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Kihara, Noriaki
Bioscience Research Center Mitsui Petrochemical Industries

Saeki, Kenji
Research Center Mitsui Petrochemical Industries

Tashiro, Masashi
Institute of Advanced Material Study Kyushu University

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SYNTHESIS AND CHARACTERIZATION OF NEW TRINUCLEAR Rh(I)-IMIDAZOLATE COMPLEXES

Noriaki KIHARA*, Kenji SAEKI**,
and Masashi TASHIRO

Trinuclear Rh-imidazolate complexes, [Rh(COD)Ims]$_3$ (Ims: imidazolate, benzimidazolate, and 4,5-dimethylimidazolate) and [Rh(CH$_2$=CH$_2$)$_2$Im]$_3$ (Im: imidazolate), were synthesized by the reaction of [Rh(COD)Cl]$_2$ or [Rh(CH$_2$=CH$_2$)$_2$ Cl]$_2$ with the corresponding imidazolate anion in THF.

In connection with biologically active molecules such as iron-heme and vitamin B, numerous transition metal complexes containing neutral imidazole molecules as a ligand have been synthesized and characterized.[1] On the other hand, such complexes having imidazolate anions instead, have been less studied; some of recent examples include the Fe(II),[2] Cu(II),[3] Ni(II),[4] Ir(II),[5] and Cr(III)[6] systems.

Previously, two of the present authors reported in a Japanese patent,[7] the preparation of several kinds of trinuclear Rh(I) complexes having imidazolate as an anionic ligand; the first successful synthesis of this type of Rh(I) complexes to our knowledge. Later, Tripicchio et al. prepared imidazolate-Rh(I) and Ir(I) complexes and found that the complexes having diolefins as a ligand exists mainly in a trinuclear complex, while those having dicarbonyl compounds as a ligand does in a tetranucleous form.[8]

The purpose of the present paper is to give the full details of our earlier report.

Results and Discussion

Trinuclear [Rh(COD)Im]$_3$ was synthesized by four different methods (procedure *a-b*) as shown in Scheme 1.

A slurry of [Rh(COD)Cl]$_2$ in THF was mixed with an equimolar mixture of imidazole and a base (BuLi, LiOH, or NaOEt) at $-65\sim-60$°C and the mixture was then stirred at room temperature for several hours to give yellow crystalline [Rh(COD)Im]$_3$ in 31-68% yield (procedure *a*). This reaction proceeds via [Rh(COD)(ImLi)Cl] or [Rh(COD)(ImNa)Cl] as an intermediate since dehydrochlorination of [Rh(COD)(ImH)Cl], which was obtained by the reaction of [Rh(COD)Cl]$_2$ with imidazole, did not take place. The benzimidazolate complex [Rh(COD)BzIm]$_3$ was similarly prepared in 52% yield.

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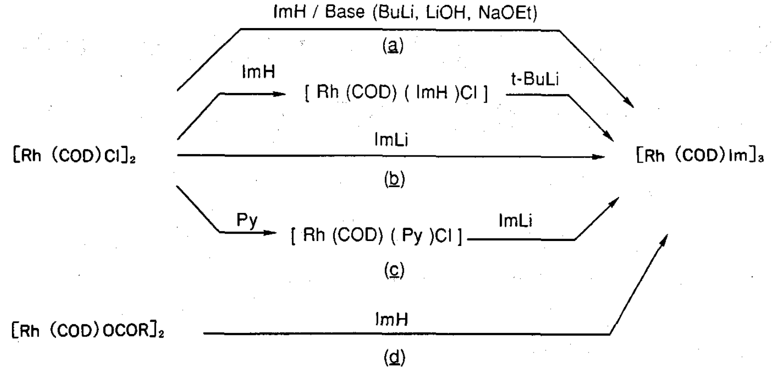
* Bioscience Research Center, Mitsui Petrochemical Industries
** Research Center, Mitsui Petrochemical Industries



COD : cyclooctadiene. ImH : imidazole. Im : imidazolate
Py : pyridine. R : CH_3-, CH_2=CH-.

Scheme 1

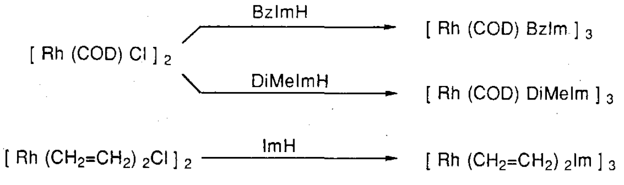
The $[Rh(COD)Im]_3$ complex was also obtained (91% yield) in the reaction of $[Rh(COD)Cl]_2$ with lithium imidazolate (LiIm) (procedure *b*). Moreover, monomeric [Rh(COD)(Py)Cl] gave the Rh-complex, albeit with poor 12% yield, when treated with lithium imidazolate in THF (procedure *c*). Interestingly, the acyloxy anion-coordinated $[Rh(COD)OCOR]_2$ reacted with imidazole in the absence of a base, giving $[Rh(COD)Im]_3$ in 31-71% yield (procedure *d*).

The trinuclear Rh-complex of the 4, 5-dimethylimidazolate anion, $[Rh(COD)DiMeIm]_3$, was prepared by procedure *b* in 39% yield. The imidazolate-Rh-complex with two ethylenes as a neutral ligand, ($[Rh(CH_2{=}CH_2)_2Im]_3$), was similarly prepared (52% yield). (Scheme 2).

Analytical and spectral data of the complexes mentioned previously are given in Table 1. The trinuclear structure of the Rh-complexes was revealed by the molecular weight determination by FD-MS and the vapor pressure osmometric method.

The chemical shift values of the imidazolate ring protons of $[Rh(COD)Im]_3$ and $[Rh(CH_2{=}CH_2)_2Im]_3$ are given in Table 2, together with those of imidazole, sodium imidazolate, and [Rh(COD)(ImH)Cl] for comparison.

The ring-proton signals of the C-2, C-4, and C-5 positions of the neutral imidazole appeared in almost the same region as those of the anionic imidazolate. On the other hand, signals of protons on the C-4 and C-5 positions of the imidazolate ring of $[Rh(COD)Im]_3$ and $[Rh(CH_2{=}CH_2)_2Im]_3$ appeared at 6.63 and 6.68 ppm, respectively, and those values are 0.17-0.12 ppm higher than the one (6.80 ppm) for [Rh(COD)(ImH)Cl]. Interestingly, the C-2 proton of the trinucleaous complexes



BzIm : benzimidazolate. DiMeIm : 4,5-dimethylimidazolate.
Im : Imidazolate.

Scheme 2

Table 1. Properties of Trinuclear Rh-Ims Complexes

complex	anal. found (calcd.)			^{1}H-NMR	IR	FD-MS	MW
	C	H	N	(ppm, $CDCl_3$)	(cm^{-1}, KBr disk)	(m/z)	(Ebullioscopically)
$[Rh(COD)Im]_3$	47.95 (47.50)	5.62 (5.44)	9.99 (10.07)	1.80(m, 4H), 2.40(m, 4H) 4.05(m, 4H), 6.17(s, 1H), 6.63(s, 2H)	2800-3000(6 bands, in COD), 1475, 1460, 1082	834 (M^+)	834 (in 3.395 g/l of CHC13)
$[Rh(CH_2=CH_2)_2Im]_3$	36.84 (37.18)	4.81 (4.91)	12.20 (12.39)	3.00(s, 8H), 6.10(S, 1H), 6.68(s, 2H)	3000 and 3070(ν_{CH} in $CH_2=CH_2$), 1470, 1070, 978, 753, 735	b) —	c) —
$[Rh(COD)BzIm]_3$	53.96 (53.89)	5.29 (5.22)	8.02 (8.02)	a) —	2800-3000(6 bands, in COD), 1605, 1232, 735	983 (M^+-H)	1000 (in 1.208 g/l of C_6H_6)
$[Rh(COD)DiMeIm]_3$	49.98 (50.99)	6.13 (6.25)	8.54 (9.15)	a) —	2800-3000(6 bands in COD), 1470, 1440, 1220, 1210	918 (M^+)	c) —

a) Not measured because of the poor solubility in $CDCl_3$
b) Not detected (M^+, M^+-H)
c) Not measured

showed a large up-field shift of 1.65 ppm, compared with the corresponding signal (7.80 ppm) of [Rh-(COD)(ImH)Cl]. This result is tentatively reasoned that in trinucleaous Rh-complexes having a cyclic structure with alternate rhodium atoms and imidazolate rings (Figure 1), the inside C-2 proton of the imidazolate ring is much more influenced by the rhodium atoms than the outside C-4 and C-5 protons.

At the present time, the preparation of a suitable single crystal for X-ray analysis for precise structure determination of the Rh-complexes has been unsuccessful.

Table 2. Chemical Shifts of C-2, C-4 and C-5 Protons in Different Type of Imidazole Compounds

compound	chemical shift (ppm, $CDCl_3$)	
	C-2	C-4 and C-5
ImH[a]	7.86	7.25
ImNa[a), b)]	7.80	7.21
[Rh(COD)(ImH)Cl]	7.80	6.80
$[Rh(COD)ImH]_3$	6.17	6.63
$[Rh(CH_2=CH_2)_2Im]_3$	6.10	6.68

a) G. B. Barlin and J. B. Batterham, J. Chem. Soc., (B), *1967*, 516
b) In 2N-NaOH

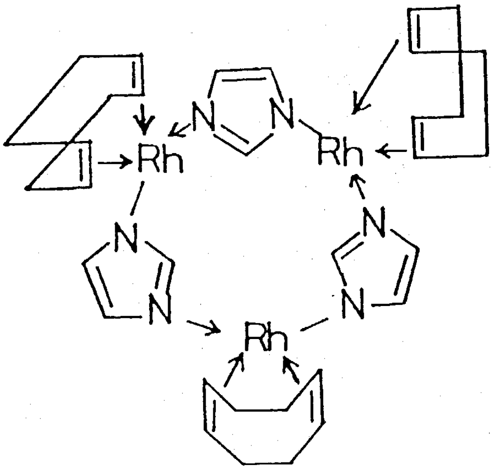


Fig. 1 Structure of $[Rh(COD)Im]_3$

Experimental

All reactions were carried out under argon atmosphere and anhydrous conditions. IR spectra were measured with a JASCO DS-701 spectrometer. ^{1}H-NMR spectra were recorded on a JEOL

JNM-4H-100 spectrometer with TMS as an internal standard. Mass spectra were obtained on a JEOL JMS-DX 303. Molecular weights were measured with a Hitachi 117 vapor pressure osmometer. The concentration of BuLi in haxane was determined by the reported method.$^{9,10)}$ Complexes such as [Rh(COD)Cl]$_2$$^{11)}$, [Rh(COD)(Py)Cl]$^{11)}$, [Rh(CH$_2$=CH$_2$)$_2$Cl]$_2$$^{12)}$, and [Rh(COD)(OCOMe)]$_2$$^{11)}$ were prepared according to the literature.

Preparation of [Rh(COD)Im]$_3$.

A) Procedure *a*. Imidazole (0.067 g, 1.00 mmol) was added to a suspension of [Rh(COD)Cl]$_2$ (0.25 g, 0.50 mmol) in 15 cm^3 of THF at −65∼−60°C, producing a yellow solution. To the mixture, 1.2 M solution (0.83 cm^3) of BuLi in haxane was added dropwise at the same temperature. The reddish yellow mixture was then stirred at room temperature for 1.5 h. Yellow crystals that precipitated were collected by filtration, washed throughly with THF, and dried in vacuo to give [Rh(COD)Im]$_3$ (0.19 g, 68% yield). When LiOH and NaOEt were used in place of BuLi, the yields were 54 and 31%, respectively.

B) Procedure *b*.. [Rh(COD)Cl]$_2$ (3.60 g, 7.30 mmol) was added to a suspension of a 1 : 1-adduct of lithium imidazolate and THF (2.13 g, 14.6 mmol) in THF (18 cm^3). The mixture was stirred at room temperature for 0.5 h and treated as already described to give [Rh(COD)Im]$_3$ (3.68 g, 91%)

C) Procedure *c*. A 1.2 M solution (0.29 cm^3) of BuLi in haxane and a solution of imidazole (0.75 g, 1.10 mmol) in THF (1.00 cm^3) were added successively to a suspension of [Rh(COD)(Py)-Cl] (0.36 g, 1.10 mmol) in THF (10 cm^3) at −65∼−60°C. The mixture was stirred at the same temperature for 4 h and worked up as already described to give [Rh(COD)Im]$_3$ (0.05 g, 12%)

D) Procedure *d*. A mixture of [Rh(COD)OCOMe]$_2$ (0.21 g, 0.40 mmol) and imidazole (0.055 g, 0.80 mmol) in THF (50 cm^3) was stirred at room temperature for 0.5 h and worked up as already described to give [Rh(COD)Im]$_3$ (0.17 g, 77%)

Similarly, the complex was obtaied in 31% yield (0.06 g) starting from [Rh(COD)OCOCH=CH$_2$]$_2$ (0.21 g, 0.37 mmol).

Preparation of [Rh(COD)BzIm]$_3$.

To a suspension of [Rh(COD)Cl]$_2$ (0.77 g, 1.55 mmol) in THF (20 cm^3) was added a hexane solution of BuLi (2.61 cm^3, 3.1 mmol) and 0.37 g (3.1 mmol) of benzimidazole at −65∼−60°C. The mixture was stirred for 3 h at the same temperature and worked up as already described to give 0.52 g (39%) of the titled complex.

Preparation of [Rh(COD)DiMeIm]$_3$.

To a solution of 4,5-dimethylimidazole (0.51 g, 5.3 mmol) in THF (5 cm^3) was added a hexane solution of BuLi (4.5 cm^3, 5.3 mmol) at 4∼5°C for 0.5 h, giving a 1 : 0.75-complex of lithium 4, 5-dimethylimidazolate and THF (1.11 g, 81%). This complex (0.72 g, 2.80 mmol) was added to a suspension of [Rh(COD)Cl]$_2$ (0.69 g, 1.40 mmol) in THF (20 cm^3) at room temperature. The mixture was stirred for 9 h at the same temperature to give 0.73 g (85%) of the titled complex.

Preparation of $[Rh(CH_2=CH_2)_2Im]_3$.

To a solution of imidazole (4.08 g, 60 mmol) in THF (100 cm^3) was added a hexane solution of BuLi (54.5 cm^3, 60 mmol) at 4~5°C for 5 h, giving a 1 :1-complex of lithium imidazolate and THF (8.35 g, 95%). This complex (0.21 g, 1.44 mmol) was suspended in THF (2.6 cm^3) and added to a solution of $[Rh(CH_2=CH_2)_2Cl]_2$ (0.55 g, 1.41 mmol) in THF (20 cm^3) at room temperature. The mixture was stirred for 2 h at the same temperature to give 0.17 g (52%) of the titled complex.

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