

Syntheses of new diphenylphosphinoacetatorhodium(I) complexes and their catalytic reactivities in hydrogenation of aromatic compounds

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Abstract

The diphenylphosphinoacetic acid $\text{Ph}_2\text{PCH}_2\text{COOH}$ was readily converted to its silver salt $[\text{Ag}(\text{Ph}_2\text{PCH}_2\text{COO})]$ (1), and subsequent reactions of 1 with $[\text{Rh}(\text{cod})\text{Cl}]_2$ (cod=1,5-cyclooctadiene) and $[\text{Rh}(\text{CO})_2\text{Cl}]_2$ gave $[\text{Rh}(\text{cod})(\text{Ph}_2\text{PCH}_2\text{COO})]$ (2) and $[\text{Rh}(\text{CO})_2(\text{Ph}_2\text{PCH}_2\text{COO})]$ (3), respectively. Spectroscopic data and some physical properties of these new compounds are described. The complexes 2 and 3 at 50 °C showed catalytic hydrogenation activities towards benzene and a variety of substituted benzenes. The turn-over number (TN) for the arene hydrogenations with 2 under 5 kg/cm² of H₂, decreased with the following sequence: benzene > toluene > anisole > ethylbenzene > *p*- and *m*-xylenes > methyl benzoate. Benzonitrile and nitrobenzene did not yield any products with hydrogenated benzene-ring moieties, and the latter substrate gave only aniline. The activity sequence observed for the arene hydrogenation resulted from steric and electron-withdrawing effects of the substituents of the benzene rings. In benzene hydrogenation with 2 under 50 kg/cm² of H₂ at 50 °C for 36 h, the TN value was found to be about 5800. Complex 2 also showed similar hydrogenation activities towards 1,2,3,4-tetrahydronaphthalene and furan.

Introduction

Unsymmetrical bidentate chelates, especially those with a tertiary phosphine moiety as one arm of the chelate [1], have been a subject of considerable interest with respect to the design and development of new homogeneous reaction systems, catalyzed with high selectivity by their transition-metal complexes. Among them, is the diphenylphosphinoacetato group $\text{Ph}_2\text{PCH}_2\text{COO}$ [2], which has two coordination sites via both hard and soft donor atoms. There have been a few papers concerning the syntheses and coordination chemistry of its some transition-metal complexes [2], regarding applications of the complexes to the catalytic homogeneous reactions, however, to our knowledge only ethylene oligomerization with the nickel (II) complexes has been described by Keim and coworkers [3]. In the present paper, we report the syntheses of new rhodium (I) complexes (Fig. 1) with this group, and their catalytic reactivities in hydrogenation reactions of aromatic compounds [4] with molecular hydrogen under pressure.

Experimental

Materials and general procedures

The diphenylphosphinoacetic acid $\text{Ph}_2\text{PCH}_2\text{COOH}$ was synthesised by the published procedure [5] with a slight modification. The complexes $[\text{Rh}(\text{cod})\text{Cl}]_2$ (cod=1,5-cyclooctadiene) [6] and $[\text{Rh}(\text{CO})_2\text{Cl}]_2$ [7] were prepared according to methods described in the literature. All organic solvents were distilled under nitrogen and dried prior to use. As authentic samples of the hydrogenated products, cyclohexyl methyl ether was prepared following ref. 8; other reagents were commercially available, including cyclohexene, methylcyclohexane, 1-methylcyclohexene, a mixture of 3- and 4-methylcyclohexenes, 1,3- and 1,4-dimethylcyclohexanes, methyl cyclohexanecarboxylate, cyclohexanecarbonitrile, cyclohexylamine, ethylcyclohexane, and decahydronaphthalene. All preparative procedures were performed under nitrogen with use of standard Schlenk techniques.

Melting points were determined with a Yanagimoto MP-S3 microstage apparatus in evacuated capillary tubes and are uncorrected. ¹H, ¹³C and ³¹P NMR spectra were recorded on a JEOL model GX-400 spectrometer operating at 399.8, 100.5 and 161.9 MHz, respectively, using tetramethylsilane as internal standard for the

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former two nuclei and 85% H_3PO_4 as external standard for the third. The chemical shifts δ are reported in parts per million from these standards, and down-field shifts are noted as positive in all cases. IR spectra (Nujol) were recorded by use of a JASCO A-100 spectrometer. Fast atom bombardment (FAB) mass spectra were obtained on a JEOL model JMS-DX-303 instrument, using *m*-nitrobenzyl alcohol as a matrix material. The instrument was used also for the observation of gas chromatograph-mass spectra (GC-MS).

Preparation of silver diphenylphosphinoacetate

Diphenylphosphinoacetic acid (1.0 g, 4.1 mmol) was dissolved in a solution of sodium carbonate (0.22 g, 2.1 mmol) in water and ethanol (1/1) (100 ml). Then, silver nitrate (0.70 g, 4.1 mmol) in water (10 ml) was added dropwise to the solution with stirring. After 30 min, the resulting grey precipitates of silver diphenylphosphinoacetate [$\text{Ag}(\text{Ph}_2\text{PCH}_2\text{COO})$] (**1**) as a monohydrate were collected and washed with water, ethanol and diethyl ether, successively. Yield 96%. $\nu(\text{C}=\text{O})$, 1570 cm^{-1} .

Preparation of $[\text{Rh}(\text{cod})(\text{Ph}_2\text{PCH}_2\text{COO})]$

Silver salt **1** (220 mg, 0.62 mmol) was added in portions to a dichloromethane solution (15 ml) of $[\text{Rh}(\text{cod})\text{Cl}]_2$ (150 mg, 0.31 mmol). After stirring for 6 h at room temperature, the solvent was removed *in vacuo* and the residue was recrystallized from benzene and diethyl ether. Yellow microcrystals were obtained and characterized as $[\text{Rh}(\text{cod})(\text{Ph}_2\text{PCH}_2\text{COO})]$ (**2**) in 52% yield. $\nu(\text{C}=\text{O})$, 1640 cm^{-1} .

Preparation of $[\text{Rh}(\text{CO})_2(\text{Ph}_2\text{PCH}_2\text{COO})]$

The carbonyl complex $[\text{Rh}(\text{CO})_2\text{Cl}]_2$ (200 mg, 0.51 mmol) in dichloromethane (20 ml) was treated with **1** (370 mg, 1.05 mmol), and the mixture was stirred for 3 h at ambient temperature. Some insoluble materials were removed by filtration, and the yellow filtrate obtained was concentrated into a small volume. Addition of diethyl ether afforded a yellow powder of $[\text{Rh}(\text{CO})_2(\text{Ph}_2\text{PCH}_2\text{COO})]$ (**3**) as a $(1/3)\text{CH}_2\text{Cl}_2$ solvate in 30% yield. $\nu(\text{C}\equiv\text{O})$, 1980 and 1965 cm^{-1} ; $\nu(\text{C}=\text{O})$, 1665 cm^{-1} .

Catalytic hydrogenations of aromatic compounds

A 50 ml thick-walled glass reactor TEM-V-50 (Taiatsu Scientific Glass Co.) was used for hydrogenation reactions under 5 kg/cm^2 of molecular hydrogen. The complex catalysts (2.5×10^{-2} mmol) were dissolved in neat aromatic compounds (25 ml) in the reactor under nitrogen. Then, the reactor was evacuated with an aspirator for a short period and filled with molecular hydrogen under a high pressure. Release of H_2 to atmospheric pressure and recharging up to the former

pressure were repeated three times. Hydrogenations of the test solutions were carried out at $50\text{ }^\circ\text{C}$ for 4 h in the reactor with mechanical stirring. In the case of hydrogenations under 50 kg/cm^2 of H_2 , 1 ml samples of the test solutions were hydrogenated similarly at $50\text{ }^\circ\text{C}$ in a 50 ml stainless steel bottle TVS-1 (Taiatsu Scientific Glass Co.) with a magnetic stirrer.

The unreacted substrates and hydrogenated products were identified gas-chromatographically by comparison with authentic samples, or were determined with the help of the GC-MS system. Quantitative evaluations were performed on Shimadzu GC-8AIT and Ohkura 802-D gas chromatographs with TCD detectors. The following column-packing materials in stainless steel columns ($3\text{ mm} \times 5\text{ m}$) were used: 10% PEG-20M on Chromosorb W NAW, 5% OV-17 on Uniport HP, 10% Silicone SE-30 on Uniport B.

Results and discussion

Syntheses of diphenylphosphinoacetatorhodium(I) complexes

According to the methods of Issleib and Thomas [5] with a slight modification, pure diphenylphosphinoacetic acid was obtained in a 63% yield from the reaction of lithium diphenylphosphide with ethyl chloroacetate in THF at $-78\text{ }^\circ\text{C}$ and subsequent hydrolysis of the resulting ethyl ester. White microcrystals of the acid were isolated from its aqueous solution by adjustment to *c.* pH 5.5. The acid was readily converted to its silver salt **1**, which was expected to be a useful starting material for the syntheses of various diphenylphosphinoacetato transition-metal complexes. In the present study, by use of **1** we obtained two kinds of rhodium(I) complexes, i.e. $[\text{Rh}(\text{cod})(\text{Ph}_2\text{PCH}_2\text{COO})]$ (**2**) and $[\text{Rh}(\text{CO})_2(\text{Ph}_2\text{PCH}_2\text{COO})]$ (**3**) (Fig. 1). The former cod complex **2** was stable both in the solid state and in solutions of common organic solvents in air, whereas the carbonyl complex **3**, particularly in solutions was decomposed readily in air. Table 1 summarizes yields and analytical data of the new compounds **1**–**3**. FAB-MS of **2** showed the $(M+H)^+$ parent-ion peak centered at m/z 455, which confirmed its formulation as $[\text{Rh}(\text{cod})(\text{Ph}_2\text{PCH}_2\text{COO})]$. In the case of **3**, the

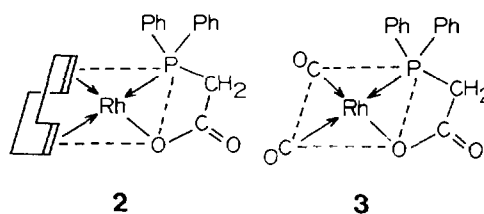


Fig. 1. New (diphenylphosphinoacetato)rhodium(I) complexes.

TABLE 1. Yields and analytical data of the new compounds

	Yield (%)	m.p. ^c (°C)	Found (calc.) (%)	
			H	C
[Ag(Ph ₂ PCH ₂ COO)] (1) ^a	87	221–225	3.37 (3.82)	45.84 (45.56)
[Rh(cod)(Ph ₂ PCH ₂ COO)] (2)	52	210–220	5.43 (5.32)	58.16 (58.16)
[Rh(CO) ₂ (Ph ₂ PCH ₂ COO)] (3) ^b	51	238–250	3.33 (2.97)	45.35 (45.59)

^aMonohydrate. ^b(1/3) CH₂Cl₂ solvate. ^cWith decomposition.

(M+H)⁺ peak was not detected, however, a (M+H-CO)⁺ peak was observed at *m/z* 375.

Two strong IR bands of **1** at 1570 and 1360 cm⁻¹ were attributed to ν(C=O) and ν(C-O) of the coordinated acetato moiety in the Ph₂PCH₂COO group, respectively, and the considerably insoluble character of **1** in common organic solvents suggested its oligo-nuclear structure, linked through both ligating diphenylphosphino and acetato moieties. Complexes **2** and **3** showed strong ν(C=O) bands at 1640 and 1665 cm⁻¹, respectively, and these high wave-numbers confirmed monodentate coordination of the acetato moieties [9] in the complexes.

NMR spectroscopic data of **2** and **3** are summarized in Table 2. Assignments of the NMR signals for **2** were confirmed by ¹³C-¹H (Fig. 2) and ¹H-¹H COSY observations.

¹H NMR spectra of **2** in CD₂Cl₂ showed two slightly broad singlets at δ 3.54 and 5.43, attributable to the olefinic protons in the cod ligand, and their couplings with ³¹P nucleus were not detected. As for ¹³C NMR, the coupling with ³¹P nucleus in 13.7 Hz was observed

on the signal (δ 69.69) for the carbons of the cod-olefinic moiety located in the position *trans* to the ligating diphenylphosphino group, whereas the signal (δ 105.98) for the other olefinic moiety in the *cis* position did not show any significant coupling. It was noteworthy that the ligating acetato part of the Ph₂PCH₂COO chelate in **2** was assumed to withdraw some electron density via rhodium, leading to the low-field shifts of the ¹H and ¹³C NMR signals for the cod-olefinic moiety situated in the *trans* position to the acetato part, in contrast to the signals for the other olefinic moiety in the *cis* position. The carbonyl complex **3** in CD₂Cl₂ gave NMR signal patterns of the diphenylphosphinoacetato group, similarly to those of **2**. A weak ¹³C NMR signal was observed at δ *c.* 188 and was attributed to the carbonyl carbons, however the coupling constants with ³¹P and ¹⁰³Rh nuclei were not determined explicitly owing to the low solubility of **3**.

³¹P NMR spectra of these complexes were observed in CD₂Cl₂ also, and the diphenylphosphino groups in **2** and **3** resonated at δ 9.84 and 33.07 as doublets coupled with ¹⁰³Rh in 146.5 and 166.0 Hz, respectively.

TABLE 2. ¹H, ¹³C and ³¹P NMR data for new (diphenylphosphinoacetato)rhodium complexes^a

Complex	δ (Ph ₂ PCH ₂ COO group)					δ (Coexisting ligands)		
	Ph ₂ PCH ₂ - [J _{RhP}]	P-CH ₂ - [J _{PH}]	P-CH ₂ - [J _{PC}]	-COO- [J _{PC}]	C in Ph [J _{PC}]	H in cod [J _{HH}]	C in cod [J _{PC}]	
2	9.84(d) [146.5]	3.26(d) [11.0]	37.54(d) [27.4]	178.57(d) [15.6]	<i>ipso</i> , 130.93 <i>ortho</i> , 133.05(d) [11.8] <i>meta</i> , 129.49(d) [11.7] <i>para</i> , 131.28	CH ₂ , 2.08(d) ^b [9.2] ~ 2.43(c) ^{b,c} CH, 3.54 ^d 5.43 ^e	CH ₂ , 28.53 33.16 CH, 69.69(d) ^d [13.7] 105.98 ^e	
	3 ^f	33.07(d) [166.0]	3.36(d) [10.6]	34.18(d) [31.3]	172.92	<i>ipso</i> , 131.29		
						<i>ortho</i> , 132.98(d) [11.7]		
						<i>meta</i> , 129.52(d) [11.7]		
<i>para</i> , 131.91								

^aObserved in CD₂Cl₂; chemical shifts δ in ppm from TMS for ¹H and ¹³C NMR and from 85% H₃PO₄ for ³¹P NMR; Signal multiplicity except (broad) singlet is shown in parentheses, d=doublet, c=complex due to overlapping of two proton resonances; coupling constants *J* in Hz are described in square brackets just under the numerical values of δ. ^bGeminal coupling between axial and equatorial CH₂ protons. ^cWeak vicinal couplings were observed with two CH signals. But the constants *J* were not determined.

^dIn the position *trans* to the coordinated diphenylphosphino moiety. ^eIn the position *trans* to the coordinated acetato moiety.

^fA weak ¹³C NMR signal observed at δ *c.* 188 was probably attributed to the carbonyl carbons in **3**; see text.

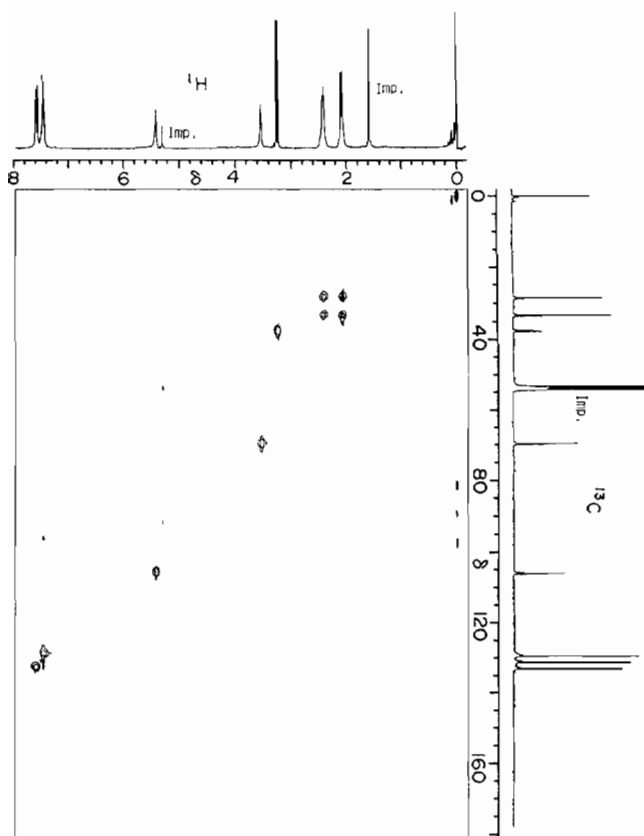


Fig. 2. The ^{13}C - ^1H COSY spectrum of $[\text{Rh}(\text{cod})(\text{Ph}_2\text{PCH}_2\text{COO})]$ in CD_2Cl_2 (imp., H_2O and CH_2Cl_2).

The low-field chemical shift of the latter resonance was due to the electron-withdrawing effect of the coexisting carbonyl ligands in **3**.

Catalytic hydrogenations of aromatic compounds

The cod complex **2** was dissolved in benzene and the mixture was charged with molecular hydrogen under 5 kg/cm^2 as an initial pressure. At 50°C , hydrogenation of benzene proceeded to give cyclohexane in 134 turn-over number (*TN*) per catalyst **2** for 4 h. As for reaction by-products, only a small amount of cyclohexene, a tetrahydro intermediate reduction product from benzene was detected by gas chromatography, together with cyclooctane formed stoichiometrically from the cod moiety on rhodium. Cyclohexadiene as a dihydro product was not obtained.

Similar hydrogenations were also performed for many substituted benzenes, and the results are summarized in Table 3. The *TN* values of the reactions decreased with the following sequence: benzene > toluene > anisole > ethylbenzene > *p*- and *m*-xylenes > methyl benzoate > benzonitrile \approx nitrobenzene.

In the hydrogenation reactions of *m*- and *p*-xylenes for 4 h, mixtures of *trans*- and *cis*-dimethylcyclohexanes were formed. Furthermore, considerable amounts of

TABLE 3. Hydrogenation of aromatic compounds with **2** under 5 kg/cm^2 of H_2 ^a

Substrate	Turn-over numbers of products	
	Cyclohexanes	Other products
Benzene	134	2 (cyclohexene)
Toluene	121	12 (1-methyl-1-cyclohexene)
Anisole ^b	82	18 (methoxycyclohexene)
Ethylbenzene	62	7 (ethylcyclohexene)
<i>p</i> -Xylene	22 (<i>cis</i>)	8 (1,4-dimethylcyclohexenes)
	10 (<i>trans</i>)	
<i>m</i> -Xylene	18 (<i>cis</i>)	5 (1,3-dimethylcyclohexenes)
	8 (<i>trans</i>)	
Methyl benzoate	24	
Benzonitrile	0	
Nitrobenzene	0	58 (aniline)

^aAromatic compounds, 25 ml; complex **2**, 2.5×10^{-2} mmol; at 50°C ; 4 h. ^bGas chromatograph of the reaction mixture showed formation of two trace products additionally, which were tentatively assigned to 1,2- and/or 1,3-dimethoxycyclohexanes on the basis of GC-MS data.

dimethylcyclohexenes were produced also, whereas dimethylcyclohexadienes were not detected gas-chromatographically. These findings indicated dissociation of dimethylcyclohexenes formed on rhodium, that is, existence of the coordination equilibrium of dimethylcyclohexenes. One might consider an alternative mechanistic scheme in which the benzene ring moieties remained attached to rhodium until some cyclohexyl species are formed [4], however, this scheme is expected to yield only *cis*-dimethylcyclohexanes through essential *cis* addition of three moles of molecular hydrogen, and is not the case for the present hydrogenations with **2**. Moreover, the present authors suggested that the production of dimethylcyclohexenes besides dimethylcyclohexanes was associated with the decrease in hydrogenation rates of the benzene rings in xylenes, which was due to the steric effects of the two methyl substituents [10]. In the hydrogenation of other substituted benzenes, similar formation of cyclohexene derivatives was observed, as shown in Table 3.

Benzonitrile and nitrobenzene bearing electron-withdrawing cyano and nitro substituents, respectively, did not show hydrogenation of their benzene rings under the present reaction conditions. The latter substrate yielded only aniline, i.e. the product of the nitro-substituent hydrogenation. These electron-withdrawing substituents were assumed to decrease electron density on the rings, and the resulting low electron density probably suppressed coordination of these substituted benzenes to rhodium [10]. Owing to a similar effect, decrease in the *TN* value occurred also in the hydrogenation of methyl benzoate.

Benzene hydrogenation was carried out with **2**, also under 50 kg/cm^2 of H_2 at 50°C for 36 h, and the *TN*

value was found to be about 5800 for cyclohexane formation. Under similar reaction conditions*, known complexes $[\text{RhCl}_2\{\eta^5\text{-C}_5(\text{CH}_3)_5\}]_2$ [4d] and $[\text{RhCl}(\text{cod})(\text{PPh}_3)]$ showed 2400 and 2200 as the *TN* values per Rh metal, respectively, and these results indicated comparatively high catalytic activities of **2** in the arene hydrogenations.

As for the carbonyl complex **3**, catalytic hydrogenation of benzene to cyclohexane proceeded for 4 h to a *TN* value of 40, under reaction conditions similar to the case of **2** with 5 kg/cm² of H₂. Comparatively low catalytic activity of **3** was probably due to its low solubility and some decomposition. Extensions of our studies to the hydrogenations of polycyclic and heterocyclic aromatic compounds, using **2**, are in progress, and some results have already been obtained. For example, 1,2,3,4-tetrahydronaphthalene was hydrogenated with **2** under 50 kg/cm² of H₂ at 50 °C to give *cis*- and *trans*-decahydronaphthalene with *TN* values of 66 and 11 after 4 h, respectively. On the other hand, hydrogenation of furan proceeded to afford tetrahydrofuran in significantly high yields, with a *TN* value of 740 after 4 h even under more mild reaction conditions with 5 kg/cm² of H₂ at 25 °C.

Acknowledgments

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*For the two known complexes, the hydrogenations were performed with NEt₃ in 30-fold moles per Rh metal.

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