Journal of Organometallic Chemistry, 65 (1974) 253—266

CHEMISTRY OF DIBENZYLIDENEACETONE—PALLADIUM(0) COMPLEXES

I. NOVEL TRIS(DIBENZYLIDENEACETONE)DIPALLADIUM(SOLVENT) COMPLEXES AND THEIR REACTIONS WITH QUINONES

TOSHINAO UKAI, HIROSHI KAWAZURA** and YOSHIO ISHII*
Department of Synthetic Chemistry, Faculty of Engineering, Nagoya University, Chikusa, Nagoya, 464 (Japan)

J.J. BONNET*** and JAMES A. IBERS
Department of Chemistry, Northwestern University, Evanston, Illinois 60201 (U.S.A.)

(Received April 2nd, 1973; in revised form June 12th, 1973)

Summary

Recrystallization of bis(dibenzylideneacetone)palladium from various solvents affords novel binuclear palladium—dibenzylideneacetone complexes of composition Pd_2(Dibenzylideneacetone)$_3$(Solvent). These new complexes were identified by spectroscopic (IR, NMR, UV, and mass) and thermogravimetric analyses, together with a confirmative crystallographic structure determination. The C=C bonds of a given dibenzylideneacetone ligand coordinate separately to two palladium atoms to yield a binuclear complex in which each palladium atom exhibits trigonal coordination. The Pd—Pd distance is 3.245 Å.

Ligand exchange reactions, oxidative addition reactions, and complex formation reactions with *p*- and *o*-quinones were investigated and found to yield a variety of new organopalladium complexes.

Introduction

In 1970 a novel zerovalent palladium complex, $Pd(DBA)_2$ [DBA: dibenzylideneacetone (PhHC=CHCOCH=CHPh)], was reported [1]. Among the nickel triad, $Ni(COD)_2$ and $Pt(COD)_2$ are well known zerovalent complexes containing an organic ligand. Since $Pd(COD)_2$ is unknown, $Pd(DBA)_2$ is a useful and interesting zerovalent complex. Hitherto, ligands used for the pre-

---

* Address correspondence to this author.

** On leave from Central Laboratory of Japan Synthetic Rubber Co., Ikuta, Kawasaki 214, Japan.

*** On leave from Department de Chimie Inorganique, The University, Toulouse, France.

paration of palladium(0) complexes have been limited to phosphines [2 - 4], phosphites [2], arsines [2], isocyanides [3] and carbon monoxide [5].

Moseley and Maitlis found analogous platinum complexes, $Pt(DBA)_2$ and $Pt(DBA)_3$ [6]. Both groups (Maitlis and Ishii) published papers on the reactions with acetylenic [7,8] and olefinic compounds [9].

In this paper, the preparation of novel binuclear $Pd_2(DBA)_3$(Solvent) complexes and their structural elucidation (IR, NMR, UV, mass, and X-ray diffraction) are reported. Furthermore various reactions of these binuclear complexes are described.

Results and discussions

An attempt to elucidate the structure of $Pd(DBA)_2$ [1] led us to a discovery of novel binuclear palladium complexes. Recrystallization of $Pd(DBA)_2$ in chloroform gives purplish needle-like crystals whose composition shows good agreement with the formula $Pd_2(DBA)_3(CHCl_3)$ (Ia). Use of benzene or toluene as a recrystallization solvent also gives purple crystals satisfying the composition $Pd_2(DBA)_3(C_6H_6)$ (Ib) and $Pd_2(DBA)_3(C_6H_5CH_3)$ (Ic), respectively. In addition a complex with decadeuteriodibenzylideneacetone $(C_6D_5CH{=}CH)_2CO$ (II), and a complex with *p,p'*-dimethoxydibenzylideneacetone, $(p\text{-}CH_3OC_6H_4CH{=}CH)_2CO$ (III), were prepared. Both of these are binuclear. While (III) has no chloroform, (II) does.

Physical characteristics of the complexes (Ia) - (Ic), (II), and (III)

M.p. and elemental analysis of these new complexes are summarized in Table 1. These five complexes appear as deep purple needles, fairly stable in air in the solid state. They decompose gradually in organic solvents to precipitate metallic palladium. The complexes are slightly soluble in CH_2Cl_2, $CHCl_3$, C_6H_6 and THF to give deep violet solutions.

Interconversions between (Ia), (Ib) and (Ic) may be effected through recrystallization from the appropriate solvent. The yield was found to be highest in $CHCl_3$ and lowest in $C_6H_5CH_3$.

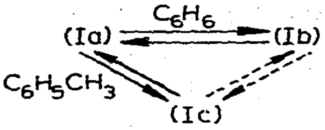


TABLE 1

YIELD, M.P. AND ANALYSIS OF THE COMPLEXES (Ia)—(Ic), (II) AND (III)

Complex	Yield (%)	M.p. (°C dec.)	Analysis found (calcd.) (%) C	H
(Ia)	80	122—124	60.15 (60.34)	4.23 (4.19)[a]
(Ib)	62.5	142—144	68.88 (68.89)	4.92 (4.87)
(Ic)	36	140—141	68.86 (69.12)	5.07 (5.00)
(II)	80	132—133		
(III)	72	141—143	62.59 (62.47)	5.06 (4.97)

[a] (Ia) Cl 10.04 (10.27); O 4.81 (4.64); Pd 20.76 (20.56).

TABLE 2

INFRARED VIBRATIONAL FREQUENCIES (cm^{-1}) OF (Ia) AND (II) [KBr]

(Ia)	DBA	(II)	DBA-d_{10}[a]	Assignment
1620 vs(sh)	1657 m(sh)	1620 m(sh)	1658 m(sh)	ν(C=O)
1614 vs	1651 vs	1615 vs	1651 vs	
	1627 m		1627 m	ν(C=C)
1600 m(sh)	1591 vs(br)	1591 m(sh)	1594 m	ν[C=C(arom.)]
1574 m	1574 s	1550 m		
[975 w(br)]	983 vs	[977 w(br)]	983 vs	δ[CH(trans)]

[a] Decadeuteriodibenzylideneacetone.

Spectroscopic analyses of the complexes (Ia) and (II)

Assignable infrared active vibrational frequencies of (Ia) and (II) are summarized in Table 2 along with those of the corresponding free ligand molecules. Notable differences in the spectra of (Ia) and (II) in comparison with those of dibenzylideneacetone and dibenzylideneacetone-d_{10} may be depicted as follows: a characteristic δ[CH(*trans*)] vibration observed at 983 cm^{-1} in the free ligands disappears almost completely in (Ia) and (II) though a weak broad band appears at a slightly lower frequency (975 cm^{-1} w, br) in both. The CO stretching bands of (Ia) and (II) are shifted about 40 cm^{-1} to lower frequencies compared with those of the free ligands. Although the behavior of the ν(C=C) bands in (Ia) and (II) is uncertain because of accidental masking by the strong CO bands, the spectra, as described, are completely consistent with coordination of DBA to the metal through the C=C moiety.

The incorporation of chloroform in complex (II) was substantiated by the presence of absorption bands of medium intensity at 747 and 766 cm^{-1} [assignable to ν(C—Cl)]. The bands are hidden in the spectrum of (Ia) by strong δ[CH(arom)] absorptions.

Electronic spectra

Electronic absorption maxima of (Ia) and DBA in THF are shown in Table 3 along with a tentative assignment. Both the n—π^* and π—π^* transitions of (Ia) remain unchanged from those of the free ligand. These observations strongly suggest the coordination of the ligand to palladium by its olefinic double bond and not by its carbonyl moiety as suggested by Moseley and Maitlis for $Pd(DBA)_2$ [6].

TABLE 3

ELECTRONIC ABSORPTION MAXIMA (nm) OF (Ia) AND DBA (IN THF)

(Ia)	DBA	Assignment
236 m	234 m	π—π^*
300 (sh)		
321 s	321 s	n—π^*
374 w		C.T.
520 vw		d—d

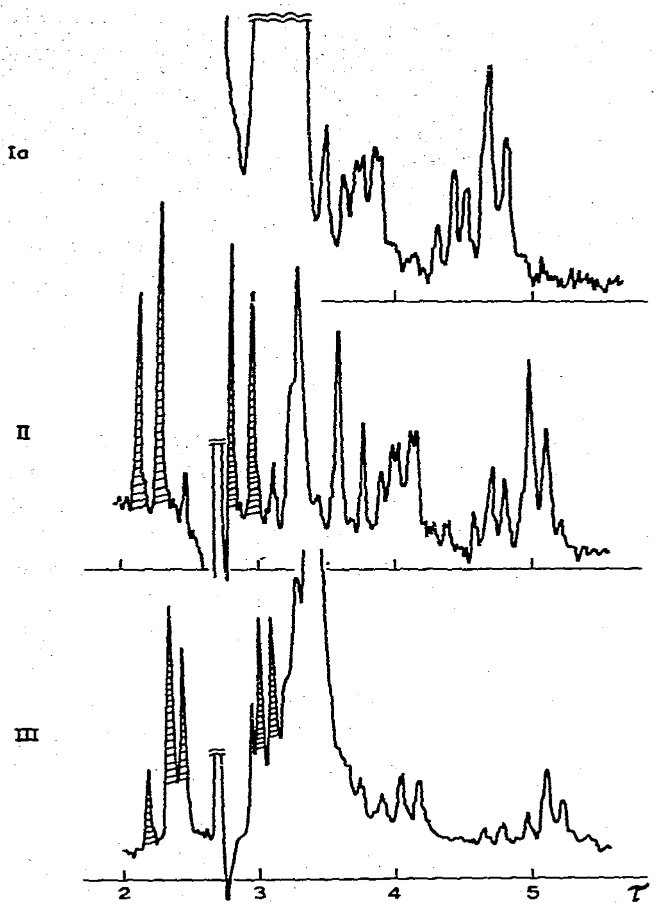


Fig. 1. The ^1H NMR spectra of complexes (Ia), (II) and (III) taken in $CDCl_3$ or CD_2Cl_2. Resonances resulting from the presence of free DBA are cross-hatched.

NMR

^1H NMR spectra of (Ia) were measured in $CDCl_3$ or in CD_2Cl_2 and the interpretation of the spectra was assisted by the availability of ^1H NMR spectra of (II) and (III) in these solvents. Owing to the low solubility of these complexes, repeated scans were necessary in order to obtain comparatively good signal to noise ratios (Fig. 1). During the long time necessary for such repeated scans part of the coordinated DBA was liberated, as is evident from the intensity changes. The resonances resulting from the free ligand are shown as striped lines in Fig. 1.

In the spectrum of (Ia) a multiplet centered at 3.5 τ is the ten ring-proton resonance of the coordinated DBA as confirmed by its disappearance in the spectrum of (II). The eight ring-proton resonance of the coordinated *p*-methoxy-DBA in (III) appears as a multiplet in the same region. Olefinic proton resonances of the coordinated DBA spread over 2.5 to 5.5 τ while, as expected, for the DBA-d_{10} complex (II) the spread is smaller (3.5 to 5.5 τ).

In coordinated DBA the olefinic proton resonances are shifted considerably to high field as are the phenyl ring proton resonances. This observation not only implies an influential role of the olefinic double bond but also a contribution of the phenyl ring to the coordination of dibenzylideneacetone to palladium.

Mass spectra

Mass spectra of the complexes (Ia) and (II) clearly indicate the presence of $CHCl_3$, DBA, and DBA-d_{10} in the complexes as evidenced by the appearance of the fragments $CHCl_2^+$ (*m/e* 83, 85, 87), $CHCl_3^+$ (*m/e* 118, 121), $(C_6H_5\text{-}CH{=}CH)_2CO^+$ (*m/e* 234), and $(C_6D_5CH{=}CH)_2CO^+$ (*m/e* 244).

Mass spectroscopic analyses of the complexes (Ib) and (Ic) were also conducted and gave fragments $C_6H_6^+$ (*m/e* 78) and tropylium cation $C_7H_7^+$ (*m/e* 91), respectively, which are indicative of the presence of C_6H_6 in (Ib) and of $C_6H_5CH_3$ in (Ic).

Thermogravimetric analysis

The results of a thermogravimetric analysis of (Ia) in air indicate that the complex loses weight in steps. The first decrease of about 12% of the total weight corresponds to liberation of $CHCl_3$; the second decrement amounts to 46%, exactly corresponding to loss of two DBA molecules in the complex; and the third step, though rather gentle, may be interpreted as liberation of the final DBA ligand. A final plateau at about 24.3% is attributed to formation of palladium oxide.

X-ray structural analysis of the complex (Ia)

$Pd_2(DBA)_3(CHCl_3)$ (Ia) crystallizes in space group $C_{2h}{}^5$—$P2_1/c$ of the monoclinic system with four formula units in a cell of dimensions: *a* 13.536(3), *b* 13.474(2), *c* 25.415(4) Å, β 109.5(1)°. Intensity data were collected on a FACS-1 automatic x-ray diffractometer out to 2θ(Cu-K_α) 106°. A total of 3819 unique reflections having $F_o{}^2 > 3\sigma(F_o{}^2)$ were obtained and were corrected for the effects of absorption. The structure was solved by standard methods and refined by full-matrix least-squares techniques to a final conventional *R* index of 6.7%.

The molecular structure of (Ia) is shown in Fig. 2. The binuclear complex consists of two Pd atoms (Pd—Pd 3.245 Å) bridged by the three DBA molecules. Coordination of the Pd atoms to these DBA molecules is through the C=C olefin portions of the ligands. The coordination about Pd is trigonal if one considers only the centers of the double bonds. Average distances in the molecule are Pd—C 2.25(1); C=C 1.20(3); C—C 1.54(2) and C=O 1.19(4) Å. The Pd—C distances are approximately 0.15 Å longer than in typical Pt—olefin π-complexes. The extreme shortness of the C=C distance is most surprising, and may be partially the result of the foreshortening of these bonds through excessive thermal motion.

Independently, Mazza and Pierpont [10] have carried out a structural

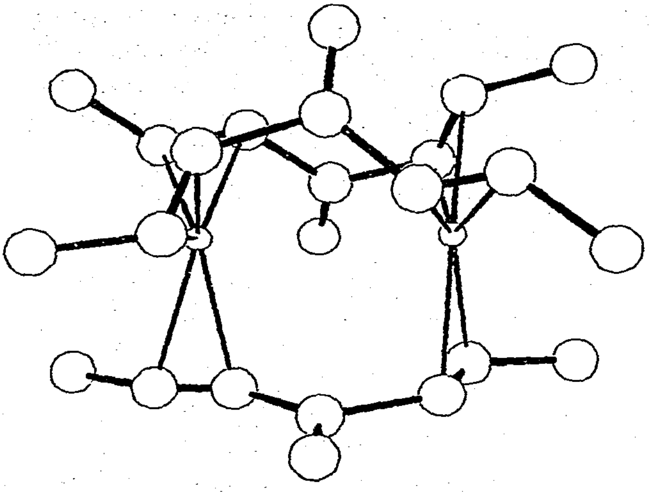


Fig 2. A drawing of the $Pd_2(DBA)_3$ molecule, showing the *s-cis, s-trans* conformation of each of the DBA ligands. Only the α-C atoms of the phenyl rings are shown. The H atoms are omitted for the sake of clarity.

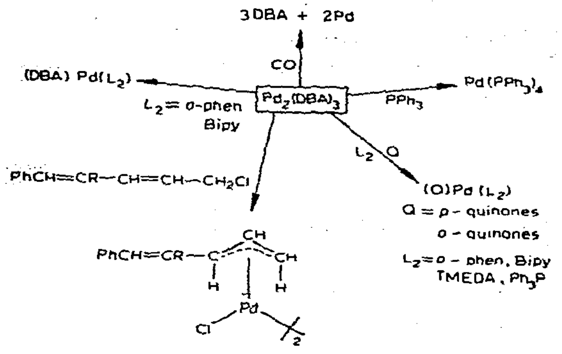
study of $Pd_2(DBA)_3 \cdot CH_2Cl_2$. The structure of the $Pd_2(DBA)_3$ molecule is essentially that reported here, the major difference being that Mazza and Pierpont find two DBA molecules in the *s-cis, s-trans* conformation and one in the more symmetric *s-cis, s-cis* conformation, whereas we find all three to be in the *s-cis, s-trans* conformation (Fig. 2). Mazza and Pierpont find a more reasonable value of 1.36(2) Å for the C=C distance upon application of approximate corrections for vibrational disorder in some instances. Their Pd—Pd distance of 3.240(2) Å is in excellent agreement with the value of 3.245(2) Å found here. Thus while a change of solvent from $CHCl_3$ to CH_2Cl_2 results in a change in conformation of one of the DBA ligands, it has little effect on the bond distances within the molecule.

Discussion of the structure of $Pd_2(DBA)_3 \cdot$Solvent

The spectral and X-ray evidence presented here leaves no doubt that $Pd_2(DBA)_3 \cdot$Solvent is formed under the conditions noted and that the bonding of the DBA ligands to the Pd is through the olefinic double bonds. Moseley and Maitlis [6] have suggested that coordination of DBA is through the carbonyl group in $Pd(DBA)_2$. This interpretation may not be valid as the composition of the Pd complex appears to be markedly solvent dependent. Thus there is the possibility of dissociation of the complex in $CHCl_3$. Moreover, the low-frequency shift of about 40 cm^{-1} in ν(C=O) seems rather small for CO coordination when compared with a shift of about 150 cm^{-1} for metal—CO coordination in $Mo(CO)_2(Acrolein)_2$ [11].

We have re-examined the IR and electronic spectra and find almost the same spectral patterns from $Pd(DBA)_2$ [1] as those from complex (Ia), except for a superposition of free DBA bands on the spectra. Since various solvents appear to crystallize easily with $Pd_2(DBA)_3$ we suggest that a DBA solvent of crystallization is a distinct possibility, leading to the characterization of $Pd(DBA)_2$ [1] as $Pd_2(DBA)_3 \cdot DBA$.

SCHEME 1
REACTIONS OF $Pd_2(DBA)_3$



Reactions of $Pd_2(DBA)_3$

The new binuclear palladium(0) complexes $Pd_2(DBA)_3$(Solvent), (Ia), (Ib), (Ic) and (III) have the same reactivity patterns reported earlier for $Pd(DBA)_2$ [1]. Shown in Scheme 1 are the reactions of $Pd_2(DBA)_3$ with carbon monoxide (decomposition into Pd and DBA), with triphenylphosphine or with Bipy, with *o*-Phen (ligand exchange reaction), with allylic halides (oxidative addition reaction), and with *p*- and *o*-quinones.

Ligand exchange reactions

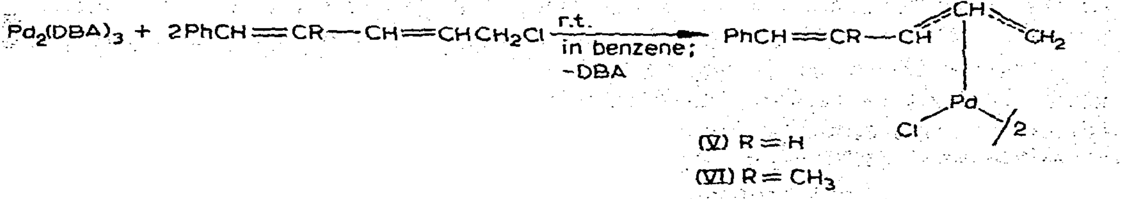
The reaction of (Ia) with carbon monoxide (DBA was recovered quantitatively) and the reaction with excess of PPh_3 in benzene at room temperature under nitrogen to give $(Ph_3P)_4Pd^0$ in high yield are consistent with the π-bonding of the DBA ligand to the Pd atom.

In the reaction between (Ia) and a large excess of Bipy in acetone yellow-orange coloured crystals of the complex (DBA)Pd(Bipy) (IV), m.p. 135° dec. in 87% yield, were obtained. The complex (IV) is unstable in air and decomposes in a few days.

Analogous complexes were prepared: (DBA)Pd(*o*-Phen)(H_2O), (DBA)Pd(Bipy)(Acetone), (DBA-d_{10})Pd(Bipy)(Acetone), and (DBA-d_{10})Pd(*o*-Phen)(H_2O).

Oxidative addition reactions

Into a benzene suspension of (Ia), excess 1-chloro-5-phenyl-2,4-pentadiene was added, and the reaction at room temperature under nitrogen gives free DBA and a yellowish π-allylic complex (V), dec. 195 - 197° in 85% yield.



(V) R = H
(VI) R = CH_3

By reaction with Tl(Acac), (V) was converted into the Acac derivative of (V), m.p. 128 - 130° dec. in 77% yield. This complex is soluble in $CHCl_3$ and C_6H_6 and was identified by its NMR spectrum.

With 1-chloro-4-methyl-5-phenyl-2,4-pentadiene the corresponding π-allylic chloro complex (VI) (yellow, m.p. 171 - 174°, 76% yield) and Acac derivative (yellow-orange, m.p. 96 - 97° dec., 61% yield) were obtained.

Preparation of palladium—p-quinone—ligand complexes

Schrauzer prepared a number of Ni^0—duroquinone complexes [12]. Takahashi and Hagiwara prepared $(Ph_3P)_2Pd(p\text{-}Q)$ complexes in the reactions of $Pd(PPh_3)_4$ with *p*-benzoquinone and 1,4-naphthoquinone in benzene [13].

$Pd_2(DBA)_3$ has been found to be an excellent starting material for the preparation of Pd—*p*-quinone π-coordinated complexes. When an acetone suspension of (Ia) is treated with *p*-quinone (Q)(*p*-benzoquinone, duroquinone, 1,4-naphthoquinone, and 2-methyl-1,4-naphthoquinone) at room temperature under nitrogen, the complexes $(Q)PdL_2$ (VII) crystallize in good yield.

$$Pd_2(DBA)_3 + 4L + 2Q \xrightarrow[RT]{N_2} 2\underset{(VII)}{(Q)PdL_2} + 3DBA$$

The complexes (VII) with *o*-Phen or Bipy ligand are obtained as yellow-red crystals. The complexes are stable in the solid state. With the exception of duroquinone complexes with TMEDA they are also stable in solution.

Quinone—Pd—PPh_3 complexes (*p*-benzoquinone and 1,4-naphthoquinone) have already been reported [13]. However they are prepared more readily and with higher purity and yield by the method outlined here.

Yield, m.p., colour and $\Delta\nu(CO)$ of the complexes (VII) are tabulated in Table 4. Also in Table 4 values of $\Delta\nu(CO)$, the carbonyl stretching frequency of the coordinated quinone ligand compared with that of the free quinone, are tabulated. Generally a 30 - 100 cm^{-1} shift of $\nu(CO)$ to lower frequencies is observed. These values may be compared with $\Delta\nu(CO)$ (36, 31 cm^{-1}) of π-olefinic—Pd complexes $(Ph_3P)_2Pd(Olefin)$ (Olefin: dimethyl fumarate, dimethyl maleate) and $\Delta\nu(CO)$ (76 cm^{-1}) of (Duroquinone)Ni(COT) [14] and are very different from $\Delta\nu(CO)$ (150 cm^{-1}) observed for oxygen coordination to the metal atom in $Mo(CO)_2(Acrolein)_2$ [11]. Therefore, it seems likely that the coordination of *p*-quinones to the Pd atom involves the olefinic double bonds and not the carbonyl moiety.

The order of $\Delta\nu(CO)$ (TMEDA > Bipy ⩾ *o*-Phen > Ph_3P) reflects the polarity of the carbonyl group of the quinone ligand in the complexes (VII). The higher $\Delta\nu(CO)$ value indicates greater polarity.

In the NMR spectra of these complexes (VII) (in $CDCl_3$), olefin protons of the quinone ligands show a high field shift, for example 1.34 τ (TMEDA) and 0.71 τ(Bipy) in $(BQ)PdL_2$. Such shifts are consistent with the coordination of *p*-benzoquinone to Pd as a diolefin. The protons adjacent to the nitrogen atoms of Bipy and *o*-Phen ligands in (VII) show a low field shift (0.2 - 0.3 τ) consistent with coordination of the nitrogen atoms of the ligands to the Pd atom. In the NMR spectra of (NQ)Pd(TMEDA) and (K_3)Pd(TMEDA) complexes, the *N*-methyl protons of the TMEDA ligand appear as two (NQ) and

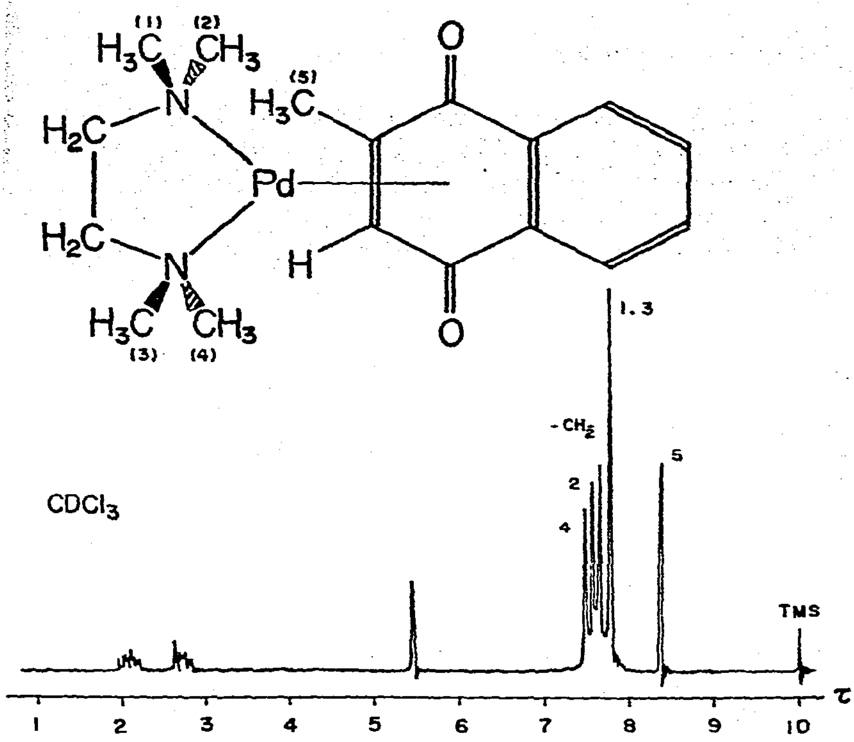


Fig 3. The NMR spectrum and proposed structure of $(K_3)Pd(TMEDA)$.

three (K_3) peaks, respectively. This indicates the nonequivalence of two methyl groups on a nitrogen atom of TMEDA and restricted free rotation because of the coordination of the N atom to Pd. The NMR spectrum and molecular structure derived for (K_3)Pd(TMEDA) are depicted in Fig. 3.

TABLE 4

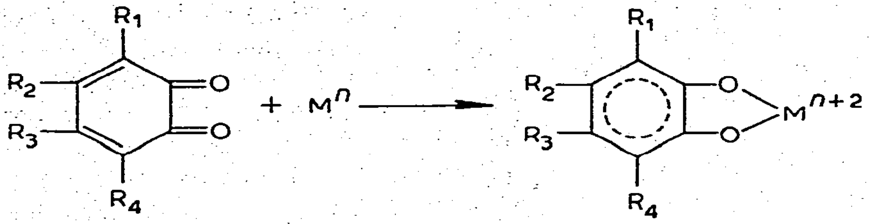
YIELD AND PHYSICAL PROPERTIES OF THE QUINONE COMPLEXES (VII)

Complex[a]	Yield (%)	M.p.(dec.)	Colour	$\Delta\nu$(CO) (cm^{-1})
BQ				(1662, 1647)
(BQ)Pd(*o*-Phen)	90	240	Ruby-red	51
(BQ)Pd(Bipy)	94	190	Red-orange	56
(BQ)Pd(TMEDA)	76	133—135	Red	(65)
$(BQ)Pd(PPh_3)_2$	92	155—157	Dark red	35
DQ				(1637)
$(DQ)Pd(o\text{-Phen})(H_2O)$	85	205	Deep red	112
(DQ)Pd(Bipy)	85	210	Deep red	75
(DQ)Pd(TMEDA)	59	130	Brown-red	95
NQ				(1662)
(NQ)Pd(o-Phen)	95	285	Orange	60
(NQ)Pd(Bipy)	84	215	Yellow-orange	61
(NQ)Pd(TMEDA)	89	130—132	Ruby-red	62
$(NQ)Pd(PPh_3)_2$	86	161—163	Red-orange	21
K_3				(1668)
$(K_3)Pd(o\text{-Phen})(H_2O)$	85	235	Orange	81
$(K_3)Pd(Bipy)$	85	225	Yellow-orange	72
$(K_3)Pd(TMEDA)$	58	138—140	Yellow-orange	74
$(K_3)Pd(PPh_3)_2$	77	128—130		37

[a] BQ *p*-benzoquinone; DQ duroquinone; NQ 1,4-naphthoquinone and K_3 2-methyl-1,4-naphthoquinone.

Preparation of Pd—o-quinone complexes

There is an extensive literature on oxidative addition reactions of low valent metal complexes [15 - 18]. Among these, oxidative addition reactions of tetrachloro-1,2-benzoquinone with $M^0(PPh_3)_4$ (M = Pt, Pd), $M^I(CO)Cl(PPh_3)_2$ (M = Rh, Ir) [19] and *trans*-$Ru(CO)_3(PPh_3)_2$ as well as that of 9,10-phenanthrenequinone with $Ir(CO)Cl(PPh_3)_2$ [21] are well established. In general, the reaction scheme is:



We find reactions between (Ia) and *o*-quinones in the presence of ligand afford new *o*-quinone—Pd complexes, such as (*o*-Q)PdL_2. When an N-donor ligand (*o*-Phen, Bipy, TMEDA, and Py) was added to an acetone suspension of (Ia), the colour of the solution changed to yellow. Then the addition of *o*-quinone caused a sudden colour change of the solution, and the crystallization of the *o*-quinone—Pd complex. Yield and physical properties of (*o*-Q)PdL_2 (VIII) are shown in Table 5. These complexes are stable in the solid state, but decompose in solution in air. The strong ν(CO) (1650 - 1700 cm^{-1}) band of the original *o*-quinones disappears in all (VIII), and a characteristic *o*-diolato absorption band emerges. Therefore, it seems that contrary to the π-olefin—Pd complexes of *p*-quinone, the two carbonyl oxygen atoms of *o*-quinone (pseudo-butadiene structure) coordinate to the Pd atom.

TABLE 5

YIELD AND PHYSICAL PROPERTIES OF THE COMPLEXES (VIII)[a]

Complex	Color	Yield (%)	M.p. (°C) (dec.)
(9,10-PQ)Pd(*o*-Phen)	Blue	95	300 <
(9,10-PQ)Pd(Bipy)	Green	97	300 <
(9,10-PQ)Pd$(Py)_2$	Yellow	88	210—218
(9,10-PQ)Pd(TMEDA)	Yellow	89	145—150
(1,2-NQ)Pd(*o*-Phen)	Blue	91	300 <
(1,2-NQ)Pd(Bipy)	Blue	81	300 <
(4,5-MeO-1,2-BQ)Pd(*o*-Phen)	Blue	95	≈ 284
(4,5-MeO-1,2-BQ)Pd(Bipy)	Blue	98	≈ 250
(4,5-MeO-1,2-BQ)Pd$(Py)_2$	Yellow-brown	80	≈ 155
(4-t-Bu-1,2-BQ)Pd(*o*-Phen)	Blue-violet	83	300 <
(4-t-Bu-1,2-BQ)Pd(Bipy)	Violet	91	300 <
(4-t-Bu-1,2-BQ)Pd$(Py)_2$	Purple	52	≈ 165

[a] 9,10-PQ 9,10-phenanthrenequinone; 1,2-NQ 1,2-naphthoquinone; 4,5-MeO-1,2-BQ 4,5-dimethoxy-1,2-benzoquinone; 4-t-Bu-1,2-BQ 4-tert-butyl-1,2-benzoquinone.

Experimental

Materials

Dibenzylideneacetone (DBA) was prepared by a condensation of acetone and benzaldehyde [22]. The analogous decadeuterio-DBA and *p,p'*-dimethoxy-DBA were also prepared by the same method by using the corresponding aldehyde. DBA-d_{10}: m.p. 102 - 104°, 91% yield. Commercial guaranteed grade $PdCl_2$ was used without any purification.

Preparations of the binuclear complexes

Tris(dibenzylideneacetone)dipalladium(chloroform) (Ia). Palladium chloride, 1.05 g (5.92 mmole), was added to hot (ca. 50°) methanol, 150 ml, containing DBA 4.60 g (19.6 mmole) and sodium acetate 3.90 g (47.5 mmole). The mixture was stirred for 4 h at 40° to give a reddish-purple precipitate and allowed to cool to complete the precipitation. The precipitate was removed by filtration, washed successively with water and acetone and dried in vacuo. The precipitate, 3.39 g, was dissolved in hot chloroform, 120 ml, and filtered to give a deep violet solution. To the solution, diethyl ether, 170 ml, was added slowly. Deep purple needles precipitated. These were removed by filtration, washed with diethyl ether, and dried in vacuo. The complex (Ia), m.p. 122 - 124° dec., satisfying the composition $Pd_2(DBA)_3(CHCl_3)$ was obtained in 80% yield.

Tris(dibenzylideneacetone)dipalladium(benzene) (Ib). As the recrystallization solvent in the above procedure benzene was used instead of chloroform to give a similar deep-violet needle-like crystalline complex (Ib), m.p. 142 - 144° dec., satisfying the composition $Pd_2(DBA)_3(C_6H_6)$. The compound was obtained in 62.5% yield.

Tris(dibenzylideneacetone)dipalladium(toluene) (Ic). Toluene as a recrystallization solvent gave a similar deep violet needle-like crystalline complex (Ic), m.p. 140 - 141° dec., satisfying the composition $Pd_2(DBA)_3(C_6H_5CH_3)$. It was obtained in 36.0% yield.

Tris(decadeuteriodibenzylideneacetone)dipalladium(chloroform) (II). By a method similar to that used to prepare (Ia), deep violet needle-like crystalline complex (II), m.p. 132 - 133° dec., satisfying the composition $Pd_2(DBA\text{-}d_{10})_3$-$(CHCl_3)$ was obtained in 80% yield.

Tris(p,p'-dimethoxy-DBA)dipalladium (III). Also by the similar method, deep violet needle-like crystalline complex (III), m.p. 141 - 143° dec., satisfying the composition Pd_2(*p,p'*-dimethoxy-DBA)$_3$ was obtained in 72.3% yield.

Physico-chemical measurements

Electronic, infrared, NMR, and mass spectra were measured by using

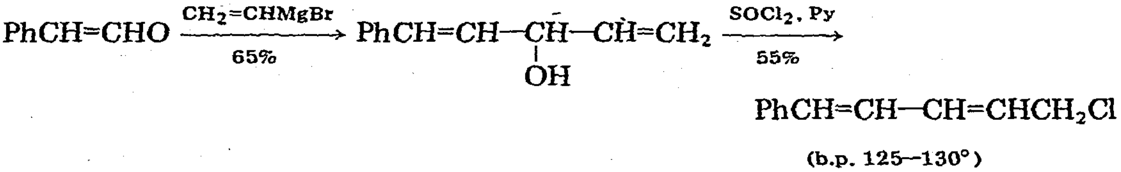
Hitachi Model 124, Jasco Model 403-G, Jeol Model HA-100 with S/N booster, and Hitachi Model RMS-4 instruments, respectively. Thermogravimetric analysis was carried out using a Kahn Electrobalance. X-ray structural analysis was carried out using a FACS-1 automatic X-ray diffractometer.

Reactions of $Pd_2(DBA)_3(CHCl_3)$complex (Ia).

Ligand exchange reactions. The dark red coloured suspension of (Ia) (48.5 mmole) and PPh_3 (779 mmole) in benzene gave yellowish crystals. After purification by washing with benzene and then ether, the complex $(Ph_3P)_4Pd^0$ was obtained in 82% yield.

The reaction of (Ia) (1.05 mmole) with Bipy (10 mmole) at RT under N_2 in ether took place with the precipitation of yellow-orange coloured crystals of the complex (DBA)Pd(Bipy) (IV), m.p. $>$ 135° dec. in 87% yield. (Found: C, 65.11; H, 4.55; N, 5.68. Calcd.: C, 65.27; H, 4.46; N, 5.64%.) When acetone was used as a solvent, a complex (DBA)Pd(Bipy)(acetone), m.p. 110°, was obtained in 71% yield.

Oxidative addition reactions. The preparation of 1-chloro-5-phenyl-2,4-pentadiene was carried out as follows:



$$PhCH{=}CHO \xrightarrow[65\%]{CH_2{=}CHMgBr} PhCH{=}CH{-}\underset{OH}{CH}{-}CH{=}CH_2 \xrightarrow[55\%]{SOCl_2,\ Py} PhCH{=}CH{-}CH{=}CHCH_2Cl$$

(b.p. 125—130°)

To a benzene suspension of (Ia) (1.00 g) $PhCH{=}CH{-}CH{=}CHCH_2Cl$ (0.36 g) was added at RT under N_2, and after 24 h an 85% yield of the complex (V), m.p. 195 - 197°, was obtained. Because of its extremely low solubility in organic solvents, recrystallization of (V) was unsuccessful. $PhCH{=}C(CH_3){-}CH{=}CHCH_2Cl$ was prepared similarly, and the corresponding complex (VI) (yellow, m.p. 171 - 174°, 76% yield) was obtained.

Preparation of palladium—p-quinone complexes (VII)

Preparation of p-quinones. *p*-Benzoquinone, 1,4-naphthoquinone, and 2-methyl-1,4-naphthoquinone used were guaranteed grade reagents. Duroquinone was prepared by a literature method [23], starting from nitration of durene, in a yield of 35% (overall).

Preparation of (quinone)PdL_2 (VII) complexes. As an example, the preparation of (BQ)Pd(*o*-Phen), m.p. 240° dec., is described. To an acetone suspension of (Ia), *o*-phenanthroline was added at RT under N_2, and when the colour of the solution became yellow addition of *p*-benzoquinone in acetone caused the crystallization of ruby-red needle-like crystals. After recrystallization from chloroform/acetone, 90% yield of the complex was obtained. (Found: C, 58.78; H, 3.29; N, 6.38. Calcd.: C, 59.41; H, 3.17; N, 6.30%.) IR;

ν(CO) 1610, 1597 cm^{-1} and NMR ($CDCl_3$) 4.20 (s,4) (coordinated quinone ligand) [free Q 3.35 (s)], 2.23 (q,2), 2.11 (s,2), 1.56 (dd,2) and 1.15(dd,2)τ (coordinated *o*-Phen).

Analyses of other (VII) complexes. (BQ)Pd(Bipy): (Found: C, 51.68; H, 3.31; N, 7.52. Calcd.: C, 51.84; H, 3.26; N, 7.56%.) *(DQ)Pd(o-Phen)*(H_2O). (Found: C, 56.88; H, 4.77; N, 5.98. Calcd.: C, 56.36; H, 4.73; N, 5.98%.) *(DQ)Pd(Bipy).* (Found: C, 55.91; H, 4.74; N, 6.57. Calcd.: C, 56.29; H, 4.72; N, 6.56%.) *(NQ)Pd(o-Phen).* (Found: C, 59.07; H, 3.30; N, 6.23. Calcd.: C, 59.41; H, 3.17; N, 6.30%.) *(NQ)Pd(Bipy).* (Found: C, 56.82; H, 3.45; N, 6.68. Calcd.: C, 57.09; H, 3.35; N, 6.66%.) *(NQ)Pd(TMEDA).* (Found: C, 50.17; H, 5.79; N, 7.21. Calcd.: C, 50.47; H, 5.83; N, 7.36%.) *(K_3)Pd(Bipy).* (Found: C, 57.51; H, 3.76; N, 6.47. Calcd.: C, 58.01; H, 3.71; N, 6.44%.) *(K_3)Pd(o-Phen)(H_2O).* (Found: C, 57.56; H, 3.53; N, 5.75. Calcd.: C, 57.94; H, 3.80; N, 5.87%.) *(K_3)Pd(PPh_3)$_2$.* (Found: C, 70.05; H, 4.81. Calcd.: C, 70.29; H, 4.77%.)

Preparation of palladium—o-quinone complexes (VIII)

Preparation of o-quinones. Both of the quinones, 1,2-naphthoquinone and 9,10-phenanthrenequinone, were recrystallized from commercial reagents. 4-tert-Butyl-*o*-benzoquinone was synthesized by Fremy's salt oxidation of *p*-tert-butylphenol, m.p. 65 - 66°, 73% yield [24]. 4,5-Dimethoxy-1,2-benzoquinone, m.p. 234 - 235°, was prepared by Wanzlick and Jahnke's method [25].

Preparation of palladium—o-quinone complexes (VIII). When the colour of the solution [*o*-Phen was added to an acetone suspension of (Ia) under N_2] became yellowish, the addition of 9,10-phenanthrenequinone changed instantaneously the colour of the solution to green, and 24 h later bluish crystals precipitated. The complex (9,10-phenanthrenequinone)Pd(*o*-Phen), m.p. > 300° was obtained. (Found: C, 62.14; H, 3.49; N, 5.74. Calcd.: C, 63.11; H, 3.26; N, 5.66%.)

As shown in Table 5, twelve complexes (VIII) were obtained in good yield. Analyses of them are given here. *(9,10-PQ)Pd(Bipy).* (Found: C, 59.52; H, 3.66; N, 5.76. Calcd.: C, 61.33; H, 3.43; N, 5.95%.) *(9,10-PQ)Pd(Py)$_2$.* (Found: C, 60.95; H, 3.85; N, 5.87. Calcd.: C, 60.97; H, 3.84; N, 5.92%.) *(9,10-PQ)Pd(TMEDA).* (Found: C, 54.25; H, 5.39; N, 6.40. Calcd.: C, 55.76; H, 5.62; N, 6.50%.) *(1,2-NQ)Pd(o-Phen).* (Found: C, 58.61; H, 3.46; N, 6.22%.) *(1,2-NQ)Pd(Bipy).* (Found: C, 56.57; H, 3.41; N, 6.64. Calcd.: C, 57.10; H, 3.35; N, 6.66%.) *(4,5-MeO-1,2-BQ)Pd(o-Phen).* (Found: C, 50.47; H, 3.52; N, 5.89. Calcd.: C, 52.82; H, 3.55; N, 6.16%.) *(4,5-MeO-1,2-BQ)Pd(Bipy).* (Found: C, 49.68; H, 3.74; N, 6.18. Calcd.: C, 50.19; H, 3.77; N, 6.50%.) *(4,5-MeO-1,2-BQ)Pd(Py)$_2$.* (Found: C, 49.98; H, 4.28; N, 6.48. Calcd.: C, 49.96; H, 4.19; N, 6.47%.) *(4-t-Bu-1,2-BQ)Pd(o-Phen).* (Found: C, 59.20; H, 3.20; N, 6.42. Calcd.: C, 59.41; H, 3.17; N, 6.30%.) *(4-t-Bu-1,2-BQ)Pd(Bipy).* (Found: C, 56.12; H, 4.75; N, 6.63. Calcd.: C, 56.29; H, 4.72; N, 6.56%.) *(4-t-Bu-1,2-BQ)Pd(Py)$_2$.* (Found: C, 54.90; H, 5.19; N, 6.44. Calcd.: C, 56.02; H, 5.17; N, 6.53%.)

Acknowledgements

Y.I. is indebted to Ministry of Education in Japan for financial support. J.J.B. is indebted to the North Atlantic Treaty Organization for a Fellowship which made his stay at Northwestern University possible. Part of this research was supported by the U.S. National Science Foundation.

References

1 Y. Takahashi, Ts. Ito, S. Sakai and Y. Ishii, J. Chem. Soc. D, (1970) 1065.
2 L. Malatesta and N. Angoletta, J. Chem. Soc., (1957) 1186.
3 E.O. Fischer and H. Werner, Chem. Ber., 95 (1962) 703.
4 S. Takahashi, K. Sonogashira and N. Hagiwara, J. Chem. Soc. Jap., 87 (1966) 610.
5 A. Misono, Y. Uchida, M. Hidai and K. Kudo, J. Organometal. Chem., 20 (1969) 7.
6 K. Moseley and P.M. Maitlis, J. Chem. Soc. D, (1971) 982.
7 K. Moseley and P.M. Maitlis, J. Chem. Soc. D, (1971) 1604.
8 Ts. Ito, S. Hasegawa, Y. Takahashi and Y. Ishii, J. Chem. Soc., Chem. Commun., (1972) 629.
9 Ts. Ito, Y. Takahashi and Y. Ishii, J. Chem. Soc., Chem. Commun., (1972) 629.
10 M.C. Mazza and C.G. Pierpont, J. Chem. Soc., Chem. Commun., (1973) 207.
We are indebted to Prof. Pierpont for a preprint of this work. See also C.G. Pierpont and M.C. Mazza, abstract INORG-74, 165th A.C.S. Meeting, Dallas, Texas, April, 1973.
11 D.P. Tate, A.A. Buss, I.M. Augl, B.L. Ross, J.G. Grasselli, W.H. Ritchey and F.J. Knoll, Inorg. Chem., 4 (1965) 1323.
12 G.N. Schrauzer, Advan. Organometal. Chem., 2 (1964) 17.
13 S. Takahashi and N. Hagiwara, J. Chem. Soc. Jap., 88 (1967) 1306.
14 G.N. Schrauzer and H. Thyret, Z. Naturforsch. B, 16 (1961) 353; B, 17 (1962) 73.
15 J.P. Collman and W.R. Roper, Advan. Organometal. Chem., 7 (1968) 53.
16 J.P. Collman, Accounts Chem. Res., 1 (1968) 136.
17 L. Vaska, Accounts Chem. Res., 1 (1968) 335.
18 J. Halpern, Accounts Chem. Res., 3 (1970) 386.
19 Y.S. Sohn and A.L. Balch, J. Amer. Chem. Soc., 93 (1971) 1290; 94 (1972) 1144.
20 A.L. Balch and Y.S. Sohn, J. Organometal. Chem., 30 (1971) C31.
21 J.S. Valentine and D. Valentine, Jr., J. Amer. Chem. Soc., 92 (1970) 5795.
22 C.R. Conard and M.A. Dolliver, Org. Syn., Coll. Vol. 2, John Wiley, p. 167.
23 L.I. Smith, Org. Synth., Coll. Vol. 2, John Wiley, p. 254.
24 H.J. Teuber and G. Staiger, Chem. Ber., 88 (1955) 802;
R.P. Singh, Can. J. Chem., 44 (1966) 1994.
25 H.W. Wanzlick and U. Jahnke, Chem. Ber., 101 (1968) 3744.