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Syntheses and Characterization of Some New (3-Oxo-1-cyclohexenyl)palladium(II) Complexes

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trans-Chloro(3-oxo-1-cyclohexenyl)bis(triphenylphosphine)palladium(II) (**1**) reacted with 1,2-bis(diphenylphosphino)ethane (dppe), 1,10-phenanthroline (phen), sodium diethyldithiocarbamate–water (1/3), and sodium tetra(1-pyrazolyl)borate {Na[BPz$_4$]} (Pz=1-pyrazolyl) to give the corresponding new (3-oxo-1-cyclohexenyl)palladium(II) complexes, [Pd(oxch)Cl(dppe)] (oxch=3-oxo-1-cyclohexenyl) (**2**), [Pd(oxch)Cl(phen)], [Pd(oxch)(S$_2$CNEt$_2$)(PPh$_3$)], and [Pd(oxch)(BPz$_4$)(PPh$_3$)], respectively. Complex **2** was treated with carbanions derived from methyl and ethyl cyanoacetates and malononitrile, and new diorganopalladium(II) complexes were obtained. These complexes were characterized by means of elemental analyses and IR and ^{1}H-NMR spectroscopy. The stereochemical nonrigidity of the BPz$_4$ complex was discussed.

In our previous study,[1] linear and cyclic (β-carbonylvinyl)chlorobis(triphenylphosphine)palladium(II) complexes were prepared by oxidative addition reactions of [Pd(PPh$_3$)$_4$] towards the corresponding linear and cyclic chlorovinyl ketones. Little has been known about the reactivity of the (β-carbonylvinyl)palladium(II) complexes.

This paper deals with some new (3-oxo-1-cyclohexenyl)palladium(II) complexes, derived from the reactions of the cyclic β-carbonylvinyl palladium(II) complex, *trans*-chloro(3-oxo-1-cyclohexenyl)bis(triphenylphosphine)palladium(II) [Pd(oxch)Cl(PPh$_3$)$_2$] (oxch=3-oxo-1-cyclohexenyl) (**1**) towards bidentate ligands. In addition, one of the new complexes, {1,2-bis(diphenylphosphino)ethane}chloro(3-oxo-1-cyclohexenyl)palladium(II) (**2**) was treated with carbanions formed from active methylene compounds, and new stable diorganopalladium(II) complexes were obtained. Organopalladium(II) complexes have already been prepared from reactions of chloropalladium(II) complexes with the carbanions.[2—4]

Experimental

General Procedure. Melting points and IR and ^{1}H-NMR spectra were measured according to the previous paper.[1] Complex **1**, 1,2-bis(diphenylphosphino)ethane (dppe),[5] and sodium tetra(1-pyrazolyl)borate{Na[BPz$_4$]} (Pz=1-pyrazolyl)[6] were synthesized in the described methods. 1,10-Phenanthroline (phen), sodium diethyldithiocarbamate–water(1/3) {Na[dedc]·3H$_2$O}, and the other reagents were commercial samples, and were used without further purification.

*Reaction of **1** with dppe or phen.* A benzene solution (110 ml) containing **1** (1.68 mmol) and dppe (1.85 mmol) was stirred at room temperature for 48 h. The resulting greyish white solids were collected and washed with benzene and diethyl ether to give [Pd(oxch)Cl(dppe)] (**2**). Complex **1** reacted similarly with phen to afford [Pd(oxch)Cl(phen)] (**3**).

*Halogen Metathesis of **3**.* An acetone suspension (20 ml) involving **3** (0.08 mmol) and lithium bromide (0.80 mmol) was refluxed for 40 h. The resulting solids were separated and added to 20 ml of ethanol, followed by stirring for 20 h at room temperature. Off-white powders were collected and washed with ethanol and diethyl ether to yield [PdBr(oxch)(phen)] (**4**).

*Reaction of **1** with Na[dedc]·3H$_2$O.* A benzene suspension (35 ml) containing **1** (0.25 mmol) and Na[dedc]·3H$_2$O (0.28 mmol) was heated at 55 °C for 8 h. After the resulting solid was filtered off, the solvent was removed under reduced pressure. The residue was recrystallized from benzene–hexane to give [Pd(oxch)(dedc)(PPh$_3$)] (**5**).

*Reaction of **1** with Na[BPz$_4$].* A benzene suspension (30 ml) involving **1** (0.23 mmol) and Na[BPz$_4$] (0.24 mmol) was refluxed for 3 h. After the resulting precipitate was filtered off, the solvent was evaporated to dryness. The residue was recrystallized from benzene–diethyl ether to afford [Pd(oxch)(BPz$_4$)(PPh$_3$)] (**6**).

*Reactions of **2** with Carbanions Formed from Alkyl Cyanoacetates or Malononitrile.* A methanol solution (30 ml) of sodium methoxide (0.19 mmol) was added dropwise to a THF suspension (30 ml) containing **2** (0.19 mmol) and methyl cyanoacetate (0.37 mmol). The mixture was stirred at room temperature for 20 h. After filtration, the filtrate was evaporated to dryness. The residue was extracted with dichloromethane, and the solvent was removed under reduced pressure. The resulting solids were recrystallized from THF–hexane to give [Pd{CH(CN)CO$_2$Me}(oxch)(dppe)] (**7**).

Complex **2** reacted similarly with ethyl cyanoacetate and malononitrile in the presence of sodium ethoxide in an equimolar amount of **2**, followed by the analogous treatments to the case of **7**, to afford [Pd{CH(CN)CO$_2$Et}(oxch)(dppe)] (**8**) and [Pd{CH(CN)$_2$}(oxch)(dppe)] (**9**), respectively.

Results and Discussion

General Properties. The *trans*-bis(triphenylphosphine) type complex **1** underwent substitution by the bidentate ligands, dppe, phen, [dedc]$^-$, and [BPz$_4$]$^-$, affording new neutral complexes **2**, **3**, **5**, and **6**, respectively. Furthermore, the dppe type complex **2** reacted with carbanions formed from methyl and ethyl cyanoacetates and malononitrile, to give novel diorganopalladium(II) complexes, **7**—**9**, respectively. The phen-type complex **3** underwent halogen metathesis to afford the bromo complex **4**. The yields, analytical data, and some properties of these new complexes are summarized in Table 1. Complexes **2** and **5**—**9** are soluble in usual organic solvents except saturated hydrocarbons, whereas **3** and **4** are highly insoluble in the solvents.

All the new complexes showed two strong IR bands near 1630 and 1540 cm^{-1}, ascribable to ν(C=O) and ν(C=C) frequencies, respectively (Table 2). In addi-

Table 1. Yields and elemental analyses of the palladium complexes

Complex		Yield %	Color	Mp[a)] °C	Found (%) C	Found (%) H	Found (%) N	Calcd (%) C	Calcd (%) H	Calcd (%) N
[Pd(oxch)Cl(dppe)]	**2**	96	Off white	>205	60.57	4.95	0	60.49	4.92	0
[Pd(oxch)Cl(phen)]	**3**	13	Off white	>247	52.45	3.62	6.58	51.82	3.62	6.72
[PdBr(oxch)(phen)]	**4**	62	Pale yellow	236—240	47.20	3.35	6.19	46.83	3.28	6.07
[Pd(oxch)(dedc)(PPh_3)]	**5**	42	Pale yellow	157—160	56.70	5.34	2.35	56.91	5.27	2.29
[Pd(oxch)$(BPz_4)(PPh_3)$]	**6**	55	White	>180	58.39	4.64	14.74	58.20	4.61	15.08
[Pd{CH(CN)CO_2Me}(oxch)(dppe)]	**7**	56	Yellow	>109	62.07	5.14	2.01	61.95	5.05	2.01
[Pd{CH(CN)CO_2Et}(oxch)(dppe)]	**8**	28	Yellow	108—113	62.07	5.23	1.99	62.41	5.24	1.97
[Pd{$CH(CN)_2$}(oxch)(dppe)]	**9**	40	Yellow orange	>125	62.77	4.87	4.24	63.22	4.85	4.21

a) Measured in nitrogen atmosphere. All complexes except **8** decomposed without melting.

tion, each of **2** and **5**—**9** exhibited a strong band and a medium one near 1425 and 1475 cm^{-1}, respectively, characteristic of ν(P–C) frequencies.

Complexes 2—5. Complexes **2**—**5** are stable in a solid state in air. However, **2** begins to decompose in deoxygenated dichloromethane at ambient temperature after 1 h, in contrast to **1** and its 5,5-dimethyl homologue. The relatively low stability of **2** is probably due to the lowering of the bond order of the palladium-carbon bond, owing to a considerably strong *trans* influence of the phosphino group located at the *trans* position to the palladium-carbon bond.

In the ^1H-NMR spectrum of **2** in CD_2Cl_2, the olefinic proton (2-H) of the oxch moiety resonated as a multiplet at δ 5.95{$^4J(HP_{trans})=12.0$ Hz, $^4J(HP_{cis})=4.5$ Hz, and ^4J(H-6-H)$=1.3$ Hz}, indicating unambiguously that two phosphino groups were coordinated at *trans* and *cis* positions to the oxch moiety. The IR spectrum of **2** exhibited a ν(Pd–Cl) band at 300 cm^{-1}, which was higher by 20 cm^{-1} than that for **1** (Table 2). This shift to the higher wave number is associated with the difference between the *trans* influence of the phosphino group in **2** and that of the oxch moiety in **1**. The ν(Pd–Cl) frequency of **3** appeared at higher wave number, corresponding to the nitrogen donor site located at a *trans* position to the palladium-chlorine bond.

The anionic bidentate ligand [dedc]$^-$ substituted both the chloro ligand and one of the two triphenylphosphine ligands in **1**, giving the neutral complex **5**, in contrast with the neutral bidentate ligand, such as dppe or phen. It is the case with the $[BPz_4]^-$ ligand, affording the neutral complex **6**, too. The ^1H-NMR spectrum of **5** exhibited two ethyl resonances, besides proton signals attributable to the oxch moiety (Table 3) and to the phenyl groups. This proves a double bond character of the carbon-nitrogen bond in the dedc ligand.[7)]

Table 2. Characteristic IR bands of the complexes[a)]

Complex	ν(C=O)	ν(C=C)	ν(C≡N)	ν(Pd–Cl)
1	1640	1540	—	280
2	1630	1540	—	300
3	1625	1540	—	325
4	1620	1538	—	—
5	1630	1535	—	—
6	1640	1545	—	—
7	1620	1535	2180	—
8	1630	1535	2180	—
9	1630	1535	2204 2150	—

a) In cm^{-1}, in KBr disk.

The [BPz_4] *Complex* 6. Complex **6** shows a considerably high stability not only in the solid state in the air, but also in the solution of benzene, chloroform, or dichloromethane. It is worthy to note that the [BPz_4] ligand serves as a stabilizing ligand for the palladium-carbon bond, presumably owing to the electronic and steric effects of the ligand. The [BPz_4] ligand in **6** was believed to act as a bidentate chelate, since a relatively electron-rich palladium atom in **6** prevents coordination to the third pyrazolyl group in similar fassion to its related BPz_4–palladium(II) complexes.[8—10)]

The ^1H-NMR spectra of **6** in $CDCl_3$ showed a temperature dependency in the region 50—−31 °C, implying a stereochemically nonrigid motion of the BPz_4 ligand (Fig. 1). The pyrazolyl proton resonances

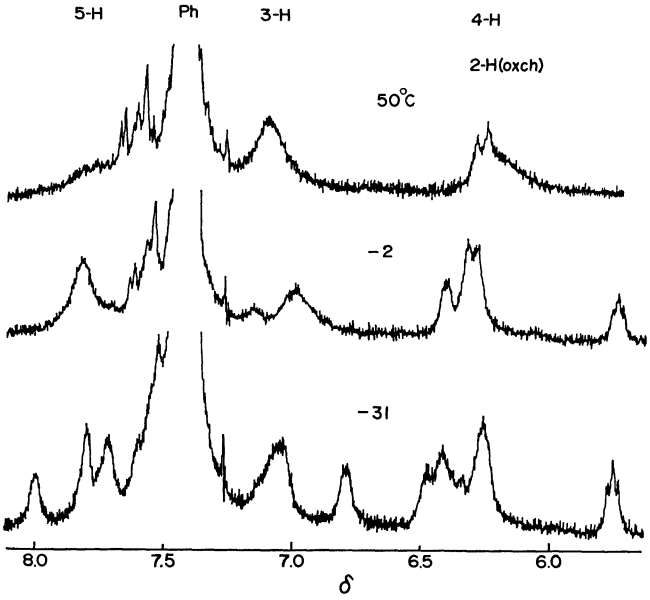
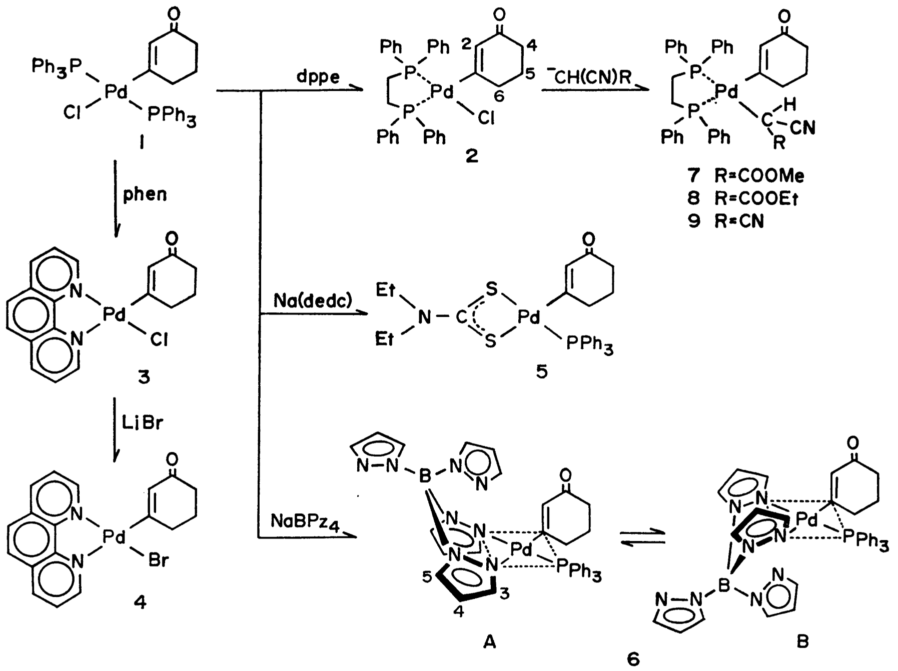


Fig. 1. Low field region of the ^1H-NMR spectra of **6**.

TABLE 3. ^{1}H-NMR DATA OF THE PALLADIUM COMPLEXES[a)]

Complex	The oxch moiety							The other group[b)]				
	2-H		4-H		5-H	6-H		-C$\underline{H}$-		-C$\underline{H}_2$-		-C$\underline{H}_3$
	δ/ppm	J_{PH}/Hz	δ/ppm	J/Hz	δ/ppm	δ/ppm	J/Hz	δ/ppm	J_{PH}/Hz	δ/ppm	J/Hz	δ/ppm
2	5.95(m)[c)]	12 4.5	2.4(b)[d)]	—	1.5(m)	1.96(m)	6.1	—	—	—	—	—
5[e)]	6.22(d)	1.7	2.42(t)	5.5	1.5(m)	1.92(m)	6.1	—	—	3.71(q) 3.77(q)	7.3 7.3	1.21(t) 1.28(t)
6[e,f)]	6.27(d)	4.3	←0.9—2.4(c)→					6.21(b, 4-H) 7.10(b, 3-H) 7.75(b, 5-H)		—	—	—
7	5.99(b, d)	11.5	←1.5—2.5(c)→					3.43(d)	9.8	—	—	3.34(s)
8	5.97(b, d)	13.0	←1.5—2.5(c)→					3.43(d)	9.8	3.34(q)	7.0	1.15(t)
9	6.24(b, d)	11.7	2.68(t)	8.3	1.5(m)	1.98(t)	6.7	3.71(d)	6	—	—	—

a) δ value from TMS. In CD_2Cl_2, except for **5** and **6**. Abbreviations used; b=broad, c=complicated, d=doublet, m=multiplet, q=quartet, s=singlet, and t=triplet. b) Phenyl protons and the ethylene protons of the dppe ligand were omitted. c) Coupling constant to 6-H's was 1.3 Hz. d) Overlapping with the ethylene protons of the dppe ligand. e) In $CDCl_3$. f) At room temperature.



Scheme 1.

at 50 °C indicate that the four pyrazolyl groups are spectroscopically equivalent and move in a tumbling process[8)] at a fairly fast rate on the NMR time scale, while the fast-exchange limiting spectrum was not obtained.

At −2 °C, the 4-H signal of the BPz_4 ligand separated into a slightly broad triplet at δ 5.76 (1H, $^3J_{HH}=2$ Hz) and two broad signals at δ 6.3 (2H, overlapping with 2-H of the oxch moiety) and 6.43 (1H). The larger broad signal at δ 6.3 was ascribed to two uncoordinated pyrazolyl groups, which exchanged rapidly with each other, accompanied both by the inversion of the Pd-(N-N)$_2$-B boat-type six-membered ring and by the fluttering of two coordinated pyrazolyl groups (**6A** and **6B** in Scheme 1). The third pyrazolyl group, corresponding to the smaller broad signal at δ 6.43, was one of the two coordinated pyrazolyl groups and exchanged slowly with the former two uncoordinated pyrazolyl ones. The fourth pyrazolyl group, associated with the triplet at δ 5.76, was virtually fixed at this temperature. Similar type of motion of the BPz_4 ligand has been reported concerning [Pd(cdamb)(BPz_4)] (cdamb=2-chloro-3-dimethylamino-3-methyl-1-butenyl-1-*C*,*N*)[10)] and its related complexes.[10)]

At −31 °C, the larger broad signal separated into two broad signals at δ 6.28 (1H) and 6.50 (1H), indicating that the motion of the BPz_4 ligand turned considerably sluggish. However, **6** gave no slow-exchange limit spectrum even at this temperature.[11)]

The Diorganopalladium(II) Complexes ***7—9***. The IR and ^{1}H-NMR data of **7**—**9** indicate undoubtedly that each of **7**—**9** retains the oxch moiety unchanged and the dppe chelate, while the ^{1}H-NMR spectra of **7** and **8** exhibit complicated signals near δ 1.5—2.5 for 4-, 5-, and 6-H's of the oxch moiety. The nonionic character of these complexes was confirmed by their low molar conductivities (Λ=2.5—5.0 Ω^{-1} cm^2 mol^{-1} in 1.0 mmol/dm^3 acetone solution). The IR spectrum of **7** showed a moderate band at 2180 cm^{-1}, which was assigned to a ν(C≡N) frequency but not to a ν(C=C=N) one in a keteniminato type [Pd-N=C=CH(CO$_2$Me)].[2,12] In addition, the methine proton of the cyano(methoxycarbonyl)methyl moiety in **7** resonated as a doublet at δ 3.43 ($^3J_{HP}$=9.8 Hz). The chemical shift is considerably similar to those of the methine protons in [Pd{CH(CN)CO$_2$Me}(pip)] {pip=2-(2-picolylimino)-4-pentanonato-*N,N,O*} and its related complexes.[4] The value of the coupling constant $^3J_{HP}$ is consistent with the protons adjacent to the carbon atom located at a *trans* position to a tertiary phosphine.[13,14] This evidence comfirms unambiguously that the cyano(methoxycarbonyl)methyl moiety in **7** is bonded to the palladium atom with the methine-carbon-palladium σ-bond but not with a nitrogen-palladium bond in the keteniminato type. It is the case with **8**, the ethyl ester homologue of **7**, or with **9**, which has a dicyanomethyl moiety in place of the cyano(methoxycarbonyl)methyl one in **7**.

Complexes **7**—**9** are considerably stable both in the solid state and in the deoxygenated solution of dichloromethane. Moreover, **7**—**9** are inactive to alcohol in THF, as expected from the preparative methods, and are in contrast to [PdMe$_2$(PEt$_3$)$_2$].[15] It seems likely that the thermal stability of **7**—**9** is actually comparable with that of [PdMe$_2$(dppe)] and related dimethylpalladium complexes.[14,15] However, **7**—**9** are more sluggish to aerial oxidation than the dimethylpalladium complexes.[14] These stabilities of **7**—**9** and their insensitivity to air are possibly due to the electron-delocalization effect of the electron-withdrawing substituents in the organic moieties attached to the palladium atom.

Complex **2** reacted with the carbanion derived from dimethyl malonate in a procedure similar to the preparation of **7**, giving no isolated pure product. However, **2** did not react with the carbanion formed from methyl acetoacetate, remaining the starting complex **2** recovered. The inertness of the latter carbanion was due to its lower nucleophilicity in comparison with the former carbanion or with the carbanion conducted from methyl cyanoacetate.[16] Complex **3** did not react with the carbanion from methyl cyanoacetate, probably owing to the high insolubility.

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