *Bull. Kor. Chem. Soc.*, **7**, 468 (1986).
17. J. A. Abys, G. Ogar, and W. M. Risen, Jr., *Inorg. Chem.*, **20**, 4446 (1981).

Photodissociation of CINO at 236 nm

Hong Lae Kim*, Yuxiang Mo[†], Yutaka Matsumi[‡], and Masahiro Kawasaki[‡]

Department of Chemistry, Kangweon National University, Chuncheon 200-701

[‡]Research Institute of Applied Electricity, Hokkaido University, Sapporo 060, Japan

Received November 13, 1991

The fine structure branching ratio and Doppler profiles of photofragment Cl (²P_y) atoms from photodissociation of CINO around 236 nm in the A band have been measured by the two photon resonance enhanced multiphoton ionization technique. The measured branching ratio, Cl* (²P_{1/2})/Cl (²P_{3/2}) is 0.18 ± 0.02. The Doppler profile of Cl is well reproduced assuming that one of the two components in the photofragment translational spectra reported by Haas, Felder, and Huber [*Chem. Phys. Lett.*, **180**, 293 (1990)] should correspond to Cl and that an anisotropy parameter β for the angular distribution is 0.45. The results suggest that CINO dissociation in the A band should consist of at least two non-crossing electronic states which correlate to the formation of Cl* and Cl, respectively.

Introduction

Photodissociation of small polyatomic molecules has been the subject of great interest because the system is simple enough to be studied theoretically and experimentally. Extensive theories such as the Frank-Condon theory or the sudden approximation in quantum scattering theory have been developed to explain the dynamics of the dissociation.¹ CINO is a typical bent triatomic molecule appropriate for theoretical calculations. In addition, spectroscopy of CINO and of the fragments Cl and NO has been well studied experimentally. Thus, the study of photodissociation dynamics of CINO has been focused on for many years since the pioneering work by Busch and Wilson.² Since the shape of potential energy surfaces in upper states determines the dynamics of the dissociation, electronic structure calculations can help understanding the dynamics of the process. Once the potential energy surfaces are known, the theory can predict

the detailed dynamics of the process such as mechanism and distributions of available energies among various degrees of freedom of the products. On the other hand, certain experimental observables which can explain the dynamics such as the energy and the angular distributions of the products deduce the approximate shape of the potential energy surfaces. Therefore, it is of fundamental importance to measure the energy and the angular distributions of the products in order to map out the potential surfaces in the excited state.

CINO shows several absorptions in the UV-VIS region which are called the A, B, C, D, and E bands (Figure 1).³ Recent *ab initio* calculations and experimental studies of photodissociation following the excitation of these bands can assign them as (1) E band-T₁←S₀, (2) D and C band-S₁←S₀, (3) B band-S₃←S₀, (4) A band-S₅←S₀, respectively.³⁻⁶ Extensive studies have been carried out for the dissociation from the E, C, and B bands by detecting LIF from the NO products. This LIF technique has high enough sensitivity to determine the rotational energy distributions of NO with the resolution of the λ doublet. In addition, vector properties

[†]On leave from Dalian Institute of Chemical Physics, Chinese Academy of Science, Dalian, China.