Synthesis and reactivity of organoplatinum–rhenium heterobimetallic complexes having sulfur ligands

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Abstract

New organoplatinum–rhenium heterobimetallic complexes (organic ligand = Me (1), Et (2), CH_2Ph (3), Ph (4)) with sulfur ligands have been prepared and characterized by IR, ^1H and $^{13}C\{^1H\}$ NMR, elemental analysis, and chemical reactions. Complex 1 was thermally more stable than related PtMeCl(cod) (5) and PtMe(SPh)(cod) (6). On the other hand, thermolysis reaction of 2 in diphenylmethane at 80°C afforded ethylene in a larger yield than those for PtEtCl(cod) (7) and PtEt(SPh)(cod) (8). From the estimation of electronegativity using ^1H NMR data, it was suggested that Pt in 2 was more electron deficient than in 7 and 8. It is thus proposed that $SRe(CO)_4$ units in 2 decreases the electron density at Pt, resulting in the promotion of apparent β-H elimination to form ethylene.

Keywords: Naphtha reforming; Heterobimetallic complex; Platinum–rhenium; Ligand effect; β-H elimination

1. Introduction

Bimetallic Pt–Re–S/Al_2O_3 catalysts are widely used in the industrial reforming of naphtha to gasoline of high octane value, where Re and S enhance the stability and reactivity of the catalysts [1]. Extensive work has been devoted to clarify the role of Re and S, and it has been frequently explained in terms of ensemble size effect and ligand effect [2]. The ligand effect, proposed by Barbier [2](b), in which sulfur changes the electron density of metal to result in

changes of the catalytic activity and selectivity. On the other hand, Somorjai recently proposed that the changes of catalytic selectivity depend on the ensemble sizes of Pt, which is modified by Re and S [2](d).

In this work, we have prepared new organoplatinum–rhenium heterobimetallic complexes having sulfur ligands as possible models of the Pt–Re–S/Al_2O_3 catalysts. Our interest is focused on the potential influence of ReS units on the reactivity of organic ligands on Pt. Although many Pt–Re complexes have been reported [3], these complexes are to our knowledge the first examples of the Pt–Re complexes having both organic and sulfur ligands.

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2. Results and discussion

2.1. Preparation and identification

Reactions of PtRCl(cod) (R = Me, Et, CH_2Ph, and Ph) with $[Re(SSnMe_3)(CO)_4]_2$ in CH_2Cl_2 gave new Pt–Re complexes 1–4 (Scheme 1) [4]. We expected that simple metathesis reactions would give a tetranuclear complex $[(CO)_4Re(\mu_3\text{-}S)PtR(cod)]_2$ (A), but the reaction proceeded. In a similar NMR tube reaction in CD_2Cl_2, almost quantitative formation of Me_3SnCl and partial liberation of COD were observed, suggesting that 1–4 were formed via dissociation of COD and formal trimerization of A. Complexes 1–4 were recrystallized from CH_2Cl_2. They are moderately air-stable, but handling should be done under an atmosphere of inert gas.

Complexes 1–4 have been characterized by IR, ^1H and $^{13}C\{^1H\}$ NMR, elemental analysis, and chemical reactions. Selected NMR and IR data are summarized in Table 1. IR spectrum of 1–4 showed ν_{CO} bands at ca. 2100–1900 cm^{-1}, which resembled those of starting $[Re(SSnMe_3)(CO)_4]_2$. In ^1H NMR of 1, three kinds of singlets due to methyl groups were

observed at δ 1.0–1.3 with ^{195}Pt satellites (Fig. 1). COD's olefinic protons gave four signals with ^{195}Pt satellites, and their δ and J_{PtH} values were in the typical ranges of those of square planar Pt(II) complexes with a COD ligand. The two high-field signals at δ 4.9 and 5.0 had larger J_{PtH} values than the low-field ones at δ 5.6 and 5.7. Since the trans influence of methyl groups is larger than that of thiolate groups, the lower field signals may be assigned to olefinic protons trans to Me. The existence of two kinds of high- and low-field signals suggests that 1 has two kinds of square planar PtMe(cod) units. From the integration of Me and COD signals, it is reasonably expected that 1 contains PtMe and Pt(cod) parts in a 3:2 ratio.

$^{13}C\{^1H\}$ NMR data of 1 were consistent with the above ^1H NMR data. Three signals due to Me groups appeared at δ −12.07, 10.72, and 11.19 with ^{195}Pt satellites, and the δ and J_{PtH} values were in the typical ranges of methyl Pt(II) complexes [5]. Perhaps, the signal at δ −12.07 was due to Me^1. Four COD's olefinic carbons were observed at δ 93.84, 95.67, 112.05, and 112.11, and the J_{PtC} values of the two signals at high field were larger than those of the other two signals at low field: 164–165
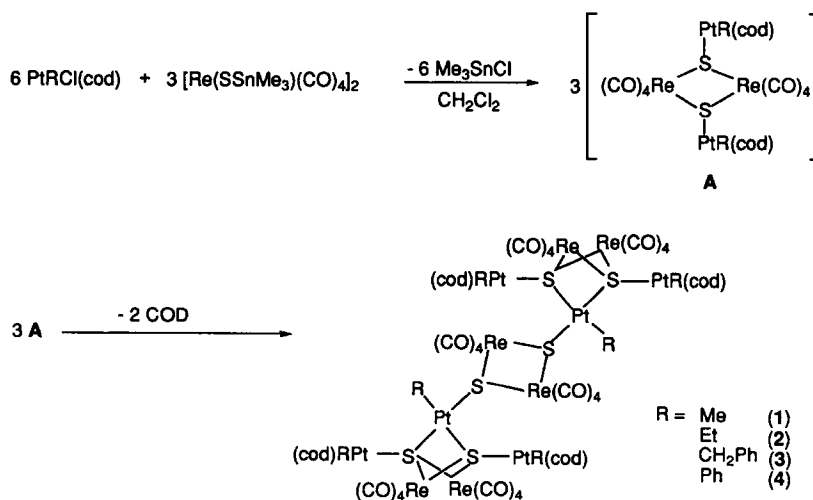
Scheme 1.
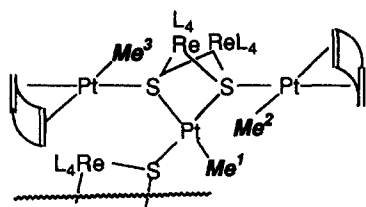
L = CO

Fig. 1. Half of the symmetrical structure of 1.

Hz vs. 26–33 Hz. According to the assignment of COD protons in ^{1}H NMR, the two high-field signals were assignable to olefinic carbons *trans* to S and the two low ones *trans* to Me. Signals due to carbonyl carbons appeared at δ 194–195.

Considering partial liberation of the COD ligand in the preparation reaction and spectroscopic data in addition to chemical reactions (see below), the expected structure of 1 is deduced as shown in Figs. 1 and 1. In Fig. 1, the two PtMe(cod)(S-) units are present in different coordination circumstances around the PtMe(S-)$_3$ unit. Thus, one Me group corresponds to Me^1
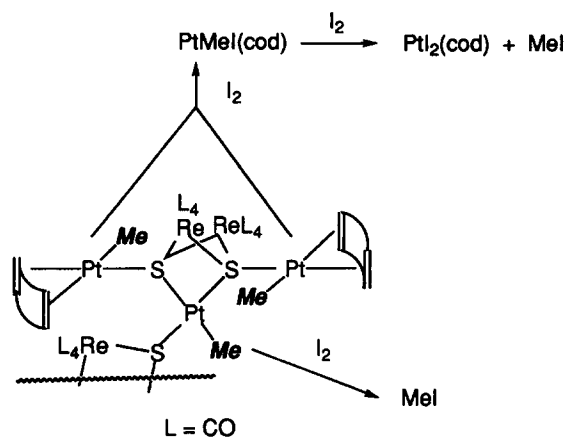
in the PtMe(S-)$_3$ unit and the other two to Me^2 and Me^3 in the PtMe(cod)(S-) units, where two kinds of COD's olefinic parts exist *cis* and *trans* to Me^1 around the square planar PtMe(S-)$_3$ unit. Accordingly, it is interpreted that the intermediate A spontaneously trimerized to give 1 with liberation of one third of COD ligands.

Satisfactory results were obtained in elemental analysis for 1 and 2. Acidolysis of 1 with excess conc. H_2SO_4 liberated methane in 620% yield per 1, supporting the presence of six methyl groups. Reaction of 1 with excess HCl in ether gave methane and PtMeCl(cod) in 150 and 270% yields, respectively, suggesting the presence of two kinds of PtMe units, i.e., PtMe(S-)$_3$ and PtMe(cod)(S-) (see Fig. 1). In reaction of 1 with excess I_2 in C_6D_6, PtMeI(cod) and MeI were initially observed in ^{1}H NMR, and finally PtI$_2$(cod) and MeI were formed in 39 and 82% yields. Perhaps, PtMe(cod)(S-) units in 1 was reacted with I_2 to give PtMeI(cod), which was further reacted with I_2 to result in the formation

Table 1

^{1}H NMR and IR data of [{(CO)$_4$Re(μ_4-S)PtR(cod)}$_2$PtR(μ_3-S)Re(CO)$_4$]$_2$

| Complex | ^{1}H NMR in CDCl$_3$ at r.t. | | | | | | IR, cm^{-1} [a] |
| | Pt–R | | | cod (–C=C–) | | cod (–CH$_2$–) | ν(CO) |
	δ, ppm	J_{Pt-H}, Hz	J_{H-H}, Hz	δ, ppm	J_{Pt-H}, Hz	δ, ppm	
PtMeCl(cod)	0.89(s, 3H)	72.0		4.50(br, 2H)	78	2.2–2.5(m, 8H)	
				5.52(br, 2H)	35		
R = Me (1)	1.08(s, 6H)	70.8		4.9(br, 4H)	66	2.3–2.7(m, 32H)	2074, 2062, 2021,
	1.11(s, 6H)	68.8		5.0(br, 4H)	71		2008, 1991br, 1891br
	1.29(s, 6H)	76.2		5.6(br, 4H)	31		
				5.7(br, 4H)	34		
R = Et (2)	1.16(t, 6H)		7.8	4.8(br, 4H)	71	2.3–2.7(m, 32H)	2102, 2054, 2003,
	1.20(t, 6H)		7.8	4.9(br, 4H)	73		1904br, 1894br
	1.37(t, 6H)		7.6	5.7(br, 4H)	35		
	1.83(q, 4H)	62	7.8	5.8(br, 4H)	27		
	1.93(q, 4H)	78	7.8				
	2.30(q, 4H)	80	7.6				
R = CH$_2$Ph (3)	3.24(s, 4H)	106.9		4.4(br, 4H)	81	2.2–2.6(m, 32H)	2057, 2023, 2007,
	3.52(s, 4H)	104.1		4.6(br, 4H)	78		1912br, 1901br
	4.01(s, 4H)	106.9		5.7(br, 4H)	33		
	7.0–7.5(m, Ph)			5.8(br, 4H)	33		
R = Ph (4)	6.7–7.2(m, Ph)			4.2(br, 4H)	66	1.2–1.9(m, 32H)	2065, 2008, 1895br
				4.4(br, 4H)	69		
				5.7(br, 4H)	27		
				6.2(br, 4H)	28		

[a] KBr disk.

Scheme 2.

of $PtI_2(cod)$ and MeI (Scheme 2). Reaction of PtMe(S-)$_3$ units with I_2 also gave MeI.

In an NMR sample tube reaction of **1** with excess PMe_2Ph in $CDCl_3$, $[PtMe(PMe_2Ph)_3]^+$ [6] species and free COD were observed in 580% and 380% yields, respectively. In this reaction, the counter anion has not been identified but may be $[SRe(CO)_4]_2^{2-}$ (Eq. 1).

$$\mathbf{1} \xrightarrow[CDCl_3, r.t.]{excess\,PMe_2Ph} 6[PtMe(PMe_2Ph)]^+$$

$$+ "3[SRe(CO)_4]_2^{2-}" + 4COD \qquad (1)$$
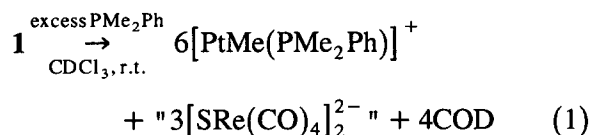
2.2. Reactivity

Thermal stability of methyl complex **1** has been compared to the related methylplatinum complexes $PtMeCl(cod)$ (**5**) and $PtMe(SPh)(cod)$ (**6**). The melting point of **1** (236–238°C, dec) was much higher than those of **5** (166–169°C, dec) and **6** (147–149°C, dec). In thermolysis reactions in C_6D_6 at 75°C for 72 h, **1** was completely unchanged while **5** and **6** were decomposed in 23% and 93% of conversions, respectively. These data show that the ReS unit greatly increases the thermal stability of Pt–Me bonds.

In thermolysis reactions of ethyl complexes **2**, $PtEtCl(cod)$ (**7**), and $PtEt(SPh)(cod)$ (**8**) in

diphenylmethane at 80°C for 3 h, ethylene and ethane were formed as organic products (Eq. 2).

$$PtEtXL_2 \xrightarrow[CH_2Ph_2, 3\,h]{\Delta(80°C)} C_2H_4 + C_2H_6 \qquad (2)$$
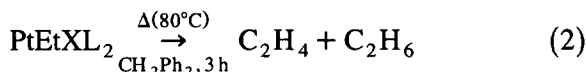
The yields of ethylene and ethane formed from the respective complexes were as follows; **2**, 42, 15%; **7**, 13, 6%; **8**, 22, 12%. Interestingly, **2** showed a higher yield of ethylene than **7** and **8**. The apparent β-H elimination process to liberate ethylene is facilitated by the $SRe(CO)_4$ ligand.

In order to explain the increased yield of ethylene from **2**, we have compared the electron density at Pt in **2**, **7**, and **8**, where the relationship between electronegativity χ of Pt and the chemical shift difference $\Delta(\delta_{CH_2} - \delta_{CH_3})$ of the ethyl group in ^1H NMR was applied: $\chi = 0.62\Delta + 2.07$ [7]. The χ values for **2**, **7**, and **8**, were calculated to be 2.5–2.6, 2.4, and 2.2, respectively, while that of Pt(0) is 1.5 (Allred–Rochow value). This suggests that the Pt atom in **2** is more electron deficient than those in **7** and **8**. Thus, we tentatively propose that the $SRe(CO)_4$ ligand in **2** may decrease the electron density at Pt, resulting in the promotion of β-H elimination to form ethylene [8]. However, detailed study is necessary to determine the mechanism of the formation of ethylene.

The above results may indicate that the ligand effect of Re and S enhances the dehydrogenation of hydrocarbons on $Pt–Re–S/Al_2O_3$ catalysts, resulting in the increase of octane value in the practical naphtha-reforming products.

3. Experimental

All manipulations were carried out using an atmosphere of N_2 with Schlenk techniques. Solvents were distilled from appropriate drying agents under N_2 prior to use. Infrared spectra were measured on a Jasco IR A302 and an FTIR 5M spectrometers. ^1H and $^{13}C\{^1H\}$ NMR spectra were obtained on JEOL FX-200 and

GX-400 spectrometers. Elemental analysis was performed with a Yanagimoto CHN Autocorder MT-2. Gases were quantitatively analyzed by gas chromatography (Shimadzu GC-8AFP, GC-3BT) using the internal standard method. The starting materials and related complexes were prepared by the literature methods: PtRCl(cod) (R = Me, Et, CH_2Ph, Ph) [9], [(CO)$_4$Re(μ_3-S)SnMe$_3$]$_2$ [10].

3.1. Preparation of complexes

A typical procedure for **1** (R = Me) is given. A Schlenk tube was charged with PtMeCl(cod) (264.7 mg, 0.6974 mmol), [(CO)$_4$Re(μ_3-S)SnMe$_3$]$_2$ (369.8 mg, 0.3742 mmol), and CH_2Cl_2 (2 ml). The mixture was refluxed for 3 min, and the resulting red–brown solution was cooled to room temperature. Addition of hexane to the solution gave yellow solid, and the filtered solid was washed with hexane. An independent NMR tube reaction in CD_2Cl_2 revealed the formation of Me$_3$SnCl (102%/Pt) and liberation of free COD (34%/Pt). Recrystallization from CH_2Cl_2 at $-20°C$ gave pale yellow plates (125.1 mg). Yield: 30% based on Pt. Mp: 236–238°C dec. Analysis, calculated for $C_{62}H_{66}O_{24}S_6Re_6Pt_6$: C, 20.26; H, 1.81. Found: C, 20.47; H, 2.09. IR and ^1H NMR data: see Table 1. $^{13}C\{^1H\}$ NMR (CDCl$_3$, r.t.): δ -12.07 (s, J_{PtC} = 502 Hz, Me), 10.72 (s, J_{PtC} = 605 Hz, Me), 11.19 (s, J_{PtC} = 614 Hz, Me), 28.55 (s, cod CH_2 trans to S), 28.62 (s, cod CH_2 trans to S), 31.33 (s, cod CH_2 trans to Me), 31.51 (s, cod CH_2 trans to Me), 93.84 (s, J_{PtC} = 162 Hz, olefinic, cod = CH trans to S), 95.67 (s, J_{PtC} = 164 Hz, olefinic, cod = CH trans to S), 112.05 (s, J_{PtC} = 18 Hz, olefinic, cod = CH trans to Me), 112.11 (s, J_{PtC} = 18 Hz, olefinic, cod = CH trans to Me), 194.07 (s, CO), 194.22 (s, CO), 194.75 (s, CO).

Complexes **2–4** were prepared by a similar method to that for **1**. **2**: yellow crystals. Yield: 15%. Analysis, calculated for $C_{68}H_{78}O_{24}S_6Re_6Pt_6$: C, 21.7; H, 2.09. Found: C, 22.3; H, 2.46. IR and ^1H NMR data: see

Table 1. $^{13}C\{^1H\}$ NMR (CDCl$_3$, r.t.): δ 7.71 (s, J_{PtC} = 528 Hz, CH_2CH_3), 16.30 (s, Me), 17.12 (s, Me), 19.94 (s, Me), 23.95 (s, J_{PtC} = 586 Hz, CH_2CH_3), 24.66 (s, J_{PtC} = 604 Hz, CH_2CH_3), 27.97 (s, cod CH_2 trans to S), 28.03 (s, cod CH_2 trans to S), 31.22 (s, cod CH_2 trans to Et), 31.39 (s, cod CH_2 trans to Et), 93.06 (s, J_{PtC} = 183 Hz, olefinic, cod = CH trans to S), 94.87 (s, J_{PtC} = 180 Hz, olefinic, cod = CH trans to S), 113.92 (s, olefinic, cod = CH trans to Et), 114.08 (s, olefinic, cod = CH trans to Et), 193.59 (s, CO), 193.89 (s, CO). Complex **3** and **4** were obtained as pale yellow powders from CH_2Cl_2/hexane. **3**: yield: 36%. **4**: yield: 30%. These complexes were identified by the spectroscopic methods. IR and ^1H NMR data: see Table 1.

Complexes **6** and **8** were prepared from PtRCl(cod) (R = Me, Et) and KSPh. Typically, a Schlenk tube was charged with PtMeCl(cod) (198.4 mg, 0.555 mmol), KSPh (100.6 mg, 0.679 mmol), and CH_2Cl_2 (2 ml), and the solution was stirred for 2 h at room temperature. After the filtered solution was evaporated to dryness, the resulting solid was extracted with CH_2Cl_2 and pale yellow blocks were obtained at $-20°C$. Yield: 75%. Mp: 147–149°C dec. Analysis, calculated for $C_{15}H_{20}SPt$: C, 42.15; H, 4.72; S, 7.50. Found: C, 42.21; H, 4.78; S, 7.25. ^1H NMR (CDCl$_3$, r.t.): δ 0.63 (s, 3H, J_{PtH} = 73.9 Hz, Me), 2.1–2.6 (m, 8H, cod CH_2), 4.5 (br, 2H, J_{PtH} = 59 Hz, cod = CH trans to SPh), 4.9 (br, 2H, J_{PtH} = 34 Hz, cod = CH trans to Me), 7.09 (t, 1H, J_{PtH} = 7.6 Hz, p-in SPh), 7.21 (t, 2H, J_{PtH} = 7.3 Hz, m-in SPh), 7.48 (d, 2H, J_{PtH} = 7.0 Hz, o-in SPh). $^{13}C\{^1H\}$ NMR (CDCl$_3$, r.t.): δ 5.01 (s, J_{PtC} = 659 Hz, Me), 28.38 (s, cod CH_2 trans to S), 31.62 (s, cod CH_2 trans to Me), 88.72 (s, J_{PtC} = 126 Hz, olefinic, cod = CH trans to S), 107.37 (s, olefinic, cod = CH trans to Me), 125.97 (s, arom CH), 127.95 (s, arom CH), 128.00 (s, arom CH), 135.12 (s, arom CH), 135.23 (s, arom CH), 139.31 (s, J_{PtC} = 38 Hz, C_6H_5 ipso bearing S). **8**: Yield: 89%. Mp: 116–117°C dec. Analysis calculated for $C_{16}H_{22}SPt$: C, 43.52; H,

5.02. Found: C, 43.13; H, 4.94. ^{1}H NMR
(CDCl$_3$, r.t.): δ 1.14 (s, 3H, $J_{PtH} = 54.0$ Hz,
$J_{HH} = 7.6$ Hz, Me), 1.37 (q, 2H, $J_{PtH} = 153$ Hz,
$J_{HH} = 7.6$ Hz, CH_2CH$_3$), 2.0–2.6 (m, 8H, cod
CH_2), 4.4 (br, 2H, $J_{PtH} = 60$ Hz, cod $=$ CH
trans to SPh), 4.9 (br, 2H, $J_{PtH} = 26$ Hz, cod $=$
CH *trans* to Me), 7.07 (t, 1H, $J_{PtH} = 7.3$ Hz,
p-in SPh), 7.19 (t, 2H, $J_{PtH} = 7.6$ Hz, *m*-in
SPh), 7.50 (d, 2H, $J_{PtH} = 7.0$ Hz, *o*-in SPh).

3.2. Reaction of 1 with PMe$_2$Ph

An NMR sample tube containing **1** (13.8 mg,
3.76 μmol) was attached to a vacuum line, and
dry CDCl$_3$ (0.4 ml) was introduced by vacuum
transfer. After excess PMe$_2$Ph (13 μl, 91 μmol)
and dioxane (0.25 μl, 3.0 μmol) were added to
the solution, the system was allowed to stand at
room temperature for 6 h. [PtMe(PMe$_2$Ph)$_3$]$^+$
(580% yield based on **1**) and free COD (380%)
were observed in ^{1}H NMR of the resulting
mixture. [PtMe(PMe$_2$Ph)$_3$]$^+$: δ 0.52 (d, 3H,
$J_{PH} = 7.5$ Hz, $J_{PtH} = 57$ Hz, Me), 1.3 (d, 6H,
$J_{PH} = 9.4$ Hz, $J_{PtH} = 17$ Hz, P*Me*$_2$Ph *trans* to
Me), 1.6 (P*Me*$_2$Ph *cis* to Me), 7.3–7.8
(PMe$_2$*Ph*). The PMe$_2$Ph *cis* to Me was rapidly
exchanged with free PMe$_2$Ph in CDCl$_3$.

3.3. Thermolysis reactions

Thermolysis reactions of methyl complexes
1, **5**, and **6** were carried out in C$_6$D$_6$ at 75°C in
NMR sample tubes. After 72 h, conversions of
the complexes were determined by ^{1}H NMR
(dioxane as internal standard).

Thermolysis reactions of ethyl complexes **2**,
7, and **8** were carried out in Schlenk tubes.
Typically, a CH$_2$Ph$_2$ (2 ml) solution of **2** (14.1
mg, 3.75 μmol) was placed in a Schlenk tube
with a serum cap and degassed. Methane (1.10

ml) was added as an internal standard, and the
solution was stirred at 80°C. Evolved gases
were analyzed by GC.

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