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CHEMISTRY OF DIBENZYLIDENEACETONE—PALLADIUM(0) COMPLEXES

II*. PREPARATION AND OXIDATION REACTIONS OF NOVEL PALLADIUM π-OLEFINIC AND π-ACETYLENIC COMPLEXES

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Summary

Reactions between the tris(dibenzylideneacetone)dipalladium complex [$Pd_2(DBA)_3$] and olefins with electron-withdrawing substituents in the presence of various ligands gave stable π-olefin—palladium—ligand complexes. The $Pd_2(DBA)_3$ complex reacted with dimethyl acetylenedicarboxylate to give either palladiacyclopentadiene complexes or π-bonded acetylenic complexes, according to the ligand used. A new complex, (bipy)$Pd^{II}(OH)_2 \cdot H_2O$, was prepared by air oxidation of $Pd_2(DBA)_3$ in the presence of bipyridyl and methanol.

Introduction

In the first paper of this series [1], novel binuclear palladium (0) complexes of type $Pd_2(DBA)_3$(solvent) were introduced, along with their structural determination and some reactions (ligand exchange, oxidative addition and with *p*- and *o*-quinones). $Pd_2(DBA)_3$(solvent) complexes were obtained by recrystallization of "$Pd(DBA)_2$" complex reported previously [2]. We have published communications on the preparation of palladium—π-olefin complexes [3] and on palladium—π-acetylenic complexes [4] via "$Pd(DBA)_2$" complex.

Hitherto, many zerovalent metal olefin and acetylene complexes of the type ML_2(olefin) or ML_2(acetylene) have been studied, where M = Ni, Pd or Pt and L = tertiary phosphine [5]. Lewis et al. [6] prepared $Pt(PPh_3)_2$ complexes of various unsaturated ligands in the reactions of $Pt(DBA)_2$, PPh_3, and excess of unsaturated ligand (C_2Cl_4, CF_3COCF_3, $CF_3C{\equiv}CCF_3$) in benzene solution. Moseley and Maitlis [7] found that $Pd(DBA)_2$ and $Pt(DBA)_2$ complexes react with

* For part I see ref. 1.

TABLE 1

YIELD AND PROPERTIES OF (OLEFIN)PdL_2 COMPLEXES

Complex	Yield (%)	M.p. (dec.)	ν(C=O)
(ma)Pd(bipy) [a]	97	229—231	1785, 1720
(ma)Pd(o-phen)	95	200	1795, 1757, 1710
(ma)Pd[P(OPh)$_3$]$_2$	96	132—133 [b]	1808, 1759, 1742
(ma)Pd[P(OMe)$_3$]$_2$	94	92—93 [b]	1798, 1769, 1732
(dmm)Pd(bipy)	74	153—155	1720
(dmm)Pd(o-phen)	73	171—172	1709, 1680
(dmf)Pd(bipy)	74	195—198	1696, 1680
(dmf)Pd(o-phen)	69	210—212	1685, 1669
(dvs)Pd(bipy)	60	143—145	
(dvs)Pd(o-phen)	81	168—171	
(an)Pd(bipy)	91	64—67	
(an)Pd(o-phen)	77	55—58	

[a] ma = maleic anhydride, dmm = dimethyl maleate, dmf = dimethyl fumarate, dvs = divinyl sulfone and an = acrylonitrile. [b] M.p. without dec.

dimethyl acetylenedicarboxylate to give palladia- and platina-cyclopentadiene complexes. They studied the crystal structure of the acid cleavage product of the palladiacyclopentadiene complex derived from $Pd(DBA)_2$ [8].

In this paper, full details of the utilization of palladium—dibenzylideneacetone complexes of the type $Pd_2(DBA)_3$(solvent) for preparing novel Pd—π-olefin complexes, and their reactions with dimethyl acetylenedicarboxylate and air oxidation to give (bipy)$Pd^{II}(OH)_2 \cdot H_2O$ are reported.

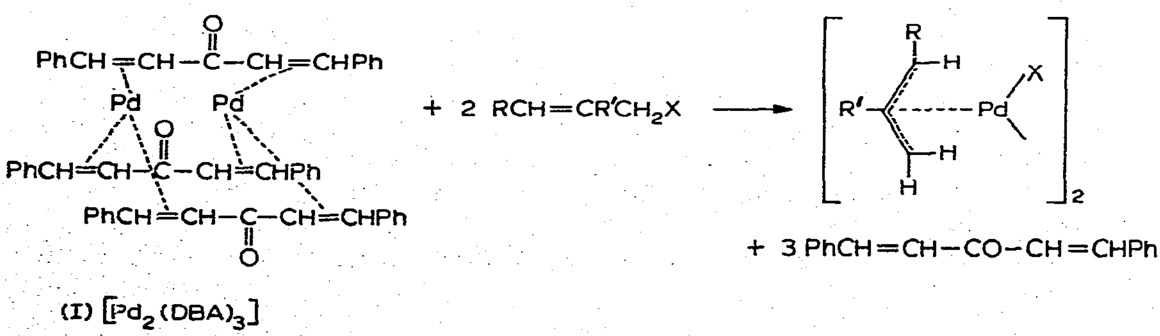
Results and discussion

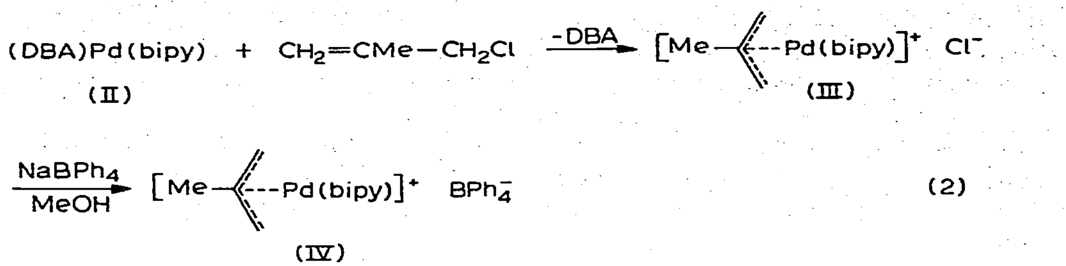
(a) Oxidative addition reactions of the $Pd_2(DBA)_3$ complex

Due to the zero-valent state of $Pd_2(DBA)_3$, oxidative addition reactions with allylic halides occurred, giving free DBA and π-allylic palladium halide complexes (eqn. 1).

The rate of the reactions of eqn. 1 varied according to R, R′ and X. The relative rate found was: allyl bromide > allyl chloride > methallyl chloride > crotyl chloride > cinnamyl chloride. The reaction was completed after 5 min in the case of allyl bromide, but 30 min was necessary in the reaction of cinnamyl chloride.

When an excess of methallyl chloride was added to (DBA)Pd(bipy) (II) (bipy = 2,2′-bipyridyl) in methanol solution, the cationic complex (III) was ob-





tained in 83% yield. Allyl bromide and methallyl chloride gave the corresponding cationic complexes in yields of 87 and 83%, respectively. As shown in eqn. 2, (III) was converted to (IV), m.p. 164—166° (dec.), in 68% yield.

(b) Formation of olefin—palladium complexes via the $Pd_2(DBA)_3$ complex

In the absence of ligand, (I) reacted with olefinic compounds in acetone solution, but stable olefin—palladium complexes could not be isolated, since they decomposed at room temperature to give metallic palladium and free DBA. However, when an excess of bipy was added to a suspension of (I) in acetone under nitrogen, further addition of olefin [e.g. dimethyl fumarate (dmf)] caused a color change from orange to yellow. Yellow crystals then precipitated. These were fairly stable in air and in benzene solution but rather unstable in chloroform. They were identified by their IR (Table 1) and NMR spectra (Table 4) and elemental analyses (Table 3).

Yields were quite high and free DBA was recovered quantitatively. Among the olefins which were examined, stable complexes were isolated only from maleic anhydride (ma), dimethyl maleate (dmm), dimethyl fumarate (dmf), divinylsulfone (dvs) and acrylonitrile (an), all of which have an *e*-value [9] above 1.2. Olefins with *e*-values below 1.2 (n-butyl acrylate 1.06, methacrylonitrile 0.81, acrylic acid 0.77, methyl vinyl ketone 0.68, ethyl acrylate 0.22) did

TABLE 2

STABILITY OF THE COMPLEXES (OLEFIN)PdL_2

Olefinic compound	*e*-value	bipy	*o*-phen	$P(OPh)_3$	$P(OMe)_3$
maleic anhydride	2.25	++ [a]	++	++	++
dimethyl fumarate	1.49	++	++	+	+
divinyl sulfone	1.33	++	++	+	+
dimethyl maleate	1.27	++	++	—	—
acrylonitrile	1.20	++	++	—	—

[a] ++ stable enough to be isolated, + complex formation possible but difficult to be isolated, and — only decomposed into metallic palladium and free DBA.

TABLE 3

ANALYSES OF (OLEFIN)PdL_2 COMPLEXES [FOUND (CALCD.) (%)]

Complex	C	H	N
(ma)Pd(bipy)	46.64(46.63)	2.68(2.79)	7.42(7.77)
(ma)Pd[$P(OPh)_3$]$_2$	58.23(58.65)	3.91(4.15)	
(ma)Pd[$P(OMe)_3$]$_2$	26.66(26.54)	4.33(4.45)	
(dmm)Pd(*o*-phen)	50.20(50.19)	3.75(3.74)	6.47(6.50)
(dmf)Pd(*o*-phen)	49.91(50.19)	3.95(3.74)	6.23(6.50)
(dmf)Pd(bipy)	47.49(47.25)	4.09(3.97)	6.86(6.89)

not afford stable olefin complexes, and complexes such as (DBA)Pd(bipy) were obtained as major products in most of these cases.

As shown in Table 2, ligands examined were bipyridyl, *o*-phenanthroline, triphenyl phosphite and trimethyl phosphite. With the two phosphites, only maleic anhydride formed stable olefin—palladium complexes and with phosphine as ligand, no olefin—palladium complex was isolated. Therefore, good σ-donor and poor π-acceptor ligands such as bipy and *o*-phen are more favorable than poor σ-donor ligands (i.e. phosphites).

The complexes thus obtained were very stable in the crystalline state and almost insoluble in common organic solvents except methanol or chloroform, in which they slowly decomposed. Only acetone was of use as solvent for *N*-donor ligands or benzene for *P*-donor ligands.

(c) Reactions of $Pd_2(DBA)_3$ with dimethyl acetylenedicarboxylate

Treatment of $Pd_2(DBA)_3$ (I) with dimethyl acetylenedicarboxylate (dmad) in acetone under nitrogen gave the palladiacyclopentadiene complex (V), which reacted with excess of ligand [L = bipy or $P(OPh)_3$] to give the monomeric palladiacyclopentadiene complex (VI). More conveniently, palladiacyclopentadiene complex (VI) could be prepared by the simultaneous addition of ligand and dmad to a suspension of (I) in acetone.

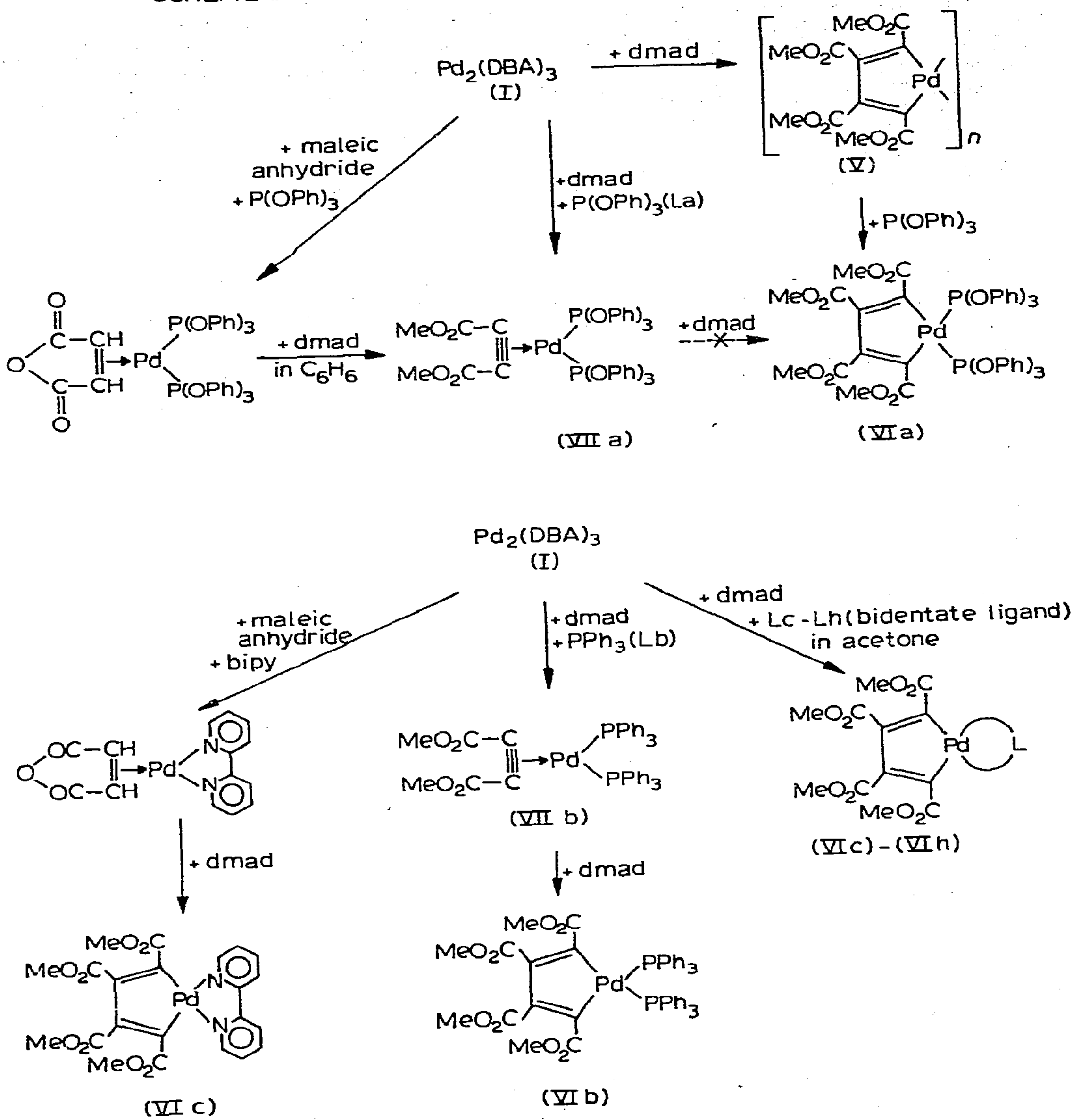
Palladiacyclopentadiene complexes (VI) also could be formed via a zero-valent π-acetylenepalladium intermediate. The addition of dmad to an excess of $P(OPh)_3$ and (I) in benzene solution gave (dmad)Pd$[P(OPh)_3]_2$ (m.p. 136—138°, 50% yield), which was identified by NMR and IR spectra and elemental analysis [ν(C≡C) 1845 cm^{-1} (KBr disc), $\tau(CDCl_3)$ 6.57 (6H, s, OMe) and 2.9 (30H, m, Ph)]. The complex (VIIa) is surprisingly stable in air and in benzene or chloroform solution. Further addition of dmad to (VIIa) did not afford the expected palladiacyclopentadiene complex [VIa; L = $P(OPh)_3$], which was prepared independently via (V).

However, with PPh_3 as ligand, the stepwise reactions (I)→(VIIb) and (VIIb)→(VIb) were successful. A similar complex (VIIb, L = PPh_3) gave (VIb) by the addition of a second molecule of dmad in benzene solution at room temperature, strongly suggesting that the π-complex (VIIb) is an intermediate in the formation of (VIb). The complex (ma)Pd$[P(OPh)_3]_2$ (Table 1) gave (VIIa) quantitatively in the reaction with dmad in benzene at room temperature, but (ma)Pd(bipy), which has a more basic ligand, gave directly the corresponding palladiacyclopentadiene complex (VIc, L = bipy) with dmad.

In conclusion, intermediate π-complexes (VII) are more stabilized as the π-acceptor character of L increases, in the order: bipy $\approx$ *o*-phen $\ll$ PPh_3 $<$ $P(OPh)_3$, indicating the following results: (1) intermediate (VII) would be stabilized by a π-acceptor ligand such as $P(OPh)_3$ and thus not give (VI); (2) the less stable intermediate (VIIb, L = PPh_3) could afford (VI), and (3) other basic ligands such as bipy (c), *o*-phen (d), tetramethylethylenediamine(tmeda) (e), dimethylglyoxime(dmg) (f), 1,2-bis(methylthio)ethane(bte) (g), and biacetyldianil(badn) (h) gave directly the corresponding palladiacyclopentadiene complexes (VIc—h), respectively.

These results are illustrated in Scheme 1.

SCHEME 1



(d) Preparation of (bipy)Pd(OH)$_2$ via Pd$_2$(TBA)$_3$

The peroxo complexes were formed in the oxygen oxidation of low valent Group VIII metal complexes [10—12]. Peroxo-isonitrile nickel and palladium complexes $(RNC)_2MO_2$ were prepared by Otsuka et al. [13].

$$M(PPh_3)_4 + O_2 \rightarrow (Ph_3P)_2M\langle{}^{O}_{O}| \quad (M = Ni, Pd, Pt) \qquad (3)$$

We attempted to obtain an oxidation product starting from (I) in the presence of a ligand. In the oxygen oxidation of (I) in the presence of 2,2′-bipyridine and methanol, another type of product, (bipy)Pd$(OH)_2$, was obtained, which has been unknown so far. This complex, m.p. 105—110° (dec.), of the composition (bipy)Pd$(OH)_2 \cdot H_2O$ (VIII), could be obtained via reduction of a peroxo intermediate (not isolated) by methanol.

$$\underset{\text{(I)}}{Pd_2(DBA)_3} + \text{bipy} + O_2 \xrightarrow{\text{MeOH}} [(\text{bipy})PdO_2] \xrightarrow[\text{—HCHO}]{\text{MeOH}} \underset{\text{(VIII)}}{(\text{bipy})Pd(OH)_2} \cdot H_2O \quad (4)$$

The complex (VIII) could be prepared by the reaction of 7% H_2O_2 with (DBA)Pd(bipy) (II) in methanol under nitrogen. Therefore, the formation of the complex (VIII) might be caused by the presence of the bipy ligand instead of PPh_3. The structure of (VIII) was confirmed by (1) addition of HCl to aqueous (VIII) gave (bipy)$PdCl_2$, (2) (VIII) and acetic acid afforded $Pd(OAc)_2 \cdot 2H_2O$ and (3) the addition of bipyridine and $HClO_4$ to aq. (VIII) gave $[(bipy)_2Pd](ClO_4)_2$, m.p. > 270°C.

(e) The reaction between $Pd_2(DBA)_3$ and oxygen in the presence of ligand with active hydrogen atom

When dimethylglyoxime (DMG—H_2) was added to an acetone suspension of (I) under an oxygen atmosphere, the purple color of the mixture turned gradually yellowish with quantitative uptake of oxygen, giving the bis(dimethylglyoximato)palladium complex (IX), $(DMGH)_2Pd$, in 90% yield (eqn. 5). Analogous reactions were realized in the cases of acetylacetone and 8-hydroxyquinoline as ligand, giving $Pd(acac)_2$ and Pd(8-OH-quinoline)$_2$, respectively. No reaction occurred under a nitrogen atmosphere.

$$\underset{\text{(I)}}{Pd_2(DBA)_3} + O_2 + 4\,DMG\text{—}H_2 \rightarrow \underset{\text{(IX)}}{2(DMGH)_2Pd} + 2H_2O + 3\,DBA \quad (5)$$

Experimental

(1) Materials

$Pd_2(DBA)_3(CHCl_3)$ (I), m.p. 122—124° (dec.), and (DBA)Pd(bipy) (II), m.p. 135° (dec.), were prepared as described in the previous paper [1].

(2) Oxidative addition reactions of (I) with allylic halides

The rate of oxidative addition reactions of various allylic halides to (I) (eqn. 1) was observed and the order was found to be as follows: allyl bromide > allyl chloride > methallyl chloride > crotyl chloride > cinnamyl chloride.

As an example, the oxidative addition reactions of methallyl chloride are given here. An excess of methallyl chloride (20.4 mmol) was added to a benzene solution of (I) (3.1 mmol) with stirring at room temperature under nitrogen. The deep purple color of the solution changed to yellow-greenish after 20 min. Upon vacuum distillation of solvent and excess methallyl chloride, the residue was washed with hexane to remove DBA and then recrystallized from methanol, giving yellow colored μ,μ'-dichlorodi-π-methallyldipalladium, m.p. 165—168°

(dec.), obtained in 75% yield [(NMR: τ(Me) 7.88 (3H), τ(H, *anti*) 7.13 (2H), τ(H, *syn*) 6.15 (2H)] [14]. Similarly, [(π-methallyl)Pd(bipy)]$^+$Cl$^-$ (III) in the reaction of methallyl chloride (8.5 mmol) with (DBA)Pd(bipy) (II) (1.7 mmol) in benzene suspension, whose NMR spectrum ($CDCl_3$) showed τ 7.73 (3H), 6.50 (2H, *anti*) and 5.97 (2H, *syn*). The reaction between (III) (1.5 mmol) and $NaBPh_4$ (2.4 mmol) in methanol gave [(π-methallyl)Pd(bipy)]$^+$$BPh_4^-$ (IV), m.p. 164—166° (dec.) in 68% yield, recrystallized from mixed solvent of MeOH and CH_2Cl_2. NMR spectrum (CH_2Cl_2): τ 7.93 (3H), 6.95 (2H) and 6.37 (2H) (Analysis: found C, 71.51; H, 5.58; N, 4.39. $C_{38}H_{35}N_2BPd$ calcd.: C, 71.66; H, 5.54; N, 4.40%).

(3) Formation of (olefin)PdL$_2$ complexes via Pd$_2$(DBA)$_3$

2,2'-Bipyridine (10.5 mmol) and maleic anhydride (8.4 mmol) in acetone (30 ml) were added to an acetone suspension of (I) (4.6 mmol) with stirring at room temperature under nitrogen and yellow needle-like crystals of (ma)Pd(bipy), m.p. 229—231° (dec.), were precipitated in 97% yield. Analyses of this complex and others are shown in Table 3. NMR data are summarized in Table 4. Yield, m.p. and IR data of twelve (olefin)PdL_2 complexes are summarized in Table 1.

(4) Reactions of Pd$_2$(DBA)$_3$ with dimethyl acetylenedicarboxylate (dmad) in the presence of ligand

Into an acetone solution (30 ml) of (I) (0.3 mmol) and an excess of a ligand (0.63 mmol), dimethyl acetylenedicarboxylate (dmad) (0.3 mmol) was added, and one h later, crystals of palladiacyclopentadiene—L_2 complex (VI) were precipitated. Ligands used in this reaction were as follows: triphenyl phosphite (a), bipy (c), *o*-phen (d), tmeda (e), dimethylglyoxime (f), 1,2-bis(methylthio)ethane (g) and biacetyldianil (h). The properties and analyses of (VIa—VIh) are tabulated in Table 5.

The addition of dmad (10.3 mmol) to an excess of $P(OPh)_3$ (0.3 ml) and (I) (0.3 mmol) in benzene solution gave (dmad)Pd[$P(OPh)_3$]$_2$ (VIIa), yellow needle-like crystals of m.p. 136—138° (dec.) in 50% yield. IR ν(C≡C) 1845 cm^{-1} and NMR τ($CDCl_3$) 6.57 (s, OMe) and 2.9 (Ph) (Analysis: found C, 58.15; H, 4.13. $C_{42}H_{36}O_{12}PdP_2$ calcd.: C, 58.04; H, 4.18%).

In the case of PPh_3 as a ligand, the complex (dmad)Pd(PPh_3)$_2$ (VIIb), m.p. 195—196° (dec.), was obtained in 52% yield. IR ν(C≡C) 1845 cm^{-1} and NMR τ($CDCl_3$) 6.8 (s, OMe). The addition of a second molecule of dmad to

TABLE 4

NMR DATA OF (OLEFIN)PdL_2 COMPLEXES (IN $CDCl_3$)

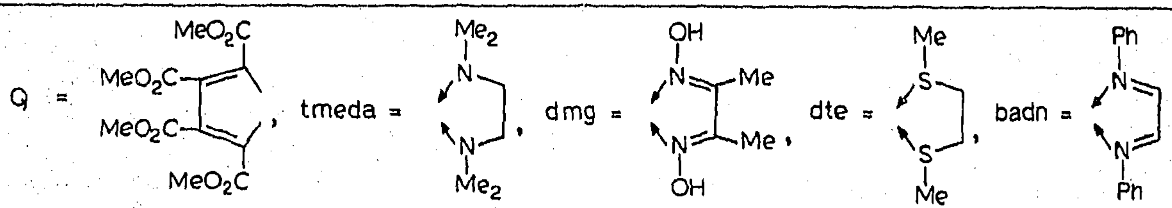
Complex	τ(CH=)	τ(L)	τ(MeO)
(ma)Pd[$P(OPh)_3$]$_2$	6.78(2H)	2.9(30H)	
(ma)Pd[$P(OMe)_3$]$_2$	5.67(2H)	6.40(18H)	
(dmm)Pd(bipy)	3.80(2H)	1.0—2.7(8H)	6.22(6H)
(dmm)Pd(*o*-phen)	3.83(2H)	1.5—2.7(8H)	6.27(6H)
(dmf)Pd(bipy)	6.14(2H)	1.4—2.9(8H)	6.44(6H)
(dmf)Pd(*o*-phen) [a]	5.89(2H)	1.0—2.3(8H)	6.35(6H)
(dmf)Pd(tmeda) [a]	6.32(2H)	7.30(12H)	6.63(6H)
(dvs)Pd(*o*-phen) [a]	4—5(6H)	0.6—2.1(8H)	
(an)Pd(*o*-phen)	4.81(2H)	0.8—2.3(8H)	

[a] DMSO-d_6.

TABLE 6

PROPERTIES AND ANALYSES OF PALLADIACYCLOPENTADIENE—L_2 COMPLEXES (VIa)-(VIh)

Complex	Structure	Color	Yield (%)	m.p.(°C, dec.)	τ(Me)($CHCl_3$)	ν(C=O) (KBr)	Analysis: Found (Calcd.) (%) C	H	N
VIa	Q Pd(OPh_3)[a] (OPh_3)	yellow	88	165-166	6.23[b], 6.34[b]	1690 1720	57.21 (57.01)	4.41 (4.19)	
VIb	Q Pd(PPh_3)(PPh_3)	yellow	70	160-164	6.35, 7.30	1650 1720	52.90 (52.68)	4.50 (4.42)	
VIc	Q Pd(bipy)	yellow	78	218-220	5.98[b], 6.12[b]	1690 1720	47.59 (48.32)	3.60 (3.69)	5.03[c] (5.12)
VId	Q Pd(*o*-phen)	yellow	53	205-210	5.95[b], 6.12[b]	1690 1715	50.68 (50.50)	3.76 (3.53)	4.64 (4.91)
VIe	Q Pd(tmeda)	yellow-brown	87	205-210	6.30, 6.38	1690 1715	43.46 (42.66)	5.52 (5.65)	5.35 (5.53)
VIf	Q Pd(dmg)	golden-yellow	50	193-196	6.25, 6.30	1685 1705	38.43 (37.92)	3.96 (3.98)	5.25 (5.53)
VIg	Q Pd(dte)	yellow-brown	28	164-165	6.26, 6.33	1690 1715	37.60 (37.47)	4.33 (4.32)	
VIh	Q Pd(badn)	golden-yellow	88	217-218	6.03, 6.35	1690 1705	53.65 (53.64)	4.61 (4.50)	4.30 (4.47)

[a]


[b] In nitrobenzene. [c] Pd 19.3(19.4).

(VIIb) in benzene at room temperature gave the palladiacyclopentadiene complex (VIb), m.p. 160—164° (dec.), in 70% yield.

(5) Preparation of (bipy)Pd(OH)$_2$ complex via Pd$_2$(DBA)$_3$

When excess molar amounts of bipyridine (1.6 mmol) was treated with a methanolic suspension of (I) (0.4 mmol) under an oxygen atmosphere, the color of the solution changed from reddish-violet to clear reddish-brown. After removal of methanol, the residue was washed with acetone and added with small amounts of water. The solution was kept in a refrigerator, and yellowish needle-like crystals (VIII), m.p. 105—110° (dec.), were precipitated in a yield of 60% (Analysis: found C, 38.77; H, 3.85; N, 8.60. $C_{10}H_{12}N_2O_3Pd$ calcd.: C, 38.18; H, 3.56; N, 8.90%). IR data ν(OH) 3400 and ν(C—N) 1450 cm^{-1}.

When bipyridine (0.6 mmol) and $HClO_4$ (0.1 ml) were added to an aqueous acetone solution of (VIII), the color of the mixture changed instantaneously to yellow, and yellow crystals, $[(bipy)_2Pd](ClO_4)_2$, m.p. > 270° were obtained. IR data ν(C—N) 1450 and $\nu(ClO_4)$ 1100 cm^{-1} (Analysis: found C, 38.67; H, 2.68; N, 9.10. $C_{20}H_{16}O_8N_4Cl_2Pd$ calcd.: C, 38.89; H, 2.61; N, 9.07%).

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References

1 T. Ukai, H. Kawazura, Y. Ishii, J.J. Bonnet and J.A. Ibers, J. Organometal. Chem., 65 (1974) 253.
2 Y. Takahashi, Ts. Ito, S. Sakai and Y. Ishii, Chem. Commun., (1970) 1065.
3 Ts. Ito, Y. Takahashi and Y. Ishii, J. Chem. Soc. Chem. Commun., (1972) 629.
4 Ts. Ito, S. Hasegawa, Y. Takahashi and Y. Ishii, J. Chem. Soc. Chem. Commun., (1972) 629.
5 R. Ugo, Coordin. Chem. Rev., 3 (1968) 319.
6 W.J. Cherwinski, B.F.G. Johnson and J. Lewis, J. Organometal. Chem., 52 (1973) C61.
7 K. Moseley and P.M. Maitlis, J. Chem. Soc. Chem. Commun., (1971) 1604.
8 D.M. Roe, P.M. Bailey, K. Moseley and P.M. Maitlis, J. Chem. Soc. Chem., Commun., (1972) 1273.
9 T. Alfrey, Jr. and L.I. Young, in G.E. Ham (Ed.), Copolymerization, Interscience, New York, 1964, p. 67.
10 G. Wilke, H. Schott and P. Heimbach, Ang. Chem. Intern. Ed., 9 (1967) 92.
11 J.P. Birk, J. Halpern and P.L. Pickard, J. Amer. Chem. Soc., 90 (1968) 4491.
12 J. Halpern and A.L. Pickard, Inorg. Chem., 9 (1970) 2798.
13 S. Otsuka, A. Nakamura and Y. Tatsuno, Chem. Commun., (1967) 836; J. Amer. Chem. Soc., 91 (1969) 6994, 7196.
14 W.T. Dent, R. Long and A.J. Wilkinson, J. Chem. Soc., (1964) 1585.