

Figure 1. The structure of  $C_5Me_5CH(p\text{-tolyl})CH_2Pd(acac)$  (**3**); all the numbered atoms are carbons and all hydrogen atoms are omitted.

derived from “*p*-tolylpalladium chloride” gave good crystals.<sup>5</sup>

The complex crystallized in the triclinic system with space group  $P\bar{1}$  and lattice parameters  $a = 11.072$  (5),  $b = 10.034$  (5),  $c = 13.515$  (5) Å;  $\alpha = 119.21$  (5),  $\beta = 88.23$  (5), and  $\gamma = 63.90$  (5)°. The unit cell contained two molecules [ $\rho_{obsd} = 1.36$  (by flotation),  $\rho_{calcd} = 1.353$  g/cm<sup>3</sup>] of two optical enantiomers; one is depicted, the other is related to it by a center of symmetry.

The structure was solved from Patterson and electron density maps using 1147 observed reflections out of 1316 measured with Mo  $K\alpha$  radiation on a Syntex automatic diffractometer. It was refined to a conventional  $R$  value of 0.055 and a weighted  $R$  of 0.078. The molecular geometry is shown (Figure 1) and the most significant bond lengths are given in Table I. The

Table I

Bond lengths, Å		Bond angles, <sup>a</sup> deg	
Pd–Ox(1)	2.048 (11)	Ox(1)–Pd–C(7)	85
Pd–Ox(2)	2.158 (9)	Ox(1)–Pd–Ox(2)	89
Pd–C(1)	2.130 (16)	Ox(2)–Pd–C(7)	172
Pd–C(2)	2.296 (17)	Pd–C(7)–C(6)	109
Pd–C(3)	3.14 (2)	C(7)–C(6)–C(5)	108
Pd–C(4)	3.48 (2)	C(7)–C(6)–C(11)	114
Pd–C(5)	3.04 (2)	C(5)–C(6)–C(11)	113
Pd–C(7)	2.025 (12)	C(6)–C(5)–C(5')	115
C(1)–C(2)	1.39 (2)	C(6)–C(5)–C(1)	108
C(2)–C(3)	1.47 (3)	C(6)–C(5)–C(4)	107
C(3)–C(4)	1.31 (2)	C(5)–C(1)–C(2)	109
C(4)–C(5)	1.54 (3)	C(1)–C(2)–C(3)	109
C(5)–C(1)	1.55 (2)	C(2)–C(3)–C(4)	110
C(5)–C(6)	1.56 (2)	C(3)–C(4)–C(5)	112
C(6)–C(7)	1.54 (2)	C(4)–C(5)–C(1)	100

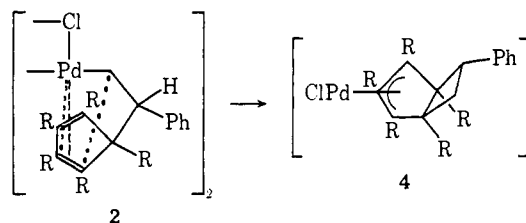
<sup>a</sup> Esd's are about 1.0°.

geometry of **3** is very unusual and consists of a cyclopentadiene which has only *one* double bond [C(1)–C(2)]

(5) The nmr spectra of **2**, and its acetylacetonate, as well as  $[C_5Me_5CH(p\text{-tolyl})CH_2PdCl]_2$  and **3** were all similar in  $CDCl_3$ . The acetylacetonates could be converted back to the chlorides and hence there is no rearrangement of the organic ligand skeleton during these interconversions.

coordinated to the metal, and which is  $\sigma$  bonded to the metal *via* a  $-CH(p\text{-tolyl})CH_2-$  bridge from C(5). As expected, the coordinated double bond is longer [C(1)–C(2) 1.39 (2) Å] than the uncoordinated one [C(3)–C(4) 1.31 (2) Å], and the coordination plane of the metal is approximately perpendicular (88°) to C(1)–C(2). The two remaining coordination sites of the square-planar palladium are occupied by the acetylacetonate. The isomers present in the crystal have the *p*-tolyl group and the *coordinated* double bond on the same side (taking the cyclopentadiene plane as horizontal). Bond angles and bond lengths are mostly very normal, in particular the angles Pd–C(7)–C(6) and C(7)–C(6)–C(5) are tetrahedral and therefore show that there is no strain present in the five-membered chelate ring (compare formula iv, above). The Pd–C  $\sigma$  bond [2.025 (16) Å] exerts a large influence on the Pd–O bond trans to itself [Pd–Ox(1) = 2.158 (9) Å, Pd–Ox(2) = 2.048 (11) Å].<sup>6</sup>

Furthermore, models of **2** and **3** show that another strain-free conformer can exist which has the coordinated double bond nearly coplanar with the coordination plane of the metal. These molecules are therefore well arranged geometrically for a variety of insertion and other reactions. For example, **2** isomerizes on standing in solution slowly to **4**;<sup>8</sup> others are described in the following communication.<sup>9</sup>



**Acknowledgment.** We thank the National Research Council of Canada for support of this work.

(6) This large trans influence may be contrasted with the situation in cyclooctenylnickel acetylacetonate where no such effect was observed.<sup>7</sup>

(7) O. S. Mills and E. F. Paulus, *Chem. Commun.*, 738 (1966).

(8) **4**: pale yellow crystalline solid; mp 145–146° dec; nmr  $\delta$  0.40, 0.91, 1.36, 1.39, 1.97 (all s, methyls), 1.97 (overlapping bd m, ca. 1 H), 3.12 (dd,  $J = 10$  and 12 Hz, 1 H), 5.01 (dd,  $J = 8$  and 10 Hz, 1 H), and 7.21 (m, aromatic). This complex was also characterized by degradation reactions, full details of which will be reported shortly.

(9) T. Hosokawa and P. M. Maitlis, *J. Amer. Chem. Soc.*, **94**, 3238 (1972).

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### A Model System for Acid and Base Reactions, Carbonylation, and $\beta$ -Hydride Elimination in Organopalladium Chemistry

Sir:

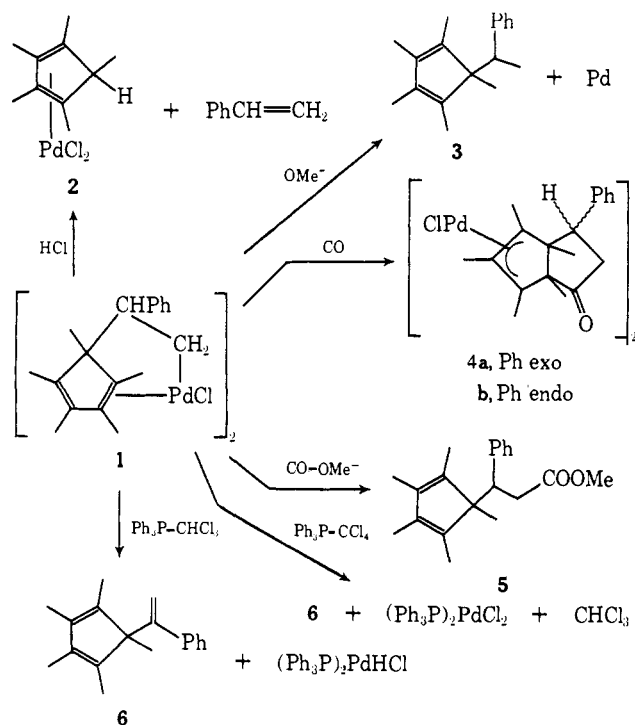
Alkylpalladium(II) complexes have been widely suggested as intermediates in a large number of catalytic reactions.<sup>1</sup> However, there has been relatively little evidence from model systems containing alkyl–Pd bonds to substantiate these mechanistic suggestions. This is largely because many of the alkylpalladium complexes

(1) P. M. Maitlis, “The Organic Chemistry of Palladium,” Vol. II, Academic Press, New York, N. Y., 1971, and references therein.

studied have tertiary phosphines or similar ligands present in order to stabilize them sufficiently for isolation and characterization, a factor which at the same time makes them kinetically rather inert and hence poor as models.<sup>2,3</sup>

In the preceding communication<sup>4</sup> we have described a novel  $\sigma, \pi$ -bonded alkylpalladium complex (**1**) which is sufficiently stable to be isolated and handled under ambient conditions but which is still reactive enough and has the right geometry to serve as a model system. We here report a number of simple reactions (see Scheme I) which occur with **1** and which shed new

Scheme I



light on the processes which occur in some catalytic reactions.<sup>5</sup>

**1. Acids and Bases.** The Pd-alkyl  $\sigma$  bond in **1** is *not directly* cleaved by acid; indeed, it undergoes only a slow reaction ( $t_{1/2} \sim 1.5$  hr) with HCl in chloroform at 25° to give dichloro(pentamethylcyclopentadiene)-palladium<sup>6</sup> (**2**) and styrene. These products cannot reasonably be derived from protonation of the Pd-C bond, and we propose that initial protonation occurs on the cyclopentadiene ring as shown in eq 1.

With base (sodium methoxide in methanol) the reaction is complete in 45 min at 25° and the Pd-C  $\sigma$  bond is attacked to give metal and 1-phenyl-1-(5'-pentamethylcyclopentadienyl)ethane (**3**).<sup>7</sup> The same

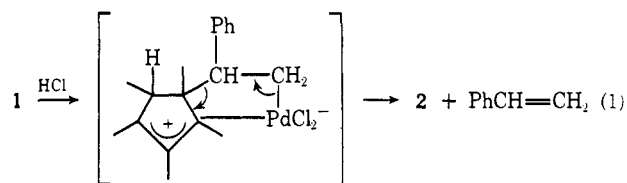
(2) See references in P. M. Maitlis, "The Organic Chemistry of Palladium," Vol. I, Academic Press, New York, N. Y., 1971, p 53, *et seq.*

(3) A group of compounds which do not have these limitations are the alkoxy-enyl complexes and studies using them as models have been carried out (ref 2, pp 74-75, 94-102). However, they suffer from the disadvantage that side reactions occur readily, for example, loss of the alkoxy groups in the presence of acid.

(4) C. Calvo, T. Hosokawa, H. Reinheimer, and P. M. Maitlis, *J. Amer. Chem. Soc.*, **94**, 3237 (1972).

(5) The reactions described here proceed essentially quantitatively. All new compounds have been isolated and characterized by analysis, molecular weight, nmr, ir, and (where appropriate) mass spectra. The carbonylation and  $\beta$  elimination reactions also occurred with the acetylacetonate complex derived from **1**.<sup>4</sup>

(6) P. V. Balakrishnan and P. M. Maitlis, *J. Chem. Soc. A*, 1721 (1971).

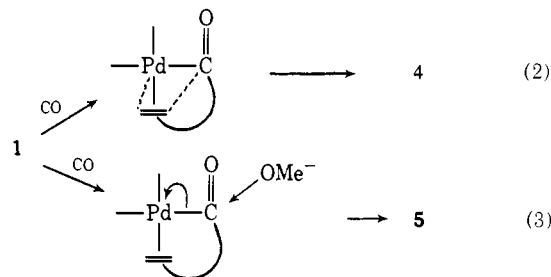


products are formed on hydrogenation in THF (1 atm, 25°) or with hydrazine in benzene.

It is likely that these reactions reflect a general property of Pd-C  $\sigma$  bonds. Reaction with bases (or hydrogen) occurs readily by an as yet undefined mechanism, which may involve a metal hydride, while reaction with acids in the absence of complicating features, is usually slow. The latter is not unexpected since Pd-C bonds are very nonpolar. The apparent greater ease of cleavage of Pt-C bonds by acid, in which the first step is an oxidative addition of H-X to Pt(II),<sup>8</sup> can be understood in terms of the greater facility with which Pt(II) undergoes oxidative addition compared to Pd(II).

**2. Carbonylation.** Although carbonylation reactions involving palladium complexes are very well known, certain anomalies exist in the literature where carbonylation is accompanied sometimes by insertion (to form cyclic ketones) and sometimes by solvolysis to give carboxylic acid derivatives.<sup>9</sup> We have now shown that the path which the reaction takes depends on the basicity of the medium.<sup>10</sup>

In benzene at 25° and 1 atm **1** reacted very rapidly with CO to give a 56:44 mixture of the exo and endo complexes **4a** and **4b**.<sup>11</sup> This reaction is unchanged in the presence of HCl, dimethyl sulfoxide, or methanol. However, in methanol in the presence of base a very fast reaction occurs to give the ester **5**<sup>12</sup> and metal. There is, therefore, a competition between two modes of reaction of the intermediate Pd-acyl complex, the one (eq 2) involving insertion of the coordinated double bond (to give **4**) and the other (eq 3) involving nucleo-



(7) **3**: colorless oil; nmr  $\delta$  0.95, 1.07 (d,  $J = 7$  Hz), 1.52, 1.56, 1.66, 1.85 (all s) methyls; 2.82 (q,  $J = 7$  Hz, 1 H), and 7.11 (m, phenyl).

(8) See, for example, U. Belluco, U. Croatto, P. Uguagliati, and R. Pietropaolo, *Inorg. Chem.*, **6**, 718 (1967); U. Belluco, M. Giustiniani, and M. Graziani, *J. Amer. Chem. Soc.*, **89**, 6494 (1967); and ref 2, p 90.

(9) Reference 1, pp 27-28; K. Bittler, N. V. Kutepow, D. Neubauer, and H. Reiss, *Angew. Chem., Int. Ed. Engl.*, **7**, 329 (1968); S. Brewis and P. R. Hughes, *Chem. Commun.*, 489 (1965); **6** (1966); *Amer. Chem. Soc., Div. Petrol. Chem., Prepr.*, **17**, B170 (1969).

(10) A somewhat similar conclusion has, very recently, been arrived at by L. F. Hines and J. K. Stille, *J. Amer. Chem. Soc.*, **94**, 485 (1972).

(11) **4a**: mp 200-202° dec; nmr  $\delta$  0.44, 0.99, 1.36, 1.43 2.06 (all s, methyls), 2.79 (dd,  $J = 20$  and 2.7 Hz, 1 H), 3.88 (dd,  $J = 10$  and 2.7 Hz, 1 H), 5.09 (dd,  $J = 10$  and 20 Hz, 1 H), and 7.20 (m, phenyl);  $\nu_{CO}$  1731  $cm^{-1}$  (KBr). **4b**: mp 189-190° dec; nmr  $\delta$  0.64, 1.02, 1.05, 1.40, 2.01 (all s, methyls), 2.65 (dd,  $J = 18$  and 8 Hz, 1 H), 3.09 (dd,  $J = 14$  and 8 Hz, 1 H), 5.14 (dd,  $J = 18$  and 14 Hz, 1 H), and 7.33 (m, phenyl);  $\nu_{CO}$  1730  $cm^{-1}$  (KBr).

(12) **5**: colorless oil; nmr  $\delta$  0.89, 1.54, 1.60, 1.69, 1.85 (all s, methyls), 2.40 (d,  $J = 4.6$  Hz, 1 H), 2.51 (d,  $J = 10.5$  Hz, 1 H), 3.27 (dd, 1 H), 3.43 (s, OMe), and 7.15 (s, phenyl);  $\nu_{CO}$  1747  $cm^{-1}$ .

philic attack, presumably at the acyl carbon, to give 5.<sup>5</sup>

**3.  $\beta$ -Hydride Elimination.** The  $\beta$  elimination of Pd-H from alkyl-Pd intermediates in catalytic and other reactions has been a frequently postulated process,<sup>13</sup> but definitive evidence for this reaction has hitherto been lacking. We now find that  $\beta$  elimination of Pd-H occurs when **1** is reacted with triphenylphosphine.

Treatment of **1** with 2 equiv of  $\text{PPh}_3$  (per Pd) in  $\text{CDCl}_3$  under an argon atmosphere gave  $\alpha$ -(pentamethylcyclopentadienyl)styrene (**6**)<sup>14</sup> and a clear solution, the nmr of which showed the presence of a high-field hydrogen (at  $\tau$  24.8) which we assign to  $(\text{Ph}_3\text{P})_2\text{PdHCl}$ .<sup>15</sup> The solution was relatively stable ( $t_{1/2}$  ca. 18 hr at 25°) but on exposure to air the hydride signal disappeared and  $(\text{Ph}_3\text{P})_2\text{PdCl}_2$  was slowly precipitated. The latter complex and **6** were formed directly when the reaction was carried out in  $\text{CCl}_4$  and in that case chloroform was detected by nmr. Full details of these and other reactions will be reported shortly.

**Acknowledgment.** We thank the National Research Council of Canada for support.

(13) Reference 2, pp 93-95; ref 1, pp 9-16; and, for example, R. F. Heck, *J. Amer. Chem. Soc.*, **90**, 5518, 5526, 5531, 5535, 5538 (1968).

(14) **6**: colorless oil; nmr  $\delta$  1.12 (s, 1 Me), 1.64 (m, 4 overlapping Me's), 5.17 (d,  $J = 1.5$  Hz, 1 H), 5.26 (d, 1 H), and 7.05 (m, phenyl).

(15) This complex was recently reported<sup>16</sup> but no nmr data were given.

(16) K. Kudo, M. Hidai, T. Murayama, and Y. Uchida, *Chem. Commun.*, 1701 (1969).

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## The Nature of Chlorotris(triphenylphosphine)rhodium in Solution and Its Reaction with Hydrogen

Sir:

Solutions of  $\text{RhCl}[\text{P}(\text{C}_6\text{H}_5)_3]_3$  are among the most efficient hydrogenation catalysts yet discovered and have occupied a central role in the development of modern homogeneous catalysis. Since the classic first paper of Wilkinson and coworkers<sup>1</sup> there has been a large number of contributions dealing with catalysis using this complex, none of which has questioned several basic features of the mechanism originally proposed.<sup>1</sup> It has been assumed that the first step involves ligand dissociation from the parent complex followed, under most conditions, by addition of molecular hydrogen, coordination of the olefin, and elimination of the hydrogenated product. In the initial publication,<sup>1</sup> molecular weight measurements were interpreted in terms of complete dissociation according to eq 1;



subsequent publications<sup>2-4</sup> have suggested that the degree of dissociation is, in fact, much smaller.

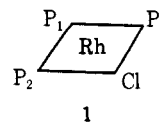
(1) J. A. Osborn, F. H. Jardine, J. F. Young, and G. Wilkinson, *J. Chem. Soc. A*, 1711 (1966)

(2) D. R. Eaton and S. R. Stuart, *J. Amer. Chem. Soc.*, **90**, 4170 (1968).

(3) D. D. Lehman, D. F. Shriver, and I. Wharf, *Chem. Commun.*, 1486 (1970).

(4) H. Arai and J. Halpern, *ibid.*, 1571 (1971).

$\text{RhCl}[\text{P}(\text{C}_6\text{H}_5)_3]_3$  (configuration **1**) is readily detected in solution using  $^{31}\text{P}$  nmr.<sup>2,5</sup> We have repeated the measurements to establish, for our spectrophotometric studies, that the trisphosphine species is the major component in solution. The  $^{31}\text{P}$  proton noise decoupled nmr spectrum for **1** is shown in the first line of Figure



**1**; the spectrum is unaffected by the addition of excess triphenylphosphine at 30°, and a new resonance appears in the position of free ligand. Similar results were obtained using the more soluble complex  $\text{RhCl}[\text{P}(p\text{-tolyl})_3]_3$ . We did not detect free  $\text{P}(\text{C}_6\text{H}_5)_3$  (expected at the position of the arrow in Figure 1) in the cw spectrum of  $\text{RhCl}[\text{P}(\text{C}_6\text{H}_5)_3]_3$ . However, by using the Fourier transform nmr technique we were able to detect a weak free phosphine resonance in a solution of 0.05 M complex in  $\text{CH}_2\text{Cl}_2$  with an intensity about 3% of that of the principal species.

Addition of molecular  $\text{H}_2$  to a solution of  $\text{RhCl}[\text{P}(\text{C}_6\text{H}_5)_3]_3$  forms a dihydride which is readily detected in the proton nmr.<sup>1</sup>  $^1\text{H}$  nmr spectra for the hydride region at two temperatures are shown in Figure 2; the spectra show well-resolved fine structure at -25° and broadening above room temperature due to phosphorus ligand exchange. Similarly the  $^{31}\text{P}$  nmr spectra with proton noise decoupling are shown for the hydride species at two temperatures in part B of Figure 1. It is clear from the spectrum at -25° that the hydride species is formed almost quantitatively and that it contains three phosphorus ligands. The structure may be unambiguously assigned as configuration **2**. Part C of

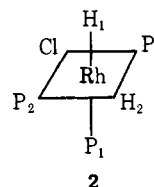
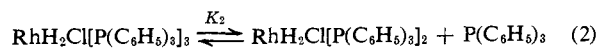


Figure 1 shows that the equilibrium may be reversed by passing  $\text{N}_2$  through the solution. No resonance for free triphenylphosphine was observed in these cw spectra.

From the spectrum in Figure 1B at 30° it is clear that phosphorus ligand dissociation is proceeding at an appreciable rate. Since the  $\text{P}_2$ -Rh coupling is preserved while the  $\text{P}_1$ -Rh and  $\text{P}_1$ - $\text{P}_2$  couplings are removed, we can deduce that under these conditions only the  $\text{P}_1$  phosphorus (the one trans to  $\text{H}_1$  in **2**) is dissociating and that it returns to the coordination site from which it left. Preliminary line-shape studies give an approximate rate constant  $k_2$  for the forward step of reaction 2 of  $\sim 400 \text{ sec}^{-1}$  at 30°. This, coupled with the absence



of line-shape effects associated with the phosphorus atoms  $\text{P}_2$  (configuration **2**), suggests a rather small degree of dissociation for the six-coordinate species. Thus it appears that the five-coordinate hydrides de-

(5) T. H. Brown and P. J. Green, *J. Amer. Chem. Soc.*, **92**, 2359 (1970).