BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN VOL 40 351—355 (1967)

The Synthesis of the Cyclohexenone Palladium Complex and Related Compounds

Akira KASAHARA, Keiko TANAKA and Kazunori ASAMIYA

Department of Chemistry, Faculty of Liberal Arts and Science, Yamagata University, Yamagata

(Received June 21, 1966)

The chloro-bridged π-allylic palladium complex has been prepared from cyclohexenone and sodium chloropalladite. 6-Oxo-4, 4-dimethylcyclohex-2-enyl, 1, 2-(4-oxo-2, 2-dimethylbutano)-π-allyl and 1, 2-(1-oxo-butano)-3-phenyl-π-allyl palladium complexes have also been prepared from the corresponding cyclic α, β-unsaturated ketones. The structures of all these compounds have been confirmed by a study of their absorption spectra and of the NMR spectra.

The preparation of chloro-bridged π-allylic palladium complex compounds has been reported using allyl alcohol,[1,2] allyl halides,[3-5] olefins,[6-7] conjugated dienes,[7,9-11] and allene.[12,13] In addition, α, β-unsaturated ketones such as mesityl oxide[2,14] and α, β- or β, γ-unsaturated carboxylic ester[15] have also been found to form π-allylic palladium complexes.

Structure studies have led to the conclusion that these π-allylic complexes occupy two ligand positions of the palladium and that, in the solid state at least, the plane determined by the three-carbon-allyl moiety is perpendicular to that of the palladium system.[16-18] Proton magnetic resonance studies in nonpolar solvents have confirmed a delocalized π-bonded structure in which two terminal allylic carbons are equivalent,[10,19,20] but in a polar solvent such as dimethyl sulfoxide, transformation to a δ-bonded structure has been reported.[21-23]

We now wish to report that π-allylic palladium complexes can be prepared from cyclic α, β-unsaturated ketones such as 2-cyclohexenone, 5, 5-dimethyl-2-cyclohexenone, 3, 5, 5-trimethyl-2-cyclohexenone (isophorone), and 2-benzalcyclohexanone.

Results and Discussion

2-Cyclohexenone. When 2-cyclohexenone was heated under reflux with sodium chloropalladite in ethanol for 15 min, di-μ-chloro-di-(6-oxo-cyclohex-2-enyl)-dipalladium was formed. This compound was stable in the air, but it decomposed slowly in a solution to give a palladium mirror. The chloro-bridged binuclear structure for this compound is supported by the molecular-weight determinations (cryoscopic in benzene),

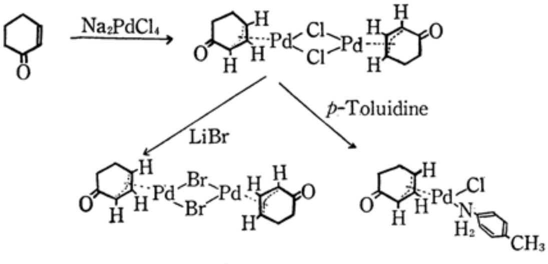

Fig. 1

---

1) J. Smidt and W. Hafner, *Angew. Chem.*, **71**, 284 (1959).

2) I. I. Moiseev, E. A. Fedorovskaya and Y. K. Syrkin, *Zh. Neorgan. Khim.*, **4**, 2461 (1959); *Russ. J. Inorg. Chem.*, **4**, 1218 (1959).

3) R. Hüttel and J. Kratzer, *Angew. Chem.*, **71**, 456 (1959).

4) E. O. Fischer and G. Burger, *Z. Naturforschung*, **16b**, 702 (1961).

5) R. Hüttel, J. Kratzer and M. Becher, *Chem. Ber.*, **94**, 766 (1961).

6) R. Hüttel and H. Christ, *ibid.*, **96**, 3101 (1963); **97**, 1439 (1964).

7) R. Hüttel, H. Dietl and H. Christ, *ibid.*, **97**, 2037 (1964).

8) R. Hüttel and H. Dietl, *ibid.*, **98**, 1752 (1965).

9) E. O. Fischer and H. Werner, *ibid.*, **93**, 2075 (1960); **95**, 695 (1962).

10) B. L. Shaw, *Chem. & Ind.*, **1962**, 1190; S. D. Robinson and B. L. Shaw, *J. Chem. Soc.*, **1963**, 4806.

11) S. D. Robinson and B. L. Shaw, *ibid.*, **1964**, 5002.

12) M. S. Lupin and B. L. Shaw, *Tetrahedron Letters*, **1964**, 883.

13) R. G. Schultz, *ibid.*, **1964**, 301; *Tetrahedron*, **20**, 2809 (1964).

14) G. W. Parshall and G. Wilkinson, *Chem. & Ind.*, **1962**, 261; *Inorg. Chem.*, **1**, 896 (1962).

15) J. Tsuji, S. Imamura and J. Kiji, *J. Am. Chem. Soc.*, **86**, 4491 (1964).

16) J. M. Rowe, *Proc. Chem. Soc.*, **1962**, 66.

17) V. F. Levdik and M. A. Porai-Koskits, *Zh. Strukturnoi Khim.*, **3**, 472 (1962).

18) W. E. Oberhansli and L. F. Dahl, *J. Organometal. Chem.*, **3**, 43 (1965).

19) H. C. Dehm and J. C. W. Chien, *J. Am. Chem. Soc.*, **82**, 4429 (1960).

20) B. L. Shaw and N. Sheppard, *Chem. & Ind.*, **1961**, 517.

21) J. C. W. Chien and H. C. Dehm, *ibid.*, **1961**, 745.

22) J. Powell, S. D. Robinson and B. L. Shaw, *Chem. Communications*, **1965**, 78.

23) G. L. Statten and K. C. Ramey, *J. Am. Chem. Soc.*, **88**, 1327 (1966).

TABLE 1. PROTON MAGNETIC RESONANCE DATA OF PALLADIUM COMPLEX AT 60 Mc/sec

Compound	Band position	Relative intensity	Assignment
Di-μ-chloro-di(6-oxo-cyclohex-2-enyl)-dipalladium (Fig. 2)	7.21—7.98 (broad)	4	H_4 and H_5
	center 5.14 (multiplet)	1	H_3
	4.72 (doublet)	1	H_1
	4.16 (triplet)	1	H_2
			$J_{1,2}=7.5$ cps
Di-μ-chloro-di(6-oxo-4, 4-di-methyl-cyclohex-2-enyl)-dipalladium (Fig. 3)	8.87 (singlet)	3	*exo*-CH_3 (5)
	8.50 (singlet)	3	*endo*-CH_3 (4)
	8.00 (doublet)	1	*exo*-H_7
	7.31 (doublet)	1	*endo*-H_6
	5.10 (doublet)	1	H_3
	4.99 (doublet)	1	H_1
	4.18 (triplet)	1	H_2
	$J_{1,2}=7.5$ cps, $J_{2,3}=6.5$ cps		
Di-μ-chloro-di[1, 2-(4-oxo-2, 2-dimethyl-butano)-π-allyl]-dipalladium (Fig. 5-A)	8.96 (singlet)	3	*exo*-CH_3 (b′)
	8.70 (singlet)	3	*endo*-CH_3 (b)
	7.88 (doublet)	1	*exo*-$H_{a'}$
	7.46 (doublet)	1	*endo*-H_a
			$J_{a,a'}=17$ cps
	7.52 (doublet)	1	*exo*-$H_{c'}$
	7.18 (doublet)	1	*endo*-H_c
			$J_{c,c'}=15$ cps
	6.83 (doublet)	1	H_2
	6.13 (singlet)	1	H_1
	5.98 (doublet)	1	H_3
			$J_{2,3}=2$ cps
Di-μ-chloro-di[1, 2-(1-oxo-butano)-3-phenyl-π-allyl]-dipalladium (Fig. 6)	7.15—8.60 (broad)	6	H_3, H_4 and H_5
	4.78—4.90 (center 4.84)	1	H_2
	3.63 (singlet)	1	H_1
	2.73	5	Phenyl protons

* NMR data is presented as τ value and deuteriochloroform was used as solvent.

its reaction with *p*-toluidine to give a readily soluble monomeric derivative, and the metathesis of the bridging-chloro ligands by such other bridging ligands as bromo (*cf.* Fig. 1).

The infrared spectrum of this complex shows a carbonyl stretching absorption at approximately the same frequency as in 2-cyclohexenone itself (1668 cm^{-1}). Evidently the ketone function is not coordinated to the metal atom. The allylic structure for this palladium complex is supported by the proton magnetic resonance spectrum, shown in Table 1.

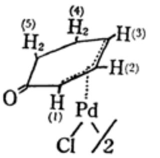

Fig. 2

The spectrum of this compound shows four bands; the three of lower fields (relative intensities 1 : 1 : 1) are assigned to the H_1, H_2, and H_3 protons in the delocalized group (see Fig. 2). The peaks at 4.16 (triplet), 4.72 (doublet), and 5.14 τ (multiplet) can be assigned to the H_2 proton at π-allylic center carbon, to the H_1 proton, and to the H_3 proton respectively. The chemical shifts of these protons are similar to those observed for the typical π-allyl complex, except that the signals shifted to lower fields; this was probably due to an electron-withdrawing substituent at the 1-position of the π-allyl group. The signals in the higher fields, with a relative intensity of 4, may be assigned to the methylene protons, H_4 and H_5.

5, 5-Dimethyl-cyclohexenone. Similarly, the reaction of 5, 5-dimethyl-cyclohexenone with sodium chloropalladite in ethanol gave the chloro-bridged 6-oxo-4, 4-dimethyl-cyclohex-2-enyl complex (Fig. 3).

The NMR spectrum of this complex showed signals at 4.18, 4.99, 5.10, 7.31, 8.00, 8.50, and 8.87 τ, with relative intensities of 1 : 1 : 1 : 1 : 1 : 3 : 3 (see Table 1). The position of the

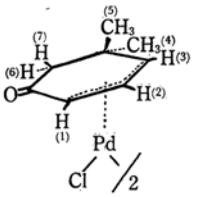

Fig. 3

three peaks in a lower field (4.18, 4.99, and 5.10 τ) and their coupling constants ($J_{1,2}=7.5$; $J_{2,3}=$ 6.5 cps) can well be accounted for by assuming the presence of a π-allyl group. The peaks at 7.31 (doublet) and 8.00 τ (doublet) have been assigned to the *endo*-proton (H_6) in methylene carbon and to the *exo*-proton (H_7) respectively. The non-equivalence of the methylene protons (H_6 and H_7) is due to their different distances from the π-allyl system. Recently, it has been reported[24] that, in benzo-bicyclo-(2, 2, 2)-octene-oxide (Fig. 4-A), the resonances of the *anti*-protons of the methylene group (H_{7a} and H_{8a}) occur in a lower field, while those of the *syn*-protons (H_{7s} and H_{8s}) occur in a higher field, than in benzo-bicyclo-(2, 2, 2)-octane (Fig. 4-B). In bicyclo-(2, 2, 1)-heptene-oxide (Fig. 4-C), the *anti*-proton resonances (H_{7n}) of the methylene group appear in a lower field and the *syn*-proton resonances (H_{7x}) occur in a higher field than in bicyclo-(2, 2, 1)-heptane (Fig. 4-D).

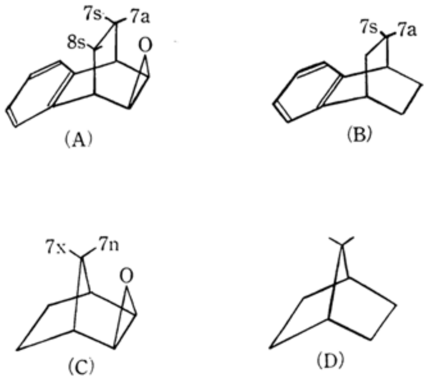

Fig. 4

Tori *et al.*[24] suggested that the separation of the resonances of methylene protons into high- and low-field groups is due to long-range shielding effects which are associated with the oxide ring system. Therefore, in this complex (Fig. 3), the shift of the *endo*-proton (H_6) towards a lower field may be due to long-range shielding effects which are associated with the chloro-palladium-bridged system.

The sharp resonance at 8.50 τ (singlet) is due to the *endo*-methyl protons (H_4), while the one at 8.87 τ (singlet) may be assigned to the *exo*-methyl protons (H_5). The non-equivalence of these methyl protons is due to their different distances from the π-allyl system, while the shift of the *endo*-methyl proton twoards a lower field may be due to long-range shielding effects which are associated with the chloro-palladium-bridged system.

2, 5, 5-Trimethyl-cyclohexenone (Isophorone). The reaction of this ketone with sodium chloropalladite in ethanol gave di-μ-chloro-di-[1, 2-(4-oxo-2, 2-dimethyl-butano)-π-allyl]-dipalladium.

The NMR spectrum shows resonances at 5.98, 6.13, 6.83, 7.18, 7.46, 7.52, 7.88, 8.70, and 8.90 τ, with relative intensities of 1 : 1 : 1 : 1 : 1 : 1 : 1 : 3 : 3 (see Table 1). The peaks at 8.70 and 8.96 τ, because of their relative intensity and sharpness, can be ascribed to the protons of the *endo*-methyl group (H_b) and the *exo*-methyl group ($H_{b'}$) respectively, suggesting the existence of two methyl groups in this complex. Therefore, this assignment can be made satisfactorily for the *exo*-cyclic structure (Fig. 5-A) rather than for the *endo*-cyclic structure (Fig. 5-B). Furthermore, as in the case of di-μ-chloro-di-(6-oxo-4, 4-dimethyl-cyclohex-2-enyl)-dipalladium (Fig. 3), the shift of the *endo*-methyl proton (H_b) towards a lower field may be due to long-range shielding effects which are associated with the chloro-palladium-bridged system.

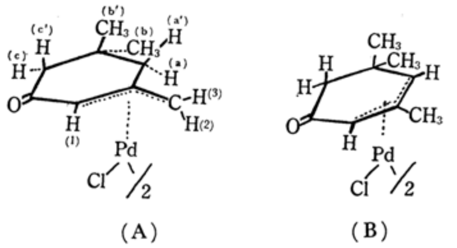

Fig. 5

The resonances at the lower fields (5.98, 6.13, and 6.83 τ) may be assigned to H_3, H_1, and H_2 respectively. The resonance at 6.13 τ (H_1) is singlet, but the signals at 5.98 τ (H_3) and 6.83 τ (H_2) form a doublet ($J_{2,3}=2$ cps). In an ordinary π-allyl complex the coupling constant between the protons on the same terminal carbon is very small or zero.[25] The observed coupling constant of H_3 and H_2, again, would be expected to be on the basis of the proposed structure (Fig. 5-A) rather than on that of the *endo*-cyclic structure (Fig. 5-B).

The two resonances at 7.18 τ (doublet) and 7.52 τ (doublet) appear to be an AB system due

---

[24] K. Tori, K. Kitahonoki, K. Takano, H. Tanida and T. Tsuji, *Tetrahedron Letters*, **1964**, 559.

[25] M. L. Green and P. L. Nagy, "Advances in Organometallic Chemistry," Vol. II, Academic Press, New York (1964), p. 331.

to the protons of the non-equivalent methylene group (H_c and $H_{c'}$, $J_{c,c'}=15$ cps), and the *endo*-proton (H_c is in a different magnetic environment from that of the *exo*-proton ($H_{c'}$). Also, the two doublets at 7.46 and 7.88 τ are assigned to the AB-pair protons of the non-equivalent methylene group (H_a and $H_{a'}$; $J_{a,a'}=17$ cps). The shift of *endo*-protons (H_a and H_c) towards lower fields may be due to long-range shielding effects which are associated with the chloro-palladium-bridged system.

2-Benzal-cyclohexanone. The reaction of this ketone with sodium chloropalladite in ethanol gave di-μ-chloro-di-[1, 2-(1-oxo-butano)-3-phenyl-π-allyl]-dipalladium (Fig. 6).

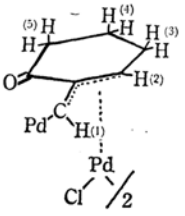

Fig. 6

The NMR spectrum (see Table 1) has four bands, with an area ratio of 5 : 1 : 1 : 6, at 2.73, 3.63, 4.78—4.90 and 7.15—8.60 τ. The peak at 2.73 τ may be ascribed to the phenyl protons on the terminal carbon in π-allyl system. On the basis of its relative intensity, the singlet peak at 3.63 τ may be assigned to the H_1 proton, the multiplet peak (4.78—4.90 τ, max. 4.84 τ) may be assigned to the H_2 proton, and the broad peak (7.15—8.60 τ) may be assigned to the six methylene protons (H_3, H_4, and H_5). In an ordinary π-allyl palladium complex, a substituent on a terminal carbon atom of the π-allyl system is in the *syn*-form, so in this complex the phenyl group on the terminal carbon atom of the π-allyl system may be in the *syn*-form.

Experimental

All melting points are uncorrected. The infrared spectra were obtained by a Hitachi Model EPI-S2 spectrometer. The NMR spectra were recorded by a Varian Model A-60 instrument in deuteriochloroform, using tetramethylsilane as an internal standard.

Materials. The following compounds were synthesized according to known procedures: 2-cyclohexenone,(26) 5, 5-dimethylcyclohexenone,(27) and benzal-cyclohexanone.(28) Commercially-available isophorone was used without further purification.

The Preparation of Chloro-π-allylic Palladium Complexes. *General Methods.* α,β-Unsaturated cyclic ketone (0.011 mol) was added to a solution of sodium chloropalladite (2.9 g) in 20—30 m*l* of ethanol, after which the mixture was heated under reflux for 15 min on a steam bath. The metallic palladium thus deposited was removed by filtration, and then the brown filtrate was evaporated to dryness under reduced pressure. The residue was chromatographed on alumina using dichloromethane. Recrystallization from benzene or benzene-cyclohexane afforded the required product. The complexes below were prepared in this manner.

Di-μ-chloro-di-(6-oxo-cyclohex-2-enyl)-dipalladium. Yellow micro-crystals (yield, 9%). Decomp. p. 156—161°C. IR Spectrum (KBr): 1668 cm^{-1} (uncoordinated C=O).

Found: C, 30.88; H, 3.04%, mol wt, 469 (in benzene). Calcd for $C_{12}H_{14}O_2Pd_2Cl_2$: C, 30.41; H, 2.97%, mol wt, 474.

Di-μ-chloro-di-(6-oxo-4, 4-dimethyl-cyclohex-2-enyl)-dipalladium. Yellow needles (yield, 10%); mp 175—178°C (decomp.). IR Spectrum (KBr) 1668 cm^{-1} (uncoordinated C=O).

Found: C, 36.95; H, 4.30%, mol wt, 529 (in benzene). Calcd for $C_{16}H_{22}O_2Pd_2Cl_2$: C, 36.70; H, 4.18%, mol wt, 530.

Di-μ-chloro-di-[1, 2-(4-oxo-2,2-dimethyl-butano)-π-allyl]-dipalladium. Yellow crystals (yield, 13%); mp 153—155°C (decomp.). IR Spectrum (KBr) 1681 cm^{-1} (uncoordinated C=O).

Found: C, 39.35; H, 4.81%, mol wt, 557 (in benzene). Calcd for $C_{18}H_{26}O_2Pd_2Cl_2$: C, 38.73; H, 4.69%, mol wt, 558.

Di-μ-chloro-di-[1, 2-(1-oxo-butano)-3-phenyl-π-allyl]-dipalladium. Yellow crystals (yield, 22%); mp 172—174°C (decomp.). IR Spectrum (KBr) 1690 cm^{-1} (uncoordinated C=O).

Found: C, 47.69; H, 3.80%, mol wt, 650 (in benzene). Calcd for $C_{26}H_{26}O_2Pd_2Cl_2$: C, 47.73; H, 4.00%, mol wt, 654.

The Preparation of Bromo-π-allylic-palladium Complexes. The corresponding chloro-complex (0.2 g) suspended in acetone (30 m*l*) was treated with lithium bromide (0.14 g), and the mixture was warmed to 40°C at 5 min. The resulting orange red solution was evaporated to dryness under reduced pressure. After chromatography with dichloromethane, recrystallization from benzene-petroleum ether gave the required product. The complexes below were prepared in this manner.

Di-μ-bromo-di-(6-oxo-cyclohex-2-enyl)-dipalladium. Yellow needles; decomposing at about 175°C without melting.

Found: C, 25.41; H, 2.26%. Calcd for $C_{12}H_{14}O_2Pd_2Br_2$: C, 25.60; H, 2.50%.

Di-μ-bromo-di-(6-oxo-4, 4-dimethyl-cyclohex-2-enyl)-dipalladium. Yellow crystals, decomposing without melting above 170°C.

Found: C, 32.94; H, 3.93%. Calcd for $C_{16}H_{22}O_2Pd_2Br_2$: C, 32.66; H, 3.58%.

Di-μ-bromo-di-[1, 2-(4-oxo-2, 2-dimethyl-butano)-π-allyl]-dipalladium. Yellow needles, decomposing without melting above 185°C.

Found: C, 33.04; H, 3.86%. Calcd for $C_{18}H_{26}O_2Pd_2Br_2$: C, 33.41; H, 4.05%.

---

26) W. F. Gannon and H. O. House, "Organic Syntheses," Vol. 40, p 14 (1960).

27) J. Colonge and J. Deux, *Compt. Rend.*, **231**, 1504 (1950).

28) W. S. Emerson, G. H. Birum and R. I. Longley, Jr., *J. Am. Chem. Soc.*, **75**, 1312 (1953).

Di-μ-bromo-di-[1, 2-(1-oxo-butano)-3-phenyl-π-allyl]-dipalladium. Yellow needles; mp 195°C (decomp.).

Found: C, 42.43; H, 3.76%. Calcd for $C_{26}H_{26}O_2Pd_2Br_2$: C, 42.02; H, 3.52%.

The Preparation of Chloro-(π-allyl)-*p*-toluidine-palladium Complexes. A solution of the chloro-bridged palladium complex (0.10 g) in dichloromethane (5 m*l*), was treated with a solution of *p*-toluidine (5% excess) in ether. After 10 min, the solvent was removed under reduced pressure, and the residue was recrystallized from a benzene-cyclohexane mixture to give the required product. The complexes below were prepared in this manner.

Chloro-(6-oxo-cyclohex-2-enyl)-*p*-toluidine-palladium. Yellow crystals; decomp. p. 160—162°C.

Found: C, 45.02; H, 4.73; N, 4.28%. Calcd for $C_{13}H_{16}ONPdCl$: C, 45.37; H, 4.68; N, 4.07%.

Chloro-(6-oxo-4, 4-dimethyl-cyclohex-2-enyl)-*p*-toluidine-palladium. Yellow needles; decomp. p. 157—158°C.

Found: C, 48.15; H, 5.48; N, 3.97%. Calcd for $C_{15}H_{20}ONPdCl$: C, 48.40; H, 5.41; N, 3.76%.

Chloro-[1, 2-(4-oxo-2, 2-dimethyl-butano)-π-allyl]-*p*-toluidine-palladium. Yellow needles; decomp. p. 158—160°C.

Found: C, 50.08; H, 5.88; N, 3.79%. Calcd for $C_{16}H_{22}ONPdCl$: C, 49.76; H, 5.74: N, 3.62%.

Chloro-[1, 2-(1-oxo-butano)-3-phenyl-π-allyl]-*p*-toluidine-palladium. Yellow needles, decomp. p. 168—170°C.

Found: C, 55.68; H, 5.33; N, 3.47%. Calcd for $C_{20}H_{22}ONPdCl$: C, 55.31; H, 5.10; N, 3.20%.

One of us (A. K.) wishes to express his gratitude to the Kawaken Fine Chemical Co. Ltd., for a gift of palladium chloride.