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NOVEL TRINUCLEAR PALLADIUM(0) COMPLEXES: TRIS(TRIBENZYLIDENEACETYLACETONE)TRIPALLADIUM(SOLVENT) COMPLEXES AND THEIR REACTIONS

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Summary

In an extension of our studies on palladium(0)—dibenzylideneacetone complexes, novel trinuclear palladium complexes with three molecules of tribenzylideneacetylacetone have been obtained and identified by elemental and spectroscopic analyses (IR, UV and NMR).

Ligand exchange reactions, oxidative addition reactions and complex formation reactions with maleic anhydride, dimethyl acetylenedicarboxylate and *para*-quinones were investigated. These were found to be similar to those of palladium(0)—dibenzylideneacetone complexes.

Introduction

Since our first introduction of a new zerovalent palladium complex "Pd-(DBA)$_2$" [DBA = dibenzylideneacetone, (PhCH=CH)$_2$CO] in 1970 [1], a number of papers on preparation and reactions of the similar complexes containing the DBA ligand have been published. Moseley and Maitlis [2] found analogous complexes, Pt(DBA)$_2$ and Pt(DBA)$_3$. Maitlis and Lee [3] obtained a rhodium—DBA complex such as (h^5-cyclo-Me$_5$C$_5$)Rh(h^4-DBA). Recrystallization of "Pd(DBA)$_2$" from solvent (chloroform, methylene chloride, benzene, toluene) afforded complexes of binuclear structure of type Pd$_2$(DBA)$_3$(solvent). The structure of Pd$_2$(DBA)$_3$(CHCl$_3$) was determined by Bonnet and Ibers [4], and that of Pd$_2$(DBA)$_3$(CH$_2$Cl$_2$) by Mazza and Pierpont [5]. The latter published the structure of Pd(DBA)$_3$ [6], which was obtained by the reaction of an excess of DBA with Pd$_2$(DBA)$_3$.

These palladium—DBA complexes are useful and interesting zerovalent complexes in which only an organic ligand is coordinated to a palladium atom. They are relatively stable in air, in contrast to Pd(CO)$_4$ or Pd(1,5-COD)$_2$ (COD =

TABLE 1

YIELDS, MELTING POINTS AND ANALYSES OF THREE COMPLEXES (Ia)—(Ic)

Complex		Yield (%)	M.p. (°C dec.)	Analysis: Found (calcd.) (%)	
				C	H
$Pd_3(TBAA)_3 \cdot CHCl_3$	(Ia)	84	133—135	61.77(61.94)	4.06(4.01) [a]
$Pd_3(TBAA)_3 \cdot CH_2Cl_2$	(Ib)	80	142—144	62.87(63.37)	4.51(4.17)
$Pd_3(TBAA)_3 \cdot C_6H_6$	(Ic)	79	154—155	67.48(67.68)	4.63(4.46) [b]

[a] (Ia) Pd, 20.45(20.84); Cl, 6.79(6.94). [b] (Ic) Pd, 22.04(21.41).

cyclooctadiene). Both groups (Maitlis and Ishii) have reported concerning reactions of Pd—DBA complexes with acetylenic [7, 8] and olefinic compounds [9]. Extensive studies of the reactions between $Pd_2(DBA)_3$ complexes and *para*- or *ortho*-quinones have been carried out in our Laboratory [4].

In this paper, the preparation of a new type of complex, the trinuclear $Pd_3(TBAA)_3$(solvent), in which TBAA is tribenzylideneacetylacetone, and their reactions are presented.

Results and discussions

(a) Preparation of tripalladium—tribenzylideneacetylacetone complexes

Tribenzylideneacetylacetone (TBAA) [PhCH=CHCOC(COCH=CHPh)=CHPh], m.p. 112—113°, was prepared in 70% yield by the alkaline condensation of three moles of benzaldehyde with acetylacetone. TBAA is a trienedione compound and has two DBA units in one molecule.

The reaction between TBAA and $PdCl_2$ in methanol in the presence of sodium acetate gave a deep purple crystalline complex in 92% yield. Recrystallization of the crude complex from chloroform gave purplish needle-like crystals whose composition showed good agreement with the formula $Pd_3(TBAA)_3(CHCl_3)$ (Ia). Use of methylene chloride or benzene as recrystallization solvent gave purple-colored crystals satisfying the composition $Pd_3(TBAA)_3(CH_2Cl_2)$ (Ib) and $Pd_3(TBAA)_3(C_6H_6)$ (Ic), respectively. Yield, m.p. and elemental analyses of these new complexes (Ia)—(Ic) are summarized in Table 1.

Interconversions among (Ia), (Ib) and (Ic) can be effected through recrystallization from the appropriate solvent. These three complexes are fairly stable in air and in the solid state. They are slightly soluble in CH_2Cl_2, $CHCl_3$, C_6H_6 and THF to give deep violet solutions. Cryoscopic molecular weight determination of (Ia) in benzene (found 1590, calcd. 1533) confirmed the trinuclear structure of the complex.

TABLE 2

INFRARED VIBRATIONAL FREQUENCIES (cm^{-1}) OF $Pd_3(TBAA)_3 \cdot CHCl_3$ AND TBAA (KBr)

$Pd_3(TBAA)_3 \cdot CHCl_3$	TBAA	Assignment
1620vs (sh)	1657m (sh)	$\nu(C=O)$
1614vs	1650vs	
1628m	1628m	$\nu(C=C)$
1590m (sh)	1591vs (sh)	$\nu(C=C_{aromatic})$
1575m	1575s	
(973)w (br)	981vs	$\delta(CH)_{trans}$

When the solvent was changed from methanol to cyclohexanol in the abovementioned preparation reaction, the solvent cyclohexanol was found to be oxidized to cyclohexanone, which was identified by the dinitrophenylhydrazone formation in 81% yield based on $PdCl_2$.

(b) Spectroscopic analyses of the complex (Ia)

Infrared, ultraviolet and nuclear magnetic resonance spectra were observed. Infrared active vibrational frequencies of (Ia) and free TBAA in KBr are shown in Table 2 with their assignments.

A characteristic $\delta(\mathrm{CH})_{trans}$ vibration observed at 981 cm^{-1} in the free ligand disappears almost completely in (Ia), though a weak broad band appears at a slightly lower frequency (973 cm^{-1} w (br)). The carbonyl stretching bands of (Ia) are shifted 36 cm^{-1} to lower frequencies compared with those of free ligand.

Electronic absorption maxima (nm) of (Ia) and free TBAA in THF were observed as follows: π—π^* transition; (Ia) 234 m, TBAA 232 m and n—π^*; (Ia) 320 s, TBAA 320 s. Due to the much lower solubility of (Ia) in THF, it was difficult to measure the absorption coefficient. Both the n—π^* and π—π^* transitions of (Ia) remain unchanged from those of the free ligand. These IR and UV spectral data suggest the coordination of the ligand to palladium by its olefinic double bonds.

The NMR spectrum of (Ia) in $CDCl_3$ was observed by Kawazura (Fig. 1). Owing to the low solubility of (Ia), 1800 scans were necessary in order to obtain comparatively good signal to noise ratios. During the long time necessary for repeated scans, a part of the coordinated TBAA was liberated and the resonances resulting from the free ligand appeared at τ 2.2—3.0. In the spectrum of (Ia), the

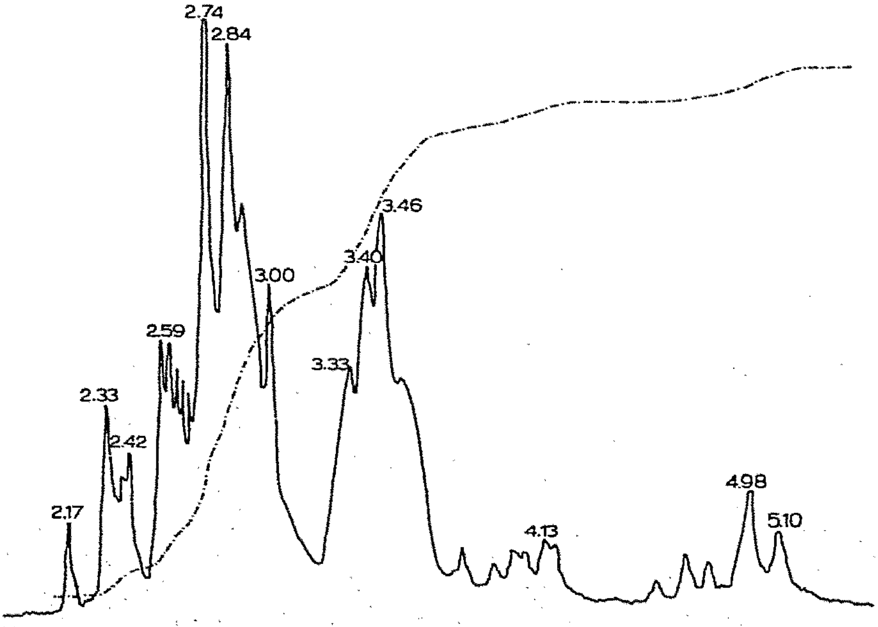


Fig. 1. NMR spectrum of (Ia) ($CDCl_3$) expanded (shown in τ).

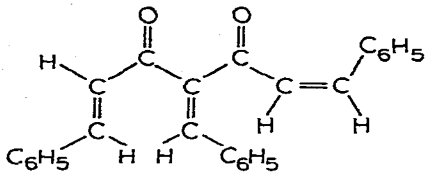
multiplet centered at τ 3.46 might be assigned to phenyl ring proton resonances of the coordinated TBAA. Olefinic proton resonances are shifted considerably to higher field (τ 4.13, 4.95 and 5.10). In coordinated TBAA of (Ia), both of the olefinic and phenyl proton resonances are shifted to higher field, as are those of DBA in $Pd_2(DBA)_3$.

IR, UV and NMR spectra of (Ia) showed clearly very similar patterns to those of $Pd_2(DBA)_3(CHCl_3)$ [4], which implies three C=C bonds of each TBAA ligand would coordinate each to three palladium atoms.

(c) Discussion of the structure of $Pd_3(TBAA)_3(CHCl_3)$ (Ia)

The structural study of $Pd_2(DBA)_3(CHCl_3)$ reported in the previous paper [4] revealed that all three DBA ligands of the complex coordinate to palladium atoms through C=C olefin portions of the ligand with the *s-cis,s-trans* conformation. On the other hand, Mazza and Pierpont [5] found that two DBA ligands in the *s-cis,s-trans* conformation and one DBA in *s-cis,s-cis* conformation from their structural study on $Pd_2(DBA)_3(CH_2Cl_2)$.

An X-ray structural determination of (Ia) by Ibers is in progress. Probably each of the three C=C bonds of one TBAA ligand is coordinated to each of the three separate palladium atoms, which would be suggested by the IR, UV and NMR data, and the conformation of TBAA ligand may be *s-cis,s-trans* as shown below (assuming the central part of TBAA fixed):



(Ia)

s-cis,s-trans form

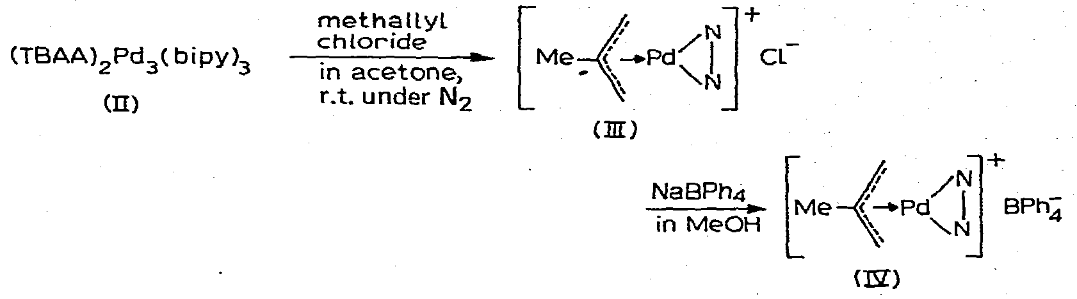
(d) Reactions of $Pd_3(TBAA)_3(CHCl_3)$ (Ia)

This new trinuclear palladium complex (Ia) was found to have similar reactivity patterns as those reported for $Pd_2(DBA)_3(CHCl_3)$ [4]. As $Pd_2(DBA)_3$ does, (Ia) was found to decompose to metallic palladium and free TBAA when carbon monoxide was passed into its solution in acetone at room temperature, and $Pd(PPh_3)_4$ was obtained in 74% yield on reaction of PPh_3 with (Ia) in ether.

Oxidative addition reactions of allylic halides with (Ia) in acetone at room temperature under nitrogen gave π-allylic palladium complexes. Thus cinnamyl bromide $PhCH{=}CHCH_2Br$ gave a 73% yield of the complex $[(\pi\text{-}PhCHCHCH_2)PdBr]_2$. The π-methallyl complex $[(\pi\text{-}CH_2CMeCH_2)PdCl]_2$ was obtained similarly.

In the reaction between (Ia) and an excess of 2,2'-bipyridine in acetone at room temperature under nitrogen, orange crystals of $Pd_3(TBAA)_2(bipy)_3$ (II) were obtained in 75% yield. Complex (II) is relatively unstable and decomposes gradually on exposure to air. The reaction of (II) with an excess of PPh_3 gave $Pd(PPh_3)_4$ in 71% yield, which confirms the low valency of palladium in (II).

The oxidative addition reaction of (II) with methallyl chloride produced a



(1)

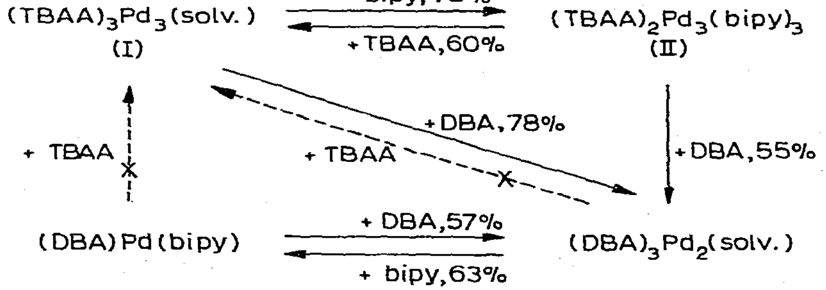
cationic π-methallylic palladium complex (III) (Eqn. 1). Complex (IV), which was prepared from (III) as shown in Eqn. 1, was identified by its NMR spectrum and elemental analysis.

Complex (II) was found to react with maleic anhydride, dimethyl maleate and dimethyl fumarate in acetone under nitrogen, giving high yields of (olefin)-Pd(bipy), which were identified by mixed m.p. with the products obtained in our previous work [9, 10]. The reaction of (II) with dimethyl acetylenedicarboxylate afforded the palladiacyclopentadiene—bipyridine complex in 96% yield, which was already obtained in the reaction with $Pd_2(DBA)_3$ [8, 10]. In a previous paper [4] p-$QPdL_2$ (p-Q = p-quinone) complexes were reported. The reactions of (II) with p-benzoquinone, duroquinone and 2-methyl-1,4-naphthoquinone took place at room temperature in acetone solution, giving such (p-Q)Pd(bipy) complexes in excellent yields.

(e) Comparison of stability and oxidizability of $Pd_3(TBAA)_3$ and $Pd_2(DBA)_3$ complexes

When an excess of TBAA was added to a benzene solution of the $Pd_2(DBA)_3$ no ligand exchange reaction took place. On the other hand, on addition of an excess of DBA to a benzene solution of $Pd_3(TBAA)_3$ at room temperature under nitrogen, the ligand TBAA was replaced by DBA, giving $Pd_2(DBA)_3$ in 78% yield. The interchangeability among $Pd_2(DBA)_3$, $Pd_3(TBAA)_3$ and their bipyridine derivatives is depicted in Scheme 1.

SCHEME 1



Both (Ia) and $Pd_2(DBA)_3(CHCl_3)$ were found to be oxidized by air oxygen in acetone solution in the presence of dimethylglyoxime (DMG), giving $[(DMG)H]_2$-Pd. When a competitive reaction was done at 25°C, the oxidation of (Ia) was complete after 2.2 h, and that of $Pd_2(DBA)_3$ after 2.5 h, which suggests that TBAA is a more labile ligand than DBA.

Experimental

General remarks

Palladium chloride was used as a commercial guaranteed grade. Infrared spectra were recorded on a Japan Spectroscopic Co. Model 403-G, electronic spectra on a Hitachi Model 124, and NMR spectra on a Japan Electronics 100 MH: FT-NMR spectrometer.

Preparation of tribenzylideneacetylacetone (TBAA)

To 60% aqueous ethanol solution (600 ml) containing sodium hydroxide (33 g), a mixture of benzaldehyde (38 g, 0.36 mol) and acetylacetone (10 g, 0.10 mol) was added slowly with stirring by cooling the solution below 25° C. Five hours later, yellow crystals precipitated were filtered, washed with water several times and dried in vacuo. The crystals recrystallized from methanol were tribenzylideneacetylacetone (TBAA), m.p. 112—113°, in a yield of 70%. IR spectral data are shown in Table 2 (Analysis: found: C, 85.22; H, 5.60. $C_{26}H_{20}O_2$ calcd.: C, 85.69; H, 5.53%).

Preparation of tris(tribenzylideneacetylacetone)tripalladium (chloroform) (Ia)

Palladium chloride (1.23 g, 6.78 mmol) was added to hot (ca. 50°) methanol (180 ml) containing TBAA (2.70 g, 27.2 mmol) and sodium acetate (3.90 g, 47.5 mmol). The mixture was stirred for 5 h at 40° to give a deep 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 (3.27 g) was dissolved in hot chloroform (140 ml) and filtered to give a deep purple solution. Diethyl ether (180 ml) was added slowly to the solution. Deep purple needle-like crystals precipitated. They were filtered, washed with diethyl ether and dried in vacuo. The complex (Ia), m.p. 132—135° (dec.), satisfying the composition $Pd_3(TBAA)_3(CHCl_3)$ was obtained in 84% yield. Analytical and IR spectral data are shown in Tables 1 and 2, respectively.

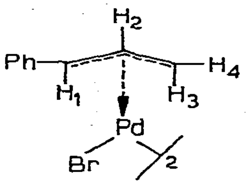
Preparation of $Pd_3(TBAA)_3(CH_2Cl_2)$ (Ib) and $Pd_3(TBAA)_3(C_6H_6)$ (Ic)

In the above procedure, methylene chloride or benzene were used as recrystallization solvent instead of chloroform to give similar deep violet needle-like (Ib), m.p. 142—144° (dec.) or deep violet (Ic), m.p. 154—156° (dec.) in 80 and 79% yield, respectively.

Oxidative addition reactions of $Pd_3(TBAA)_3(CHCl_3)$ (Ia)

The reaction between (Ia) (0.30 g, 0.22 mmol) and cinnamyl bromide (0.53 ml) in acetone occurred at room temperature under nitrogen. After removal of solvent under reduced pressure, yellow crystalline π-cinnamylpalladium bromide [11], m.p. 172—175° (dec.), was obtained in 73% yield (91 mg). NMR ($CDCl_3$): H_1 τ 5.37 (d), H_2 4.30 (sextet), H_3 7.00 (d) and H_4 6.05 (d) with $J(H_1—H_2)$ 12, $J(H_2—H_3)$ 12 and $J(H_2—H_4)$ 6.5 Hz.

Yellow colored π-methallylpalladium chloride [12], m.p. 165—168° (dec.), was obtained in 44% yield by the reaction of (Ia) (0.32 mmol) with methallyl chloride (0.63 mmol) in acetone at room temperature under nitrogen, followed



by recrystallization from methanol. Both of these π-allylpalladium halides were identified with m.p. and IR data of authentic samples.

Ligand exchange reactions

The reaction of (Ia) (0.66 mmol) and PPh_3 (11.4 mmol) in ether at room temperature under nitrogen gave yellowish crystals of $Pd(PPh_3)_4$ [13], m.p. 103—106°, in a yield of 74%, which was identical with the authentic sample [4].

The reaction of (Ia) (0.20 mmol) with bipyridine (2.56 mmol) in acetone at room temperature under nitrogen took place with the precipitation of orange-colored crystals of $Pd_3(TBAA)_2(bipy)_3$ (II), m.p. 114—115° (dec.), in a yield of 75% (Analysis: found: C, 64.94; H, 4.25; N, 5.54. $C_{82}H_{64}N_6O_4Pd_3$ calcd.: C, 64.60; H, 4.20; N, 5.51%). This complex is relatively unstable and decomposes gradually on exposure to air.

Reactions of $Pd_3(TBAA)_2(bipy)_3$ (II)

The reaction of (II) (2.1 mmol) with PPh_3 (10.5 mmol) in acetone at room temperature under nitrogen gave $Pd(PPh_3)_4$ in 71% yield.

Reaction of methallyl chloride (10.6 mmol) with (II) (3.6 mmol) in acetone took place at room temperature under nitrogen, affording the cationic π-CH_2-$CMeCH_2$—Pd(bipy) complex (III), which NMR spectrum ($CDCl_3$) shows τ 7.73 (3 H), 6.50 (2 H, *anti*) and 5.97 (2 H, *syn.*). Complex (III) was converted by reaction with $NaBPh_4$ in methanol to the known [10] cationic $[(\pi\text{-}CH_2CMeCH_2)\text{—}Pd(bipy)]^+BPh_4^-$ (IV), m.p. 164—166° (dec.), in 74% yield, which was identified by NMR spectrum (CH_2Cl_2): τ 7.93 (3 H), 6.95 (2 H) and 6.37 (2 H).

The reactions of (II) with maleic anhydride, dimethyl maleate and dimethyl fumarate were carried out in acetone at room temperature under nitrogen in the mole ratio of 1.3/15 and the corresponding complexes: (maleic anhydride)Pd(bipy) in 76% yield, (dimethyl maleate)Pd(bipy) 77% and (dimethyl fumarate)Pd(bipy) 81% were obtained, which are already reported [9, 10] and could be identified.

The reaction of (II) (0.17 mmol) with dimethyl acetylenedicarboxylate (1.41 mmol) in acetone at room temperature under nitrogen gave the known palladiacyclopentadiene—bipyridine complex (V) [8, 10], m.p. 218—220° (dec.), in 96% yield.

Similar to the reactions of $Pd_2(DBA)_3$ with *para*-quinones (*p*-Q) to give (*p*-Q)Pd(bipy) complexes [4], the reactions of (II) (0.20 mmol) with three *p*-quinones (each 1.55 mmol) in acetone at room temperature under nitrogen gave the following three complexes: (*p*-benzoquinone)Pd(bipy), m.p. 190—192° (dec.), yield 89%; (duroquinone)Pd(bipy), m.p. 209—211° (dec.), 86% yield; and (2-methyl-1,4-naphthoquinone)Pd(bipy), m.p. 215—217° (dec.), 84% yield, which were prepared and identified previously [4].

Comparison of stability and oxidizability between $Pd_3(TBAA)_3$ and $Pd_2(DBA)_3$ complexes

When an excess (3.05 mmol) of TBAA was added to a benzene solution of (II) (0.2 mmol) at room temperature under nitrogen, the product obtained was recrystallized from chloroform, giving (Ia) in 60% yield.

An excess of DBA (3.55 mmol) was added to a benzene solution of (II) (0.34 mmol) at room temperature, and the product obtained was $Pd_2(DBA)_3$-$(CHCl_3)$ in a yield of 55% after recrystallization from chloroform. While no ligand exchange was observed in the reaction of an excess of TBAA (5.0 mmol) with $Pd_2(DBA)_3(CHCl_3)$ (0.32 mmol) or (DBA)Pd(bipy) (0.26 mmol), the reaction of an excess of DBA (4.7 mmol) with (Ia) (0.46 mmol) in benzene at room temperature under nitrogen gave a 78% yield of $Pd_2(DBA)_3$ complex.

The oxidation of a mixture of (Ia) (0.33 mmol) and dimethylglyoxime (0.70 mmol) in acetone at room temperature with air oxygen gave the known dimethylglyoximato complex $[(DMG)H]_2Pd$ [14], m.p. > 290°, in 92% yield, which was identified with the authentic sample prepared by literature [15].

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