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Palladium(I) Complexes in Coordination Chemistry and Catalysis

O.N.Temkin and L.G.Bruk

The state of a rapidly developing branch of the coordination chemistry of platinum metals, namely the chemistry of palladium(I) complexes, is examined. The fundamental properties, chemical reactions, and methods of synthesis of palladium(I) complexes are described. The role of palladium(I) compounds in the mechanisms of catalytic and stoichiometric reactions is discussed.
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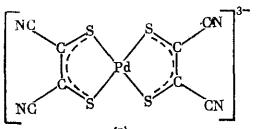
I. INTRODUCTION

Complexes of metals with the d^9 electronic configuration are known for the metals at the ends of the transition series in the Periodic System. Until recently, the family of these compounds was limited mainly to copper(II) and zerovalent cobalt complexes[1]. Although the first representatives of the coordination compounds of the nickel triad in the +1 oxidation state have been known for a fairly long time [nickel(I)—1913 [2] and palladium(I)—1942 [3]], the early studies concerning palladium(I) complexes have been treated with much scepticism. For example, there is not even a mention of palladium(I) in the monograph of Cotton and Wilkinson[1] (1965), while Livingstone's book[4] (1973) describes three complexes and notes that "the existence of univalent palladium still cannot be regarded as proved". Only Maitlis's monograph[5] (1971) presents complete information about all the few compounds of formally univalent palladium known at the time.

During the last ten years, numerous studies concerning nickel(I), palladium(I), and platinum(I) have been published, the early investigations have been re-examined, and it has become possible to speak of a new family of complexes of formally univalent nickel, palladium, and platinum. The interest in these compounds has been to a large extent stimulated by studies in the field of metal complex catalysis and in the chemistry of cluster compounds. It was found that the complexes of the metals M(I) of the nickel triad contain a wide variety of σ and π ligands and have a series of rarely encountered structural features. The present review is devoted to palladium(I) compounds whose structure and reactivity have been investigated most fully.

II. THE STRUCTURE AND PHYSICAL PROPERTIES OF PALLADIUM(I) COMPLEXES

By the beginning of 1981, more than 140 palladium(I) compounds with various σ and π ligands had been synthesised. In the vast majority of instances the palladium(I) complexes are dimeric as a result of the formation of Pd—Pd bonds and are diamagnetic in contrast to the numerous monomeric paramagnetic nickel(I) complexes[6,7]. Only one monomeric paramagnetic palladium(I) [and platinum(I)] complex (I) with a chelating thiolene ligand is known[8].



(I)

Furthermore, the formation of paramagnetic Pd^+ ions has been detected by EPR on the PdY zeolite under various conditions[9,10]. The most thoroughly investigated class of cluster complexes of palladium comprises dimers with the Pd_2^{2+} fragment, although complexes containing the following skeletons made up of palladium atoms are already known: Pd_2^{2+}, Pd_3^{2+},[11,12] Pd_3^{4+},[13-15] Pd_4^0,[16] Pd_4^{4+},[17-21] Pd_5^{4+},[22] Pd_{10}^0,[23] Pd_{10}^{8+},[24] and Pd_{12}^0.[25]

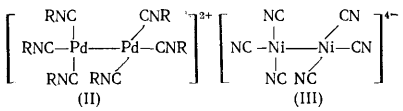
The formal oxidation state of the metal atom in the complex is defined, according to Nyholm[26], as the charge which remains on the group of metal atoms after the removal of the ligand and is referred to the number of metal atoms. It is assumed that in the leaving ligand atoms or groups of atoms (H^-, Cl^-, O^{2-}, OH^-, NH_2^-, PR_2^-, $SnCl_3^-$, CH_3^-) the electron cloud of the atom linked to the metal corresponds to the cloud of the nearest inert gas atom and that the ligands are removed in the form of neutral molecules (CO, NO, N_2, CO_2, C_2H_2, C_4H_4). Certain π-bonded organic groups (C_3H_5, C_5H_5) are believed to be anions like the σ-bonded groups ($C_3H_5^-$, $C_5H_5^-$). From this standpoint, the oxidation state of palladium in the compounds C_3H_5PdCl, $(C_3H_5)_2Pd$, and C_5H_5PdCl is +2, while in the compounds $C_3H_5Pd_2Cl$, $(C_3H_5)_2.Pd_2$, and $C_5H_5Pd_2C_3H_3$ it is +1. In view of the foregoing, compounds containing Pd^+, Pd_2^{2+}, and Pd_4^{4+} belong to the class of complexes of formally univalent palladium (+1 oxidation state). These complexes will be considered in the present review.

1. Palladium(I) Complexes with σ-Ligands

In this subsection we shall deal with palladium(I) complexes containing ligands which supply to the metal unshared σ (or *n*) electron pairs and are linked to the metal via a single centre (atom)†.

†In contrast to the π-ligands which form π-complexes, ligands of this kind can be usefully referred to as σ-ligands regardless of the predominant direction of electron transfer in the M—L bond and its multiplicity. Ligands containing π-electron pairs as well as σ-electron pairs can naturally be coordinated as π-ligands or as both σ- and π-ligands simultaneously (RCN, RNC, N_2, CO, CS_2).

Palladium(I) complexes with isonitriles (Table 1) are the most stable among the palladium(I) compounds with σ-ligands. This factor as well as the possibility of growing their single crystals made it possible in 1974 to carry out the first X-ray diffraction study on the palladium(I) complex with a σ-ligand: $[Pd_2(CH_3NC)_6](PF_6)_2 \cdot \frac{1}{2}(CH_3)_2CO$.[27,28] A characteristic feature of the structure of the complexes $Pd_2(RNC)_6^{2+}$ (II) as well as the analogous nickel(I) complex $Ni_2(CN)_6^{4-}$ (III) [29] is a square planar environment of the metal atom:



(II) (III)

This structure is apparently characteristic of all dimeric palladium(I) complexes with σ-ligands.

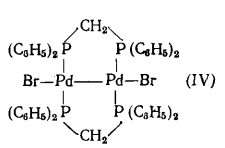
Table 1. Palladium(I) complexes with isonitrile ligands.

Complex	X	L	L′	Refs.
$[PdXL_2]_2$	Cl, Br, I	t-C_4H_9NC	—	[30, 31]
$[PdXL_2]_2$	I	CH_3NC, C_6H_5NC	—	[31]
$[PdXL_2]_2$	SCN	CH_3NC	—	[31]
$[PdXL_2]_n$	Cl, Br	CH_3NC	—	[32]
$[PdXL'L]_2$	I	t-C_4H_9NC	$P(C_6H_5)_3$	[30]
$[Pd_2L_6]X_2$	PF_6, Cl	CH_3NC	—	[27, 28]
$[Pd_2L_6]X_2$	Br	t-C_4H_9NC	—	[32, 33]
$[Pd_2L_6]X_2$	Br	C_6H_5NC	—	[32, 33]
$[Pd_2L_5L'](PF_6)_2$	—	CH_3NC	$P(C_6H_5)_3$	[33]
$[Pd_2L_4L_2'](PF_6)_2$	—	CH_3NC	$P(C_6H_5)_3$	[33]
$[PdPtL_6](PF_6)_2$	—	CH_3NC	—	[33, 34]
$[PdPtL_5L'](PF_6)_2$	—	CH_3NC	$P(C_6H_5)_3$	[31, 33]
$[PdPtL_4L_2'](PF_6)_2$	—	CH_3NC	$P(C_6H_5)_2$	[31, 33]
$[Pd_2L_2L_2'](PF_6)_2$	—	CH_3NC	$(C_6H_5)_2P(CH_2)_nP(C_6H_5)_2$; $n=2-4$	*
$[Pd_2L_2L_2'](PF_6)_2$	—	CH_3NC	$(C_6H_5)_2PCH{=}CHP(C_6H_5)_2$	*

*C.H.Lindsay, L.S.Benner, and A.L.Balch, Inorg.Chem., 1980, 19, 3503.

A typical feature of the complexes of isonitriles is the absence of bridge ligands, which, together with the diamagnetism and the short Pd–Pd distance (2.53 Å) makes it possible to infer with confidence the presence of a metal–metal bond. Thus the complexes are dsp^2 hybridised and the fourth coordination site at each palladium atom is occupied by a neighbouring palladium atom. The angle between the planes in which the PdL_3 groups are located is 86.2° for L = CH_3NC.[27,28]

Certain bidentate σ-ligands#, namely CH_3COO^-, $CH_2[As(C_6H_5)_2]_2$, and $CH_2[P(C_6H_5)_2]_2$, are bridge ligands in complexes with Pd–Pd bond (Table 2). In the case of bridge phosphine the angle between the planes of the PdL_3 groups is 39° (38.5° in the platinum analogue). However, the virtually square planar coordination around each palladium atom is retained[49]. The Pd–Pd distance in the complex $Pd_2Br_2dpm_2$ (IV) is 2.699 Å.[49]



(IV)

#Henceforth $CH_2[As(C_6H_5)_2]_2$ and $CH_2[P(C_6H_5)_2]_2$ will be designated by dam and dpm respectively.

We shall consider in greater detail the carbonyl complexes of palladium(I).[52] During the time since the publication of the first study[53], a large set of carbonyl halide complexes of palladium have been obtained under similar conditions from CO and PdX_2 with an average degree of oxidation from +0.5 to +2, which was calculated from the determinations of the contents of the elements[35–41,53–57]. According to the majority of investigators, these compounds are coordination monomers of the type $Pd_m(CO)_lX_n$. The insoluble polymeric complexes have been synthesised by various investigators and had similar spectroscopic characteristics but differed significantly in composition. It has been established[38,39] that the composition and properties of the coordination polymers are determined to a large extent by the amount of water in the reaction medium during their synthesis. The influence of the water concentration on the composition of the complexes and hence on the average degree of oxidation of palladium is apparently related to the involvement of water in the stages involving the reduction of palladium(II) and palladium(I) to zerovalent palladium via reaction (1). The interaction of the carbonyl complexes of palladium(I) with PdX_2 and Pd(0), whose ratio in the reaction system depends on the concentration of water, proceeds via Scheme (2) and leads to coordination polymers with different degrees of oxidation of palladium:

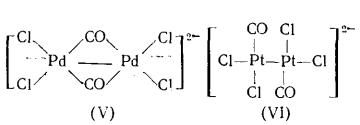
$$PdX_2 \xrightarrow{CO,H_2O} Pd^0 \xrightarrow{PdX_2} Pd_2X_2(CO)_n \xrightarrow{CO,H_2O} 2Pd^0 \quad (1)$$

$$m\,Pd_2X_2(CO)_n \begin{cases} \xrightarrow{nPdX_2} Pd_{(2m+n)}X_{2(m+n)}(CO)_n \\ \xrightarrow{pPd^0} Pd_{(2m+p)}X_{2m}(CO)_n \end{cases} \quad (2)$$

When certain conditions are maintained, it is possible to obtain polymeric complexes having the composition $(PdCOX)_n$ (Table 2, Nos.1–9).

Together with these compounds, numerous dimeric diamagnetic compounds have been synthesised, the first representatives having been obtained as early as 1942 [3] (Table 2, Nos.31–33).

A detailed study of the structures of palladium carbonyl halides by infrared and Raman spectroscopy threw some light on the question, which had been under discussion for a long time, whether the halide or the carbon monoxide functions as the bridge in the palladium(I) carbonyl halide complexes[41]. According to Goggin and Mink[41], the carbonyl groups constitute the bridges in the dimeric palladium carbonyl halides $[Pd_2(CO)_2X_4]^{2-}$ [structure (V)], while the polymeric complexes consist of dimers linked by halide bridges. It is of interest to note that the dimeric platinum(I) carbonyl halide complexes have the non-bridge structure (VI),[58,59] characteristic of palladium(I) isocyanides, in contrast to the analogous palladium(I) complexes.



(V) (VI)

The first palladium(I) carbonyl acetate cluster of the type $[Pd(CO)(OOCCH_3)]_4 \cdot 2CH_3COOH$ was obtained in a number of studies[17–19] (Table 2, Nos.10 and 14). The crystal of this compound is made up of planar tetranuclear complexes (VII) and acetic acid dimers located at the centres of symmetry. The complex (VII) contains two dimeric complex species $Pd_2(CO)_2^{2+}$ with Pd–Pd bonds (l = 2.663 Å) and carbonyl bridges linked via four acetate groups[42]. Moiseev et al.[19] and Kuz'mina and Struchkov[42] carried out the first X-ray diffraction studies on palladium(I) carbonyl complexes.

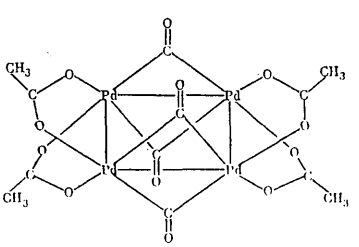
Table 2. Palladium(I) complexes with CO and other σ-ligands.

No.	Complex	X,	L′,	M+	$\nu_{CO,\,NO}$ cm^{-1}	References
			$[Pd(CO)X]_n$			
1	Pale yellow	Cl	—	—	2003, 1972, 1942	[35]
2	Yellow-green or red-violet	Cl	—	—	1975, 1925, 1892	[36]
3	Yellow-green	Cl	—	—	1978, 1940	[37]
4	Yellow, violet	Cl	—	—	1985, 1975, 1960, 1940	[38]
5	Yellow-brown	Cl	—	—	1977	40]
6	Yellow-green	Cl	—	—	2023, 2002, 1978, 1951, 1936	[41]
7	—	Br	—	—	1960, 1930	[38, 39]
8	Bright green	Br	—	—	1953	[40]
9	Yellow	Br	—	—	2008, 1996, 1987, 1953, 1938, 1922	[41]
10	$n = 4$	CH_3COO	—	—	1975, 1940	[17—19]
11	$n = 4$	C_2H_5COO	—	—	1968, 1935	[19]
			$[Pd(CO)X]_nL_m$			
12	Yellow; $n = 6, m = 2$	Cl	C_6H_5CN	—	1979, 1954c, 1948c, 1917	[41]
13	Brown; $n = 2, m = 2$	Cl	$As(C_6H_5)_3$	—	1963, 1918, 1890, 1961, 1816	[41]
14	Yellow; $n = 4, m = 2$	CH_3COO	CH_3COOH	—	1975, 1934	[17—19, 42]
15	$n = 4, m = 2$	CD_3COO	CD_3COOD	—	1965, 1931	[17—19]
16	$n = 4, m = 2$	C_6H_5COO	C_6H_5COOH	—	1980, 1958	[17—19]
			$Pd_4(CO)_2L_nX_4$			
17	Black; $n = 4$	CH_3COO	phen	—	1800	[20, 21, 43]
	»	Cl, CCl_3COO	phen	—	—	[44]
	»	CF_3COO, CNS	phen	—	—	[44]
18	Brown; $n = 2$	CH_3COO	bipy	—	1800	[44]
19	Brown		$[(PdXL)_2CO]_n$			
20	Brown	Cl	$P(C_6H_5)_3$	—	1892, 1962	[45, 46]
20a	Dark cherry-red	Br	$P(C_6H_5)_3$	—	1890, 1860	[45, 46]
21	Brown	I	$P(C_6H_5)_3$	—	1902, 1862	[45, 46]
22	Red	Cl	$P(C_6H_5)(p\text{-}CH_3OC_6H_4)_2$	—	1889, 1859	[45, 46]
		Br	$P(C_6H_5)(p\text{-}ClH_3OC_6H_4)_2$	—	1891, 1864	[45, 46]
23	Dark red	Cl	$P(C_6H_5)_2(C_6H_4COOH)$	—	1898, 1867	[45, 46]
24	Bright red	Br	$P(C_6H_5)_2(C_6H_4COOH)$	—	1893, 1865	[45, 46]
25	Pale brown	Cl	$P(C_6H_5)_2(C_6H_4F)$	—	1893, 1859	[45, 46]
26	Red brown	Br	$P(C_6H_5)_2(C_6H_4F)$	—	1896, 1861	[45, 46]
27	Brown	Cl	$P(C_6H_5)_2(C_6H_4Cl)$	—	1892, 1860	[45, 46]
28	Red brown	Br	$P(C_6H_5)_2(C_6H_4Cl)$	—	1890, 1861	[45, 46]
29	Brown	Cl	$P(C_6H_5)_2(C_6H_4CH_3)$	—	1890, 1860	[45, 46]
30	Red brown	Br	$P(C_6H_5)_2(C_6H_4CH_3)$	—	1898, 1870	[45, 46]
			$[Pd_2(CO)_2X_4]M_2$			
31	Greenish yellow	Cl	—	NH_4	—	[3]
32	Bright yellow	Cl	—	$Pt(NH_3)_4^{2+}$	—	[3]
33	Yellow	Cl		$(CH_2NH_3)_2^{2+}$	—	[3]
34	Pale yellow	Cl	—	Cs	1915	[40]
35	Green	Cl	—	Rb	—	[40]
36	Greenish yellow	Cl	—	$(n\text{-}C_3H_7)_4N$	1962, 1973, 1905—1922	[41]
37	Yellow	Cl	—	$(n\text{-}C_4H_9)_4N$	1960—1966, 1898—1907	[41]
38	Brown	Br	—	Cs	1947, 1893, 1869	[40]
39	Orange	Br	—	$(n\text{-}C_3H_7)_4N$	1958—1966, 1903—1905	[41]
40	Yellow-orange	Br	—	$(n\text{-}C_4H_9)_4N$	—	[41]
41	$[Pd_4Cl_6(CO)_4][(n\text{-}C_3H_7)_4N]_2$	—	—	—	1964, 1918, 1906	[41]
			$[Pd(NO)Cl]_n$			
42	Dark brown	—	—	—	1764, 1712	[47]
43	Pale brown	—	—	—	1750, 1720	[48]
44	Pale green; $[Pd(NO)Cl]PdCl_2$	—	—	—	1672	[48]
45	Black; $(PdCl)_2NO$	—	—	—	1665	[48]
			$Pd_2(L—L)_2X_2$			
46	—	Cl, Br	dam	—	—	[40]
47	—	Cl, Br	dpm	—	—	[49]
48	—	I	dpe	—	—	[30]
48a	—	PF_6	tpde	—	—	*
			$Pd_2L_nX_2$			
49	Brown; $n = 1$	CH_3COO	bipy	—	—	[44]
50	$n = 2$	CH_3COO	$P(C_6H_5)_3$	—	—	[50]
51	Yellow-green; $n = 2$	SCN	$P(C_6H_5)_3$	—	—	[45]
			$Pd_2I_4M_2 \cdot 2H_2O$			
52	Black	—	—	Li	—	[51]
53	Black	—	—	Cs	—	[51]

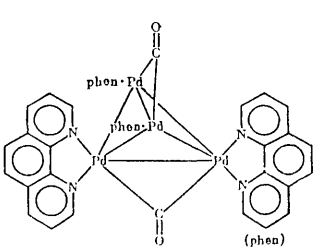
Notation: phen = *o*-phenanthroline; bipy = α,α′-bipyridyl; dpe = bis(diphenylphosphino)-ethane; tpde = $(C_6H_5)_2P(CH_2)_2P(C_6H_5)(CH_2)_2P(C_6H_5)_2$.

*C.H.Lindsay, L.S.Benner, and A.L.Balch, Inorg.Chem., 1980, **19**, 3503.

The same workers obtained a tetranuclear cluster (Table 2, No.17) with a tetrahedral Pd_4^{4+} skeleton[20,21]. X-Ray diffraction analysis of the complex $Pd_4(CO)_2(phen)_4(OOCCH_3)_4$ (VIII) showed that all four palladium atoms are equivalent and form an almost regular tetrahedron. The two Pd–Pd bonds having carbonyl bridges (the Pd–C–Pd angle is 105°) are somewhat longer (l_{Pd-Pd} = 2.890 Å) than the four Pd–Pd bonds without such bridges (2.718 Å). *o*-Phenanthroline behaves as a bidentate terminal ligand; the acetate ions are in the inner sphere of the complex[20,21].



(VII)



(VIII)

Solutions of palladium(I) carbonyl halide complexes in concentrated hydrochloric acid, obtained by the method of Colton et al.[40] and Goggin and Mink[41], were used[45,46] to synthesise the complexes $[(PdLX)_2CO]$ (Table 2, Nos.19–30). After being dried in an atmosphere of argon, these complexes are entirely stable but in solution in benzene, acetone, and ethanol they slowly disproportionate (the formation of colloidal, metallic palladium is observed). They contain only one carbonyl group for two palladium atoms and have a large dipole moment (μ = 7–9 D) and reduced stretching vibration frequencies ν(CO) of the carbonyl group (Table 2). Furthermore, their ^{31}P NMR spectra contain two bands with the chemical shifts δ_1 = −22 – −24 p.p.m. and δ_2 = −19 to −21 p.p.m., which apparently indicates different types of coordination of the two phosphine ligands[46].

In conclusion we shall consider briefly the possibility of using the parameters of the infrared spectra, in particular the frequencies ν(CO), for the analysis of the structure of the complex and the determination of the oxidation state of the metal. The range of variation of ν(CO) for the palladium and platinum complexes is very large, reaching ~500 cm^{-1}.[60,61] The main factors influencing ν(CO) are (a) the nature of the coordination of the CO group (terminal or bridge groups), (b) the type of bridge, (c) the degree of oxidation of the metal (metals), and (d) the nature of the other ligands. The influence of the degree of oxidation of platinum and palladium on ν(CO) can be traced from the following examples. The change in the stretching vibration frequency of the terminal CO group $\Delta\nu$(CO) on passing from platinum(II) to platinum(0) is ~30 cm^{-1} and that on passing from platinum(II) to platinum(I) is 52–71 cm^{-1} (Table 3). Similarly in the case of the Pd(II) → Pd(0) transition the value of $\Delta\nu$(CO) is low (~70 cm^{-1}). The change in the type of coordination (transition from the terminal to the bridge CO group) leads to a considerable decrease of ν(CO).

Table 3. The influence of the degree of oxidation of the metal and of the type of coordination of carbon monoxide on ν(CO).

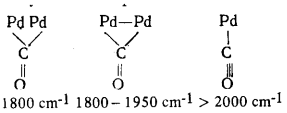
Metal (degree of oxidation)	Complex	ν(CO), cm^{-1}	References
Pt(II)	$PtCl_3(CO)^-$	2098	[61]
Pt(I)	$Pt_2(CO)_2Cl_4^{2-}$	2047, 2027	[58]
Pt(0)	$[Pt(CO)_2]_n$	2068	[58]
Pd(II)	$PdCl_3(CO)^-$	2132	[61]
Pd(I)	$Pd_2(CO)_2Cl_4^{2-}$	1922, 1973	[41]
Pd(0)	$Pd(CO)_4$	2060	[62]

Thus ν(CO) for the dimer $[Pd_2(CO)_2Cl_4]^{2-}$ is reduced compared with ν(CO) for $[PdCl_3CO]^-$ by 210–160 cm^{-1}, while the decrease of ν(CO) as a consequence of the change in the oxidation state of palladium [Pd(II) → Pd(I)] should not exceed 70 cm^{-1}. The vibration frequencies of the CO group coordinated as a bridge at the Pd–Pd bond in palladium(I) complexes are in the range 1800–1980 cm^{-1}.[16–21,23,41] This wide range of ν(CO) is apparently associated with the number of CO groups (strong π-acceptors), coordinated to the Pd_2 group, and with the characteristics of the Pd_2CO fragment (the Pd–C–Pd angle and the Pd–Pd bond length) rather than with the influence of other ligands. Thus ν(CO) for the complexes $[Pd(CO)(OOCCH_3)]_4$, $[Pd(CO)Cl]_n$, and $[Pd_2(CO)_2Cl_4]^{2-}$ are in the range 1900 to 1980 cm^{-1}, while those for the complexes $(PdLX)_2CO$ or $[Pd_4(CO)_2Phen_4]^{4+}$ are in the range 1800–1890 cm^{-1}. The vibration frequencies of the CO groups coordinated in the form of bridges in the zerovalent palladium clusters are in the same range[16,23]. There is no doubt that there is a correlation between ν(CO) and the characteristics of the Pd_2CO fragment—the Pd–C–Pd angle of the Pd–Pd bond length (Table 4). In the limiting case (Table 4, No.5) CO is inserted in the Pd–Pd bond, the Pd–C–Pd angle is ~120°, and ν(CO) has the usual values characteristic of the carbonyl group in organic compounds (see Section III, subsection 4).

Table 4. Relation between ν(CO) and the characteristics of the Pd_2CO fragment.

No.	Complex	ν(CO), cm^{-1}	l_{Pd-Pd}, Å	$\alpha_{Pd-C-Pd}$, °	l_{Pd-C}, Å	Refs.
1	$[Pd(CO)CH_3COO]_4$	1940, 1975	2.663	84.5	1.99	[18,19,42]
2	$Pd_4[P(C_6H_5)_2CH_3]_4(CO)_4$	1840, 1820	2.75	82.5	2.085	[16]
3	$Pd_{10}(CO)_{12}[P(n\text{-}C_4H_9)_3]_6$	1800, 1853, 1890	2.70; 2.82	83	2.05	[23]
4	$[Pd_4(CO)_2phen_4]^{4+}$	1800	2.890	105	—	[20, 21]
5	$[Pd(dam)Cl]_2CO\cdot 3C_6H_{14}$	1720	3.274	119	1.9	[63]

Thus the following limiting frequencies ν(CO) can be used for a preliminary assessment of the nature of the coordination of the CO group in palladium compounds on the basis of infrared spectroscopic data:



Palladium(I) complexes with terminal CO groups and palladium(II) complexes with CO groups coordinated in the form of bridges are hitherto unknown, but the frequencies ν(CO) for such compounds should apparently be within the limits indicated.

The first binary palladium(I) complex of the type $M_2Pd_2I_4 \cdot 2H_2O$, where M = Li or Cs, has been synthesised[51] from the complex $H_2Pd_2(CO)_2Cl_4$ obtained by the method of Colton et al.[40] and Goggin and Mink[41]. These compounds are diamagnetic and are apparently coordination polymers, because they dissolve in alcohols, acetone, dimethylformamide (DMF), and tetrahydrofuran only in the presence of an excess of I^- ions. When the complex $Li_2Pd_2I_4 \cdot 2H_2O$ is treated repeatedly with deaerated concentrated hydrochloric acid in an inert atmosphere, a compound is obtained whose elemental analysis leads to the formula $(PdI \cdot H_2O)_n$.

The complex $(LPdOOCCH_3)_2$ has been obtained[52] in the study of the mechanism of the formation of the active forms of hydrogenation catalysts in the $L_2Pd(OOCCH_3)_2$–H_2 system. The complex $\boxed{Si}$–P_2–$Pd_2(OOCCH_3)_2$ with a similar composition has been synthesised by the reduction of palladium acetate immobilised on a phosphinated silica gel surface[64].

The first palladium(I) nitrosyl complex was synthesised in 1960.[47] Several other nitrosyl complexes, tentatively of palladium(I) (Table 2, Nos.43–45), were described later but their structure was not established[48,65]. It has been suggested that they are coordination polymers with Pd–Pd bonds like the complexes $[Pd(CO)Cl]_n$.

A comparatively high thermal stability of palladium(I) complexes has been noted in a number of studies (Table 5). Some of the data on the thermal stability of palladium(I) compounds (Table 5, Nos.1–9a) have been obtained as a result of visual observations and are approximate. The stability of the complexes $[Pd(CO)Cl]_n$ (Table 5, No.9b),

$Li_2Pd_2I_4 \cdot 2H_2O$, and $(PdLX)_2CO$ has been investigated by the thermographic method. The degradation of the complex $Li_2Pd_2I_4 \cdot 2H_2O$ is preceded by the elimination of water (120–320 °C), which is followed by the liberation of I_2 (one mole per mole of the initial compound in the temperature range 320–600 °C).[51] The first stage in the thermal transformations of the complexes $(PdLX)_2CO$ is isomerisation, carbon monoxide being split off on raising the temperature. At 300–400 °C the final decomposition of these compounds takes place[46,66]. The above data indicate the possibility of the existence of palladium(I) compounds under fairly severe conditions.

Table 5. Thermal stability of palladium(I) complexes.

No.	Complex	T_{decomp}, °C	References
1	$[PdCl(t\text{-}C_4H_9NC)_2]_2 \cdot C_6H_5Cl$	150	[30]
2	$[PdCl(t\text{-}C_4H_5NC)_2]_2 \cdot C_6H_6$	155	[30]
3	$[Pdldpe]_2$	300	[30]
4	$[Pd_2(t\text{-}C_4H_9NC)_6]_2(PF_6)_2$	140	[32]
5	$[(n\text{-}C_3H_7)_4N]_2[Pd_2Cl_4(CO)_2]$	155	[41]
6	$[(n\text{-}C_3H_7)_4N]_2[Pd_2Br_4(CO)_2]$	145	[41]
7	$[PdCl(CO)As(C_6H_5)_3]_2$	110	[41]
8a	$[Pd(CO)Br]_n$	120	[40]
8б	$[Pd(CO)Br]_n$	145	[41]
9a	$[Pd(CO)Cl]_n$	60	[40]
9б	$[Pd(CO)Cl]_n$	180	[37]
10	$Li_2Pd_2I_4 \cdot 2H_2O$	320	[51]
11	$[PdP(C_6H_5)_3Cl]_2CO$	76; 110	[46, 66]
12	$[PdP(C_6H_5)_3Br]_2CO$	130; 130	[46, 66]
13	$[PdP(C_6H_5)_3P]_2CO$	136; 140	[46, 66]
14	$[PdP(C_6H_5)(C_6H_4OCH_3)_2Cl]_2CO$	79; 130	[46, 66]
15	$[PdP(C_6H_5)_2(C_6H_4COOH)Cl]_2CO$	40; 160	[46, 66]
16	$[PdP(C_6H_5)_2(C_6H_4F)Cl]_2CO$	60; 110	[46, 66]
17	$[PdP(C_6H_5)_2(C_6H_4Cl]_2CO$	78; 135	[46, 66]

Note. For compounds Nos.11–17, the isomerisation temperature is indicated first and the second figure denotes the temperature at which the elimination of CO groups begins.

2. Palladium(I) Complexes with π-Ligands

The π-complex of palladium(I) was synthesised in 1965 [67] by Fischer's method ($PdCl_2 + AlCl_3 + Al + C_6H_6$) (Table 6, No.1). X-Ray diffraction studies[67,68] established that complexes Nos.1 and 2 contain a Pd–Pd fragment [see structures (IX) and (X)].

Both compounds consist of centrosymmetric molecules containing benzene rings with virtually identical C–C bond lengths. Complexes Nos.1 and 2 differ in the position of the benzene rings relative to the Pd–Pd bond. In complex No.1 the two benzene rings located in parallel planes have at least two different orientations relative to the Pd–Pd bond [structure (IX)], differing from the orientation in the rings in complex No.2 [structure (X)] (Fig.1). The centres of the rings are displaced from the projection of the centre of symmetry of the complexes by 0.18 Å in structure (IX) and by 0.43 Å in structure (X).

Table 6. π-Complexes of palladium(I).

No.	Complex	Characteristic	Refs.
1	$Pd_2(C_6H_6)_2(Al_2Cl_7)_2$	l_{Pd-Pd}=2.57 Å dark brown	[67]
2	$Pd_2(C_6H_6)_2(AlCl_4)_2$	l_{Pd-Pd}=2.57 Å dark brown	[68]
3	$Pd_2(C_6H_5CH_3)_2(AlCl_4)_2$	—	[69]
4	$Pd_2[C_6H_4(CH_3)_2]_2(AlCl_4)_2$	—	[69]
5	$Pd_2(C_6H_6)_2(ClO_4)_2(H_2O)_2$	red-violet	[70]
6	$Pd_2(C_6H_6)_2(HSO_4)_2$	—	[71, 72]
7	$Pd_2(C_6H_6)(OOCCH_3) \cdot {}^1/_2Sol$ *	red	[73]
8	$Pd_2SO_4 \cdot Q$ ** $\cdot 3H_2O$	—	[74]

*Sol = CH_3COOH or CH_2Cl_2.
**Q = *p*-benzoquinone.

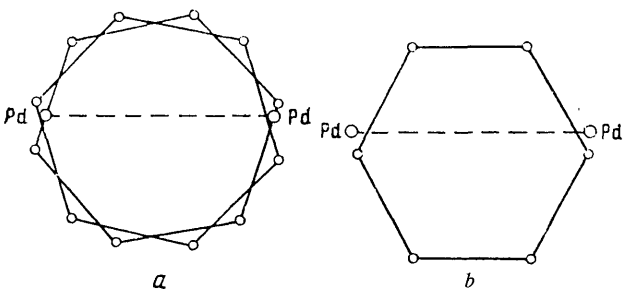
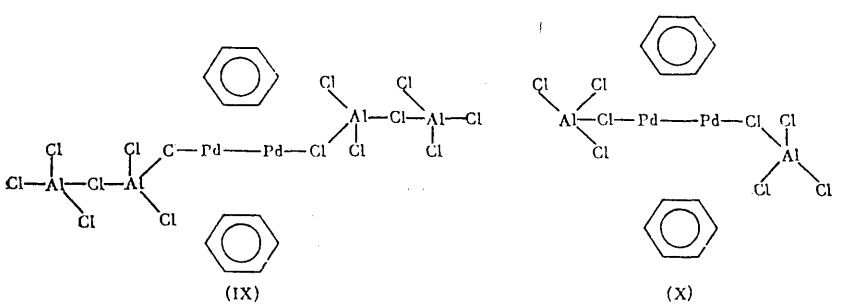
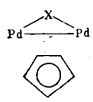
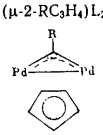
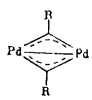
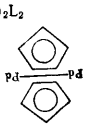
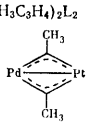
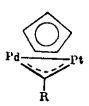
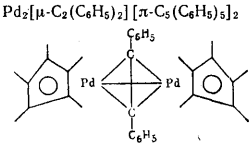


Figure 1. The disposition of the carbon atoms of the benzene rings relative to the Pd–Pd fragment in bis-π-arene complexes: *a*) complex (IX); *b*) complex (X).



The π-complexes of palladium(I) with benzene apparently have structures similar to those of complexes Nos.1 and 2 described by Davidson and Triggs[70] (Table 6, No.5) and Rudakov and co-workers[71,72] (Table 6, No.6). The studies of Rudakov and co-workers[71,72] showed that complex No.5 is diamagnetic, despite the view of Davidson and Triggs[70], and has a singlet due to benzene protons in the ^{1}H NMR spectrum, displaced upfield by 0.76 p.p.m. relative to benzene. The π-complex No.6 (Table 6) has been obtained[71,72] by the oxidation of cyclohexane or cyclohexene with palladium

Table 7. Palladium(I) complexes with allyl and cyclopentadienyl ligands.

No.	Formula	L	R	X	References
1	$Pd_2(\mu\text{-}2\text{-}RC_3H_4)(\mu\text{-}X)L_2$ 	$P(C_6H_5)_3$	H	I	[79] *
		$P(C_6H_5)_3$	H	Br	[80]
		$P(iso\text{-}C_3H_7)_3$	CH_3	I, Cl	[81, 82]
		$P(t\text{-}C_4H_9)_3$	CH_3	Cl	[81, 82]
		$P(C_6H_{11})_3$	CH_3	Cl	[82]
		$P(iso\text{-}C_3H_7)_3$	H, CH_3, *iso*-C_3H_7, t-C_4H_9	CH_3COO	[83]
		$P(iso\text{-}C_3H_7)_3$	*iso*-C_3H_7, t-C_4H_9	C_6H_5COO	[83]
		$P(iso\text{-}C_3H_7)_3$	*t*-C_4H_9	CF_3COO	[83]
2	$Pd_2(\mu\text{-}C_5H_5)(\mu\text{-}X)L_2$ 	$P(iso\text{-}C_3H_7)_3$	—	Br	[84] **
		$P(iso\text{-}C_3H_7)_3$	—	Cl, I, $S(C_6H_5)$	[80, 84]
		$P(C_6H_5)_3$, $P(C_6H_{11})_3$	—	Br	[80, 84]
		$P(C_6H_5)_3$	—	$S(C_6H_5)$	[80]
		$P(iso\text{-}C_3H_7)_3$	—	C_6H_5COO	[85]
		$P(iso\text{-}C_3H_7)_3$	—	CH_3COO	[83]
3	$Pd_2(\mu\text{-}C_5H_5)(\mu\text{-}2\text{-}RC_3H_4)L_2$ 	$P(C_6H_5)_3$	CH_3	—	[78] ***
		$P(OC_6H_5)_3$, $P(OCH_3)_3$	CH_3	—	[78]
		$P(C_6H_5)_3$	H, t-C_4H_9	—	[86]
		$P(C_6H_5)_2CH_3$, $P(iso\text{-}C_3H_7)_3$	CH_3	—	[86]
		$P(iso\text{-}C_3H_7)_3$, $P(C_6H_5)_2CH_3$	t-C_4H_9	—	[86]
		$P(O\text{-}o\text{-}C_6H_4CH_3)_3$	CH_3	—	[86]
		$P(O\text{-}o\text{-}C_6H_4CH_3)_3$	t-C_4H_9	—	[86] ****
		$P(iso\text{-}C_3H_7)_3$	H, Cl	—	[81]
		$P(C_6H_{11})_3$	CH_3	—	[81]
		$P(C_6H_5)(CH_3)_2$	CH_3, t-C_4H_9	—	[87]
		$P(n\text{-}C_4H_9)_3$	CH_3, t-C_4H_9	—	[87]
		$P(OCH_3)_3$, $P(OC_6H_5)_3$	t-C_4H_9	—	[87]
		$As(iso\text{-}C_3H_7)_3$, $As(CH_2C_6H_5)_3$	H, CH_3	—	[88]
		$P(CH_3)_3$, $P(iso\text{-}C_4H_9)_3$	CH_3	—	[88]
		$P(t\text{-}C_4H_9)(C_6H_5)_2$, $P(C_6H_{11})_2C_6H_5$	CH_3	—	[88]
		$P(O\text{-}iso\text{-}C_3H_7)_3$	CH_3	—	[88]
		$P(iso\text{-}C_4H_9)_3$, $P(t\text{-}C_4H_9)(C_6H_5)_2$	t-C_4H_9	—	[88]
		$P(C_6H_{11})_2(C_6H_5)$, $As(iso\text{-}C_3H_7)_3$	t-C_4H_9	—	[88]
4	$Pd_2(\mu\text{-}2\text{-}RC_3H_4)_2L_2$ 	$P(iso\text{-}C_3H_7)_3$	H	—	[80]
		$P(iso\text{-}C_3H_7)_3$	CH_3	—	[81]
		$P(C_6H_{11})_3$	CH_3	—	[82]
5	$Pd_2(\mu\text{-}C_5H_5)_2L_2$ 	$P(iso\text{-}C_3H_7)_3$	—	—	[85]
		$P(OC_6H_5)_3$	—	—	[89]
6	$PdPt(\mu\text{-}2\text{-}CH_3C_3H_4)_2L_2$ 	$P(iso\text{-}C_3H_7)_3$	—	—	[90]
7	$PdPt(\mu\text{-}2\text{-}RC_3H_4)(\mu\text{-}C_5H_5)L_2$ 	$P(iso\text{-}C_3H_7)_3$, $P(C_6H_{11})_3$	H, CH_3	—	[90]
8	$Pd_2[\mu\text{-}C_2(C_6H_5)_2][\pi\text{-}C_5(C_6H_5)_5]_2$ 	—	—	—	[77]

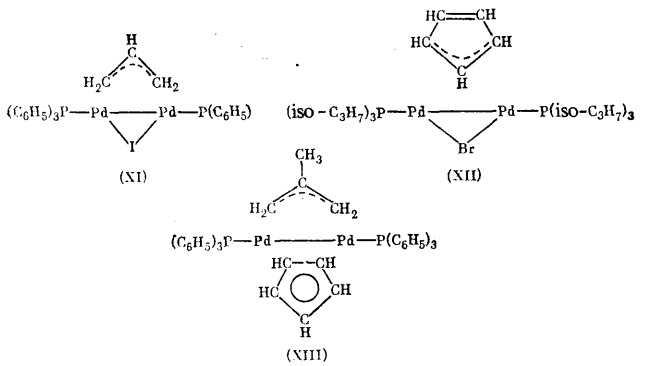
*l_{Pd-Pd} = 2.686 Å, **l_{Pd-Pd} = 2.609 Å, ***l_{Pd-Pd} = 2.679 Å, ****l_{Pd-Pd} = 2.689 Å.

sulphate and also from benzene and H_2 in 90% of sulphuric acid. Complexes Nos.5 and 6 disproportionate following the addition of Cl^- or dilution of the solutions with water.

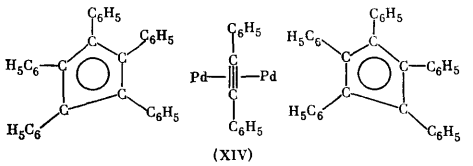
The reaction of $Pd(OOCCF_3)_2$ in CF_3COOH with benzene or naphthalene results in the formation of complexes with an involved composition[75] which the authors regard as π-arene complexes on the basis of infrared spectroscopic and NMR data as well as chemical reactions. It has been suggested that $Pd_2(OOCCF_3)_2$, formed on reduction of palladium(II), coordinates aryl groups to form $ArPdOOCF_3$.

Two π-complexes, tentatively of palladium(I) (Table 6, Nos.7 and 8), have been obtained under the conditions of the oxidation of cyclohexa-1,4-diene in acetic acid[73] and of ethylene in sulphuric acid[74] in the presence of palladium(II) salts. According to Postnikov[76], the compounds of palladium and graphite (Pd_2Cl_2-graphite) which he synthesised are π-complexes of the type of compounds Nos.1–6 in Table 6.

The palladium(I) compounds containing π-allyl and π-cyclopentadienyl ligands are also believed[32,77,78] to constitute a large group of very interesting π-complexes (Table 7). The first examples of compounds containing π-allyl and π-cyclopentadienyl ligands coordinated at an M–M bond [compounds (XI), (XII), and (XIII)] and the first examples of symmetrical bis-π-allyl and bis-π-cyclopentadienyl sandwich compounds with an M–M fragment are encountered within this group. The bond lengths l_{Pd-Pd} in these complexes are similar, exceeding slightly l_{Pd-Pd} in the bis-π-arene complex of palladium(I).



The C_5H_5 group can be regarded as one non-coordinated double bond (l = 1.331 Å) and an allyl fragment (1.48 and 1.52 Å) linked mainly to two palladium atoms (Table 7, No.2).[84] Mixed complexes with a Pd–Pt bond have been obtained as a result of the interaction of $(C_5H_5)Pt(2\text{-}CH_3C_3H_4)$ and $Pt(2\text{-}CH_3C_3H_4)_2$ with PdL_2 (Table 7, Nos.6 and 7). The interesting π-complex of palladium(I) with $(C_6H_5)_2C_2$ (XIV)



is a structural analogue of the complex $[\mu\text{-}(C_6H_5)_2C_2].Ni_2(\pi\text{-}C_5H_5)_2$.[91]

3. X-Ray Photoelectron Spectra of Palladium(I) Complexes

Relatively extensive data have now accumulated on the X-ray photoelectron (XPE) spectra of palladium(I) complexes, which permit the estimation of the range of variation of the binding energies of the palladium(I) electrons and the influence of the ligand on $E(3d_{5/2})$.[92–100] Table 8 and Fig.2 show that the ranges of variation of $E(3d_{5/2})$ for complexes containing palladium in different oxidation states (0, +1, or +2) have no distinct limits and partially overlap.

Table 8. The binding energies $E(3d_{5/2})$.

No.	Complex	$E(3d_{5/2})$, eV	References
	Pd(0)		
1	Pd_{met}	335.8	[95]
	Pd_{met}	335.7±3	[98]
2*	PdL_4	336.2	[95, 95]
3*	$Pd(CO)L_3$	337.9	[94]
4*	Pd_2L_2	336.8	[95]
	Pd(I)		
5	$Pd_2dpm_2Cl_2$	337.3	[96]
6	$Pd_2dam_2Cl_2$	337.4	[96]
7	$Pd_2dpm_2Cl_2(\mu\text{-}CO)$	337.5	[96]
8*	$Pd_2L_2(OOCCH_3)_2$	337.1	[95]
9	Pd_2Cl_2· (graphite)	336.8	[76]
10	$[PdI\cdot H_2O]_n$	336.9	**
11	$Cs_2Pd_2I_4\cdot 2H_2O$	337.3	**
12	$[Pd_2(CH_3NC)_6](PF_6)_2$	338.0	[96]
	Pd(II)		
13	$PdCl_2$	337.9±0.3	[98]
	$PdCl_2$	338.0	[76]
	$PdCl_2$	338.1	[94]
14	$PdCl_2$· (graphite)	338.0	[76]
	$PdCl_2$· (graphite)	337.9±0.3	[98]
15*	$PdCl_2L_2$ (*trans*)	338.3	[76]
16	K_2PdCl_4	338.4±0.2	[98]
17*	PdI_2L_2 (*trans*)	337.7±0.4	[98]
18*	$Pd(OOCCH_3)_2L_2$	338.1	[95]
19*	$[Pd(OOCCH_3)_2L]_2$	338.5	[95]
20	$PdI_2(CH_3NC)_2$	338.9	[96]
21	$[Pd(OOCCH_3)_2]_n$	338.8	[95]
22	$Pd(CH_3NC)_4(PF_6)_2$	339.5	[96]
23	$Pd(CN)_2$	339.6	[98]
24	$Pd(OOCCF_3)_2$	339.7	[99]
	Pd(IV)		
25	K_2PdCl_6	340.3±0.3	[98]
26	K_2PdF_6	342.8	[100]

*L = $P(C_6H_5)_3$. **Spectra obtained by Yu.G.Borod'ko and T.S.Moravskaya (OIKhF, USSR Academy of Sciences).

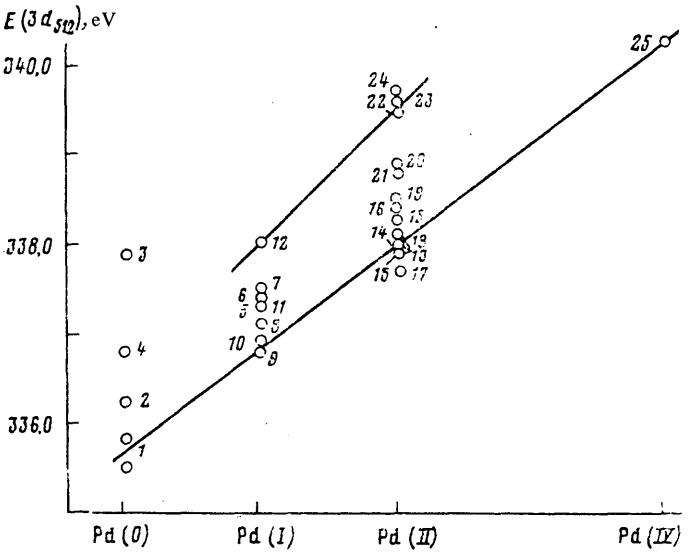


Figure 2. XPE spectra of metallic palladium and palladium compounds; the numbers against the points correspond to the numbers of the compounds in Table 8.

The influence of the ligands on the position of the $E(3d_{5/2})$ level is very strong, for the oxidation states 0 and +1 the range of variation of E as a function of the ligand is on average ~1.5 eV, and for palladium(II) it is as much as 2 eV. The binding energies in complexes with ligands having pronounced π-acceptor properties (Table 8, Nos.12, 22, and 23) increase to a particularly marked extent also in the case of $Pd(OOCCF_3)_2$. The high values of $E(3d_{5/2})$ for complexes Nos.3 and 4 give rise to some doubts—this may be a possible consequence of the oxidation of zerovalent palladium.

The spectrum of PdI_2, obtained by Kumar et al.[98], also deviates from the general pattern of the XPE spectra presented in Fig.2, the value $E(3d_{5/2}) = 336.6 \pm 0.1$ eV for PdI_2 actually lying below the values obtained for palladium(I). A probable explanation is the possible reduction of the surfaces of the PdI_2 specimens on irradiation in the course of the recording of the spectra.

If a line is drawn in Fig.2 through points *1*, *13*, and *25* corresponding to Pd(0), $PdCl_2$ and K_2PdCl_6, then the value of $E(3d_{5/2})$ for the Pd_2Cl_2-graphite complex lies on this line (Table 8, No.9). The values of $E(3d_{5/2})$ for all the remaining compounds lie above this line and below the line drawn through points *12* and *22*, corresponding to $Pd(CNR)_4^{2+}$ and $Pd_2(CNR)_6^{2+}$. Points *2*, *5*, and *15*, which correspond to phosphine-containing zerovalent palladium, palladium(I), and palladium(II) complexes, lie somewhat above the line drawn through points *1*, *9*, *13*, and *25*. We are aware of two studies of palladium carbonyl complexes by XPE spectroscopy. The binding energies $E(3d_{5/2})$ for PdL_3CO [94] and $[Pd(CO)(OOCCH_3)]_4.2CH_3COOH$ [17] are 337.9 and 338.7 eV respectively. The replacement of $P(C_6H_5)_3$ by CO in the complexes PdL_4 (Table 8, No.2) and $Pd_2L_2(OOCCH_3)_2$ (Table 8, No.8) should increase the binding energy $E(3d_{5/2})$ owing to the pronounced π-acceptor properties of the CO group; however, the observed increase of $E(3d_{5/2})$ by 1.6–1.7 eV appears to be very surprising.

Thus the interpretation of the XPE spectroscopic data for the purpose of the identification of palladium(I) complexes should be approached with caution. It is desirable to compare the spectra of complexes with similar sets of ligands or with ligands which have only a slight influence on the electron density of the central atom (Cl, Br, PR_3, CH_3COO, AsR_3).

III. SYNTHESIS AND REACTIONS OF PALLADIUM(I) COMPLEXES

We shall consider the principal methods of synthesis of palladium(I) complexes, their oxidation-reduction properties, and their oxidation-reduction reactions. These problems are mostly inter-related, because the principal difficulties in the synthesis of compounds of palladium in the intermediate +1 oxidation state are due to the capacity of palladium(I) for oxidation, reduction, and disproportionation.

The first palladium(I) complexes were obtained by the reduction of palladium(II) compounds, but at the present time numerous palladium(I) complexes have been synthesised [directly] and information has been obtained about their chemical properties. Ligand substitution reactions are therefore widely used for the synthesis of new palladium(I) compounds.

1. Ligand Substitution Reactions Involving Palladium(I) Complexes

The polymeric carbonyl halides $[Pd(CO)X]_n$ or the dimer $H_2Pd_2(CO)_nCl_4$ in hydrochloric acid solutions are frequently used as the starting compounds. Thus the complexes $Pd_2L_2X_2$ have been synthesised[40] by treating $[Pd(CO)X]_n$ (X = Cl or Br, L = dpm or dam) with the ligand in methylene chloride. The addition of lithium or caesium iodide to the hydrochloric acid solution of $H_2Pd_2(CO)_nCl_4$ leads to the evolution of CO and the formation of the complex $M_2Pd_2I_4.2H_2O$ (M = Li or Cs) [51] (Table 2).

The complexes $[Pd_2X_2L_2]CO$ [45] (Table 2), in which one CO group corresponds to two Pd atoms, have been isolated as a result of the reaction of a hydrochloric acid solution of $P(C_6H_5)_3$ with $H_2Pd_2(CO)_nCl$ using the proportions [L] : [Pd] = 1.5. The ligand substitution reactions involving palladium(I) carbonyl halide complexes may be accompanied by extremely complicated processes. Thus the reaction of $[Pd(CO)Cl]_n$ with dam involve the insertion of CO in the Pd–Pd bond[63] (see below) and the interaction of $H_2Pd_2(CO)_nCl_4$ with MI results in the evolution of small amounts of CO_2 and H_2 together with CO.[51]

The mode of the substitution reaction and the product composition depend on the nature of the substituting ligand, the [L] : [Pd] ratio, and other factors. Thus, when the carbonyl acetate complex $[Pd_2(CO)_2(CH_3COO)_2]_2$ [17–19] was used as the starting material for the synthesis of palladium(I) complexes with other ligands, it was established[44] that unstable complexes are formed for the initial reactant ratio [L] : [Pd] = 0.25, where L = $(C_6H_5)_3$, C_5H_5N, ½ bipy, or ½ phen. For [L] : [Pd] = 0.5, the state of palladium(I) is stabilised by triphenylphosphine 2,2-bipyridyl, and o-phenanthroline. Treatment with pyridine and its alkyl derivatives leads to the evolution of the entire carbon monoxide bound in the initial carbonyl acetate and the precipitation of metallic palladium; palladium(II) complexes are detected in solution.

The substitution reactions are different for different palladium(I)-stabilising ligands. Treatment with $P(C_6H_5)_3$ also leads to the complete evolution of carbon monoxide and the formation of the complex $Pd_2[P(C_6H_5)_3]_2.(CH_3COO)_2$ [44] (Table 2). The composition of the ligand substitution reaction products when o-phenanthroline and bipyridyl are employed is determined by the initial concentrations of these ligands and palladium(I) carbonyl acetate for [L] : [Pd] = 0.5. In bipyridyl solutions at concentrations ≥0.5 M the entire carbon monoxide is evolved:

$$[Pd_2(CO)_2(OOCCH_3)_2]_2 + 2bipy \rightarrow 2Pd_2bipy(CH_3COO)_2 + 4CO.$$

For [bipy] ≤ 0.5 M, half of the carbon monoxide remains in the coordinated form:

$$[Pd_2(CO)_2(OOCCH_3)_2]_2 + 2bipy \rightarrow 2Pd_2(CO)bipy(CH_3COO)_2 + 2CO.$$

Whatever its concentration, phenanthroline displaces half of the CO molecules present in the carbonyl acetate complex:

$$[Pd_2(CO)_2(OOCCH_3)_2]_2 \xrightarrow{[phen]<10^{-3}\ M} 2Pd_2(CO)\,phen\,(CH_3COO)_2 + 2CO;$$
$$[Pd_2(CO)_2(OOCCH_3)_2]_2 \xrightarrow{[phen]\geq 0.5\ M} 2Pd_2(CO)\,phen_2\,(CH_3COO)_2 + 2CO.$$

In the carbonyl complexes with bipyridyl and phenanthroline as ligands, the acetate is reversibly substituted by the anion X (X = ClO_4^-, Cl^-, CCl_3COO^-, CF_3COO^-, or CNS^-).[44]

The ligand and outer anion substitution reactions involving the isonitrile complexes of palladium(I) have been investigated[31,33]. The methylisocyanide groups in the cationic complexes $[(CH_3NC)_6Pd_2]^{2+}$ are exchanged at a high rate with free methyl isocyanide in acetone solution in the temperature range +40– –50 °C. On treatment with an excess of $t\text{-}C_4H_9NC$ or C_6H_5NC under conditions ensuring the removal

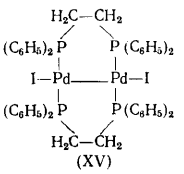
of the methyl isocyanide molecules to be substituted, it is possible to replace completely the methyl isocyanide groups and to isolate the complexes $[(t\text{-}C_4H_9NC)_6Pd_2](PF_6)_2$ and $[(C_6H_5NC)_6Pd_2](PF_6)_2$.[31,33] The same workers obtained complexes containing one or two triphenylphosphine groups (Table 1) in the axial coordination positions. It is not possible to substitute more than two methylisocyanide groups by triphenylphosphine[31,33].

Complexes of the type $[Pd_2(\text{diphosphine})_2(CH_3NC)_2](PF_6)_2$ have been obtained recently§ by the substitution of isonitrile ligands in the complex $[Pd_2(CH_3NC)_6](PF_6)_2$ by the diphosphines $(C_6H_5)_2P(CH_2)_nP(C_6H_5)_2$ (n = 2–4) or *cis*-$(C_6H_5)_2PCH=CHP(C_6H_5)_2$. According to NMR data, these complexes have a symmetrical non-bridged structure in which the diphosphine ligand is bound to one palladium atom. When the triphosphine $(C_6H_5)_2P(CH_2)_2P(C_6H_5)(CH_2)_2P(C_6H_5)_2$ is used in an analogous reaction, the isonitrile ligands are fully substituted and crystals of the complex $\{Pd_2[(C_6H_5)_2P(CH_2)_2P(C_6H_5)(CH_2)_2P(C_6H_5)]_2\}(PF_6)_2$ are formed. The absence of reactions of the isonitrile complexes with CO, pyridine, 2,2′-bipyridyl, cyclo-octa-1,5-diene, and tetrachloroethylene has been noted[31-34].

The complexes $Pd_2X_2(CNR)_4$ have been obtained by the substitution of some of the isonitrile groups by the corresponding ligands (X = I or SCN; R = CH_3, t-C_4H_9, or C_6H_5) in the complexes $[Pd_2(RNC)_6](PF_6)_2$.[31,33] The complex $Pd_2I_2(t\text{-}C_4H_9NC)_4$ has been used[30] to synthesise palladium(I) complexes with phosphorus-containing ligands:

$$Pd_2I_2(t\text{-}C_4H_9NC)_4 \xrightarrow{2P(C_6H_5)_3} Pd_2I_2(t\text{-}C_4H_9NC)_2[P(C_6H_5)_3]_2;$$
$$\xrightarrow{[P(C_6H_5)_2CH_2]_2} Pd_2I_2[(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2]_2.$$

Presumably the complex with the diphosphine ligand has structure (XV), analogous to the structure of the complexes with bis(diphenylphosphino)methane[49].

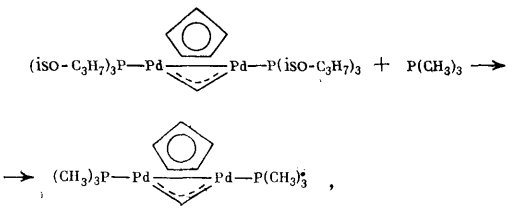


(XV)

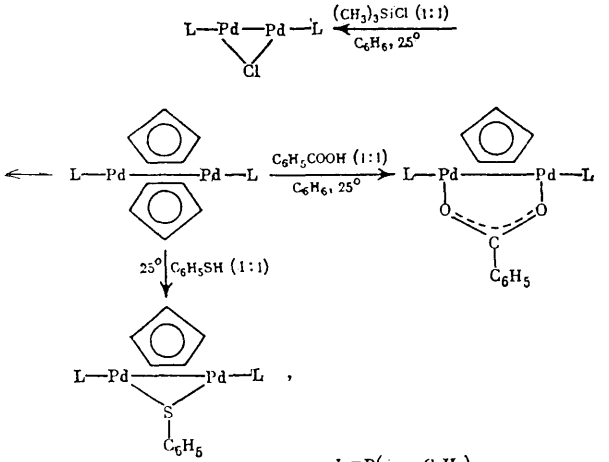
There is virtually no information about substitution reactions involving π-complexes of palladium(I). The possibility of the substitution of the ClO_4^- anion in Davidson's complex has been demonstrated[71]:

$$[Pd(ClO_4)(H_2O)(C_6H_6)]_2 \xrightarrow{H_2SO_4} [Pd_2(C_6H_6)_2](HSO_4)_2.$$

The substituion of a neutral ligand[88],

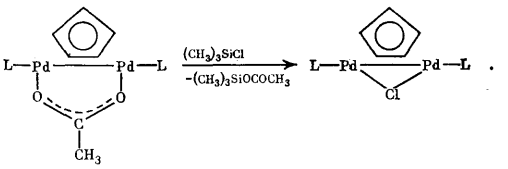


and of a single cyclopentadienyl ligand by Cl^-, $C_6H_5COO^-$, or $C_6H_5S^-$,[85]

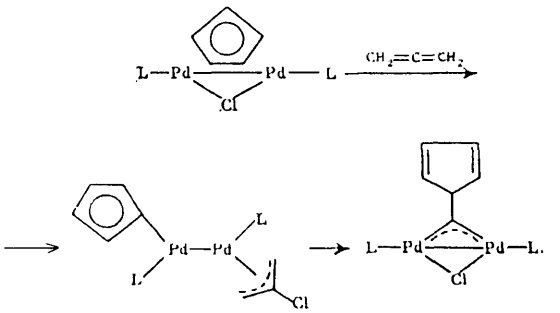


$L = P(\text{iso-}C_3H_7)_3$,

has been reported. The acetate ligand in the analogous complex can be substituted by Cl^-:[83]



The only reaction of the π-ligands without change in the oxidation state of palladium(I) has apparently been described by Kühn and Werner[88]:



$L = \text{iso-}C_3H_7$

It follows from the substitution reactions described above that this method of synthesis of palladium(I) complexes is fairly convenient and extremely effective.

2. Synthesis of Palladium(I) Complexes by the Reduction of Palladium(II) Compounds

The reduction of palladium(II) compounds constitutes the most general method of synthesis of palladium(I) complexes. When this reaction is carried out, it is necessary to employ ligands which stabilise the intermediate palladium(I) oxidation state and prevent the disproportionation reaction

$$Pd_2^I \rightarrow Pd^{II} + Pd^0. \qquad (3)$$

In some cases the same substance can fulfill the functions of the reductant and the ligand:

$$Pd^{II} + L\,(\text{Red}) \rightarrow Pd^IL + L'\,(\text{Ox}).$$

§C.H.Lindsay, L.S.Benner, and A.L.Balch, Inorg.Chem., 1980, 19, 3503.

CO,[3,40,41] C_6H_6,[70] C_6H_8,[73] and RNC [27,32,34] have been used as such bifunctional reagents. However, this type of combination of functions is not always possible and palladium(I) complexes are therefore usually synthesised in accordance with the equation

$$Pd^{II} + Red + L \rightarrow Pd^{I}L + Ox .$$

The following combinations of reductants and ligands, in which the reductant fulfilled in many instances also the function of an additional ligand, have been used to synthesise π- and σ-complexes: $Na/Hg-CN^-$,[101] $CO-CH_3COO^-$,[17-19] $Al-C_6H_6$,[67,68] CO–phen, CO–bipy,[43,44] $H_2-C_6H_6$,[71,72] $C_6H_{12}-C_6H_6$,[71,72] $H_2-P(C_6H_5)_3$,[50] and $C_2H_2-I^-$, $CrCl_2-I^-$,[51,102] and C_2H_4–*p*-benzoquinone[74]. For example, the bis-π-arene complex of palladium(I) was obtained for the first time by the reaction[67]:

$$2PdCl_2 + 4AlCl_3 + \tfrac{2}{3}Al + 2C_6H_6 \rightarrow Pd_2(C_6H_6)_2(Al_2Cl_7)_2 + \tfrac{2}{3}AlCl_3 .$$

The series of reductants Mg, Na/Hg, LiAlH $(t\text{-}C_4H_9O)_3$, $LiAlH_4$, $NaBH_4$, and $n\text{-}C_4H_9MgBr$ [80,84] have been used to synthesise the complexes $[(\mu\text{-}C_5H_5)(\mu\text{-}X)Pd_2(PR_3)_2]$ (X = Br, R = iso-C_3H_7, C_6H_5, or C_6H_{11}; X = Cl or I, R = iso-C_3H_7). A paramagnetic palladium(I) complex with thiolene ligands is synthesised by the electrochemical reduction of the corresponding palladium(II) compound[8].

One of the possible mechanisms of the formation of palladium(I) complexes with a Pd–Pd bond in the instances enumerated consists in the reaction of the zerovalent palladium complex formed initially with palladium(II), i.e. involves a reaction which is the opposite of the disproportionation reaction (3), for example:

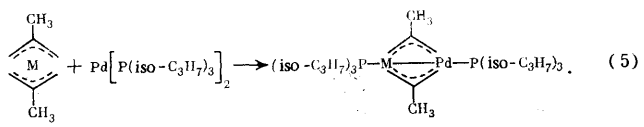
$$\begin{gathered}\tfrac{1}{2}(C_3H_5PdI)_2 + 3P(C_6H_5)_3 \rightarrow [C_3H_5P(C_6H_5)_3]^+I^- + Pd[P(C_6H_5)_3]_2 ;\\ \tfrac{1}{2}(C_3H_5PdI)_2 + Pd[P(C_6H_5)_3]_2 \rightarrow [C_3H_5Pd_2IL_2] ;\\ 2(\pi\text{-}C_6H_5)Pd(2\text{-}CH_3C_3H_4) + 2PR_3 \rightarrow (C_6H_5)Pd_2(2\text{-}CH_3C_3H_4)(PR_3)_2 + C_6H_5C_3H_4CH_3 ;\\ L = P(C_6H_5)_3 .\end{gathered} \quad (4)$$

The compound $[C_3H_5P(C_6H_5)_3]^+I^-$ has been isolated[79].

The possibility of reactions of this type has been demonstrated by direct synthesis of palladium(I) complexes *from palladium(II) and zerovalent palladium complexes*. Thus the isonitrile complexes of palladium(I) of the type $Pd_2X_2(t\text{-}C_4H_9NC)_4$ have been obtained by the reaction of $Pd(t\text{-}C_4H_9NC)_2$ with $PdX_2(t\text{-}C_4H_9NC)_2$ (X = Cl, Br or I) at −30 °C in chlorobenzene[30]. Analogous complexes have been prepared from $PdCl_2(C_6H_5NC)_2$ and $Pd(dba)_n$¶ (*n* = 2 or 3) in the presence of an excess of the isonitrile[32]. The reaction of platinum(II) and zerovalent palladium complexes results in the formation of compounds containing the Pt–Pd fragment[26,29]:

$$2[(CH_3NC)_4Pt][PF_6]_2 + Pd_2(dba)_3\cdot CHCl_3 \xrightarrow[CH_3NC]{CH_3CN} 2[(CH_3NC)_6PdPt][PF_6]_2 .$$

The complex $Pd_2[P(C_6H_5)_3]_2(CH_3COO)_2$ has been synthesised by the reaction of $Pd_2[P(C_6H_5)_3]_2$ with $[(C_6H_5)_3PPd\cdot(CH_3COO)_2]_2$.[50] Numerous π-complexes with cyclopentadienyl and allyl ligands have been obtained in accordance with the same scheme (Table 7), for example:



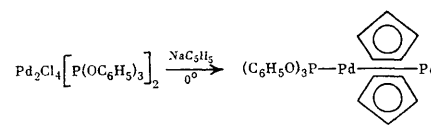
$$+ Pd[P(iso\text{-}C_3H_7)_3]_2 \rightarrow (iso\text{-}C_3H_7)_3P\text{–}M\text{–}Pd\text{–}P(iso\text{-}C_3H_7)_3 . \quad (5)$$

The coordination-unsaturated zerovalent palladium complex of the type PdL_2 or the zerovalent palladium complex $Pd_m(dba)_n$ which readily loses ligands is involved in reactions via Scheme (5). It is therefore extremely important to follow the ratio L/Pd in the syntheses of complexes with π-allyl and π-cyclopentadienyl ligands. Thus, when L/Pd > 4, the complex PdL_4 is formed instead of the palladium(I) complexes [reaction (4)].

Owing to the absence of the complex $Pd(C_5H_5)_2$, the bis-cyclopentadienylpalladium(I) complex has to be synthesised by a more complicated procedure[85]:

$$\begin{gathered}Pd_2Cl_2L_2(\mu\text{-}OOCCH_3)_2 \xrightarrow{TlC_5H_5} 2C_6H_5PdL(OOCCH_3) \rightarrow\\ \xrightarrow[C_6H_6]{NaK_{2.8}} Pd_2(\mu\text{-}C_5H_5)_2L_2 ;\\ L = P(iso\text{-}C_3H_7)_3 .\end{gathered}$$

An analogous complex has also been obtained via the reaction[89]



$$Pd_2Cl_4[P(OC_6H_5)_3]_2 \xrightarrow[0°]{NaC_5H_5} (C_6H_5O)_3P\text{–}Pd\text{–}Pd\text{–}P(OC_6H_5)_3 .$$

The reactions of zerovalent palladium and palladium(II) complexes have been used to synthesise palladium(I) dimers fixed on the surface of silica gel[64]:

$$\boxed{Si}\text{–}P_2Pd(OOCCH_3)_2 \xrightarrow{Red} \boxed{Si}\text{–}P_2Pd \xrightarrow{Pd(CH_3COO)_2} \boxed{Si}\text{–}P_2Pd_2(OOCCH_3)_2$$

where $\boxed{Si}$–P_2 is silica gel with grafted groups containing tertiary phosphines and Red is formic acid.

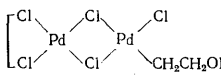
Other mechanisms of the formation of palladium(I), involving the reactions of hydride and σ-organopalladium intermediates, are also possible[102]:

$$HPdX + PdX_2 \rightarrow HX + Pd_2X_2 .$$

This mechanism probably operates in the reduction of palladium(II) with carbon monoxide, acetylene, and alcohol[103], as well as hydrogen[71], and in other reactions leading to the appearance of hydride complexes:

$$RPdX + PdX_2 \rightarrow \begin{cases} \rightarrow RX + Pd_2X_2 \\ \rightarrow R_{-H} + Pd_2X_2 + HX . \end{cases} \quad (6)$$

This mechanism, involving the oxidative demetallation of RPdX, does not include a stage in which zerovalent palladium is formed. The demetallation of a dimeric σ-organopalladium compound and the formation of palladium(I) in the oxidation of olefins by palladium(II) chloride probably take place in precisely this manner[104]:



$$\rightarrow Pd_2Cl_4^{2-} + CH_3CHO + HCl . \quad (7)$$

3. The Oxidation-Reduction Properties and Reactions of Palladium(I) Complexes

As already mentioned above, palladium(I) complexes exhibit in their reactions the properties of both reductants and oxidants, which is reflected primarily in the disproportionation reaction (3), which is very characteristic of palladium(I). The ligand coordinated to palladium(I) or a nucleophile interacting with the coordinated ligand (CH_3COO^-, RO^-, H_2O, ROH) can play the role of the reductant. Thus on heating to 70 °C *in vacuo*, the complex $Pd_2(C_6H_8)(OOCCH_3)_2$ undergoes the reaction[73]

$$Pd_2(C_6H_8)(OOCCH_3)_2 \rightarrow 2Pd_{met} + C_6H_6 + 2CH_3COOH .$$

¶Here and henceforth dba = dibenzylideneacetone.

The reaction of the complex $[Pd_2(CO)_2(OOCCH_3)_2]_2$ in the presence of CH_3COONa in acetic acid at 90 °C is of interest[105]:

$$Pd_2(CO)_2(OOCCH_3)_2 \xrightarrow{CH_3COONa} 2Pd_{met} + CO_2 + (CH_3CO)_2O \,. \qquad (8)$$

The probable mechanism of reaction (8) involves attack by the acetate ion on the coordinated carbon monoxide[105]:

$$Pd_2(CO)_2(OOCCH_3)_2 + CH_3COO^- \rightarrow Pd_2(CO)(OOCCH_3)_2(\overset{\overset{O}{\|}}{COOCCH_3})^- \rightarrow$$

$$\xrightarrow[-CO_2]{} Pd_2(CO)(OOCCH_3)_2(\overset{\overset{O}{\|}}{CCH_3})^- \rightarrow 2Pd_{met} + CO + CH_3COO^- + (CH_3CO)_2O \,.$$

As already mentioned above, palladium(I) carbonyl halides are readily reduced by H_2O. Thus treatment of $[Pd(CO)Cl]_n$ [$\nu(CO)$ = 1975, 1930 cm^{-1}] with water leads to the slow formation of CO_2 and metallic palladium[106]. The rate of formation of CO_2 increases sharply following the addition of $Cr_2O_7^{2-}$ or *p*-benzoquinone in an acid medium[106]. The same palladium(I) carbonyl in methanol or in methanol containing CH_3ONa gives rise to $ClCOOCH_3$, i.e. the product of the reductive elimination reaction[107]:

$$ClPd{-}PdCOOCH_3 \rightarrow 2Pd_{met} + ClCOOCH_3 \,.$$

This mechanism has been confirmed by the following reaction[107]:

$$\frac{2}{n}[Pd(CO)Cl]_n + CH_3COOHgCOOCH_3 \rightarrow [Pd_2(COOCH_3)Cl(CO)_2] \rightarrow$$

$$\rightarrow ClCOOCH_3 + 2Pd_{met} + 2CO + Cl^- \,.$$

In the decomposition of $[Pd(CO)Cl]_n$ in alcohol in the presence of *p*-benzoquinone, the reaction pathway changes and dimethyl oxalate is mainly formed[107]. Treatment of $[Pd_2(CO)_2(OOCCH_3)_2]_2$ with water and ethanol also leads to the formation of CO_2 and the product of the oxidative carbonylation of methanol, namely dimethyl carbonate[105].

The behaviour of palladium(I) complexes with respect to a reductant such as H_2 depends greatly on the nature of the ligands. For example, the reduction of the palladium(I) acetate complex[50] leads to the formation of the diamagnetic cluster Pd_2L_2:

$$Pd_2(OOCCH_3)_2L_2 + H_2 \rightarrow Pd_2L_2 + 2CH_3COOH \,,$$

while the compounds $Pd_2(C_6H_6)_2(HSO_4)_2$ and $Pd_2(CH_3NC)_6 \cdot (PF_6)_2$ are not reduced by hydrogen.

Palladium(I) in complexes is oxidised by various oxidants (O_2, I_2, Br_2, MnO_4^-, $Cr_2O_7^{2-}$, *p* benzoquinone, etc.), including coordinated ligands, for example NO:[47]

$$2Pd(NO)Cl + 8CN^- + H_2O \rightarrow 2Pd(CN)_4^{2-} + N_2O + 2Cl^- + 2OH^- \,.$$

The quantitative characteristics of the oxidation-reduction properties have so far been obtained only for several palladium(I) complexes, but extensive experimental data have been accumulated on reactions of the oxidation-reduction type which it would be useful to analyse and to estimate at least approximately the oxidation-reduction properties of palladium(I). For this purpose, we shall consider in greater detail the disproportionation reaction

$$Pd_2^I \rightleftarrows Pd^0 + Pd^{II} \,.$$

The complexes $Pd_2(C_6H_6)_2^{2+}$ do not disproportionate in acetic and sulphuric acid solutions and only the addition of Cl^- leads to a rapid oxidation-reduction process. This finding is in good agreement with the hypothesis[108,109] that $Pd_2Cl_4^{2-}$, formed via reaction (7), tends to disproportionate in accordance with the mechanism

$$Pd_2Cl_4^{2-} \rightleftarrows Pd_{met} + PdCl_4^{2-} \,. \qquad (9)$$

It can be easily shown that the free energy ΔG° of reaction (9) is negative if the standard oxidation-reduction potentials ε_2^0 and ε_1^0 in the scheme below

$$PdCl_4^{2-} \xrightarrow{\varepsilon_1^0} \tfrac{1}{2}Pd_2Cl_4^{2-} \xrightarrow{\varepsilon_2^0} Pd_{met} \qquad (10)$$

$$\varepsilon_3$$

satisfy the inequality $\varepsilon_2^0 > \varepsilon_1^0$. In this case $\varepsilon_1^0 < 0.62$ V and $\varepsilon_2^0 > 0.62$ V when $\varepsilon_3^0 = 0.62$ V.[110] Since according to some data[108,109] *p*-benzoquinone (Q) oxidises $Pd_2Cl_4^{2-}$ in acid media and the potential of benzoquinone ε_Q varies from 0.7 to 0.6 V in the pH range 0–2, one may conclude that ε_1^0 is indeed smaller than 0.6 V. If it is assumed that the reaction of the palladium(I) complex with an oxidant (Ox) reaches equilibrium[11],

$$Pd_2^I = Ox \rightleftarrows 2Pd^{II} + Red \,, \qquad (11)$$

it is possible to achieve a further refinement of the values of ε_1^0 and ε_2^0. Since the expression for ε_1^0 corresponding to reaction (11) assumes the form (in terms of the concentration approximation)

$$\varepsilon_1^0 = \varepsilon_{Ox/Red}^0 - \frac{RT}{2F}\ln\frac{[Red][Pd^{II}]^2}{[Ox][Pd_2^I]} \,, \qquad (12)$$

it is possible to estimate Δ in Eqns.(12) and (13) by specifying different degrees of conversion of $Pd_2(I)$ and using the real concentrations of all the components:

$$\varepsilon_1^0 = \varepsilon_{Ox/Red}^0 - \Delta \,. \qquad (13)$$

In the calculation of Δ it is of course necessary to take into account the concentration of H^+ ions and the ligands involved in the reaction (11). When account is taken of Δ (estimated from the data of Moiseev and Pestrikov[108]), the potential ε_1^0 for $Pd_2Cl_4^{2-}$ can be $\varepsilon_1^0 \leqslant 0.5$ V; then $\varepsilon_2^0 \geqslant 0.74$ V.

The complex $Pd_2SO_4 \cdot Q$ [74] is formed in an acid medium with $[H^+] = 0.1$–0.2 M. Since metallic palladium cannot be oxidised by *p*-benzoquinone to $PdSO_4$ in sulphuric acid solutions[110], one may assume that metallic palladium is oxidised to Pd_2SO_4, which is additionally stabilised by *p*-benzoquinone:

$$2Pd_{met} + 2Q + H_2SO_4 \rightarrow Pd_2SO_4 \cdot Q + QH_2 \,.$$

Hence, without taking into account the complex formation reaction of Q with Pd_2SO_4, we obtain $\varepsilon_2 \leqslant 0.7$ V [the designation of the potentials is analogous to that in scheme (10)]. If it is assumed that ε_3^0 for $PdSO_4/Pd_{met}$ does not differ greatly from $\varepsilon^0_{Pd^{2+}/Pd_{met}} = 0.987$ V,[110] we obtain $\varepsilon_1^0 \geqslant 1.1$ V (for $HgSO_4$, $\varepsilon_1^0 = 0.92$ V and $\varepsilon_2^0 = 0.789$ V). The complex $Pd_2SO_4 \cdot Q$ does not disproportionate precisely because in this case $\varepsilon_2^0 < \varepsilon_1^0$ and in addition there is a possibility of some stabilisation of palladium(I) on treatment with p-benzoquinone. The addition of concentrated hydrochloric acid to $Pd_2SO_4 \cdot Q$ leads immediately to the oxidation of palladium(I) and the formation of hydroquinone and $PdCl_4^{2-}$ (because Cl^- displaces Q and SO_4^{2-} from the coordination sphere of palladium and lowers ε_1^0).[74]

The complex $Pd_2(C_6H_6)_2(ClO_4)_2$ [70] is oxidised by O_2, Br_2, and $KMnO_4$. However, $Cr_2O_7^{2-}$ and $Pb(OCOCH_3)_4$ in acetic acid oxidise this complex only in the presence of Cl^-. The high potential of $Cr_2O_7^{2-}$ in the six-electron reduction ($\varepsilon^0_{Ox/Red} = 1.33$ V) in a weakly acid medium is probably low in the first stages of the oxidation [Cr(VI) → Cr(V) → Cr(IV)] and for this reason $Cr_2O_7^{2-}$ does not oxidise the stabilised cation $Pd_2(C_6H_6)_2^{2+}$ in the absence of Cl^-; only in concentrated 90% H_2SO_4 is that cation oxidised by dichromate[74].

The complex $Li_2Pd_2I_4 \cdot 2H_2O$ in butanol is oxidised by I_2.[51] In the presence of an excess of LiI, at a concentration of 0.5 M for $[Pd_2^I] = 0.01$ M, the complex probably exists in

the form $Pd_2I_6^{4-}$. In this case the oxidation reaction can be formulated as the equilibrium

$$Pd_2I_6^{4-} + I_2 \rightleftarrows 2PdI_4^{2-}. \qquad (14)$$

The standard potentials of the I_2/I^- and I_3^-/I^- pairs in water are 0.62 and 0.55 V [$\varepsilon^0_{Ox/Red}$ in Eqns.(12) and (13)]. Judging from potentiometric data[97], equilibrium (14) is almost completely displaced to the right. For a degree of conversion of PdI_2 of 0.99 and at the real concentrations of the reactants, $\Delta = 0.15$ V in Eqn.(13). If it is assumed that in butanol $\varepsilon^0_{Ox/Red}$ for I_2 does not differ greatly from the value in aqueous solutions and amounts to ~0.6 V, then ε_1^0 in scheme (15) is $\varepsilon_1^0 \leqslant 0.45$ V†:

$$PdI_4^{2-} \xrightarrow{\varepsilon_1^0} \tfrac{1}{2}Pd_2I_6^{4-} \xrightarrow{\varepsilon_2^0} Pd^0_{met}\,, \quad PdI_4^{2-} \xrightarrow{\varepsilon_3^0} Pd^0_{met} \qquad (15)$$

According to Fasman[111], the overall instability constant of the complex PdI_4^{2-} in water at $I = 1$ is close to 10^{-24}. Then (on the same assumptions) $\varepsilon_3^0 \cong 0.3$ V and $\varepsilon_2^0 \geqslant 0.15$ V. The above estimate makes it possible to explain the stability of the palladium(I) iodide complex with respect to the disproportionation reaction ($\varepsilon_2^0 < \varepsilon_1^0$). The potentials of system (15) are probably very similar to those of the system $HgBr_4^{2-} \rightarrow \tfrac{1}{2}Hg_2Br_2 \rightarrow Hg^0$ [110] ($K_{inst} = 2.3 \times 10^{-22}$, $\varepsilon_1^0 = 0.31$ V, $\varepsilon_2^0 = 0.14$ V, and $\varepsilon_3^0 = 0.227$ V).

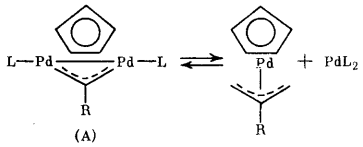
The complex $Pd_2(CH_3NC)_6^{2+}$ proved to be very stable with respect to oxidants. It is not oxidised by O_2 and chloranil[34], but is oxidised by iodine (and bromine) via the reaction

$$Pd_2L_6^{2+} + I_2 \rightarrow PdL_4^{2+} + PdI_2L_2\,.$$

Here I_2 in essence displaces the disproportionation equilibrium to the right:

$$PdL_2^0 + I_2 \rightleftarrows PdI_2L_2\,.$$

The disproportionation reaction proceeds also in the case of π-cyclopentadienyl-π-allyl complexes[88]. Thus the equilibrium in the reaction



(A)

is usually strongly displaced to the left (see Section III, subsection 2 above), but is displaced to the right in the presence of substituents giving rise to an appreciable steric hindrance (R = t-C_4H_9 and L = PR_3). The complexes (A) are readily oxidised by I_2, CH_3I, and even HCl, but in this instance the primary reaction products are those resulting from the oxidative addition of I_2 and CH_3I (as well as HCl) to PdL_2^0:[80]

$$(A) + I_2 \rightarrow [(C_6H_5)\,Pd\,(R - C_3H_4) + L_2PdI_2] \rightarrow (C_6H_5)\,PdLI + (R - C_3H_4)\,PdLI\,.$$

In conclusion of this Section, we shall consider the results of polarographic studies of palladium(II) and palladium(I) complexes. The number of studies devoted to the polarography of palladium(II) is small. At a mercury electrode, polarographic waves can be detected for complexes whose oxidation potential ε^0 is in excess of 0.25 V [i.e. above the potential of the saturated calomel electrode (s.c.e.)].[112] The measured values of $E_{\frac{1}{2}}$ for palladium(II) are therefore in the range between −0.3 and −1.96 V (relative to s.c.e.) or in the range −0.05– −1.65 V (relative to the hydrogen electrode). Thus the $E_{\frac{1}{2}}$ refer to complexes in which the state of palladium(II) is much more stable than the zerovalent palladium and palladium(I) states [C_5H_5N, NH_3, $P(OR)_3$, dpe, CN^-, acac$^-$, $S_2C_2(CN)_2^{2-}$].[8,112–116]#

Polarographic studies of palladium(II) cyanide complexes[113] yielded for the first time the electrochemical characteristics of the palladium(I) cyanide complex. The value of $E_{\frac{1}{2}}$ (relative to s.c.e.) for the reaction $Pd(CN)_4^{2-} + 2e \rightarrow Pd(CN)_4^{4-}$ is −1.6 V (reversible reaction). The product of the dimerisation of $Pd(CN)_4^{3-}$, namely $Pd_2(CN)_6^{4-}$, does not give rise to a cathodic wave. The anodic half-wave potential of this intermediate (−0.85 V) is close to the anodic half-wave potential of the product of the reduction of $Pd(CN)_4^{2-}$ by sodium amalgam (−0.93 V). In order to estimate ε_1^0 for the transition $Pd(CN)_4^{2-} \rightarrow \tfrac{1}{2}Pd_2(CN)_6^{4-}$ from the potential of the anodic wave, we shall assume that the transition is reversible. Then $\varepsilon_1^0 = -0.65$ V (relative to the hydrogen electrode). Using the value $K_{inst} = 10^{-51}$ for $Pd(CN)_4^{2-}$,[111] we obtain $\varepsilon_3^0 = -0.51$ V and $\varepsilon_2^0 = -0.38$ V. It follows from these estimates that CN^- stabilises palladium(II) to a much greater extent than zerovalent palladium and palladium(I) and the postulated complex $Pd_2(CN)_6^{4-}$ is therefore a very powerful reductant. The half-wave potential of the reversible cathodic Pd(II)/Pd(I) transition was first measured with a dithiolenepalladium(II) complex[8]. The reaction

$$Pd\,(mnt)_2^{2-} + e \rightleftarrows Pd\,(mnt)_2^{3-} \qquad (16)$$

where mnt = $(NC)_2C_2S_2^{2-}$, in acetonitrile leads to the formation of the only known paramagnetic palladium(I) (d^9) complex. The complex is stable in acetonitrile and dimethoxyethane and is not reduced further up to a potential of −2.8 V. The value of $E_{\frac{1}{2}}$ for reaction (16) is −1.9 V relative to the aqueous saturated calomel electrode. After a number of assumptions have been made, $\varepsilon^0_{Pd(II)/Pd(I)}$ for this complex is in the range between −1.6 and −1.65 V. Thus the above palladium(I) complex is an exceptionally powerful reductant.

The formation of univalent palladium has been detected also in the polarographic reduction of palladium(II) oxinate and acetylacetonate complexes in DMF.[115] The complexes $Pd(oxine)_2$§ and $Pd(acac)_2$ are reduced in two one-electron stages. In the case of $Pd(oxine)_2$, the potential $E_{\frac{1}{2}}$[Pd(II)/. .Pd(I)] (relative to s.c.e.) corresponds to a reversible reaction and amounts to −1.46 V. The lifetime of palladium(I) is ~0.18 s, the first stage in the reduction of $Pd(acac)_2$ is not fully reversible ($E_{\frac{1}{2}} = -1.29$ V), and the palladium(I) complex decomposes faster (lifetime ~0.02 s).

The first oscillopolarographic characteristics of palladium(I) complexes have been obtained recently in a saturated solution of KCl in 98% acetic acid[46,117]. The complex $K_2Pd_2(CO)_2Cl_4$ has a cathodic reduction potential $E_1 = -0.576$ V (relative to s.c.e.). The complexes $(PdXL)_2CO$ in acetic acid have similar potentials[46,117]. Their electrochemical behaviour has been studied by cyclic voltamperometry[46,117] in DMF and acetonitrile. The reduction potentials of the complexes $(PdXL)_2CO$, reversible in DMF, are in the range −0.56 to −0.63 V (relative to the aqueous hydrogen electrode).

Table 9 presents the values of ε_1^0 and ε_2^0 which we estimated (see above) from indirect or polarographic data or they were measured polarographically. Evidently the oxidation-reduction properties of palladium(I) vary within very wide limits as a function of the nature of the ligands.

†Presumably the equilibrium constant of $PdI_3^- + I^- \rightleftharpoons PdI_4^{2-}$ is small and does not alter ε_1^0 appreciably.

#Here and henceforth acac$^-$ = acetylacetonate anion.

§Oxine = 8-hydroxyquinolinate anion.

4. Reactions Involving the Insertion of Various Molecules in a Pd–Pd Bond

The first complex containing a CO molecule inserted in a Pd–Pd bond was synthesised in 1973,[40] but its structure was interpreted erroneously. The diamagnetic complex $Pd_2dam_2.Cl_2(CO)$ was obtained by the reaction[40,63]

$$\frac{2}{n}(PdCOCl)_n + 2\,dam \rightarrow Pd_2(dam)_2Cl_2(CO) + CO\ .$$

Table 9. Estimated standard potentials for palladium(I) complexes [the notation is based on Scheme (10)].

Complex	Solvent	ε_1^0, V	ε_2^0, V
$Pd_2SO_4 \cdot Q$	water	$\geqslant 1.1$	$\leqslant 0.7$
$Pd_2Cl_4^{2-}$	water	$\leqslant 0.5$	$\geqslant 0.74$
$Pd_2I_6^{4-}$	n-butyl alcohol	$\leqslant 0.45$	$\geqslant 0.15$
$[PdX(PR_3)]_2CO$ *	CH_3CN, DMF	−0.56 – −0.63	—
$Pd(CN)_6^{4-}$ *	water	−0.65 **	−0.38
$Pd(oxine)_2^-$ *	DMF	−1.21	—
$Pd[S_2C_2(CN)_2]_2^{3-}$ *	CH_3CN	−1.6 – −1.65	—

*The potentials relative to the aqueous hydrogen electrode are quoted.

**$\varepsilon_1^0 \cong \varepsilon_{1/2}$.

The surprisingly low vibration frequency of the carbonyl group [$\nu(CO) = 1720\ cm^{-1}$] was explained with the aid of X-ray diffraction analysis[63]. Thus the parameters of a fragment of complex No.1 (Table 10 and Fig.3) indicate the absence of a metal–metal bond. The Pd–C–Pd angle appreciably exceeds the angles in metal carbonyls having the M>C–O<M bridge (<88°) and even in aldehydes and ketones (108–113°).

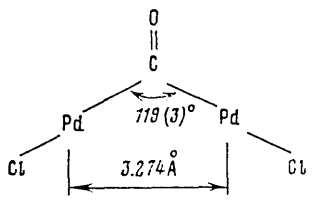


Figure 3. Fragment of the complex $Pd_2(dam)_2Cl_2(\mu\text{-}CO)$.[63]

If the complex $Pd_2dpm_2X_2$ is kept in methylene chloride at p_{CO} = 1 atm, a red crystalline product $(Pd_2dpm_2X_2)CO$ (X = Cl or Br), for which $\nu(CO) = 1704\ cm^{-1}$ when X = Cl, is formed[118]. The RNC molecule behaves similarly to carbon monoxide[118,119] (Table 10), being inserted in the Pd–Pd bond in the following reactions:

$$Pd_2(dpm)_2X_2 + RNC \rightarrow Pd_2(dpm)_2X_2(\mu\text{-}RNC)\ ;$$
$$Pd_2(RNC)_6(PF_6)_2 + 2\,dpm \xrightarrow[-3RNC]{} [Pd_2(dpm)_2(RNC)_2(\mu\text{-}RNC)](PF_6)_2\ .$$
(XVI)

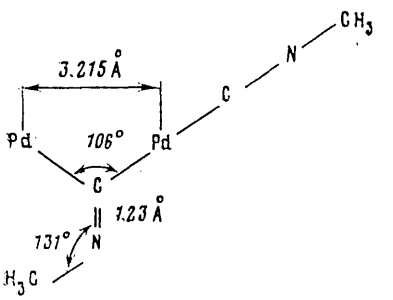


Figure 4. Fragment of the complex $Pd_2(dpm)_2(\mu\text{-}CH_3NC).(CH_3NC)_2(PF_6)_2$.[118]

The stretching vibration frequency of the CN bridge group (μ-RNC) (1640–1680 cm^{-1}) is appreciably reduced compared with that of the terminal ligand (2183–2231 cm^{-1}). The fragment of complex (XVI) (Fig.4) has parameters analogous to those of the fragment of the complex with an inserted CO group, although the Pd–C–Pd angle is appreciably smaller. The products of insertion in a Pd–Pd bond have also been isolated in the case of SO_2 molecules[120], ArN_2^+,[121] alkynes[122], and atomic sulphur[123] (Table 10).

Table 10. Products of the insertion of molecules in a Pd–Pd bond.

Y	L–L	X	L′	$^1J_{Pd-Pd}$	References
		$Pd_2(L-L)_2(\mu\text{-}Y)X_2$			
CO	dam	Cl	—	3,274 (8)	[40,63]
CO	dpm	Cl, Br	—	—	[118]
CO	dpm	I, SCN, NCO, N_3	—	—	[119]
SO_2	dpm	Cl	—	3,383 (2)	[120]
SO_2	dpm	Br	—	3,221 (2)	[120]
SO_2	dam	Cl	—	—	[120]
$C_2(CF_3)_2$	dpm	Cl	—	3,492 (1)	[122]
$C_2(COOCH_3)_2$	dpm	Cl	—	—	[122]
S	dpm	Cl	—	—	[123]
CH_3NC, C_6H_5NC, $p\text{-}CH_3C_6H_4NC$	dpm	Cl, Br	—	—	[118]
$C_6H_{11}NC$, CH_3NC	dpm	I, SCN, NCO, N_3	—	—	[119]
		$Pd_2(L-L)_2(\mu\text{-}Y)L_2'X_2$			
CH_3NC	dpm	PF_6	CH_3NC	3,215 (2)	[118]
$p\text{-}CH_3C_6H_4NC$	dpm	PF_6	$p\text{-}CH_3—C_6H_4$	—	[118]
		$Pd_2(L-L)_2(\mu\text{-}Y)L'X_2$			
CH_3NC	dpm	I, SCN	CH_3NC	—	[119]

CO and SO_2 molecules are inserted reversibly while RNC, S, and RN_2^+ are inserted irreversibly. A somewhat idealised structure of all the complexes with an iserted group Y is illustrated in Fig.5. The environment of the Pd atom is planar and almost square. Only in the case of $C_2(CF_3)_2$ does the C–Pd–C angle (~165°) differ appreciably from 180°.

The marked reduction of the ν(CO) and ν(NC) frequencies, the absence of the Pd–Pd interaction, the change in the hybridisation of the carbon atom in the CO, RNC, and C_2R_2 complexes (for example, the C–C=C angles[122] are 122.8° and 124.7°), and the increase in the length of the N=C bonds in RNC and of the C=C bonds in C_2R_2 are all facts indicating that the oxidative addition of various molecules and atoms to palladium(I) complexes takes place via the dissociation of the Pd–Pd bond. Thus the formation of a disubstituted palladium(II) sulphide takes place in essence in the reaction

$$(dpm)_2Pd_2Cl_2 + {}^1/_8S_8 \rightarrow S(PdCl)_2(dpm)_2\ .$$

In the reaction involving CO the characteristics of the inserted carbon monoxide approach those of the carbonyl group in ketones and it is therefore entirely appropriate to regard these complexes as derivatives of dimetallated formaldehyde[124]. Naturally the insertion of C_2R_2 molecules as well as those of $C_2(CN)_4$ and CS_2 [122] in the Pd–Pd bond is an oxidative addition reaction. The reaction involving the insertion of alkenes in an M–M bond is known for nickel(I), cobalt(II), zerovalent cobalt, and molybdenum(I) complexes.

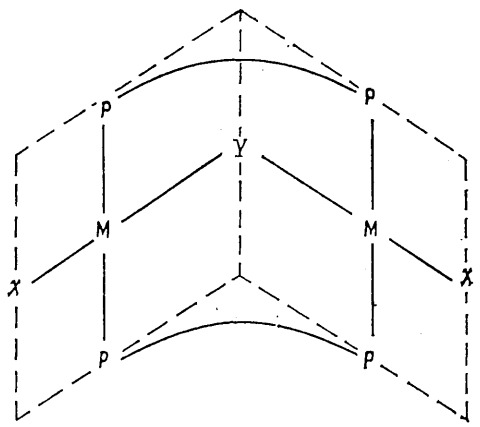


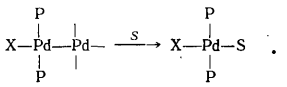
Figure 5. Idealised structure of complexes containing the M–Y–M fragment.

However, studies of the XPE spectra of palladium(I) complexes and the products of the insertion of various molecules have shown[96] that it is impossible to detect appreciable charge transfer and changes in the degree of oxidation of the palladium atoms. This factor led Balch et al.[122] to the conclusion that the question of the degree of oxidation of palladium and of the type of insertion reaction is to a large extent semantic. We shall consider this problem in greater detail. In all cases where it has been possible to measure the binding energy of the electrons at the atom linked directly to two palladium atoms, there is an entirely appreciable decrease of the binding energy on passing from a free to an inserted species. Thus $E(2p_{3/2})$ = 161.6 eV for the S atom in the complex $S(PdCl)_2(dpm)_2$ is lower by 2.4 eV than $E(2p_{3/2})$ for S_8. The transition from free SO_2 to μ-SO_2 decreases the $2p_{3/2}$ binding energy for sulphur by 1.4 to 1.5 eV. Thus there is partial charge transfer to the sulphur atoms. The slight change in $E(3d_{5/2})$ for palladium atoms is also entirely explicable:

(a) electron density is transferred to the inserted species (μ-Y) from two palladium atoms, which decreases the absolute magnitude of the effect;

(b) apart from the two palladium atoms, four (!) powerful σ-donor ligands (P and As) atoms are involved in the charge transfer;

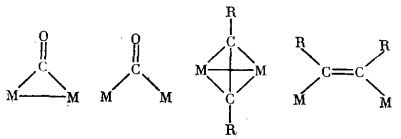
(c) the $3d_{5/2}$ binding energy for palladium (see Section II, subsection 3) depends greatly on the ligand environment (within the limits of 1 eV and more for a constant degree of oxidation). There is therefore a possibility of the mutual cancelling of two effects—the increase of E on transition to palladium(II) and its decrease on transition from the palladium atom as the ligand to, for example, a sulphur atom or CO and SO_2 molecules:



The solution of this problem still requires further study.

The achievement of extremely interesting reactions involving the insertion of various molecules in a Pd–Pd bond expands our ideas concerning the nature of the possible intermediates in catalytic and stoichiometric reactions.

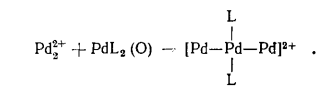
On the basis of the data described above, the types of coordination of CO and acetylenes at the two metal atoms in palladium and platinum complexes can be represented by structures (B), (C), (D), and (E):



(B) (C) (D) (E)

In the case of platinum, a type (C) complex is formed from $Pt_2Cl_2(dpm)_2$ and CO in dichloromethane [ν(CO) = 1638 cm^{-1}] [125–127] and also from the complex $Pt_2(CO)_2Cl_4^{2-}$ and dpm.[125–127]

Within the framework of this Section, which is devoted to reactions involving insertion in a Pd–Pd bond, mention should be made also of the insertion of the PdL_2 complex[11], which can be called a "reductive" addition reaction:



The formal degree of oxidation of palladium approaches +2/3 in this instance.

Thus the Pd–Pd bond in palladium(I) complexes is able to react with both electron acceptors (oxidants—for example, sulphur) and with electron donors (reductants—for example, zerovalent palladium).

IV. THE ROLE OF PALLADIUM(I) COMPOUNDS IN STOICHIOMETRIC AND CATALYTIC REACTIONS

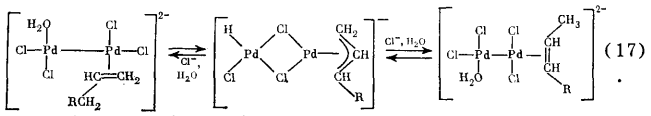
As already mentioned above, the increase of interest in palladium(I) complexes is associated to a large extent with the acquisition of information concerning the involvement of palladium(I) compounds in stoichiometric and catalytic reactions as catalysts and intermediates or about the formation of reaction products containing palladium(I). In this Section we shall consider the available data on the functions of palladium(I) complexes in various reactions. We believe it is useful to mention also the studies in which the postulates of the involvement of palladium(I) are merely working hypotheses and have not yet been sufficiently convincingly demonstrated.

1. The Positional Isomerisation of Olefins

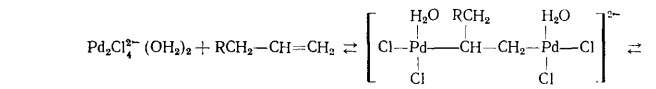
The isomerisation of olefins was apparently the first reaction the results of the study of which were quite convincingly interpreted within the framework of the mechanism of an unbranched chain reaction with a palladium(I) complex as the chain carrier (the catalyst of the isomerisation stages).[104,108,109]. This reaction has been recently discussed in detail[128,129] and we shall therefore mention only its principal features. As a result of the oxidation of an olefin (butenes) with

palladium(II) chloride, a palladium complex is formed [tentatively $Pd_2Cl_4^{2-}$: reaction of type (7)] and catalyses the isomerisation of butenes (α-$C_4H_8 \rightarrow \beta$-C_4H_8). As a consequence of its instability, the complex $Pd_2Cl_4^{2-}$ disproportionates (Section III, subsection 3), which terminates the kinetic chain. The chain termination occurs also after the addition of p-benzoquinone (Q), which oxidises palladium(I).[108] Within the framework of this mechanism, it was possible to explain the surprising proportionality of the rate of isomerisation of α-C_4H_8 to its concentration and the concentration of the total olefins $[C_4H_8]_\Sigma$. These results constitute kinetic proof that the isomerisation of olefins is catalysed by a palladium(I) compound. It has been shown[39] that the insoluble palladium carbonyl chloride $[Pd(CO)Cl]_n$ catalyses the isomerisation of liquid hept-1-ene to *cis,trans*-hept-2-enes. These experiments were repeated under homogeneous conditions[51]. The complex $[Pd(CO)Cl]_n$ was synthesised by the method of Kushnikov et al.[38] and was dissolved in DMF saturated with LiCl. The isomerisation of but-1-ene takes place at 20 °C without an inductive period, comes to a complete stop after the addition of p-benzoquinone in amounts comparable to those of palladium(I), and is resumed after the reduction of p-benzoquinone. It has been shown quite recently[69] that aromatic π-complexes of palladium(I) catalyse the isomerisation of butenes, pentenes, and hexenes at a high rate at room temperature without an inductive period and the hypothesis put forward by Moiseev and co-workers[108,109] has been thereby confirmed.

The mechanism of the isomerisation in the presence of palladium(I) complexes is based on the hypothesis of the transformation of the π-allyl complex, formed as a result of the oxidative addition of $H_2C = CH-CH_2R$ to the complex $Pd_2Cl_4^{2-}$ with dissociation of a C–H bond[104,109]:


(17)

The existence of the dimeric allylpalladium(II) hydride complex has not so far been confirmed. Presumably allylpalladium chloride interacts with the complex $HPdCl_2^-$ and is converted into $Pd_2Cl_4^{2-}$ and $CH_3CH = CHR$. In the light of new data concerning the possibility of the insertion of various molecules in the Pd–Pd bond in palladium(I) complexes, another version of the C–H bond dissociation mechanism can be suggested:



The highly reactive σ-allylpalladium chloride can interact directly with $HPdCl_2^-$ or can be first converted into a π-allyl complex as in scheme (17).

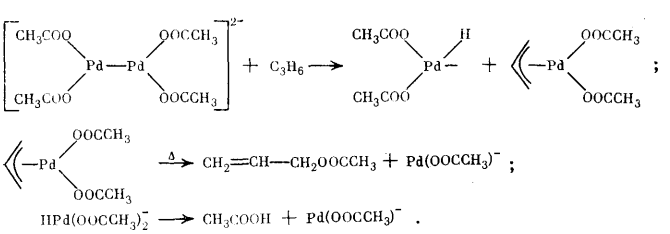
2. The Oxidation of Organic Compounds

As we have seen above, palladium(I) complexes were regarded as the final reaction products in olefin oxidation reactions. This hypothesis was confirmed chemically by Davidson and Triggs[70]. A benzenepalladium(I) complex is formed (Table 6, No.5) on reduction of palladium(II) acetate with hex-1-ene in perchloric acid-containing acetic acid in the presence of 25% of benzene. An analogous complex is formed also in the oxidative dimerisation of benzene. Under the conditions of the oxidation of cyclohexa-1,4-diene catalysed by $Pd(OOCCH_3)_2$, a palladium(I) complex was also isolated[73] (Table 6, No.7). The reduction of $PdSO_4$ by ethylene in the presence of p-benzoquinone (Q) results in the formation of the complex $Pd_2SO_4.Q$.[74] As mentioned above, the formation of palladium(I) in the reactions considered may be a consequence of two processes—the decomposition of intermediate organometallic σ-compounds [reaction (6)] or the reduction of palladium(II) by a zerovalent palladium complex stabilised by some kind of π ligand:

$$PdSO_4 + C_2H_4 + H_2O + Q \rightarrow Pd^0 \cdot Q + H_2SO_4 + CH_3CHO\ ;$$
$$Pd^0 \cdot Q + PdSO_4 \rightarrow Pd_2SO_4 \cdot Q\ .$$

The palladium(I) formed in the oxidative dehydrogenation of cyclohexane to benzene[71,72] exhibits an interesting "protecting" function—the benzene bound in a complex with palladium(I) is not sulphonated in 98% H_2SO_4. When oxidants capable of oxidising palladium(I) are added, only benzene sulphonation products are formed.

It is believed[130–135] that the palladium(I) complexes $[Pd_2(OOCCH_3)]_2$ (or clusters with a large number of atoms) are involved in the heterogeneous catalytic oxidative acetoxylation of olefins. The study of the XPE spectra of the catalyst $[Pd(OOCCH_3)_2 - CH_3COOK]/Al_2O_3$, prepared in different ways before and after tests for catalytic activity, showed that the specimens which have the 336.2 ± 0.1 eV band $[E(3d_{5/2})]$ in the XPE spectrum are active in the acetoxylation of propene. Politanskii et al.[135] assigned this band to the $CH_3COOPd-PdOOCCH_3$ fragment located on the catalyst surface. The specimens whose XPE spectra contain only the 335.3 or 336.8 eV bands, which the authors assigned to Pd(0) and PdO/Al_2O_3 respectively, have no catalytic activity in the process investigated[135]. A mechanism, close to the mechanism of the isomerisation of olefins, which does not specify in detail the possible modes of coordination of acetate groups, was proposed[131]:



The interaction of zerovalent palladium or of the hydride and allyl complexes with oxygen leads to the regeneration of the catalytically active form of palladium(I).

As mentioned above, the formation of paramagnetic palladium(I) centres has been established by EPR in a study of the interaction of the PdY zeolite with H_2 and CO.[9,10] Treatment of this specimen with oxygen at 500 °C with subsequent evacuation converts ~1% of palladium to the +3 state. If the same specimen is then treated with hydrogen at 25 °C, the zeolite blackens, the EPR signal corresponding to palladium(III) disappears, and the signals of two different palladium(I) states appear (8% of the total amount of palladium). The palladium(I) signals vanish when the specimen is treated with oxygen at 300 °C. The action of carbon monoxide on the specimens treated beforehand with oxygen or hydrogen leads to the disappearance of the EPR signals detected previously and to the appearance of a triplet signal, which the authors attributed to palladium(I) carbonyl[9]. Analogous results were obtained later in a different study[10]. When the zeolite specimen was treated in succession with hydrogen, carbon monoxide, and oxygen, the formation of carbon dioxide was observed. The involvement of palladium(I) carbonyl in this reaction is extremely probable[9].

Taking into account the comparatively high thermal stability of the palladium(I) complexes with isonitrile, carbonyl, and other ligands, one must bear in mind the possibility of the involvement of palladium(I) compounds as intermediates or catalysts in heterogeneous processes catalysed by palladium.

3. Oxidation of Carbon Monoxide

The oxidation of CO in solutions of palladium(I) complexes has been known since 1894 [136] and has been studied in fair detail[102,137,138]. Nevertheless, the role of the palladium(I) complexes in this reaction has started to become clear comparatively recently. It is known that CO reduces palladium(II) to palladium(I) (this is a method of synthesis of carbonyl complexes[38-41]), while $[Pd(CO)Cl]_n$ or $Pd_2(CO)_2Cl_4^{2-}$ decompose in aqueous solutions to CO_2 and zerovalent palladium[36]:

$$Pd^{II} \xrightarrow[-CO_2]{CO,\ H_2O} Pd^{I}CO \xrightarrow[-CO_2]{H_2O} Pd^0 .$$

The rate of decomposition of $[Pd(CO)Cl]_n$ increases greatly in the presence of an oxidant (Q, $Cr_2O_7^{2-}$). However, the characteristic features of the transformation of $[Pd(CO)Cl]_n$, investigated by Zhir-Lebed' and Golodov[106], left open the question of the role of palladium(I) in the CO oxidation process. Autocatalytic phenomena and a stepwise character of the reduction of palladium(II) have been observed in studies[139-141] of the reaction of $PdCl_2$ with CO without an oxidant. The inductive period was abolished after the introduction of the complex $[Pd(CO)Cl]_n$ into the initial solution ($PdBr_2$–H_2O–dioxan), and the rate of oxidation of CO increased. It follows from these findings that not only are palladium(I) complexes formed in the course of the reduction of palladium(II) but (in the absence of an oxidant) they also play the role of a catalyst of the oxidation of CO. The catalytic cycle (the chain propagation stages) in this process can be represented schematically as follows[102]:

$$[Pd_2(CO)_2X_4]^{2-} \xrightarrow{H_2O} Pd_2(COOH)(CO)X_3^{2-};$$

$$Pd_2(COOH)(CO)X_3^{2-} + PdX_2 + CO \rightarrow Pd_2(CO)_2X_4^{2-} + Pd^0 + CO_2 + HX .$$

In the presence of oxidants, the role of palladium(I) can change, but the stages involving the formation of palladium(I) complexes and their conversion into CO_2 can take place[141-143]. Studies of the kinetics of this reaction in the $PdCl_2$–$FeCl_3$–HCl–H_2O system led Brailovskii and co-workers[142,143] to the conclusion that zerovalent palladium complexes (carriers of the kinetic chain) play an important role in this system, while palladium(I) complexes are formed as a result of chain termination [Pd(0) + Pd(II)], which lowers the rate of formation of CO_2.

According to current information, there is a possibility of the direct transfer of an oxygen atom to CO from O_2 under homogeneous conditions. Thus the oxidation of CO by oxygen takes place selectively in the $Pd_4(phen)_2(CO)\cdot(OOCCH_3)_4$ cluster in acetic acid solution:[99]

$$Pd_4(phen)_2(CO)(OOCCH_3)_4 + \tfrac{1}{2}O_2 \rightarrow Pd_4(phen)_2(OOCCH_3)_4 + CO_2 .$$

4. Oxidative Carbonylation of Alcohols and Certain Other Oxidation-Reduction Reactions of Carbon Monoxide

A study of the kinetics of the catalytic carbonylation of methanol in the presence of $PdCl_2$,[102,107,144]

$$2CO + 2CH_3OH + Q \xrightarrow{PdCl_2} (COOCH_3)_2 + QH_2 , \qquad (18)$$

established that, under conditions where the rate of formation of dimethyl oxalate r_{DMO} is independent of p_{CO}, the dicarbonyl complex $PdCl_2(CO)_2$ is involved in the reaction. The rate of reaction is then described by the equation

$$r_{DMO} = \frac{k[PdCl_2(CO)_2]_\Sigma \cdot [Q]}{1 + k_1[PdCl_2(CO)_2]_\Sigma^n} ,$$

where $n = 1-2$, depending on the range of variation of $[PdCl_2]_\Sigma$. One of the hypotheses which explained the variable and fractional order of the reaction with respect to $[PdCl_2]_\Sigma$ is the possibility of the formation of palladium(I) carbonyl chloride clusters. We already noted above (Section III, subsection 3) that $[Pd(CO)Cl]_n$ is converted into the chloride carbonate in alcoholic solutions, while in the presence of *p*-benzoquinone it is converted into dimethyl oxalate. The carbonylation of phenol to diphenyl carbonate and salicylate also takes place in the presence of palladium(I) carbonyl halides[145,146]. However, a study[107] of the kinetics of the reaction (18) catalysed by $[Pd(CO)Cl]_n$ showed that the rate of reaction in this system under steady-state conditions (under conditions of independence of p_{CO}) is described by another equation:

$$r_{DMO} = k_2[Pd_2(CO)_2Cl_4^{2-}]_\Sigma \cdot [Q] .$$

In the region of first order of the reaction with respect to the catalyst, the constant k_2 is greater than k by a factor of 1.6. For $[Pd]_\Sigma = 0.06$ M, the rate of reaction in palladium(I) solutions is 4.5 times higher than r_{DMO} in palladium(II) solutions, other conditions being equal.

In $[Pd(CO)Cl]_n$ solutions in the presence of an excess of LiCl [when account is taken of the CO content in the initial palladium(I) carbonyl halide], one mole of CO is absorbed per gram-atom of palladium, i.e. dimeric dicarbonyl complexes, probably $Pd_2(CO)_2Cl_4^{2-}$, are formed in these solutions. Thus the results of the above investigations lead to a remarkable consequence: in a CO atmosphere in alcoholic solutions of *p*-benzoquinone, palladium(II) and palladium(I) form two different catalytic systems which are not interconverted to an appreciable extent. This conclusion has been confirmed in a study of the kinetics of the model reaction

$$2CH_3COOHgCOOCH_3 + Q + 2HX \rightarrow (COOCH_3)_2 + QH_2 + Hg(OOCCH_3)_2 + HgX_2$$

catalysed by $PdCl_2$ and $[Pd(CO)Cl]_n$. Different dependences of the rates of reaction on [Q] were obtained in this instance, and, for identical reactant concentrations under the conditions of first order of the reaction with respect to both Q and the catalyst, the second-order rate constant is higher by a factor of 4.2 for $PdCl_2$ than in $Pd_2(CO)_2Cl_4^{2-}$ solutions. The mechanism of the synthesis of dimethyl oxalate in palladium(I) solutions is described by the scheme[107]

$$Pd_2(CO)_2Cl_4^{2-} + Q \underset{}{\overset{K}{\rightleftarrows}} \underset{(XVII)}{QPd_2(CO)_2Cl_3^-} + Cl^- ;$$

$$(XVII) \begin{cases} \xrightarrow[\xleftarrow{H^+,\ Cl^-}]{ROH} QPd_2(COOR)(CO)Cl_2^- + Cl^- \ (XVIII) ; \\ \xrightarrow[k_2']{CH_3COOHgCOOR} (XVIII) ; \end{cases}$$

$$(XVIII) \begin{cases} \xrightarrow[\xleftarrow{H^+}]{ROH} QPd_2(COOR)_2Cl_2^{2-} \ (XIX) ; \\ \xrightarrow[k_3',\ -CO]{CH_3COOHgCOOR} (XIX) ; \end{cases}$$

$$(XIX) + 2HCl \rightarrow Pd_2Cl_4^{2-} + QH_2 + (COOR)_2 ;$$

$$Pd_2Cl_4^{2-} + 2CO \rightarrow Pd_2(CO)_2Cl_4^{2-} .$$

It has been reported that the carbonyl chloride $[Pd(CO)Cl]_n$ [147] and the carbonyl acetate $[Pd(CO).(OOCCH_3)]_4$ [148] are involved in the oxidative carbonylation of olefins:

$$CH_2{=}CHR + ArOH + [Pd(CO)Cl] \xrightarrow[CH_2Cl_2;\ CO\ (1\ atm)]{R_3N;\ 20^\circ} \begin{cases} \longrightarrow ArOOCCH(OAr)CH_2R \\ \longrightarrow ArOOCCH{=}CHR \end{cases} + Pd_{met};$$

$$C_6H_5CH{=}CH_2 + CH_3OH + [Pd(CO)(OOCCH_3)]_4 \xrightarrow[28^\circ]{CO\ (1\ atm)} C_6H_5CH{=}CHCOOCH_3 + Pd_{met}.$$

The same reactions occur in catalytic systems based on palladium(II) in the presence of oxidants[102,149]. The elucidation of the role of palladium(I) compounds in the oxidative carbonylation of olefins requires further study.

The oxidative carbonylation of amines resembles closely the reactions considered in this Section[150-152]. The short inductive period in the $PdCl_2$–$CuCl_2$ system in the synthesis of dibutylurea

$$4RNH_2 + CO + CuCl_2 \xrightarrow{PdCl_2} RNHCONHR + 2CuCl + 2\overset{+}{R}NH_3Cl^-,$$

and the fractional order of the reaction with respect to $PdCl_2$ (~0.5) is treated[151,152] as a consequence of the catalysis of this reaction by palladium(I) complexes. This hypothesis cannot yet be regarded as sufficiently well founded.

Palladium complexes catalyse an interesting reaction involving the reductive carbonylation of nitro-compounds[153]:

$$RNO_2 + 3CO \rightarrow RNCO + 2CO_2.$$

It has been suggested that palladium(I) carbonyl halide complexes can participate in this reaction. Its mechanism is apparently close to that of the stoichiometric reduction of ArNO by carbon monoxide coordinated to palladium(I).[154] When equimolar amounts of ArNO and Pd(CO)Cl interact in dichlorobenzene at 90 °C, ArN–NAr and CO_2 are formed via the reaction

$$2Pd(CO)Cl + 2ArNO \rightarrow ArN{=}NAr + 2CO_2 + [Pd_2Cl_2]$$
$$[Pd_2Cl_2] \rightarrow PdCl_2 + Pd_{met}.$$

In the case of C_6H_5NO the products are ~90% of azoxybenzene and 10% of azobenzene relative to the initial C_6H_5NO.[154]

The oxidative dehydration of acetic acid is a very interesting reaction[155]:

$$2CH_3COOH + CO + \tfrac{1}{2}O_2 \xrightarrow{Pd(CH_3COO)_2} (CH_3CO)_2O + CO_2 + H_2O.$$

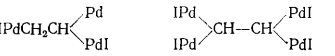
It is a coupled process. There is reason to regard palladium(I) complexes as intermediates in this reaction. It has been suggested that the reaction proceeds via the formation and transformation of the carbonyl acetate cluster [see reaction (8)]:

$$Pd(OOCCH_3)_2 \xrightarrow{CO} Pd_2(CO)_2(OOCCH_3)_2 \xrightarrow{NaOOCCH_3} (CH_3CO)_2O + CO_2 + 2Pd^0.$$

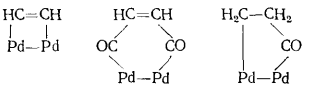
There is also a possibility of the formation of the anhydride and CO_2 in the stage leading to palladium(I). The oxidation of zerovalent palladium by oxygen or another oxidant makes the process catalytic.

5. Alkoxycarbonylation of Acetylene

The first hypothesis of the involvement of palladium(I) complexes in the oxidative alkoxycarbonylation of acetylene was put forward in a study[156] of the synthesis of maleic and fumaric diesters in the $PdCl_2$–$SC(NH_2)_2$–ROH system. The first evidence for the catalysis by palladium(I) complexes of the reactions of acetylene with RO and ROH was obtained in a study of the coupled reaction involving the synthesis of acrylic, propionic, maleic, fumaric, and succinic acid esters in the Li_2PdI_4–ROH–HCl system[51,97,102]. The potentiometric study of the active catalyst formation stage and the study of the influence of oxidants and reductants on this stage and on the rate of reaction under steady-state conditions led to the conclusion that the alkoxycarbonylation of acetylene is catalysed by palladium(I) complexes. Tests of the activities of a number of palladium(I) compounds, namely $[Pd(CO)Cl]_n$, $Cs_2Pd_2(CO)_2Cl_4$, and $Li_2Pd_2I_4.2H_2O$,[51,97] in this reaction in the LiI–C_4H_9OH system showed that palladium(I) complexes catalyse the synthesis of the acid mono- and di-esters and that the catalytic properties of $Li_2Pd_2I_4.2H_2O$ and its potentiometric characteristics are very close to the properties and characteristics of the catalytic system formed from Li_2PdI_4 after the attainment of the steady state. A study of the kinetics of this complex coupled reaction showed that the experimental dependences of the rate of formation of all the products (and their ratio) on p_{CO} and $[H^+]$ are not described by the mechanisms proposed previously[97] and not even by their combination. In order to account for the set of experimental findings, it proved essential to resort to the information about specific properties of the palladium(I) complexes and about the reactions involving the Pd–Pd bond; the products of the insertion of C_2H_2 and CO in the Pd–Pd bond (IPd–CO–CH=CH–PdI, IPd–CO–CH=CH–CO–PdI) as well as the polynuclear organometallic σ-compounds[157]



and metal-containing cyclic compounds



formed in the system were regarded as intermediates.

The study of the $PdBr_2$–$P(C_6H_5)_3$–C_4H_9OH–DMF system in the same acetylene alkoxycarbonylation reactions showed that oxidants and reductants influence the process parameters in the same way as in the Li_2PdI_4–C_4H_9OH system[158]. This influence is particularly strong in the stage involving the formation of the active complex. The hypothesis of the involvement of low-valence forms of palladium [palladium(I)] in this system does not conflict with recent data, according to which the complex $[PdClP(C_6H_5)_3]_2CO$ [$\nu(CO)$ = 1860, 1890 cm^{-1}] proved to be catalytically active in the DMF–C_4H_9OH system; the overall rate of reaction and the rates of formation of individual esters are comparable to the rates of alkoxycarbonylation in the $PdBr_2$–$P(C_6H_5)_3$–DMF–C_4H_9OH system[159].

6. The Hydrogenation, Dimerisation, and Cyclo-oligomerisation of Unsaturated Molecules

The important role of palladium(I) compounds in the mechanism of the formation of catalytically active complexes—catalysts of the hydrogenation of dienes and alkynes in the $[(C_6H_5)_3PPd(CH_3COO)_2]_2$–$H_2$ system in various solvents—has been established[50,160]. It has been shown convincingly that the interaction of the complex $[(C_6H_5)_3PPd(CH_3COO)_2]_2$ with H_2 constitutes an autocatalytic process whose mechanism has been accounted for by the formation of the zerovalent palladium complex Pd_2L_2 [$L = P(C_6H_5)_3$] catalysing the reduction of $[LPd(CH_3COO)_2]_2$ via the intermediate palladium(I) complex $Pd_2(OOCCH_3)_2L_2$, which undergoes hydrogenolysis faster than $[LPd(CH_3COO)_2]_2$ with formation of Pd_2L_2:[160]

$$[LPd(OOCCH_3)_2]_2 + H_2 \rightarrow L_2Pd_2(OOCCH_3)_3H + CH_3COOH;$$
$$L_2Pd_2(OOCCH_3)_3H \rightarrow Pd_2(CH_3COO)_2L_2 + CH_3COOH;$$
$$Pd_2(CH_3COO)_2L_2 + H_2 \rightarrow Pd_2L_2 + 2CH_3COOH.$$

On interaction with $[LPd(CH_3COO)_2]_2$, the Pd_2L_2 formed leads to $Pd_2(CH_3COO)_2L_2$:

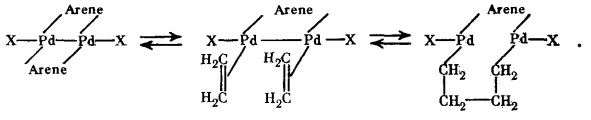
$$Pd_2L_2 + [LPd(CH_3COO)_2]_2 \rightarrow 2Pd_2(CH_3COO)_2L_2 ;$$
$$2Pd_2(CH_3COO)_2L_2 + 2H_2 \rightarrow 2Pd_2L_2 + 4CH_3COOH .$$

It has been established recently that the palladium cluster $Pd_5L'_2$ [$L' = P(C_6H_5)$], active in hydrogenation, is formed from Pd_2L_2 and palladium(II) [22] via the scheme

$$Pd^{II} \rightarrow Pd^{I} \rightarrow Pd_2L_2 \xrightarrow{Pd^{II}} Pd_5L'_2 .$$

Palladium clusters having the composition $\boxed{Si}\begin{matrix}P\\ \diagdown\ \diagup\\ P\end{matrix}Pd_n \cdot (OOCCH_3)_2$ (where n = 2, 3, 4, or 5) and immobilised on the surface have been obtained by the reaction of $Pd(CH_3COO)_2$ with zerovalent palladium on a silica gel surface modified by the diphosphine ligand $\boxed{Si}-P_2$ and also from the complex $[Pd_2(CO)_2(OOCCH_3)_2]_2$ and $\boxed{Si}P_2$.[64] The complex with n = 2 [formally of palladium(I)] resembles closely palladium(I) complexes according to XPE spectroscopy and is converted by triphenylphosphine into the complex $Pd_2(OOCCH_3)_2L_2$ described by Berenblyum et al.[50¶] The immobilised complex with n = 2 catalyses the hydrogenation of cyclopentadiene; the ratio of the rates of hydrogenation of cyclopentadiene and cyclopentene is in the range 0.2–1.[161]

The first information about the catalytic dimerisation of ethylene in solutions of palladium(I) complexes has appeared recently[69]. The aromatic π-complexes $(ArH)_2Pd_2(Al_2Cl_7)_2$ and $(ArH)_2Pd_2(AlCl_4)_2$ in benzene and toluene (ArH = benzene, toluene, or p-xylene) form a mixture of *trans*-but-2-ene (80%) and *cis*-but-2-ene (14–20%) at room temperature at a rate greatly exceeding the rate of dimerisation in palladium(II) solutions (~25 moles of butene per hour per gram-atom of palladium). The catalytic system is stable only in aromatic solvents. A mechanism incorporating a stage involving the oxidative addition of two ethylene molecules to the Pd-Pd bond has been proposed:

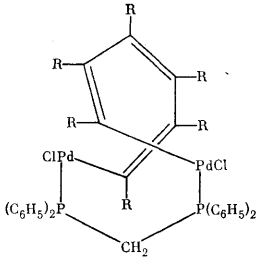


(XX) (XXI) (XXII)

According to Pertici and Vitulli[69], the reaction of compound (XXII) takes place synchronously because palladium atoms promote the transfer of two hydrogen atoms with formation of the primary product—*trans*-but-2-ene.

The possible involvement of palladium(I) complexes also in the polymerisation of propene to polyethylene, catalysed by palladium(II) cyanide, has been suggested[104]. The transfer of hydrogen from one propene molecule to another can take place via a mechanism similar to that of the isomerisation of butene [reaction (17)] on the fragment containing NCPd–PdCN. The available information about the existence of the complex $Pd_2(CN)_6^{4-}$ even in aqueous solutions (see Section III, subsection 3) makes this hypothesis entirely probable.

In connection with the synthesis of the products of the insertion of acetylenes and olefins in a Pd–Pd bond[122], the activity of the complex $Pd_2(dpm)_2Cl_2$ in the cyclotrimerisation of dimethyl acetylenedicarboxylate was tested. The complex proved to the active, like the complex $Pd_2(dpm)_2 \cdot [\mu\text{-}C_2(COOR)_2]Cl_2$, formed under reaction conditions and capable of being an intermediate in the synthesis of hexamethyl mellitate. The reaction takes place at room temperature with formation of 10–13 moles of the product per hour per mole of the complex. The subsequent insertion of three alkyne molecules in the Pd–Pd and Pd–C bonds can lead to the intermediate (XXIII) in which the Pd atoms linked to the bisphosphine ligand are in a position convenient for the reductive elimination reaction with ring closure [like the complex $(RC_2R')_3Co_2(CO)_4$] [163] and the formation of benzene derivatives.



(XXIII)

In conclusion of this Section, we may note that, for the understanding of the mechanisms of a large number of catalytic processes, it is useful to resort to the hypothesis of the involvement of the Pd–Pd cluster bond of palladium(I) complexes in the formation of intermediates compounds in catalytic reactions. The presence of the Pd–Pd fragment in the catalytically active complexes may promote the formation of metal-containing rings with a metal–metal bond and can lead to partial reduction of a number of substrates (CO, RNC, C_2R_2) as a result of their oxidative addition to Pd_2, to the formation of Pd–C bonds as a consequence of the rupture of the Pd–Pd bonds, and to the homolytic rupture of C–H bonds at two centres. Judging from all the considerations, palladium(I) complexes are in general convenient models for the study of catalysis by metal clusters.

* * *

Thus compounds of palladium in the +1 oxidation state constitute a fairly numerous family with a number of structural features associated with the presence of a metal–metal bond. The possibility of the extensive variation of the oxidation-reduction properties of palladium(I) by varying the nature of the ligands is extremely important for catalysis by palladium(I) complexes because the range of variation of the standard electrode potential of the Pd(II)/Pd(I) pair is very large, amounting to ~2.7 V.

The data presented above show that palladium(I) compounds can exist in aqueous, non-aqueous, and non-polar media under different conditions, including high temperatures and in the presence of oxidants (oxygen, *p*-benzoquinone). The appearance of palladium(I) compounds under the conditions of catalytic processes can lead to the operation of unusual mechanisms due to the presence of the Pd–Pd bond.

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Lomonosov Moscow Institute of Fine Chemical Engineering