Journal of Organometallic Chemistry, 454 (1993) 221–228

JOM 23485

Studies on binuclear complexes. Synthesis and catalytic behaviour of Fe–M complexes (M = Mo, Ni, Rh, Cu, Hg) using *trans*-$Fe(Ph_2Ppy)_2(CO)_3$ [Ph_2Ppy = 2-(diphenylphosphino)pyridine] as a neutral tridentate ligand. Molecular structure of $FeHg(\mu\text{-}Ph_2Ppy)_2(CO)_3(SCN)_2$

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(Received October 23, 1992; in revised form December 18, 1992)

Abstract

trans-$Fe(Ph_2Ppy)_2(CO)_3$ reacts as a neutral tridentate ligand with $Mo(CO)_6$, $Ni(NCS)_2$, $[Rh(CO)_2Cl]_2$, CuX (Cl, Br, I) and $Hg(SCN)_2$ to form binuclear complexes including an Fe–M bond. Crystal and molecular structures of the Fe–Hg complex has been determined by X-ray diffraction. The Fe–Hg bond distance is 2.648 Å. The effects have been evaluated of these complexes as homogeneous catalysts on the carbonylation of ethanol to ethyl propionate. The Fe–Rh complex possesses very high activity and selectivity.

1. Introduction

Following the initial studies by Balch many hetero- and homobinuclear complexes have been prepared using 2-(diphenylphosphino)pyridine (Ph_2Ppy) as a bridging ligand [1–10]. However consideration of bis(diphenylphosphino)methane (dppm) suggests that the ligand Ph_2Ppy should be much more widely applicable to the preparation of binuclear complexes, especially heteronuclear ones. In this work, it was found that the complex *trans*-$Fe(Ph_2Ppy)_2(CO)_3$ can act as a neutral organometallic tridentate ligand, reacting with metal compounds to give several heterobinuclear complexes including $FeHg(\mu\text{-}Ph_2Ppy)_2(CO)_3(SCN)_2$ whose molecular structure has been determined by X-ray diffraction. The catalytic activities and selectivities of these complexes on the carbonylation of ethanol to ethyl propionate have been evaluated.

2. Results and discussion

2.1. Synthesis and reaction

It is well known that some iron(0) complexes can act as donors reacting with certain metal compounds to form heterobinuclear complexes with the Fe–M bond

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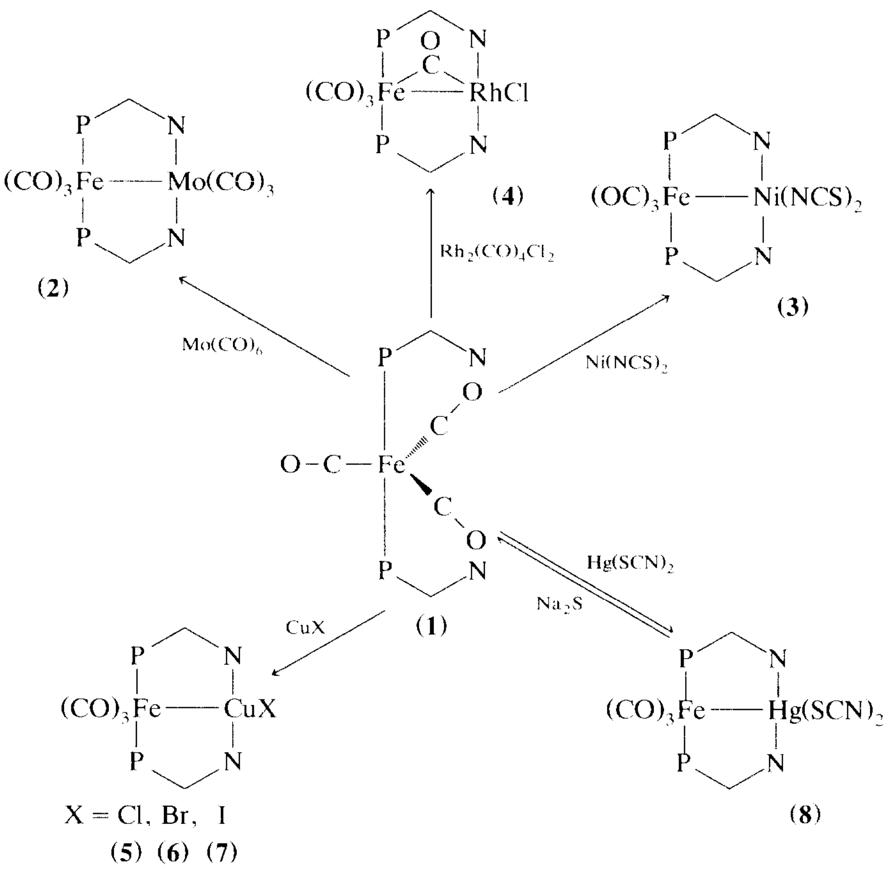

Fig. 1. Syntheses of Fe–M complexes using *trans*-$Fe(Ph_2Ppy)_2(CO)_3$ as a tridentate ligand.

[11–13]. We found that $Fe(CO)_5$ reacts with Ph_2Ppy in n-butane to give *trans*-$Fe(Ph_2Ppy)_2(CO)_3$ (**1**) in high yield. Using the donor characters of the Fe and N atoms and the rigidity of the ligand Ph_2Ppy, the complex (**1**) as a tridentate ligand can react with $Mo(CO)_6$, $Ni(NCS)_2$, $[Rh(CO)_2Cl]_2$, CuX (X = Cl, Br, I) and $Hg(SCN)_2$ to give high yields of binuclear complexes with Fe–M bond (**2–7**) (Fig. 1). The IR spectrum of complex **4** shows three terminal carbonyl (2030, 1990, 1954 cm^{-1}) and a bridging carbonyl (1795 cm^{-1}) stretch vibrations and $^2J(P-Rh) = 146$ Hz is observed in ^{31}P NMR, so the complex may be described as $FeRh(\mu\text{-}Ph_2Ppy)_2(\mu\text{-}CO)(CO)_3$.

Complex **8** can react with Na_2S to yield *trans*-$Fe(Ph_2Ppy)_2(CO)_3$ quantitatively. The analyses and physical properties of complexes **1–8** are given in Table 1, and the IR and ^{31}P NMR data are in Table 2. Complex **1**, as a tridentate ligand, would be expected

TABLE 1. Analyses and physical properties of complexes **1–8**

	Complex	Colour	m.p. (°C)	Analyses					
				C (%)		H (%)		N (%)	
				Calcd	Found	Calcd	Found	Calcd	Found
1	$Fe(Ph_2Ppy)_2(CO)_3$	yellow	230–2	66.67	65.86	4.20	3.79	4.20	4.36
2	$FeMo(Ph_2Ppy)_2(CO)_6$	red	170(dec.)	56.73	56.65	3.31	3.29	3.31	3.62
3	$FeNi(Ph_2Ppy)_2(CO)_3(NCS)_2$	yellow	180(dec.)	55.65	55.58	3.33	3.23	6.66	6.12
4	$FeRh(Ph_2Ppy)_2(CO)_4Cl$	orange	177–9	54.94	55.03	3.37	3.39	3.37	3.40
5	$FeCu(Ph_2Ppy)_2(CO)_3Cl$	orange	176–8	58.04	57.39	3.66	3.47	3.66	3.66
6	$FeCu(Ph_2Ppy)_2(CO)_3Br$	yellow	182–4	54.85	55.38	3.46	3.66	3.46	3.61
7	$FeCu(Ph_2Ppy)_2(CO)_3I$	yellow	120–2	51.84	52.47	3.27	3.23	3.27	3.44
8	$FeHg(Ph_2Ppy)_2(CO)_3(SCN)_2$	yellow	152–4	47.63	47.48	2.85	2.82	5.70	5.78

TABLE 2. IR and ^{31}P NMR data of complexes **1–8**

Complex	IR ν(CO) (cm^{-1})	^{31}P NMR δ (ppm, H_3PO_4)
1	1874s	8.75
2	1980m, 1928s, 1910s	
	1882s, 1824s, 1800s	84.37
3	2000m, 1960s, 1930s	
4	2030s, 1990s, 1954m	
	1795s	42.80, J(P–Rh) 146 Hz
5	1980m, 1916s, 1890s	85.07
6	1980m, 1910s, 1884s	84.54
7	1975m, 1890s, 1880s	83.59
8	2020s, 1970s, 1896m	70.94

to have a rich chemistry especially in its reactions with high valence metal compounds, and further work is being carried out.

2.2. Catalytic behaviour

Results of using the above heterobinuclear complexes as homogeneous catalysts for carbonylation of ethanol to form ethyl propionate are given in Table 3. Evidently the Fe–Rh complex **4** is superior in activity and selectivity. Comparison of catalytic behaviour between **4** and Rh(Ph$_3$P)$_3$Cl at different reaction temperatures (Table 4) shows that **4** is distinctly superior to Rh(Ph$_3$P)$_3$Cl at 200°C for the conversion of ethanol (99.5%) and selectivity to propionate (98.6%) although Rh(Ph$_3$P)$_3$Cl has better activity at 160°C. Recently, it has been reported that some Fe–Rh bimetallic carbonyl clusters can act as molecular precursors for preparation of Fe–Rh bimetallic catalysts. These catalysts can be used to catalyze olefin hydroformylation and are effective for insertion of migratory CO. The Fe atom promotes migratory CO insertion at the Rh atom thus [14]:

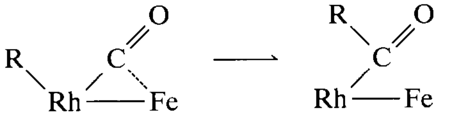

TABLE 3. Activities and selectivities of calalytic effects of Fe–M complexes on carbonylation of ethanol to ethyl propionate

Complex	Conversion of ethanol (%)	Selectivity (%)	
		ethyl ether	ethyl propionate
2	88.5	81.3	18.7
3	95.2	52.3	47.7
4 [a]	92.4	48.0	52.0
5	91.4	76.0	24.0
8	94.4	73.2	26.8
Rh(Ph$_3$P)$_3$Cl [a]	96.5	52.4	47.6

Reaction conditions: temperature, 220°C; pressure, 35 kg/cm^2; time 4 h; reagent ratio, ethanol:ethyl iodide:toluene = 86:61:95 (mmol) and amount of catalyst, 0.060 mmol; [a] Temperature, 180°C and amount of catalyst, 0.048 mmol.

TABLE 4. Catalytic behaviours of Fe–Rh complex **4** and Rh(Ph$_3$P)$_3$Cl at different reaction temperature on carbonylation of ethanol to ethyl propionate

Reaction temperature	Catalyst	Conversion of ethanol (%)	Selectivity (%)	
			ethyl ether	ethyl propionate
160°C	Rh(PH$_3$P)$_3$Cl	46.9	61.6	38.4
	Fe–Rh complex **4**	38.9	66.1	33.9
180°C	Rh(Ph$_3$P)$_3$Cl	90.5	52.4	47.2
	Fe–Rh complex **4**	92.4	48.0	52.0
200°C	Rh(Ph$_3$P)$_3$Cl	96.4	32.3	67.7
	Fe–Rh complex **4**	99.5	1.4	98.6

Analogous synergistic behaviour might be expected in our catalytic process. However, at lower reaction temperatures and because of the presence of the Fe atom, the oxidative addition of RI towards the Rh atom is probably hindered, and this is the rate-determining step in the carbonylation of alcohols.

2.3. Structure of FeHg(μ-Ph$_2$Ppy)$_2$(CO)$_3$(SCN)$_2$ (8)

X-ray diffraction analysis of **8** shows that it has HH configuration (Fig. 2). Bond lengths and angles are shown in Table 5. The Fe atom exhibits an octahedral geometry and the Hg coordination geometry is very interesting. The coordination chemistry of mercury has been studied in detail by Grdenic [15] and Canty [16], and according to their hypothesis there is effective coordination between Hg and L when ligands fulfil the condition D(Hg–L) < R(Hg) + R(L) (R = van der Waals radii). The Hg–N distances of 2.595 and 2.867 Å in **8** are well within the sum of van der Waals radii (Hg, 1.5 Å [15] and N, 1.5 Å [17]), so that the Hg atom may be considered as having trigonal bipyramidal configuration. However, the Hg atom interacts only weakly with the N(52) atom. Because of the rigidity of the Ph$_2$Ppy ligand the Fe–Hg distance is larger than previously reported in Fe–Hg compounds (Table 6). This kind of bonding model is novel in Ph$_2$Ppy-bridging binuclear complexes.

3. Experimental section

2-(Diphenylphosphino)pyridine [3] and Rh$_2$(CO)$_4$Cl$_2$ [23] were obtained by routes described elsewhere.

3.1. Physical measurements

Microanalyses of C, H and N were carried out on a Perkin Elmer model 240 analyzer. Infrared spectra (KBr disc) were recorded on a WFD-14 spectrophotometer. An AC-P 200 NMR spectrometer was used to record ^{31}P NMR at 81.02 Hz (solvent: CDCl$_3$, external standard: 85% H_3PO_4). FD-MS were performed with a

TABLE 5. Bond distances (Å) and angles (°) in $FeHg(\mu\text{-}Ph_2Ppy)_2(CO)_3(SCN)_2$ (**8**)

(i) Coordination geometry about Hg atoms			
Hg–Fe	2.6483(8)	Hg–C(3)	2.709(6)
Hg–S(1)	2.544(3)	Hg–N(32)	2.595(6)
Hg–S(2)	2.535(2)	Hg–N(52)	2.867(6)
Hg–C(1)	2.750(6)		
Fe–Hg–S(1)	127.55(8)	S(2)–Hg–C(1)	162.5(1)
Fe–Hg–S(2)	124.92(5)	S(2)–Hg–C(3)	85.8(2)
Fe–Hg–C(1)	37.6(1)	S(2)–Hg–N(32)	97.6(1)
Fe–Hg–C(3)	39.1(1)	S(2)–Hg–N(52)	93.6(1)
Fe–Hg–N(32)	88.5(1)	C(1)–Hg–C(3)	76.7(2)
Fe–Hg–N(52)	84.7(1)	C(1)–Hg–N(32)	83.8(2)
S(1)–Hg–S(2)	105.55(8)	C(1)–Hg–N(52)	85.4(2)
S(1)–Hg–C(1)	91.5(2)	C(3)–Hg–N(32)	93.7(2)
S(1)–Hg–C(3)	161.7(1)	C(3)–Hg–N(52)	86.6(2)
S(1)–Hg–N(32)	98.9(1)	N(32)–Hg–N(52)	168.8(2)
S(1)–Hg–N(52)	78.4(1)		
(ii) Coordination geometry about Fe atom			
Fe–P(1)	2.259(2)	Fe–C(2)	1.785(8)
Fe–P(2)	2.265(2)	Fe–C(3)	1.795(8)
Fe–C(1)	1.742(7)		
Hg–Fe–P(1)	91.23(5)	P(1)–Fe–C(3)	91.0(3)
Hg–Fe–P(2)	94.73(5)	P(2)–Fe–C(1)	92.1(2)
Hg–Fe–C(1)	74.4(3)	P(2)–Fe–C(2)	86.8(2)
Hg–Fe–C(2)	177.9(2)	P(2)–Fe–C(3)	91.2(3)
Hg–Fe–C(3)	72.2(2)	C(1)–Fe–C(2)	107.0(4)
P(1)–Fe–P(2)	174.02(7)	C(1)–Fe–C(3)	146.6(3)
P(1)–Fe–C(1)	89.1(2)	C(2)–Fe–C(3)	106.3(3)
P(1)–Fe–C(2)	87.3(2)		
(iii) Thiocyanato groups			
S(1)–C(4)	1.60(2)	S(2)–C(5)	1.45(2)
N(1)–C(4)	1.17(1)	N(2)–C(5)	1.06(2)
Hg–S(1)–C(4)	103.6(3)	Hg–S(2)–C(5)	101.0(4)
S(1)–C(4)–N(1)	178(1)	S(2)–C(5)–N(2)	174(2)
(iv) Carbonyl groups			
O(1)–C(1)	1.184(8)	O(3)–C(3)	1.132(7)
O(2)–C(2)	1.134(8)		
Hg–C(1)–Fe	68.0(3)	Hg–C(3)–Fe	68.6(3)
Hg–C(1)–O(1)	115.6(5)	Hg–C(3)–O(3)	115.6(5)
Fe–C(1)–O(1)	176.3(6)	Fe–C(3)–O(3)	175.3(6)
Fe–C(2)–O(2)	178.1(7)		
(v) Diphenylpyridylphosphino ligands			
P(1)–C(11)	1.853(7)	P(2)–C(41)	1.818(6)
P(1)–C(21)	1.809(6)	P(2)–C(51)	1.827(6)
P(1)–C(31)	1.838(7)	P(2)–C(61)	1.831(7)
C(11)–C(12)	1.39(1)	C(41)–C(42)	1.380(9)
C(11)–C(16)	1.414(9)	C(41)–C(46)	1.40(1)
C(12)–C(13)	1.42(2)	C(42)–C(43)	1.42(2)
C(13)–C(14)	1.43(2)	C(43)–C(44)	1.39(1)
C(14)–C(15)	1.37(2)	C(44)–C(45)	1.38(2)
C(15)–C(16)	1.44(1)	C(45)–C(46)	1.42(2)
C(21)–C(22)	1.389(9)	C(51)–N(52)	1.321(8)
C(21)–C(26)	1.406(9)	C(51)–C(56)	1.386(8)
C(22)–C(23)	1.43(2)	N(52)–C(53)	1.39(1)
C(23)–C(24)	1.37(2)	C(53)–C(54)	1.32(2)
C(24)–C(25)	1.36(2)	C(54)–C(55)	1.38(2)
C(25)–C(26)	1.42(1)	C(55)–C(56)	1.420(9)
C(31)–N(32)	1.316(8)	C(61)–C(62)	1.396(9)

TABLE 5 (continued)

C(31)–C(36)	1.38(1)	C(61)–C(66)	1.40(1)
N(32)–C(33)	1.38(1)	C(62)–C(63)	1.43(2)
C(33)–C(34)	1.42(2)	C(63)–C(64)	1.40(1)
C(34)–C(35)	1.33(1)	C(64)–C(65)	1.39(1)
C(35)–C(36)	1.42(1)	C(65)–C(66)	1.43(2)
Fe–P(1)–C(11)	114.2(2)	Fe–P(2)–C(41)	112.2(2)
Fe–P(1)–C(21)	115.3(2)	Fe–P(2)–C(51)	117.0(2)
Fe–P(1)–C(31)	117.4(2)	Fe–P(2)–C(61)	116.4(2)
C(11)–P(1)–C(21)	102.3(3)	C(41)–P(2)–C(51)	103.9(3)
C(11)–P(1)–C(31)	103.4(3)	C(41)–P(2)–C(61)	103.9(3)
C(21)–P(1)–C(31)	102.3(3)	C(51)–P(2)–C(61)	101.8(3)
P(1)–C(11)–C(12)	120.0(6)	P(2)–C(41)–C(42)	120.7(5)
P(1)–C(11)–C(16)	116.9(6)	P(2)–C(41)–C(46)	117.9(5)
C(12)–C(11)–C(16)	123.0(6)	C(42)–C(41)–C(46)	121.3(6)
C(11)–C(12)–C(13)	120.0(7)	C(41)–C(42)–C(43)	118.9(7)
C(12)–C(13)–C(14)	117.5(7)	C(42)–C(43)–C(44)	120.3(8)
C(13)–C(14)–C(15)	121.9(7)	C(43)–C(44)–C(45)	120.3(8)
C(14)–C(15)–C(16)	121.6(8)	C(44)–C(45)–C(46)	119.9(8)
C(11)–C(16)–C(15)	115.9(6)	C(41)–C(46)–C(45)	119.3(7)
P(1)–C(21)–C(22)	122.3(5)	P(2)–C(51)–N(52)	112.9(5)
P(1)–C(21)–C(26)	117.5(6)	P(2)–C(51)–C(56)	124.0(5)
C(22)–C(21)–C(26)	120.3(6)	N(52)–C(51)–C(56)	123.1(6)
C(21)–C(22)–C(23)	118.4(7)	Hg–N(52)–C(51)	111.0(5)
C(22)–C(23)–C(24)	120.7(7)	Hg–N(52)–C(53)	116.1(5)
C(23)–C(24)–C(25)	121.3(8)	C(51)–N(52)–C(53)	116.9(6)
C(24)–C(25)–C(26)	119.6(7)	N(52)–C(53)–C(54)	123.9(8)
C(21)–C(26)–C(25)	119.5(7)	C(53)–C(54)–C(55)	120.1(8)
P(1)–C(31)–N(32)	114.5(6)	C(54)–C(55)–C(56)	117.7(7)
P(1)–C(31)–C(36)	122.1(5)	C(51)–C(56)–C(55)	118.1(6)
N(32)–C(31)–C(36)	123.1(6)	P(2)–C(61)–C(62)	118.7(6)
Hg–N(32)–C(31)	118.4(5)	P(2)–C(61)–C(66)	118.4(5)
Hg–N(32)–C(33)	117.1(5)	C(62)–C(61)–C(66)	123.0(7)
C(31)–N(32)–C(33)	120.3(6)	C(61)–C(62)–C(63)	116.2(7)
N(32)–C(33)–C(34)	118.3(8)	C(62)–C(63)–C(64)	121.0(9)
C(33)–C(34)–C(35)	121.2(7)	C(63)–C(64)–C(65)	122.0(9)
C(34)–C(35)–C(36)	119.5(7)	C(64)–C(65)–C(66)	117.4(8)
C(31)–C(36)–C(35)	117.5(7)	C(61)–C(66)–C(65)	120.3(7)

Numbers in parentheses are estimated standard deviations in the least significant digits.

Finnigan MAT-90 apparatus. GC were carried out on a 2305 chromatogram analyzer (column filling GDX-301; column temperature 180°C).

3.2. Synthesis of compounds

3.2.1. trans-Fe(Ph$_2$Ppy)$_2$(CO)$_3$ (1)

To a solution of NaOH (0.17 g, 4.4 mmol) in n-butane (20 ml) was added Fe(CO)$_5$ (0.28 ml, 2.12 mmol) and the mixture was stirred for 30 min at room temperature. Then Ph$_2$Ppy (1.40 g, 5.32 mmol) was added and the mixture was refluxed for 2 h. During the reaction CO gas was evolved and a yellow precipitate was formed. After the solution was cooled this was collected by filtration and recrystallized from dichloromethane and methanol. Yield: 1.12 g (80%).

3.2.2. FeMo(μ-Ph$_2$Ppy)$_2$(CO)$_6$ (2)

A solution of Fe(Ph$_2$Ppy)$_2$(CO)$_3$ (0.40 g, 0.60 mmol) and Mo(CO)$_6$ (0.16 g, 0.60 mmol) in benzene (25 ml) was heated under reflux for 12 h. After the solution was cooled a red solid was precipitated. This was collected by filtration and washed with benzene and ethyl ether and vacuum dried. Yield: 0.35 g (60%). FD-MS, *m/e* (relative intensity, %): 842 (M^+, 15), 666 ($M^+ -$ Mo(CO)$_3$, 100).

3.2.3. FeNi(μ-Ph$_2$Ppy)$_2$(CO)$_3$(NCS)$_2$ (3)

A solution of Fe(Ph$_2$Ppy)$_2$(CO)$_3$ (0.40 g, 0.60 mmol) in dichloromethane (10 ml) was mixed with a solution of Ni(NCS)$_2$ (0.11 g, 0.60 mmol) in methanol (10 ml). The mixture was stirred for 2 h to form a yellow precipitate. This was collected by filtration and washed

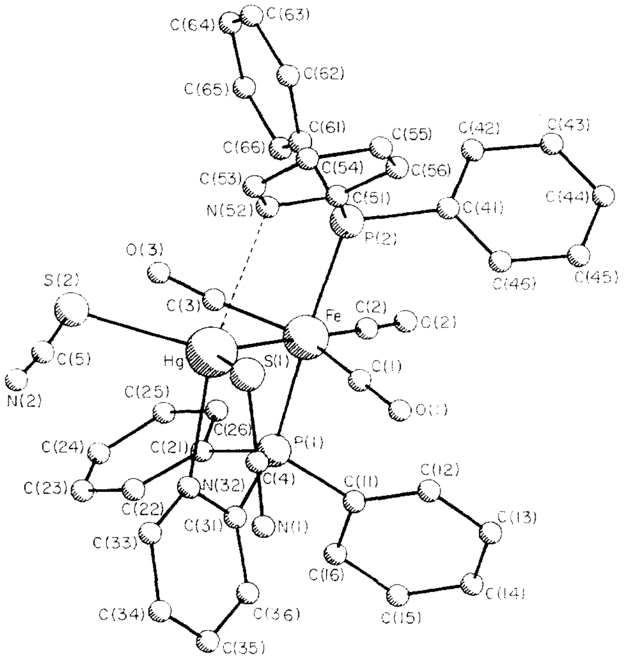

Fig. 2. Molecular structure of FeHg(μ-$Ph_2Ppy)_2(CO)_3(SCN)_2$.

with methanol, dichloromethane and ethyl ether. Yield: 0.30 g (60%).

3.2.4. *FeRh(μ-$Ph_2Ppy)_2$(μ-CO)$(CO)_3Cl_2$ (4)*

A mixture of $Rh_2(CO)_4Cl_2$ (0.10 g, 0.26 mmol) and $Fe(Ph_2Ppy)_2(CO)_3$ (0.34 g, 0.52 mmol) in dichloromethane (20 ml) was stirred for 4 h at room temperature. The volume of the solution was reduced to 5 ml by using a rotary evaporator and ethyl ether was added. An orange solid was precipitated and collected by filtration. The crude product was recrystallized from dichloromethane and ethyl ether. Yield: 0.20 g (50%). FD-MS, *m/e* (relative intensity, %): 830 (M^+, 100).

TABLE 6. Fe–Hg distances of some known complexes

Complex	Fe–Hg (Å)	Ref.
$Cl_2HgFe[CS_2C_2(CO_2Me)_2]$		
$(CO)_2(PMe_2Ph)_2$	2.546	18
$Fe(CO)_4(HgClpy)_2$	2.553	19
$[Fe(CO)_4(HgCl)(HgCl_2)]^-$	2.560	20
	2.516	
$Hg[Fe(CO)_2(NO)(PEt_3)]_2$	2.534	21
$(BrHg)_2Fe(CO)_4$	2.44	22
	2.59	
$FeHg(Ph_2Ppy)_2(CO)_3(SCN)_2$	2.648	this work

3.2.5. *FeCu(μ-$Ph_2Ppy)_2(CO)_3$X [X = Cl (5), Br (6), I (7)]*

A solution of $Fe(Ph_2Ppy)_2(CO)_3$ (0.5 mmol) in dichloromethane (15 ml) was added to a solution of CuX (0.5 mmol) at room temperature. Immediately the solution changed from yellow to orange. Stirring was continued for 30 min. After filtration the volume of the solution was reduced by a rotary evaporator. Then ethyl ether was added and the product was precipitated. Yield: (**5**) 0.30 g (85%), FD-MS, *m/e* (relative intensity, %): 729 (M^+ – Cl, 30), 589 (M^+ – $Fe(CO)_3$, 65); (**6**) 0.26 g (65%), FD-MS, *m/e* (relative intensity, %): 810 (M^+, 5), 729 (M^+ – Br, 100); (**7**) 0.17 g (40%).

3.2.6. *FeHg(μ-$Ph_2Ppy)_2(CO)_3(SCN)_2$ (8)*

$Hg(SCN)_2$ (0.16 g, 0.5 mmol) was added to a solution of $Fe(Ph_2Ppy)_2(CO)_3$ (0.33 g, 0.5 mmol) in dichloromethane (20 ml). At room temperature the mixture was stirred for 3 h and filtered. The filtrate was concentrated and ethyl ether was added to give a pale yellow precipitate. Yield: 0.40 g (83%). FD-MS, *m/e* (relative intensity, %): 926 (M^+ – 2CO, 100), 672 (M^+ – Ph_2Ppy – CO, 60).

3.2.6.1. Reaction of FeHg(μ-$Ph_2Ppy)_2(CO)_3(SCN)_2$ (8) with Na_2S. A solution of $Na_2S \cdot 9H_2O$ (0.06 g) in methanol (10 ml) was added to a solution of $FeHg(Ph_2Ppy)_2(CO)_3(SCN)_2$ (0.2 g, 0.2 mmol) in dichloromethane (20 ml). Immediately a black precipitate was formed. After stirring for 10 min at room temperature the black precipitate was filtered off and the solvent removed by a rotary evaporator. The residue was recrystallized from dichloromethane and ethyl ether. A yellow crystal was obtained. Yield: 0.14 g (100%). IR: ν(CO), 1874 cm^{-1}. ^{31}P NMR ($CDCl_3$, δ) 8.75 ppm.

3.2.6.2. X-ray crystallography of FeHg(μ-Ph_2-$Ppy)_2(CO)_3(SCN)_2$ (8). Crystal data: $C_{39}H_{28}FeHgN_4O_3P_2S_2$, monoclinic space group $P2_1/n$, $a = 16.369(5)$, $b = 13.754(3)$, $c = 17.749(2)$ Å, $\beta = 108.95(2)°$, $V = 3779.5$ Å^3, $M_r = 983.19$, $Z = 4$, $D_x = 1.73$ g/cm^3, $\mu = 56.7$ cm^{-1}, and $F(000) = 1928$.

The single crystal was obtained from CH_2Cl_2/hexane. A pale yellow crystal of approximate dimensions 0.2 × 0.3 × 0.3 mm was mounted on a glass fibre. Intensity data were collected on an Enraf-Nonius CAD4 diffractometer using graphite monochromated Mo Kα radiation ($\lambda = 0.71073$ Å). A total of 4433 independent reflections was collected in the range of $2° \leq \theta \leq 21°$ by ω-2θ scan technique at room temperature (23 ± 1°C), in which 3102 reflections with $I \geq 3\sigma(I)$ were considered to be observed and used in the succeeding refinement. Corrections for Lp factors and

TABLE 7. Fractional coordinates and thermal parameters for non-hydrogen atoms in FeHg(μ-$Ph_2Ppy)_2(CO)_3(SCN)_2$ (**8**)

Atom	x	y	z	B_{eq}/B (Å^2)
Hg	0.04431(4)	0.15916(5)	0.25730(4)	3.40(1)
Fe	0.1450(1)	0.1573(2)	0.4081(1)	2.60(5)
S(1)	−0.1170(4)	0.1245(5)	0.2031(4)	6.9(2)
S(2)	0.0811(4)	0.2413(4)	0.1446(3)	5.9(1)
P(1)	0.2075(3)	0.0170(3)	0.3892(3)	2.9(1)
P(2)	0.0909(3)	0.2968(3)	0.4406(3)	2.7(1)
O(1)	−0.0070(7)	0.0458(9)	0.4083(7)	4.4(3)
O(2)	0.2608(8)	0.156(1)	0.5725(7)	6.0(4)
O(3)	0.2381(8)	0.2684(9)	0.3213(8)	5.2(3)
N(1)	−0.127(1)	−0.076(1)	0.187(1)	6.1(5)
N(2)	−0.021(1)	0.165(2)	0.022(1)	9.1(6)
C(1)	0.053(1)	0.092(1)	0.4057(9)	2.9(3)
C(2)	0.216(1)	0.155(1)	0.508(1)	4.2(4)
C(3)	0.2002(9)	0.224(1)	0.3520(9)	2.8(3)
C(4)	−0.122(1)	0.008(2)	0.195(1)	5.7(5)
C(5)	0.021(1)	0.194(2)	0.076(1)	6.4(5)
C(11)	0.236(1)	−0.067(1)	0.4757(9)	3.2(3)
C(12)	0.186(1)	−0.068(1)	0.526(1)	3.9(4)
C(13)	0.206(1)	−0.133(2)	0.591(1)	5.5(5)
C(14)	0.278(1)	−0.196(1)	0.602(1)	5.1(5)
C(15)	0.325(1)	−0.196(1)	0.551(1)	4.7(4)
C(16)	0.306(1)	-0.130(1)	0.485(1)	4.2(4)
C(21)	0.310(1)	0.030(1)	0.3713(9)	3.3(3)
C(22)	0.323(1)	−0.006(1)	0.303(1)	4.6(4)
C(23)	0.408(1)	0.002(2)	0.297(1)	5.4(5)
C(24)	0.473(1)	0.047(2)	0.355(1)	5.1(5)
C(25)	0.459(1)	0.087(1)	0.420(1)	4.7(4)
C(26)	0.376(1)	0.080(1)	0.429(1)	4.3(4)
C(31)	0.146(1)	−0.061(1)	0.3057(9)	3.3(3)
N(32)	0.1017(9)	−0.013(1)	0.2411(9)	4.4(3)
C(33)	0.060(1)	−0.062(2)	0.172(1)	5.1(5)
C(34)	0.067(1)	−0.165(2)	0.172(1)	4.7(4)
C(35)	0.110(1)	−0.213(1)	0.238(1)	4.6(4)
C(36)	0.153(1)	−0.161(1)	0.309(1)	4.0(4)
C(41)	0.0830(9)	0.292(1)	0.5403(9)	2.7(3)
C(42)	0.124(1)	0.361(1)	0.597(1)	5.0(4)
C(43)	0.119(1)	0.352(2)	0.675(1)	6.4(5)
C(44)	0.074(1)	0.276(2)	0.694(1)	5.3(5)
C(45)	0.035(1)	0.206(2)	0.637(1)	5.6(5)
C(46)	0.039(1)	0.214(2)	0.559(1)	5.1(5)
C(51)	−0.0174(9)	0.332(1)	0.3779(9)	2.9(3)
N(52)	−0.0263(9)	0.333(1)	0.3012(9)	5.0(3)
C(53)	−0.105(1)	0.362(2)	0.250(1)	5.4(5)
C(54)	−0.171(1)	0.388(2)	0.272(1)	5.3(5)
C(55)	−0.164(1)	0.386(1)	0.352(1)	4.8(4)
C(56)	−0.083(1)	0.357(1)	0.407(1)	4.0(4)
C(61)	0.153(1)	0.408(1)	0.4408(9)	3.2(3)
C(62)	0.108(1)	0.495(1)	0.416(1)	4.7(4)
C(63)	0.159(1)	0.579(2)	0.418(1)	5.6(5)
C(64)	0.250(1)	0.574(2)	0.443(1)	6.6(6)
C(65)	0.294(1)	0.487(2)	0.469(1)	5.8(5)
C(66)	0.243(1)	0.402(1)	0.468(1)	4.4(4)

Anisotropically refined atoms are given in the form of the equivalent isotropic thermal parameter defined as: $(4/3) * [a^2 * \beta(1,1) + b^2 * \beta(2,2) + c^2 * \beta(3,3) + ab(\cos r) * \beta(1,2) + ac(\cos \beta) * \beta(1,3) + bc(\cos a) * \beta(2,3)]$.

for the absorption by empirical formula were applied to the data.

The structure was solved by the direct method. The positions of the Fe atom and Hg atom were found from the E-map. The coordinates of the other non-hydrogen atoms were obtained through several difference Fourier syntheses. With anisotropic thermal parameters for the Fe, Hg, P, S, N, and O atoms and isotropic thermal parameters for the C atoms, a unit weights full-matrix least-squares refinement converged at a final convention R factor of 0.057 and the R_w is 0.064. The highest peak on the final difference Fourier map had a height of 0.72 e/Å^3.

All calculations were performed on a PDP 11/44 computer using SDP-PLUS program system.

Fractional atomic coordinates and thermal parameters for the non-hydrogen atoms are given in Table 7.

3.2.7. Catalytic reaction

In a 170 ml autoclave with a magnetic stirrer are placed a certain quantity of ethanol, ethyl iodide and toluene (see Table 3). The autoclave is purged with CO three times, then filled with CO to pressure. The mixture is stirred and heated to the reaction temperature. After the reaction the autoclave is quickly cooled to the room temperature. The reaction mixture is taken out and analyzed by GC.

Acknowledgment

The financial support of the National Science Foundation and Elemento-Organic Chemistry Laboratory, Nankai University is gratefully acknowledged.

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