Journal of Organometallic Chemistry 693 (2008) 3638–3642

Contents lists available at ScienceDirect

Journal of Organometallic Chemistry

journal homepage: www.elsevier.com/locate/jorganchem

High selectivity for L-cysteine residue at axial solvated site of trigonal–bipyramidal palladium(II) complex with tripodal tetradentate phosphine

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ARTICLE INFO

Article history:
Received 1 August 2008
Received in revised form 3 September 2008
Accepted 4 September 2008
Available online 10 September 2008

Keywords:
Trigonal–bipyramidal palladium(II)
Selective coordination
Thiolate sulfur atom
L-Cysteine residue

ABSTRACT

The five-coordinate trigonal–bipyramidal palladium(II) and platinum(II) complexes with sulfur-coordinated glutathione at the axial position, $[Pd(gluta)(pp_3)](BF_4)$ and $[Pt(gluta)(pp_3)](PF_6)$ (gluta = glutathionate, pp_3 = tris[2-(diphenylphosphino)ethyl]phosphine), were prepared and characterized by ^{31}P NMR spectroscopy. The dimeric square-planar platinum(II) complex $[Pt(pp_3)]_2(PF_6)_4$ gave the monomeric five-coordinate solvated complex, $[Pt(pp_3)(CH_3CN)]^{2+}$, in acetonitrile. Extraction experiments for amino acids from the aqueous solution to the chloroform layer were carried out by using $[Pd(pp_3)(CH_3CN)]^{2+}$, $[Pt(pp_3)(CH_3CN)]^{2+}$, and $[Pd(p_3)(CH_3CN)]^{2+}$ (p_3 = bis[2-(diphenylphosphino)ethyl]phenylphosphine) as extractants. High selectivity for the thiolate sulfur atom in L-cysteinate was observed at the solvated coordination site in $[Pd(pp_3)(CH_3CN)]^{2+}$. The selectivity was applied to extraction of L-cysteinate from a mixture of some amino acids and, further, the reduced form of glutathionate from a mixture of the reduced and oxidized forms of glutathione.

1. Introduction

A variety of donor atoms such as carbon, nitrogen, oxygen, phosphorus, sulfur, and halogens can form relatively stable four-coordinate square-planar palladium(II) and platinum(II) complexes. On the other hand, five-coordinate trigonal–bipyramidal palladium(II) and platinum(II) complexes are formed preferably by the ligands with donor atoms in the third and fourth periods such as phosphorus, sulfur, arsenic, and selenium [1–9] because the higher energy levels of the donor orbitals are effective in formation of the longer σ bonds to reduce the electronic repulsion in the higher coordination numbers. Such a preference of the five-coordinate palladium(II) and platinum(II) complexes can be of great advantage in distinguishing the sulfur-containing functional groups from the invariably contained nitrogen and oxygen donors in biological systems.

Since L-cysteine and L-cysteine residue play important roles in biochemical reactions, we have investigated the selectivity for the thiolate sulfur atom in L-cysteinate by using the five-coordinate palladium(II) complexes with the tripodal tetradentate phosphine, $[Pd(pp_3)(CH_3CN)]^{2+}$ (pp_3 = tris[2-(diphenylphosphino)ethyl]phosphine) [10], in which the solvated coordination site is available to the entering donor atom. The selectivity at the solvated site has been compared to those of the corresponding platinum(II) complex and the four-coordinate square-planar palladium(II) complex with the tridentate phosphine, $[Pd(p_3)(CH_3CN)]^{2+}$ (p_3 = bis[2-(diphenylphosphino)ethyl]phenylphosphine) [11]. To clarify the selectivity for the thiolate sulfur atom in L-cysteine, we have examined extraction experiments by using four kinds of amino acids, L-cysteine, L-penicillamine, L-methionine, and L-alanine (Scheme 1). Furthermore, we have applied the selectivity to separation of a mixture of the reduced and oxidized forms of glutathione (γ-L-glutamyl-L-cysteinyl-glycine) (Scheme 2), redox of which is quite important in the biological detoxification systems [12].

2. Experimental

2.1. Materials and instruments

Tris[2-(diphenylphosphino)ethyl]phosphine (pp_3), bis[2-(diphenylphosphino)ethyl]phenylphosphine (p_3), tetrakis(acetonitrile)palladium(II) tetrafluoroborate ($[Pd(CH_3CN)_4](BF_4)_2$), silver hexafluorophosphate, L-penicillamine, and glutathione (reduced form) were purchased from Aldrich, potassium tetrachloroplatinate(II) ($K_2[PtCl_4]$), tetra-*n*-butylammonium iodide (n-Bu_4NI), L-cysteine, L-methionine, and L-alanine, from Wako, and glutathione (oxidized form), from ACROS. ^{31}P and ^1H NMR spectra were recorded on a JEOL JNM-A400 FT-NMR spectrometer operating at 160.70 and 399.65 MHz, respectively. In order to determine the ^{31}P NMR chemical shifts, a 3-mm-o.d. NMR tube containing the sample solution was coaxially mounted in a 5-mm-o.d. NMR

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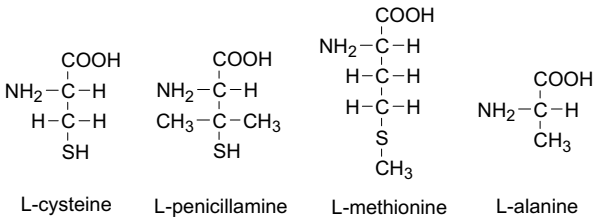
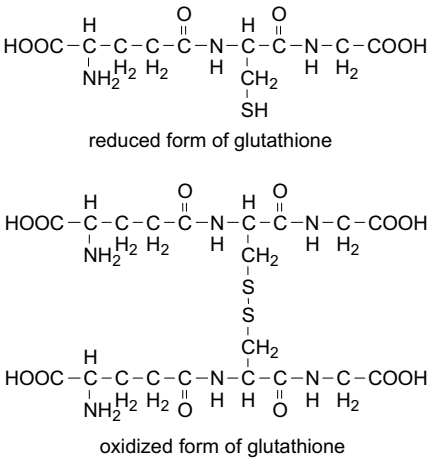
doi:10.1016/j.jorganchem.2008.09.001



Scheme 1.



Scheme 2.

tube containing deuterated water as a lock solvent and phosphoric acid as a reference. UV–Vis absorption spectra were recorded on a Perkin–Elmer Lambda 19 spectrophotometer.

2.2. Preparation of complexes

2.2.1. $[Pd(pp_3)](BF_4)_2$ (**1**) and $[Pd(p_3)(CH_3CN)](BF_4)_2$ (**2**)

The palladium complexes with pp_3 and p_3 were prepared by procedures similar to those reported [10,11].

2.2.2. $[Pt(pp_3)]_2(PF_6)_4$ (**3**)

The preparation of the chloride-free platinum(II) complex reported by King et al. [13] was modified by using $AgPF_6$ instead of NH_4PF_6 to effectively remove the chloride ions. To a solution containing $[PtCl(pp_3)]Cl$ [13] (0.538 g, 0.574 mmol) in chloroform (15 cm^3) was added a solution containing $AgPF_6$ (0.300 g, 1.186 mmol) in acetonitrile (15 cm^3) and the solution was stirred at room temperature for 18 h. Precipitated AgCl was filtered off and the filtrate was concentrated to ca. 3 cm^3, followed by addition of ethanol. The resultant colorless crystals were filtered, and then dried. Anal. Calc. for $C_{84}H_{84}F_{24}P_{12}Pt_2 \cdot CHCl_3$: C, 42.00; H, 3.52; N, 0.00. Found: C, 41.70; H, 3.59; N, 0.00%. $^{31}P\{^1H\}$ NMR (CH_3NO_2): δ13.1 (d, $^2J_{P-P}$ = 298 Hz, $^1J_{P-Pt}$ = 2478 Hz), 43.9 (s, $^1J_{P-Pt}$ = 2366 Hz), 101.2 (d, $^2J_{P-P}$ = 298 Hz, $^1J_{P-Pt}$ = 2132 Hz), 165.4 (se, $^2J_{P-F}$ = 710 Hz); $^{31}P\{^1H\}$ NMR (CH_3CN): δ−14.1 (s, $^1J_{P-Pt}$ = 1914 Hz), 36.5 (s, $^1J_{P-Pt}$ = 2479 Hz), 114.1 (s, $^1J_{P-Pt}$ = 2641 Hz), 165.1 (se, $^2J_{P-F}$ = 706 Hz).

2.2.3. $[Pd(gluta)(pp_3)](BF_4)$ (gluta = glutathionate) (**4**)

To a solution containing **1** (0.405 g, 0.426 mmol) in acetonitrile (20 cm^3) was added an alkaline solution (5 cm^3, pH 9) containing the reduced form of glutathione (0.135 g, 0.439 mmol), and the solution was concentrated by gradual evaporation of the solvent to give red crystals. Anal. Calc. for $C_{52}H_{58}N_3BF_4P_4SPd \cdot H_2O$: C, 50.28; H, 5.35; N, 3.38. Found: C, 50.72; H, 5.49; N, 3.54%. $^{31}P\{^1H\}$ NMR (CH_3CN/H_2O (1:2 v/v)): δ32.3 (s), 138.1 (s). UV–Vis (0.03 M NaOH aq): λ_{max}/nm ($\log(\varepsilon/M^{-1}\,cm^{-1})$) 520 (3.38), 414 (3.68).

2.2.4. $[Pt(gluta)(pp_3)](PF_6)$ (**5**)

The yellow platinum(II) complex with glutathionate was prepared by a procedure similar to that for **4** using **3** instead of **1**. $^{31}P\{^1H\}$ NMR (CH_3CN/H_2O (3:1 v/v)): δ21.7 (s, $^1J_{P-Pt}$ = 2600 Hz), 127.6 (s, $^1J_{P-Pt}$ = 2019 Hz), 164.8 (se, $^2J_{P-P}$ = 707 Hz). UV–Vis (CH_3CN/H_2O (3:1 v/v)): λ_{max}/nm ($\log(\varepsilon/mol^{-1}\,kg\,cm^{-1})$) 434 (3.37), 367 (3.66).

2.3. Extraction procedures

To a solution containing **1** (0.0082 g, 0.0087 mmol) in acetonitrile (ca. 5 cm^3) was added an aqueous solution (ca. 5 cm^3) containing L-cysteine (0.0022 g, 0.0174 mmol). The resultant complex was extracted with chloroform and characterized by the ^{31}P NMR spectrum. To the chloroform layer containing the extracted complex was added a small amount of chloroform solution (ca. 2 cm^3) of n-Bu_4NI (0.0032 g, 0.0087 mmol). The chloroform solution was stirred with water (ca. 5 cm^3) for several minutes, and the water layer was concentrated to dryness, followed by the ^1H NMR measurement. Similar extraction procedures were carried out by using L-penicillamine, L-methionine, L-alanine, a equimolar mixture of L-cysteine, L-penicillamine, L-methionine, and L-alanine, the reduced and oxidized forms of glutathione, and a 1:1 mixture of both forms. The above extraction procedures for the amino acids were carried out by using **2** (0.0074 g, 0.0087 mmol) and **3** (0.010 g, 0.0041 mmol).

3. Results and discussion

3.1. Characterization

As shown in Fig. 1, the ^{31}P NMR spectrum of **3** in nitromethane is consistent with the dimeric square-planar structure proposed by King et al. [13] showing the three ^{31}P NMR signals coupled with ^{195}Pt corresponding to the bridging phosphorus atom (P_1), the two terminal ones (P_2), and the central one (P_3) and, further, the relatively strong coupling between P_1 and P_3 characteristic of the phosphorous atoms trans to each other [14]. From

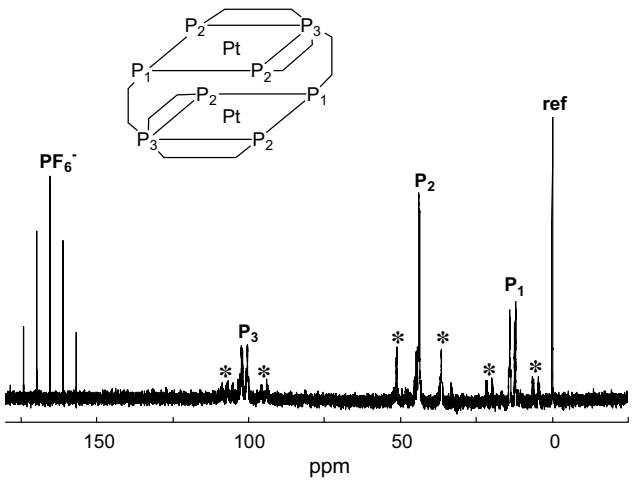


Fig. 1. ^{31}P NMR spectrum of **3** in nitromethane. **Ref** and asterisks denote the signal for D_3PO_4 in outer D_2O and the satellite signals due to the coupling with ^{195}Pt, respectively.

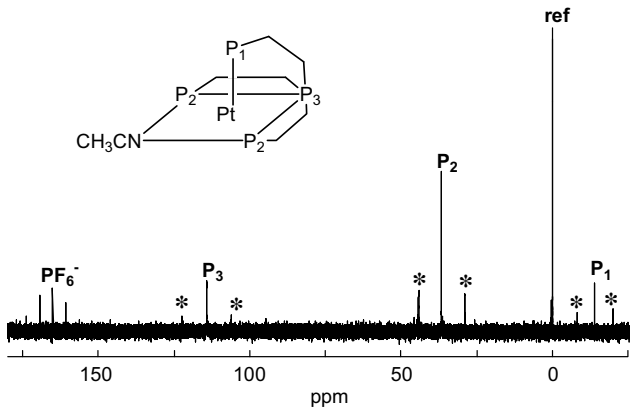


Fig. 2. ^{31}P NMR spectrum of **3** in acetonitrile. **Ref** and asterisks denote the signal for D_3PO_4 in outer D_2O and the satellite signals due to the coupling with ^{195}Pt, respectively.

disappearance of the P_1–P_3 coupling in Fig. 2, it is indicated that the dimeric structure is broken up into the monomeric one without bridging P_1 in a diluted acetonitrile solution. The relatively weak P–Pt coupling of P_1 ($^1J_{P-Pt}$ = 1914 Hz) can be attributed to the weak coordination of P_1 in the apical site of the square-pyramidal acetonitrile-solvated complex, $[Pt(pp_3)(CH_3CN)]^{2+}$, as shown in Fig. 2.

The glutathionato Pd(II) and Pt(II) complexes with pp_3, **4** and **5**, take the trigonal–bipyramidal structure with C_3 symmetry showing the two ^{31}P NMR signals for the equatorial and axial phosphorus atoms (see Section 2). Because the ^{31}P NMR chemical shifts of the equatorial and axial phosphorus atoms are quite variable with σ and π donicities of the axial ligand, one can assign the axially coordinated donor atom of the pp_3 complexes by the ^{31}P NMR chemical shifts [10]. The chemical shifts of the equatorial and axial phosphorus atoms for **4** and **5** are quite close to those of $[M(pt)(pp_3)](BF_4)$ (M = Pd [3,15], Pt [5,16]; pt = 1-propanethiolate), respectively, indicating that the glutathionato ligand is coordinated with its thiolato sulfur atom in both cases. These structures of **4** and **5** are supported by their absorption spectra quite similar to those of $[M(pt)(pp_3)](BF_4)$ (M = Pd [3,15], Pt [5,16]), respectively, showing the two absorption bands characteristic of the five-coordinate trigonal–bipyramidal geometry that can be assigned to the transitions from $^1A_1'$ to $^1E'$ and $^1E''$ [9]. From the fact that the ^{11}B NMR signal for BF_4^- and ^{31}P NMR signal for PF_6^- were observed for **4** and **5**, respectively, both complexes are regarded as cationic in the solid. It is reasonable to consider that both complexes are monocationic ones having monoanionic thiolato-coordinated glutathionate because the neutral thiolato-coordinated glutathione having noncharged carboxyl groups and cationic ammonium group is hardly formed in the basic conditions used for the preparations (see Section 2).

3.2. Extraction

The ^{31}P NMR spectrum of the chloroform layer obtained by the extraction of L-cysteine in water by using **1** as an extractant showed two main signals at 32.6 and 136.7 ppm assignable to the equatorial and axial phosphorus of the trigonal–bipyramidal complex with the axially coordinated thiolato sulfur atom from agreement with the chemical shift of $[Pd(pt)(pp_3)](BF_4)$ [15] and **4** (Fig. 3a). The minor signals at 31.4 and 134.0 ppm close to the main signals were increased by using an alkaline aqueous solution of L-cysteine. Accordingly, the major and minor signals can be assigned to $[Pd(L\text{-Hcys})(pp_3)]^+$ and $[Pd(L\text{-cys})(pp_3)]$, where L-Hcys and L-cys denote the monoprotonated monoanionic L-cysteinato ligands and the deprotonated dianionic one, respectively. In the case

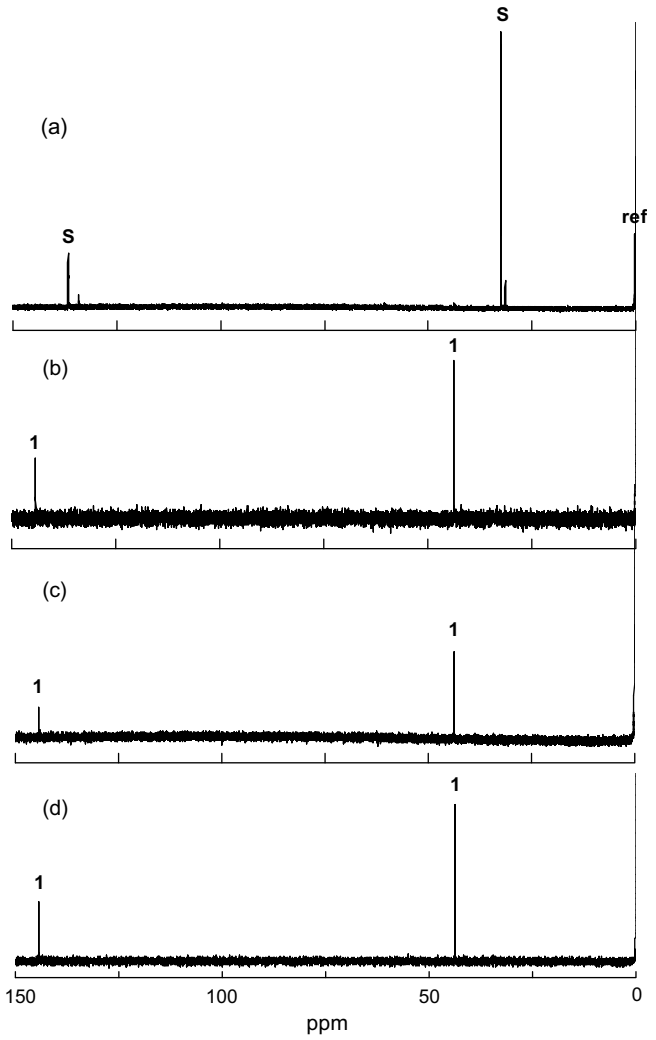


Fig. 3. ^{31}P NMR spectra of chloroform layers obtained by the extraction with **1** for L-cysteine (a), L-penicillamine (b), L-methionine (c), and L-alanine(d). **Ref** denotes the signal for D_3PO_4 in outer D_2O.

of the extraction of L-penicillamine, L-methionine, and L-alanine, the chloroform layers showed only the two signals for the solvated extractant **1**, $[Pd(pp_3)(CH_3CN)](BF_4)_2$ [10], at around 43.8 ppm and 144.3 ppm (Fig. 3b–d). These facts indicate that the axial coordination site of the present trigonal–bipyramidal palladium(II) complex with pp_3 has a much stronger affinity for the thiolate sulfur atom in L-cysteinate compared with the amine nitrogen, carboxylate oxygen, and acetonitrile nitrogen atoms. It is obvious that the thiolate sulfur atom in L-penicillamine was not coordinated due to the steric repulsion of the two adjacent methyl groups with the surrounding phenyl groups of the pp_3 ligand in the trigonal–bipyramidal geometry. No complexation with L-methionine is mainly attributed to the weak donicity of the thioether sulfur atom and, in addition, to the steric repulsion of the methyl group on the sulfur atom.

In the case of the extraction of L-cysteine using the platinum(II) complex **3** as an extractant, two sets of ^{31}P NMR signals for the trigonal–bipyramidal Pt(II) complexes were observed in the chloroform layer besides the signals for the monomeric form of **3**, $[Pt(pp_3)(CH_3CN)]^{2+}$ (Fig. 4). The major signals (23.4 and 129.5 ppm) except those for the extractant can be assigned to the thiolato complex with the sulfur-coordinated L-cysteinato ligand by comparison with the chemical shift of **5** and $[Pt(pt)(pp_3)]^+$ [16]. The minor signals (27.8 and 121.5 ppm) are probably due to formation of the trigonal–bipyramidal complex with the nitro-

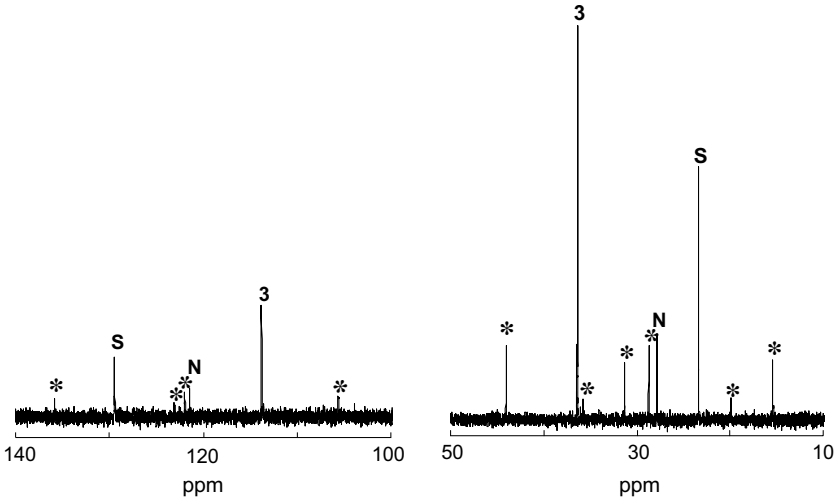


Fig. 4. ^{31}P NMR spectra of chloroform layers obtained by the extraction with **3** for L-cysteine. **3**s, **S**s, **N**s, and asterisks denote the signals for the monomeric form of **3** and the sulfur- and nitrogen-bound pp_3 platinum(II) complexes, and the satellite signals due to the coupling with ^{195}Pt, respectively.

gen-coordinated L-cysteinato ligand considering a preference of the Pt(II) complex for the amine nitrogen over the carboxylate oxygen [17]. For the extraction of L-penicillamine, the chloroform layer exhibited no signals of the thiolato complex but the minor signals at 27.8 and 121.5 ppm for the nitrogen-bound complex besides the large signals for the extractant (Fig. S1b), which is attributed to the steric hindrance between the two methyl groups adjacent to the thiolate sulfur atom and the surrounding phenyl groups. The chloroform layers obtained by the extraction for L-methionine and L-alanine showed no clear signals other than those for the extractant as in the case of the corresponding palladium(II) extractant mentioned above (Figs. S1c and d) [18]. These results indicate that acetonitrile is coordinated competitively at the axial site of the trigonal–bipyramidal platinum(II) complex with the pp_3 ligand and the selectivity for the thiolate sulfur atom is relatively low compared with the corresponding palladium(II) complex.

To compare the coordinative selectivity for amino acids between the five-coordinate trigonal–bipyramidal and four-coordinate square-planar palladium(II) complexes, similar extraction procedures were carried out by using **2** as an extractant. The main ^{31}P NMR signals at 50.3 and 106.7 ppm observed for the chloroform layer in the case of the extraction of L-cysteine (Fig. 5a) is assignable, respectively, to the terminal and central phosphorus atoms in the square-planar palladium(II) complexes by comparison of the ^{31}P NMR signals for $[PdX(p_3)]^+$ (X = pt$^-$, Cl$^-$, Br$^-$, I$^-$) [19]. It is reasonable to assume that L-cysteinate is coordinated with the thiolate sulfur atom because the signals for the extractant **2** were observed as the main signals in the case of the extraction of L-alanine and L-methionine, which have no thiol group (Fig. 5c and d). The minor signals observed for the above three amino acids are tentatively assigned to the nitrogen-bound square-planar palladium(II) complexes because of their preference for the amine nitrogen over the carboxylate oxygen under the neutral conditions [17]. In the case of the extraction of L-penicillamine, the chloroform layer showed no signal for the extractant but the complicated spectrum including the nitrogen-bound complex (Fig. 5b) probably due to partial dissociation of the p_3 ligand by sterically repulsive coordination of the thiolate group with the adjacent methyl groups and subsequent chelation with the amino group. These results revealed that the square-planar extractant **2** is less selective toward the thiolate sulfur atom and, consequently, L-cysteine compared with the trigonal–bipyramidal extractant **1**.

By comparison between the five-coordinate trigonal–bipyramidal palladium(II) and platinum(II) complexes with the same tetradentate phosphine bound ligand and between the five-coordinate trigonal–bipyramidal and four-coordinate square-planar palladium(II) complexes with the multidentate phosphine ligands, it

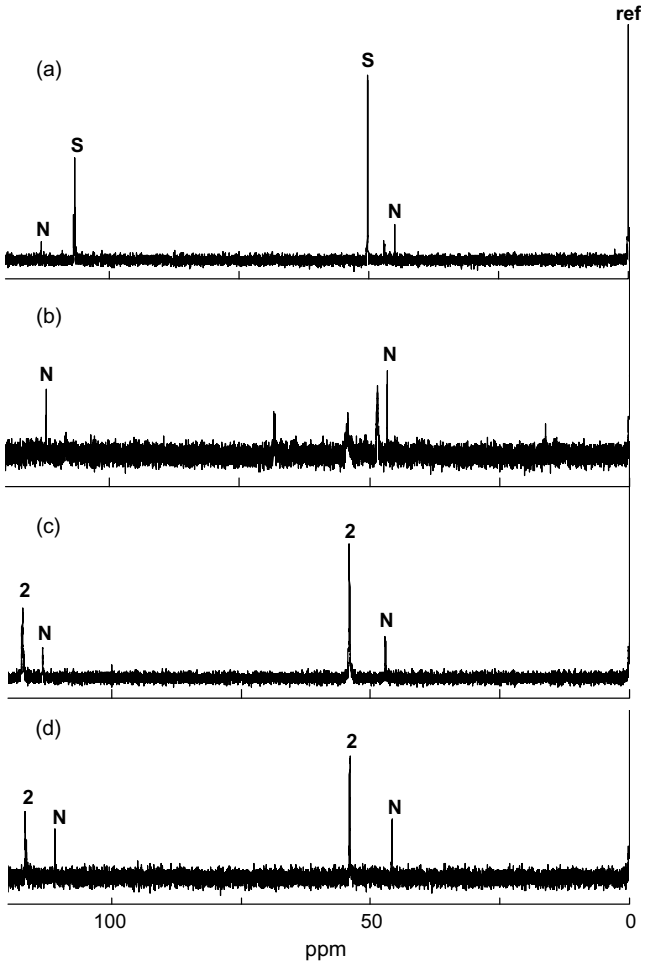


Fig. 5. ^{31}P NMR spectra of chloroform layers obtained by the extraction with **2** for L-cysteine (a), L-penicillamine (b), L-methionine (c), and L-alanine(d). **2**s, **S**s, **N**s, and **Ref** denote the signals for **2**, the sulfur- and nitrogen-bound p_3 palladium(II) complexes, and D_3PO_4 in outer D_2O, respectively.

was confirmed that the axial coordination site of the trigonal–bipyramidal palladium(II) complex with the pp_3 ligand shows the remarkable selectivity for the thiolate group in L-cysteine. In order to apply such selectivity to separation of amino acids, a similar extraction procedure using the extractant **1** was carried out for the aqueous solution containing equimolar four kinds of amino acids, L-cysteine, L-penicillamine, L-methionine, and L-alanine. Since only the ^{31}P NMR signals of the sulfur-bound L-cysteinato complex was observed in the chloroform layer, the L-cysteinato ligand was replaced by an iodide ion by using a chloroform solution of n-Bu_4NI and subsequently the dissociated L-cysteinate was back-extracted with water. The water layer showed only the ^1H NMR signals of L-cysteinate besides the signals for n-Bu_4N^+ and the solvents (Fig. 6).

The selectivity of the extractant **1** can also be applied to separation of peptides. Though the reduced and oxidized forms of glutathione usually act as a multidentate ligand to form metal complexes with complicated structures [20–22], **1** maintains the trigonal–bipyramidal thiolato structure excluding the coordination of the carboxylate, amino, and amide groups. Taking advantage of the selectivity at the axial site, the reduced form of glutathione, which is an important reductant in the biological redox and detoxification systems, was separated from the oxidized form, in which the two thiol groups are oxidized to form the disulfide bond. In the extraction using the aqueous solution containing the reduced form of glutathione, only the thiolato complex **4** was observed in the chloroform layer besides the extractant **1** (Fig. S2a) and the coordinated glutathionate was back-extracted with water by adding n-Bu_4NI, which was confirmed by the ^1H NMR spectrum (Fig. 7). Contrarily, the oxidized form was not extracted at all to show no ^{31}P NMR signals other than those of the extractant **1** (Fig. S2b). For the 1:1 mixture of the reduced and oxidized forms, only the reduced form was extracted with chloroform by using the extractant **1** and subsequently back-extracted with water by adding n-Bu_4NI.

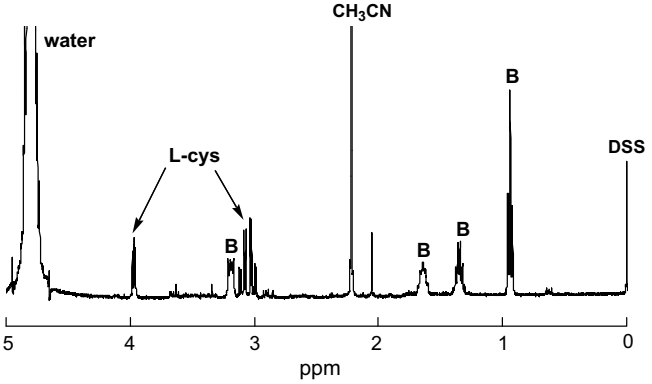


Fig. 6. ^1H NMR spectra of water layer obtained by back-extraction after the extraction with **1** for the mixture of L-cysteine, L-penicillamine, L-methionine, and L-alanine. **B**s denote the signals for n-Bu_4N^+.

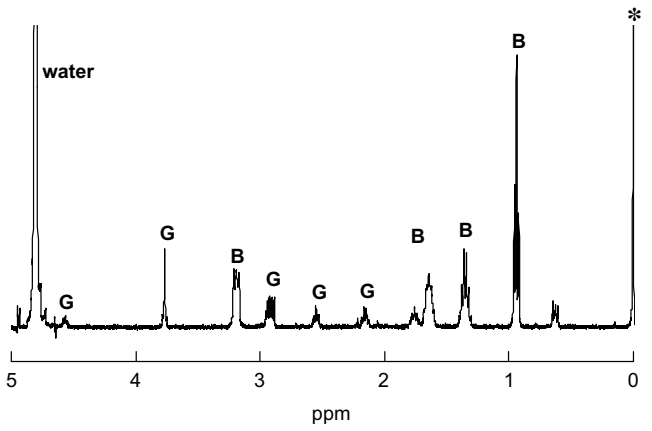


Fig. 7. ^1H NMR spectra of water layer obtained by back-extraction after the extraction with **1** for reduced form of glutathione. **G**s, **B**s, and asterisks denote the signals for reduced form of glutathione, n-Bu_4N^+, and DSS, respectively.

4. Conclusion

The five-coordinate trigonal–bipyramidal palladium(II) and platinum(II) complexes with glutathionate that acts as a monodentate thiolato ligand were prepared from $[Pd(pp_3)](BF_4)_2$ (**1**) and $[Pt(pp_3)]_2(PF_6)_4$ (**3**), respectively. High selectivity for thiolate sulfur atom in L-cysteinate and L-cysteine residue was observed at the solvated coordination site of $[Pd(pp_3)(CH_3CN)]^{2+}$ compared to $[Pt(pp_3)(CH_3CN)]^{2+}$ and $[Pt(p_3)(CH_3CN)]^{2+}$. The selective extractions for L-cysteine and the reduced form of glutathione were successfully carried out by using $[Pd(pp_3)(CH_3CN)]^{2+}$ as an extractant.

Appendix A. Supplementary material

The ^{31}P NMR spectra of the chloroform layers obtained by the extraction with **3** for amino acids and with **1** for the reduced and oxidized forms of glutathione. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2008.09.001.

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[15] $^{31}P\{^1H\}$ NMR ($CHCl_3$): δ30.3 (d, $^3J_{P-P}$ = 10 Hz), 134.5 (q, $^3J_{P-P}$ = 10 Hz). UV–Vis ($CHCl_3$): λ_{max}/nm (log(ε/mol^{-1} kg cm^{-1})) 551 (3.31), 409 (3.82).
[16] $^{31}P\{^1H\}$ NMR ($CHCl_3$): δ20.2 (s, $^1J_{P-Pt}$ = 2650 Hz), 126.3 (s, $^1J_{P-Pt}$ = 1940 Hz). UV–Vis ($CHCl_3$): λ_{max}/nm (log(ε/mol^{-1} kg cm^{-1})) 449 (3.52), 360 (3.95).
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[18] It is assumed that the nitrogen-bound complexes with L-cys and L-pen are monocationic complexes with thiolate and carboxyl groups while those with L-met and L-ala would be dicationic ones with a carboxyl group if they were formed. Such a difference in the positive charge can make a difference in extractability of the nitrogen-bound complexes.
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