Russian Journal of General Chemistry, Vol. 71, No. 6, 2001, pp. 888–892. Translated from Zhurnal Obshchei Khimii, Vol. 71, No. 6, 2001, pp. 946–951.

Structure of Complexes and Catalytic Oxidation of Triarylphosphine in the Reaction of 9-Phenyl-9-phosphafluorene with Bis(acetylacetonato)palladium

O. V. Tyukalova, G. V. Ratovskii, and F. K. Shmidt

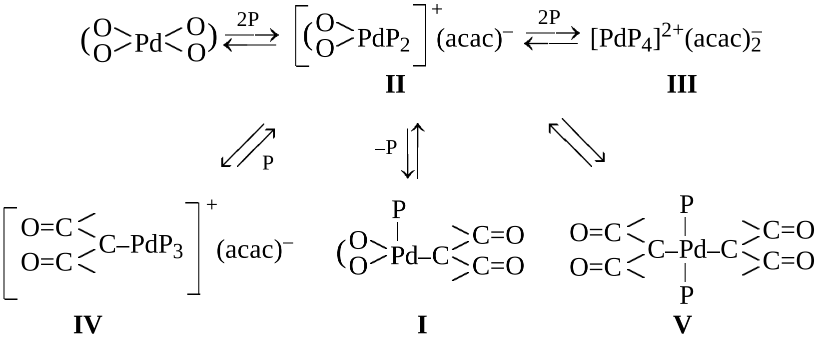
Institute of Petroleum and Coal Chemical Synthesis, Irkutsk State University, Irkutsk, Russia

Received January 25, 2000

Abstract—Complex formation of 9-phenyl-9-phosphafluorene with bis(acetylacetonato)palladium in benzene and acetonitrile was studied by means of NMR, IR, and UV spectroscopy. The structure of the resulting complexes, as well as specific features of catalytic oxidation of the arylphosphine and the reduction of Pd(II) to Pd(0) to form the complex $Pd(PC_{18}H_{13})_4$ were explored. 9-Phenyl-9-phosphafluorene gives two types of complexes with $Pd(acac)_2$. The first ones are similar to triphenylphosphine complexes, and the others (π complexes) are formed by coordination of the planar aromatic π system of the phosphine to the plane of $Pd(acac)_2$.

Systematic studies on reaction of phosphines with Pd(*acac*)$_2$ in organic media by means of IR, UV, and NMR spectroscopy showed that the resulting complexes can contain different forms of acetylacetonate ligands, depending on the nature and excess of the phosphine [1–4].

9-Phenyl-9-phosphafluorene ($PC_{18}H_{13}$) is a representative of triarylphosphines which are widely used as ligands in transition metal complexes. The structural peculiarities of this phosphine are associated with the presence of an additional C^2–C^2 bond between the two aromatic fragments. As a result, a five-membered ring including a phosphorus atom and benzene carbon atoms residing in the same plane is formed. The involvement of the lone electron pair of phosphorus in *p*–π conjugation with the aromatic system [5] determines some specific features $PC_{18}H_{13}$ exhibits in complex formation and catalytic oxidation reactions, as compared with PPh_3. In the previous works [1, 6] we showed that triphenylphosphine reacts with $Pd(acac)_2$ to form complexes containing from one to four molecules of triphenylphosphine in the coordination sphere of palladium. Depending on the number of phosphine molecules, complexes with one or two monodentate C^3-bound ligands and complexes with one or two acetylacetonate anions in the outer coordination sphere (compounds **I**–**V** are formed. The reaction of Pd(*acac*)$_2$ with PPh_3 in a 1 : 1 P : Pd ratio in various solvents gives an extremely stable complex Pd(acac)(acac-C^3)PPh_3 (**I**) with one chelate and one C^3-bound acetylacetonate ligand. The reaction of $Pd(acac)_2$ with PPh_3 in the presence of oxygen forms a system for the catalytic oxidation of PPh_3 to the corresponding phosphine oxide, followed by regeneration of complex **I** or the starting $Pd(acac)_2$.



1070-3632/01/7106-0888 $25.00 ©2001 MAIK "Nauka/Interperiodica"

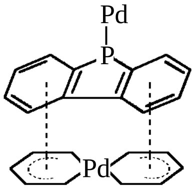
Table 1. Values of ε for the UV absorption bands of mixtures of $Pd(acac)_2$ and $PC_{18}H_{13}$ in benzene

P : Pd	Time, h	Absorption band, λ, nm			
		284	295	330	390
1 : 1	0.1	10100	8000	8700	640
	1	9900	7900	8700	
	2.5	10100	8100	9500	
	24	10600	8700	11800	
	72	10400	8450	11800	
	220	10500	8600	12000	510
3 : 1	0.1	27000	20900	10600	1400
	1	26700	20800	10300	
	4	26400	20800	10300	
	24	26400	20600	11700	
	190	25300	20300	12400	790
5 : 1	0.1	50200	36900	14700	11700
	1	44500	34100	14300	1600
	3			14100	1500
	24	44500	34100	16700	1400
	72			16700	1300
	240	40700	31300	17100	850
9 : 1	0.1	106100	70800	20400	19400
	1	87000	64900	19900	8300
	3	85500	64100	19300	7100
	24	78000	61900	19600	2150
	48	74000	58200	20000	2000

Table 2. Values of ε for the UV absorption bands of mixtures of $Pd(acac)_2$ and $PC_{18}H_{13}$ in acetonitrile

P : Pd	Time, h	Absorption band, λ, nm				
		272	284	295	327	357
1 : 1	0.1	17800	13300	10600	8700	2880
	1	15500	12600	9900	8000	2640
	3	15200	12600	9600	8000	2560
	24	15200	12300	9800	8200	2400
	168	14200	11800	9300	9000	1760
	890	10800	9000	7300	11400	800
3 : 1	0.1	34600	30600	22400	9650	6270
	1	31800	28200	19500	8130	4740
	2	31400	28200	19500	7930	4400
	24	31000	27400	19500	9150	4150
	144	28200	25800	17800	10840	2710
	860	22600	19300	15800	14060	1020
5 : 1	0.1	48700	45800	33500	12260	5500
	1	46600	43600	32000	10370	4240
	3	50200	43600	32000	10530	3770
	24	48000	46500	35600	12100	4720
	144	40700	45800	34900	13200	3300
	550	42200	41500	32700	16170	1410

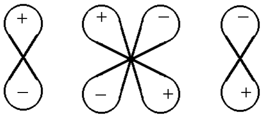
We earlier showed [1, 6] that in the course of the reaction of $Pd(acac)_2$ with PPh_3 in a 1 : 1 ratio the intensity of the absorption band at 300 nm in the UV spectrum of the system, that characterizes electronic transitions in the chelate acetylacetonate rings of $Pd(acac)_2$ (ε 11000), nearly halves, implying formation of complex **I**. At the same time, the UV spectrum contains no bands relating to other types of acetylacetonate ligands, and the spectral characteristics practically do not alter with time, what points to a high stability of complex **I**. Analysis of the UV spectra of benzene and acetonitrile solutions containing $Pd(acac)_2$ and $PC_{18}H_{13}$ shows that at a 1 : 1 P : Pd ratio the absorption band at 330 nm is 25% less intense than in $Pd(acac)_2$, and an absorption band at 295 nm appears, characteristic of acetylacetonate anions. The UV spectral parameters alter with time (Tables 1 and 2): The intensities of the absorption bands of the anions decrease, and the intensity of the band at 330 nm increases to values (ε 12 000) even slightly higher than those characteristic of the band of the chelate rings in $Pd(acac)_2$. With excess phosphine (P : Pd 3 : 1 and 5 : 1), initially strong bands of acetylacetonate anions are observed, whose intensity decreases with time; similtaneously, the band at 330 nm, belonging to the chelate acetylacetonate rings, sharply increases. In the reaction of $Pd(acac)_2$ with excess PPh_2 in the presence of oxygen, the decrease in the intensity of the acetylacetonate bands and the increase in the intensity of the band at 330 nm to ε 6000–9000 are associated with the occurrence of catalytic oxidation of coordinated triphenylphosphine and regeneration of complex **I** and the starting $Pd(acac)_2$ [1, 6]. Obviously, the reaction with $PC_{18}H_{13}$ involves similar oxidation of the phosphine and regeneration of $Pd(acac)_2$ and a complex like **I**. However, the fact that the intensity of the band of the chelate acetylacetonate rings increases several times compared with the starting $Pd(acac)_2$ suggests formation of some specific complexes of the latter with $PC_{18}H_{13}$, along with complexes formed by the coordination of the phosphine by the phosphorus atom, according to the above-presented scheme. Probably, such a resonance band enhancement is connected with formation of ππ complexes **VI** via interaction of the π system of the phosphafluorene fragment with the palladium ion (like π^5 interaction in complexes described in [7, 8]) and the π system of the two chelate rings in $Pd(acac)_2$, which favors electronic transitions in the pseudoaromatic system of the chelate acetylacetonate rings at palladium:



ππ complex **VI**

The fraction of such complexes much increases with increasing excess of the phosphine (at the 25 : 1 P : Pd ratio, ε_{330} = 60000). The ππ complexes formed are stable, as evidenced by the fact that the strong band at 330 nm is observed in the UV spectra for several days, even in the presence of oxygen.

As noted in [3], the intensity of the band at 330 nm is proportional to the number of the chelate acetylacetonate rings at palladium, and the band position is practically constant. That means that electronic transitions in the two coplanar chelate rings occur independently of one another. Considering the symmetry of *d* orbitals, the π systems of the chelate ligands can not interact via palladium *d* orbitals, because the *dxz* and *dyz* orbitals of the metal ion, which are antisymmetrical with respect to the molecular plain, differently overlap with π orbitals of the two acetylacetonate ligands:



pz *dxz* (*dyz*) *pz*

The interaction of π and π^* orbitals of the chelate rings with π and π^* orbitals of the phosphafluorene fragment makes possible certain correlation between electronic transitions in the acetylacetonate rings, which shows up in the resonance enhancement of the UV band.

Along with the above-mentioned bands, the UV spectra of the complexes of $Pd(acac)_2$ with $PC_{18}H_{13}$, unlike those of the complexes with PPh_3, contain a strong long-wave band near 390 (in benzene) or 357 nm (in acetonitrile). Its intensity sharply increases (analogously to the band of the anions at 295 nm) with increasing P : Pd ratio. This band may be formed by charge transfer from orbitals of coordinated $PC_{18} \cdot H_{13}$ on orbitals of the cations Pd^{2+} and $[Pd(acac)]^+$. In this case, phosphine may be coordinated to palladium by the phosphorus atom (interaction with the lone electron pair of phosphorus), as well as by π^5 coordination of the five-membered phosphafluorene ring (interaction with the π system). Fast mutual transformations between these complexes may take place. Therefore, the intensity of this band belonging to the π^5-coordinated compexes quickly decreases with time.

The formation of complex **I** from $Pd(acac)_2$ and PPh_3 (P : Pd 1 : 1) causes a twofold decrease in the intensity of the carbonyl absorption bands of the chelate rings and appearance of bands due to C^3-bound ligands in the IR spectrum. The reaction of $Pd(acac)_2$ with $PC_{18}H_{13}$ at a 1 : 1 P : Pd ratio leads to a more than twofold decrease in the intensity of bands of the chelate rings of $Pd(acac)_2$ (1560 cm^{-1}) in the IR spectra in benzene. At the same time, the amount of C^3-bound acetylacetonate ligands at palladium (1678 and 1645 cm^{-1}) is about 3 times smaller (from evaluated peak and integral intensities of the IR bands; Table 3 and 4) than with PPh_3 at the same component ratio, and at 1617 cm^{-1} a medium band of acetylacetonate anions appears.

The intensities of the absorption bands in the IR spectra undergo redistribution with time: The intensities of the C^3-bound ligand bands decrease, while the intensities of the chelate ring bands, including those of $Pd(acac)_2$ (1560 and 1517 cm^{-1}) increase. These data show that the complex $Pd(acac)(acac\text{-}C^3) \cdot (PC_{18}H_{13})$ is less stable than its triphenylphosphine analog (complex **I**). Noteworthy is also the appearance and growth of a band at 1597 cm^{-1} due to coordinated phosphine. This may be explained by formation of complex **VI**. Probably, the donor–acceptor interaction between the π system of the dibenzoheteroring of the phosphine and the quasiaromatic system of the chelate rings of $Pd(acac)_2$ produces resonance alterations in vibrational characteristics of the coordinated phosphine. Analogous alterations are observed in the IR spectra during reaction of $Pd(acac)_2$ with three parts of $PC_{18}H_{13}$ (Tables 3 and 4).

It is known [1, 6] that the reaction of $Pd(acac)_2$ with excess PPh_3 (P : Pd > 2 : 1) in the presence of oxygen is accompanied by catalytic oxidation of the phosphine to phosphine oxide, followed by regeneration of complex **I** and the starting $Pd(acac)_2$. Catalytic activity is exhibited by Pd(II) complexes **II**–**V** containing two C^3-bound or ionic acetylacetonate ligands. 9-Phenyl-9-phosphafluorene, too, undergoes catalytic oxidation in the presence of $Pd(acac)_2$, which is confirmed by IR, UV, and ^{31}P NMR spectroscopy. The oxidation of the phosphine at 1 : 1–9 : 1 P : Pd ratios in benzene and acetonitrile is accompanied by gradual decrease in the intensity of the phosphine band at

Table 3. Peak intensities of absorption bands (ε) in the IR spectra of mixtures of $Pd(acac)_2$ with $PC_{18}H_{13}$ in benzene

P : Pd	Time, h	Absorption band, ν, cm^{-1}							
		1730	1712	1678	1645	1617	1597	1578	1560
1 : 1	0.1			150	100	140	160	500[a]	430
	1			100	80	140	210	750[a]	590
	3			80	80	140	220	850[a]	660
	24			80	70	110	220	930[a]	750
	120			90	70	110	210	1000[a]	890
	360			30	60	150	230	1220[a]	1120
3 : 1	0.1			590	350	300	370	1000	380
	1			560	340	320	390	970	350
	3			510	320	330	400	960	340
	24			330	250	310	570	1320	340
	96			300	230	320	590	1260	630
5 : 1	0.1	60	80	570	340	330	420	1010	390
	1	60	80	520	340	360	450	950	360
	3	60	80	480	340	370	470	910	370
	24	60	80	330	380	480	600	840	360
	720	80	120	110	300	610	650	610	310
5 : 1[b]	0.1	280[c]	270[d]	60	190	320[e]	390	200	140
	0.5	330[c]	310[d]	70	200	350[e]	440	240	160
	1	330[c]	310[d]	70	200	350[e]	440	240	180
	3	350[c]	330[d]	90	230	350[e]	470	310	280
	24	340[c]	320[d]	90	230	350[e]	510	370	380

[a] The maximum is shifted to 1570 cm^{-1}. [b] In acetonitrile. [c] ν_{max} 1728 cm^{-1}. [d] ν_{max} 1708 cm^{-1}. [e] ν_{max} 1620 cm^{-1}.

272 nm and the acetylacetonate anion bands at 95 and 390 nm, and increase in the intensity of the band of the chelate rings at 330 nm in the UV spectra (Tables 1 and 2). The oxidation at 1 : 1 and 3 : 1 P : Pd ratios is accompanied by appearance and gradual growth of bands at 1212 and 1130 cm^{-1} due to the phosphine oxide. Simultaneously the number of complexes with C^3-bound and anionic forms of the ligands decrease, and the contents of complexes **I, II** and the starting $Pd(acac)_2$ increase (Tables 3 and 4). The signal of the phosphine in the ^{31}P NMR spectra (δ_P –9.6 ppm) disappears and the signal of the phosphine oxide appears (δ_P 30 ppm).

The rate of oxidation of $PC_{18}H_{13}$ in oxygen medium, as measured by the consumption of oxygen, is much lower than the rate of oxidation of other arylphosphines (t 37°C, C_{Pd} 0.0013 M; P : Pd 25 : 1).

Phosphine	PPh_3	$P(p\text{-}ClC_6H_4)_3$	$P(n\text{-}CH_3C_6H_4)_3$	$PC_{18}H_{13}$
V, mol O_2/(mol Pd min)	0.89	0.73	1.01	0.21

This is probably explained by the fact that the oxidation primarily involves complexes **II**–**IV** which

Table 4. Integral intensities of absorption bands (A) in the IR spectra of mixtures of $Pd(acac)_2$ with $PC_{18}H_{13}$ in benzene.

P : Pd	Time, h	Absorption band, ν, cm^{-1}				
		1730 + 1712	1678 + 1645	1617 + 1597	1580 + 1560	1517
1 : 1	0.1		5010	3640	24600	10300
	1		3900	4000	33500	17900
	3		3320	3480	38100	18700
	24		3300	3300	41900	21400
	120		3300	3300	45200	18500
	360		1500	2800	50200	21000
3 : 1	0.1		19200	8400	30200	11100
	1		18700	9300	29300	8600
	3		17900	9600	28900	7900
	24		13400	9200	42300	15800
	96		12900	9200	46900	17800
5 : 1	0.1	2900	18400	9400	28500	7400
	1	2900	17600	10300	27300	7800
	3	2900	17400	10300	27300	6600
	24	2900	11400	21400	26500	6300
	720	3900	3200	34000	17200	4000

are similar to triphenylphosphine ones (i.e., they contain two C^3-bound ligands or acetylacetonate anions) but are less active. On the other hand, the low oxidation rates can also associated with the inactivity of ππ complexes **VI** partially formed in the first stage.

Attempted oxidation of $PC_{18}H_{13}$ at 5 : 1 and 9 : 1 P : Pd ratios in benzene and acetonitrile containing traces of water and at high reactant concentrations (C_{Pd} 0.04 M), used for registration of IR spectra, gave results differing from those obtained at 1 : 1 and 3 : 1 P : Pd ratios. The IR spectra show (Tables 3 and 4) that initially the reaction solution contains C^3-bound and chelate forms of the acetylacetonate ligands, but the amount of both species decreases with time, and free acetylacetone appears in the solution (more than 50%). This follows from the appearance of three absorption bands, ν, cm^{-1}: 1730, 1712, and 1600–1615 (in benzene, a broad band) or 1620 (in acetonitrile). The solution gets dark brown. Here, evidently, the reduction of Pd(II) to Pd(0) takes place to give a zero-valent complex $Pd(PC_{18}H_{13})_4$ (**VII**):

$$\mathrm{Pd(acac)_2 + 5PC_{18}P_{13} + H_2O} \longrightarrow \mathrm{Pd(PC_{18}H_{13})_4 + 2acacH + P(O)C_{18}H_{13}}.$$

The zero-valent complex is unstable in the presence of oxygen and decomposes to phosphine oxide and brown products. With PPh_3, such reduction reaction proceeds only in an inert atmosphere, while in the presence of air oxygen the competing process of catalytic oxidation of PPh_3 with subsequent regeneration of complex **I** and $Pd(acac)_2$ takes place [6]. Evidently, with $PC_{18}H_{13}$, at high concentrations and large excesses of the phosphine, the redox process according to above equation is preferred even in the presence of oxygen. It is known that zero-valent palladium complexes like **VII** catalyze oxidation of phosphines. Probably, complex **VII** formed in the presence of oxygen is to a certain extent involved in oxidation of the phosphine and then decomposes.

Hence, 9-phenyl-9-phosphafluorene forms two types of complexes with $Pd(acac)_2$. The first ones are analogous to triphenylphosphine complexes **I**–**V**. They undergo rearrangements with time and are active in the catalytic oxidation of the phosphine. The reduction of Pd(II) to Pd(0) and the formation of complex **VII**, too, occur through formation of such complexes. The other complexes (ππ complex **VI**) are inactive in the catalytic oxidation of the phosphine. They are stable in solutions, and their formation is confirmed by spectral data.

EXPERIMENTAL

The UV spectra were recorded on a Specord UV VIS spectrophotometer in the range 50 000–15 000 cm^{-1}. Solutions for spectral measurements were prepared in picnometers (5 ml in volume) so that the concentrations of $Pd(acac)_2$ were in the range 0.005–0.001 M.

The IR spectra were measured on a Specord M-80 spectrometer in the range 4000–200 cm^{-1}. The concentrations of $Pd(acac)_2$ in the working solutions were 0.015–0.045 M.

REFERENCES

1. Ratovskii, G.V., Tyukalova, O.V., Tkach, V.S., and Shmidt, F.K., *Zh. Obshch. Khim.*, 1996, vol. 66, no. 11, pp. 1791–1795.
2. Tyukalova, O.V., Ratovskii, G.V., and Shmidt, F.K., *Koord. Khim.*, 1997, vol. 23, no. 4, pp. 288–292.
3. Ratovskii, G.V., Tyukalova, O.V., Tkach, V.S., and Shmidt, F.K., *Zh. Obshch. Khim.*, 1996, vol. 66, no. 5, pp. 708–715.
4. Ratovskii, G.V., Tyukalova, O.V., Tkach, V.S., and Shmidt, F.K., *Zh. Obshch. Khim.*, 1998, vol. 68, no. 10, pp. 1660–1668.
5. Davydov, S.N., Rodionov, A.N., Shigorin, D.N., Syutkina, O.P., and Krasnova, T.L., *Zh. Fiz. Khim.*, 1980, vol. 54, no. 2, pp. 506–508.
6. Tyukalova, O.V., Ratovskii, G.V., Belykh, L.B., and Shmidt, F.K., *Zh. Obshch. Khim.*, 1997, vol. 67, no. 1, pp. 58–92.
7. Garnovskii, A.D., Sadimenko, A.P., Vasil'chenko, I.S., and Garnovskii, D.A., Abstracts of Papers, *XIX Vserossiiskoe Chuguevskoe soveshchanie po khimii kompleksnykh soedinenii* (XIX All-Russia Chuguev Conf. on Chemistry of Complex Compounds), Ivanovo, 1999, p. 9.
8. Nief, F. and Ricard, L., *J. Organomet. Chem.*, 1994, vol. 464, no. 2, pp. 149–154.