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Preparation and Characterization of Dinuclear Metal Complexes, [(PPh₃)₂(CO)M(μ-E)M(CO)(PPh₃)₂](SO₃CF₃)₂ (M=Rh, Ir; E=1,4-Dicyanobenzene and 1,4-Dicyano-2-butene)

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Hydrocarbon solution of (PPh₃)₂(CO)MOSO₂CF₃ (M=Rh, Ir) reacts rapidly with 1,4-dicyanobenzene or 1,4-dicyano-2-butene to yield dinuclear metal complexes [(PPh₃)₂(CO)M(μ-dicyanobenzene)M(CO)(PPh₃)₂](SO₃CF₃)₂ (I: M=Rh; II: M=Ir) or [(PPh₃)₂(CO)M(μ-dicyano-2-benzene)M(CO)(PPh₃)₂](SO₃CF₃)₂ (III: M=Rh; IV: M=Ir), respectively. Compounds I, II, III, and IV were characterized by ¹H-NMR, ³¹P-NMR, and infrared spectrum. Dichloromethane solution of II and IV reacts with H₂ and I₂ to yield oxidative addition complexes [(PPh₃)₂(CO)IrX₂(μ-E)X₂Ir(CO)(PPh₃)₂](SO₃CF₃)₂ (V; E=1,4-dicyanobenzene, X₂=H₂; VI: E=1,4-dicyano-2-butene, X₂=H₂; VII: E=1,4-dicyanobenzene, X₂=I₂). All metal complexes are bridged by the cyanide groups. Compounds V, VI, and VII are characterized by conventional methods.

Introduction

The preparation of three-dimensional metal complex hosts able to accommodate aromatic molecules is of great importance in both organic and inorganic chemistry.¹ 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 coworker³ 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 approach is important because the structural design is easily controlled. Recently, we⁵ prepared dinuclear and trinuclear metal complexes [(PPh₃)₂(CO)M(μ-E)M(CO)PPh₃]₂X₂ (M=Rh, Ir; E=pyrazine, 4,4'-dipyridyl, X=SO₃CF₃; E=Pd(CN)₄, Pt(CN)₄, X=none). The syntheses of trinuclear metal complexes prompted us to prepare dinuclear metal complexes bridged by the cyanide groups. Therefore, we chose 1,4-dicyanobenzene and 1,4-dicyano-2-butene as a bridging ligand. The four bridged compounds show interesting features because they are able

to control the size and they are possible models of 1-D polymer.

In this article, we wish to report the formation of dinuclear metal complexes bridged by 1,4-dicyanobenzene or 1,4-dicyano-2-butene and oxidative addition reaction.

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, 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-NMR spectra and 85% H₃PO₄ for ³¹P-NMR spectra. IR spectra were obtained by using a Perkin-Elmer 1310 instrument. Conductivity measurement was conducted with an Industrial Instrument Model RC216B2. Elemental analyses were carried out at the Basic Science Research Center. Reagent grade ether and benzene were distilled under argon from sodium-benzophenone ketyl. Dichloromethane was distilled under Ar from calcium hydride. (PPh₃)₂(CO)MCl⁶ (M=Rh, Ir) and (PPh₃)₂(CO)MOSO₂CF₃⁷ (M=Rh, Ir) were prepared according to literature methods. 1,4-Dicyanobenzene and 1,4-Dicyano-2-bu-

tene were purchased from Aldrich. $\text{MCl}_3 \cdot x\text{H}_2\text{O}$ ($\text{M} = \text{Rh}, \text{Ir}$) was purchased from Strem.

Preparation of $[(\text{CO})(\text{PPh}_3)_2\text{Rh}(\mu\text{-NCC}_6\text{H}_4\text{CN})\text{Rh}(\text{PPh}_3)_2(\text{CO})](\text{SO}_3\text{CF}_3)_2$ (I). To a stirred benzene (10 ml) solution of $(\text{CO})(\text{PPh}_3)_2\text{RhOSO}_2\text{CF}_3$ (0.2 g, 0.248 mmol) was added 1,4-dicyanobenzene (0.016 g, 0.124 mmol) in benzene (5 ml) dropwise. Upon addition of dicyanobenzene, yellow product was immediately precipitated out. The solution was stirred at room temperature for additional 0.5 h. The yellow precipitate was filtered and washed with benzene (5 ml) and hexane (5 ml). The yield was 0.15 g (69.5%). mp. 163°C . Molar conductivity: $168.2 \text{ ohm}^{-1}\text{cm}^2\text{mol}^{-1}$. $^1\text{H-NMR}$ (CDCl_3) δ (ppm) 7.68-7.42 (m, 60H), 7.36 (s, 4H). $^{31}\text{P-NMR}$ (CDCl_3) δ (ppm) 27.88 (d, $J_{\text{Rh-P}} = 130.13 \text{ Hz}$). IR (on pellet; cm^{-1}) 3042, 2262 (m), 1996 (vs), 1578 (w), 1268 (br, vs), 1222 (m), 1182 (w), 1148 (br, s), 1095 (s), 1072 (w), 1028 (s), 1012 (w), 998 (m), 842 (m), 802 (w), 743 (s), 708 (s), 693 (s), 636 (s). Anal. Calcd for $\text{C}_{84}\text{F}_6\text{H}_{64}\text{N}_2\text{O}_8\text{P}_4\text{Rh}_2\text{S}_2$: C, 58.09; H, 3.69. Found: C, 57.62; H, 3.48.

Preparation of $[(\text{CO})(\text{PPh}_3)_2\text{Ir}(\mu\text{-NCC}_6\text{H}_4\text{NC})\text{Ir}(\text{PPh}_3)_2(\text{CO})](\text{SO}_3\text{CF}_3)_2$ (II). To a stirred benzene (10 ml) solution of $(\text{CO})(\text{PPh}_3)_2\text{IrOSO}_2\text{CF}_3$ (0.2 g, 0.22 mmol) was added 1,4-dicyanobenzene (0.014 g, 0.11 mmol) in benzene (5 ml) dropwise. Upon addition of dicyanobenzene, orange product was precipitated out. The solution was stirred at room temperature for 1 h. The orange precipitate was filtered and washed with benzene ($2 \times 5 \text{ ml}$) and ethyl ether (10 ml). The yield was 0.18 g (84%). mp. 146°C . Molar conductivity: $162.4 \text{ ohm}^{-1}\text{cm}^2\text{mol}^{-1}$. $^1\text{H-NMR}$ (CDCl_3) δ (ppm) 7.68-7.42 (m, 60H), 7.36 (s, 4H). $^{31}\text{P-NMR}$ (CDCl_3) δ (ppm) 21.50. IR (on pellet; cm^{-1}) 3025 (br, m), 2256 (m), 1996 (vs), 1568 (w), 1304 (w), 1265 (br, vs), 1218 (m), 1178 (m), 1182 (br, m), 1092 (s), 1068 (w), 1022 (s), 994 (m), 836 (w), 747 (s), 705 (s), 689 (s), 672 (s), 632 (s). Anal. Calcd for $\text{C}_{84}\text{F}_6\text{H}_{64}\text{N}_2\text{O}_8\text{P}_4\text{Ir}_2\text{S}_2$: C, 52.68; H, 3.34. Found: C, 51.92; H, 3.18.

Preparation of $[(\text{CO})(\text{PPh}_3)_2\text{Rh}(\mu\text{-NCCH}_2\text{CHCHCH}_2\text{-CN})\text{Rh}(\text{PPh}_3)_2(\text{CO})](\text{SO}_3\text{CF}_3)_2$ (III). The same procedure was taken as described in the preparation of I. The isolated yield was 85%. mp. 174°C . Molar conductivity: $160.8 \text{ ohm}^{-1}\text{cm}^2\text{mol}^{-1}$. $^1\text{H-NMR}$ (CDCl_3) δ (ppm) 7.67-7.32 (m, 60H), 4.14 (br, 2H), 2.54 (br, 4H). $^{31}\text{P-NMR}$ (CDCl_3) δ (ppm) 27.52 (d, $J_{\text{Rh-P}} = 129.82 \text{ Hz}$). IR (on pellet; cm^{-1}) 3214 (br, m), 2884 (m), 2284 (m), 1996 (vs), 1572 (w), 1398 (m), 1338 (w), 1305 (sh), 1278 (s), 1262 (br, vs), 1222 (s), 1182 (m), 1164 (s), 1140 (s), 1192 (s), 1170 (w), 1126 (s), 992 (m), 963 (m), 855 (w), 749 (s), 703 (s), 694 (s), 672 (s), 632 (s). Anal. Calcd for $\text{C}_{82}\text{F}_6\text{H}_{66}\text{N}_2\text{O}_8\text{P}_4\text{Rh}_2\text{S}_2$: C, 57.44; H, 3.85. Found: C, 68.04; H, 3.69.

Preparation of $[(\text{CO})(\text{PPh}_3)_2\text{Ir}(\mu\text{-NCCH}_2\text{CHCHCH}_2\text{-CN})\text{Ir}(\text{PPh}_3)_2(\text{CO})](\text{SO}_3\text{CF}_3)_2$ (IV). The same procedure was taken as described in the preparation of I. The yield was 61.5%. mp. 191°C . Molar conductivity: $157.4 \text{ ohm}^{-1}\text{cm}^2\text{mol}^{-1}$. $^1\text{H-NMR}$ (CDCl_3) δ (ppm) 7.82-7.14 (m, 60H), 4.06 (br, 2H), 2.63 (br, 4H). $^{31}\text{P-NMR}$ (CDCl_3) δ 21.40. IR (on pellet; cm^{-1}) 3204 (br, m), 2880 (m), 2184 (m), 1986 (vs), 1582 (w), 1395 (m), 1336 (w), 1305 (m), 1274 (s), 1264 (sh), 1255 (vs), 1221 (s), 1178 (m), 1153 (s), 1137 (s), 992 (s), 971 (w), 960 (w), 927 (s), 867 (m), 895 (m), 858 (w), 756 (sh), 749 (s), 703 (s), 695 (s), 687 (sh), 672 (s), 632 (s). Anal. Calcd for $\text{C}_{82}\text{F}_6\text{H}_{66}\text{N}_2\text{O}_8\text{P}_4\text{Ir}_2\text{S}_2$: C, 52.02; H, 3.49. Found: C, 51.22; H, 3.32.

Preparation of $[(\text{CO})(\text{PPh}_3)_2\text{H}_2\text{Ir}(\mu\text{-NCC}_6\text{H}_4\text{CN})\text{IrH}_2(\text{PPh}_3)_2(\text{CO})](\text{SO}_3\text{CF}_3)_2$ (V). The compound III (0.15 g) was dissolved in CH_2Cl_2 (15 ml). The hydrogen gas was bubbled into the solution. After 5 min, the solution was changed from yellow into colorless. The solution was bubbled for additional 0.5 h and added hexane (15 ml). The pale yellow precipitate was filtered and washed with hexane (10 ml) and dried in vacuo. The yield was 94%. mp. 130°C . Molar conductivity: $160.4 \text{ ohm}^{-1}\text{cm}^2\text{mol}^{-1}$. $^1\text{H-NMR}$ (CDCl_3) δ (ppm) 7.74-7.44 (m, 60H), 7.38 (s, 4H), -8.42 (t, $J_{\text{P-H}} = 14.12 \text{ Hz}$). IR (on pellet; cm^{-1}) 3038 (br, m), 2216 (m), 2108 (s), 2032 (s), 1574 (w), 1396 (w), 1328 (w), 1308 (sh), 1264 (br, vs), 1216 (m), 1182 (s), 1142 (br, s), 1092 (s), 1068 (w), 1022 (s), 992 (m), 868 (br, m), 842 (br, m), 792 (w), 748 (s), 732 (sh, s), 705 (s), 692 (s), 630 (s), 612 (w). Anal. Calcd for $\text{C}_{84}\text{F}_6\text{H}_{68}\text{N}_2\text{O}_8\text{P}_4\text{Ir}_2\text{S}_2$: C, 52.57; H, 3.54. Found: C, 51.85; H, 3.42.

Preparation of $[(\text{CO})(\text{PPh}_3)_2\text{H}_2\text{Ir}(\mu\text{-NCCH}_2\text{CHCHCH}_2\text{-CN})\text{IrH}_2(\text{PPh}_3)_2(\text{CO})](\text{SO}_3\text{CF}_3)_2$ (VI). The same procedure was taken as described in the preparation of V. The yield was 88%. mp. 110°C . Molar conductivity: $157.8 \text{ ohm}^{-1}\text{cm}^2\text{mol}^{-1}$. $^1\text{H-NMR}$ (CDCl_3) δ (ppm) 6.74-7.38 (m, 60H), 4.19 (br, 2H), 2.60 (br, 4H), -8.54 (t, $J_{\text{P-H}} = 14.08 \text{ Hz}$). IR (on pellet; cm^{-1}) 3042 (br, m), 2224 (m), 2108 (s), 2017 (s), 1582 (w), 1568 (w), 1327 (w), 1305 (sh), 1262 (br, vs), 1218 (s), 1185 (m), 1145 (br, s), 1098 (s), 1072 (w), 1027 (s), 996 (m), 968 (m), 874 (m), 845 (w), 751 (s), 704 (s), 692 (s), 632 (s). Anal. Calcd for $\text{C}_{82}\text{F}_6\text{H}_{68}\text{N}_2\text{O}_8\text{P}_4\text{Ir}_2\text{S}_2$: C, 51.91; H, 3.69. Found: C, 51.04; H, 3.74.

Preparation of $[(\text{CO})(\text{PPh}_3)_2\text{I}_2\text{Ir}(\mu\text{-NCC}_6\text{H}_4\text{CN})\text{IrI}_2(\text{PPh}_3)_2(\text{CO})](\text{SO}_3\text{CF}_3)_2$ (VII). To a stirred CH_2Cl_2 (10 ml) solution of II (0.12 g, 0.06 mmol) was added iodine (0.016 g, 0.12 mmol) in CH_2Cl_2 (5 ml) at room temperature. Upon addition of iodine, red color was rapidly developed and red-dish-brown product was precipitated out. The solution was stirred for additional 1 h. The product was filtered and washed with hexane (10 ml). The yield was 58%. mp. 218°C . Molar conductivity: $156.2 \text{ ohm}^{-1}\text{cm}^2\text{mol}^{-1}$. $^1\text{H-NMR}$ (CDCl_3) δ (ppm) 7.79-7.45 (m, 60H), 7.40 (s, 4H). IR (on pellet; cm^{-1}) 3028 (br, m), 2248 (m), 2042 (s), 1584 (w), 1388 (w), 1309 (w), 1269 (br, vs), 1224 (m), 1148 (br, s), 1087 (s), 1029 (s), 982 (m), 860 (br, m), 837 (br, m), 788 (w), 758 (s), 742 (sh, s), 720 (s), 684 (s), 638 (s), 632 (w). Anal. Calcd for $\text{C}_{84}\text{F}_6\text{H}_{64}\text{N}_2\text{O}_8\text{P}_4\text{Ir}_2\text{S}_2$: C, 41.64; H, 2.64. Found: C, 40.24; H, 2.39.

Results and Discussion

The dinuclear metal complexes bridged by 1,4-dicyanobenzene and 1,4-dicyano-2-butene have been prepared according to the general Eq. (1).

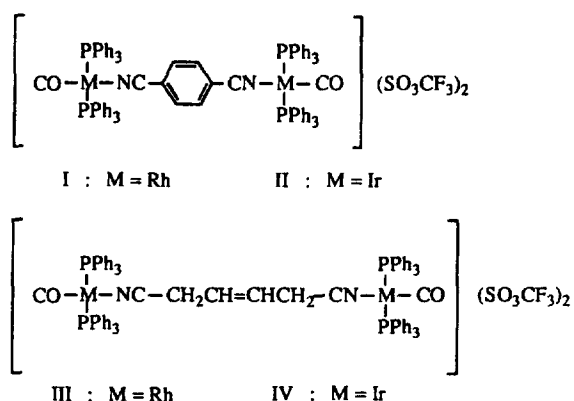


$\text{M} = \text{Rh}, \text{Ir}$; $\text{E} = 1,4\text{-dicyanobenzene}, 1,4\text{-dicyano-2-butene}$

The addition of 1,4-dicyanobenzene or 1,4-dicyano-2-butene to a stirred benzene solution of $(\text{PPh}_3)_2(\text{CO})\text{MOSO}_2\text{CF}_3$ ($\text{M} = \text{Rh}, \text{Ir}$) affords a yellow precipitate. The resulting yellow compounds, $[(\text{PPh}_3)_2(\text{CO})\text{M}(\mu\text{-1,4-dicyanobenzene})\text{M}(\text{CO})(\text{PPh}_3)_2](\text{SO}_3\text{CF}_3)_2$ and $[(\text{PPh}_3)_2(\text{CO})\text{M}(\mu\text{-1,4-dicyano-2-butene})\text{M}(\text{CO})(\text{PPh}_3)_2](\text{SO}_3\text{CF}_3)_2$ ($\text{M} = \text{Rh}, \text{Ir}$) were isolated as air-stable in high yield, as shown below. The four-coordinated

Table 1. ^1H -NMR, ^{31}P -NMR, and IR data^c

Compound	^1H Chemical shift, δ	^{31}P Chemical shift, δ	IR frequency, cm^{-1}		
			$\nu(\text{CN})$	$\nu(\text{MH})$	$\nu(\text{CO})$
I	7.36 ^a	27.88 (d, $J_{\text{Rh-P}} = 130.13$ Hz)	2262		1996
II	7.36 ^a	21.50	2256		1996
III	4.14 ^b 2.54	27.52 (d, $J_{\text{Rh-P}} = 129.83$ Hz)	2284		1996
IV	4.06 ^b 2.63	21.40	2184		1986
V	7.38 ^a -8.42 (d, $J_{\text{P-H}} = 14.12$ Hz)		2216	2108	2032
VI	4.19 ^b 2.60 -8.54 (t, $J_{\text{P-H}} = 14.08$ Hz)		2224	2108	2071
VII	7.40 ^a		2248		2042

^a 1,4-dicyanobenzene proton. ^b 1,4-dicyano-2-butene proton. ^c on pellet.

rhodium (I) and iridium (I) complexes $\text{M}(\text{CO})\text{L}_2\text{X}$ ($\text{M} = \text{Rh}, \text{Ir}$; $\text{L} = \text{PPh}_3, \text{Pcy}_3$; $\text{X} = \text{OCIO}_3, \text{OSO}_2\text{CF}_3$) was known to react with pyridine⁸, 2-methylpyridine⁸, 8-alkylquinolines⁹, imidazoles¹⁰, and unsaturated nitriles¹¹ to give four coordinate cations of the general form $[\text{M}(\text{CO})\text{L}_2\text{N}]^+$ ($\text{N} = \text{pyridine}, 2\text{-methylpyridine}, 8\text{-alkylquinolines}, \text{imidazoles}, \text{unsaturated nitriles}$). 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 perchlorato and trifluoromethanesulfonato ligands in $\text{M}(\text{CO})(\text{PPh}_3)_2\text{X}$ is so labile that it is readily replaced by various solvent molecules¹². Indeed, the reaction of $(\text{TBA})_2\text{M}(\text{CN})_4$ ($\text{M} = \text{Pd}, \text{Pt}$) with $(\text{PPh}_3)_2(\text{CO})\text{M}'\text{OSO}_2\text{CF}_3$ ($\text{M}' = \text{Rh}, \text{Ir}$) proceeded to give trinuclear metal complexes bridged by the cyanide groups. Accordingly, it is reasonable to expect that the reaction of 1,4-dicyanobenzene or 1,4-dicyano-2-butene with $\text{M}(\text{CO})(\text{PPh}_3)_2\text{X}$ ($\text{M} = \text{Rh}, \text{Ir}$; $\text{X} = \text{OSO}_2\text{CF}_3$) proceeds to give dinuclear metal complexes bridged by the cyano ligands. The structure of compounds (I-VII) were deduced from their NMR, IR spectra, conductivity measurement, and elemental analyses.

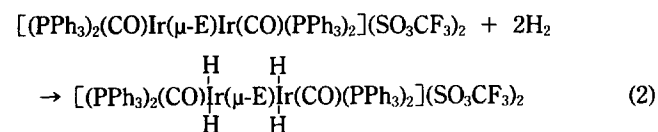
The ^1H -NMR spectrum of I taken in CDCl_3 at room temperature exhibits a resonance of 1,4-dicyanobenzene at δ 7.36 (see Table 1). The peak is shifted to upfield compared with that of free 1,4-dicyanobenzene appearing at δ 7.82. It may be attributable to the electron donating power of metal complex. The carbonyl and 1,4-dicyanobenzene ligands are presumed to be in a *trans* position in order to augment the electronic effect of π bonding. The ^{31}P -NMR spectrum of I exhibits one doublet at δ 27.88 ($J_{\text{Rh-P}} = 130.13$ Hz). The value is very close to that of the compound $[(\text{PPh}_3)_2(\text{CO})\text{Rh}(\mu\text{-pyra-}$

zine) $\text{M}(\text{CO})(\text{PPh}_3)_2](\text{SO}_3\text{CF}_3)_2$ ⁵. The spectrum tells us that the two triphenylphosphines are chemically equivalent. Therefore, it can be said that they are in a *trans* position. The infrared spectrum of I on pellet shows two strong absorptions at 2262 and 1996 cm^{-1} in the CN and CO region. The medium peak at 2262 cm^{-1} is assigned to the CN stretching mode. The significant higher shift (65 cm^{-1}) in ν_{CN} of 1,4-dicyanobenzene upon coordination suggests that the cyano group in 1,4-dicyanobenzene is coordinated through the cyano group to rhodium complex. Significant increases have been also found for ν_{CN} of II, III, and IV compared with those of free ligands. The intense peak at 1996 cm^{-1} is assigned to the CO stretching mode. It is interesting to note that the CO stretching frequency is relatively high in spite of the presence of the 1,4-dicyanobenzene containing the nitrogen atom, compared with those 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 cation. The conductivities of I-VII is in the region of 157-168 $\text{ohm}^{-1}\text{cm}^2\text{mol}^{-1}$ ¹³. The values show that the compounds are 1 : 2 electrolytes. Although the structure of I was straightforwardly deduced from spectroscopic data, one problem still remains as to how the bridging ligand is posed. The answer is that the bridging ligand is presumed to be in a vertical position with respect to the square-planar rhodium complex due to the steric crowding between the hydrogen atom of ligand and triphenylphosphine.

The reaction of $(\text{PPh}_3)_2(\text{CO})\text{MOSO}_2\text{CF}_3$ ($\text{M} = \text{Rh}, \text{Ir}$) with 1,4-dicyanobutane or 1,5-dicyanopentane led to no reaction. It seems that the rigidity of framework containing two cyanide groups is important and the coordination of cyanide group to a metal center is quite difficult due to the rapid rotation of framework.

Oxidative Addition Reaction

The dinuclear iridium complexes II and IV react with hydrogen *via* an oxidative addition reaction to give the formation of stable hydride iridium (III) complexes according to Eq. (2).



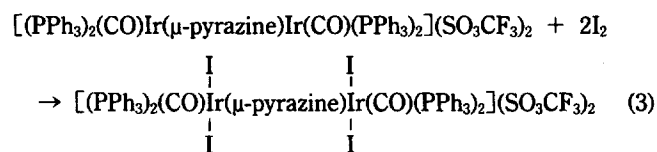
V: E = pyrazine

VI: E = 1,4-dicyanobenzene

The pale-yellow products are air-stable and soluble in CH_2Cl_2 , slightly soluble in CHCl_3 . The complexes have been identified by ^1H -NMR spectroscopy, IR spectroscopy, and elemental analyses.

The ^1H -NMR spectrum of V exhibits the resonance pattern of the hydride at $\delta -8.42$ ($J_{\text{P-H}} = 14.12$ Hz). Its pattern consists of a triplet due to the spin coupling between the hydride and two phosphines. The value is very close to that of the complexes $[\text{IrH}_2(\text{CO})(\text{PPh}_3)_3]\text{BF}_4^{14}$ and $[\text{IrH}_2(\text{CO})(\text{CH}_3\text{CN})(\text{PPh}_3)_2]\text{BF}_4^{15}$. The spin system indicates that two phosphine ligands are chemically equivalent. The small coupling constant also indicates that the hydride is *cis* to the phosphine. In addition to that, there are two peaks at δ 7.74-7.44 and 7.38, assigned to phenyl hydrogens and dicyanobenzene, respectively. The peak at δ 7.38 is essentially identical to that of compound II. The infrared spectrum of V indicates the presence of the Ir-H bond¹⁶. The peaks at 2216 cm^{-1} , 2108 cm^{-1} , and 2032 cm^{-1} are assigned to the CN, Ir-H, and CO stretching mode, respectively. The spectral data of VI is similarly assigned as that compound V. It is interesting to note that the reaction of IV with H_2 gave the hydride iridium (III) complex, rather than the addition reaction to the carbon-carbon double bond. In strikingly contrast to the iridium complexes, the rhodium complexes I and II with H_2 led to no reaction.

The dinuclear iridium complex II reacts with iodine to give the formation of the stable iodo iridium (III) complex according to Eq. (3).



The red-brown product is air-stable and soluble in DMSO. The ^1H -NMR spectrum of VII exhibits the resonance of 1,4-dicyanobenzene at δ 7.40. The peak is slightly shifted to downfield compared with that of V. The infrared spectrum of VII shows two strong absorptions at 2248 cm^{-1} and 2042 cm^{-1} . The medium peak at 2248 cm^{-1} and intense peak at 2042 cm^{-1} are assigned to the CN stretching mode and CO stretching mode, respectively. The shift to a higher frequency of VII in CO stretching mode compared with that of V may be attributable to the electron withdrawing group.

In summary, we prepared dinuclear metal complexes bridged by cyanide group. The complexes II and IV reacts with H_2 and I_2 via an oxidative addition reaction to give the hy-

drido and iodo iridium metal complexes, respectively. The complexes I-IV may give a good model for synthesizing a 1-D polymer by substituting the carbonyl ligand into the pyrazine and 1,4-dicyano-2-butene. The reaction is in progress.

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