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BONDING INTERACTION OF *p*-QUINONES WITH PALLADIUM(0)—PHOSPHINE COMPLEXES

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Summary

In the complexes of formula $L_2Pd(p\text{-}C_6H_4O_2)$ [L = n-Bu_3P, $(p\text{-}CH_3\text{-}OC_6H_4)_3P$, Ph_3P, $(p\text{-}ClC_6H_4)_3P$ and $(PhO)_3P$, $C_6H_4O_2$ = benzoquinone], the *p*-benzoquinone is bound to palladium as a bidentate ligand. The chemical shifts and the carbonyl stretching frequencies of the *p*-benzoquinone have close relationships with the basicities of the phosphorus ligand L. When L is n-Bu_3P, two types of interconvertible complexes, $(n\text{-}Bu_3P)_2Pd(p\text{-}C_6H_4O_2)$ and $[(n\text{-}Bu_3P)_2Pd]_2(p\text{-}C_6H_4O_2)$, have been isolated. In the complexes of formula $(Ph_3P)_2Pd(p\text{-}C_6H_3O_2X)$ (X = methyl, acetyl, methoxy and carbomethoxy groups), the quinone is bound as monodentate ligand, and the coordination mode of the quinone is found to depend on the electronic nature of the substituent.

Introduction

Since the discovery of palladium(0)— and platinum(0)—tertiary phosphine complexes [1], a number of olefin complexes of formula L_2M(olefin) (M = Pd, Pt; L = tertiary phosphine) have been prepared and the nature of the metal—olefin bonding was discussed on the basis of the Dewar-Chatt-Duncanson model [2]. These complexes are well known to show a great tendency to be three coordinate (16 electron configuration) [3] and, to our knowledge, no four coordinate complexes of type $L_2M(\text{olefin})_2$ have been reported.

We have studied the bonding interaction of *p*-quinones, which can be considered to have two activated olefinic functions, with palladium(0)—phosphine complexes, and discuss here their bonding on the basis of IR, ^1H NMR and ^{13}C NMR data.

TABLE 1

^{1}H NMR[a] AND IR[b] DATA FOR p-BENZOQUINONE IN $L_2Pd(p\text{-}C_6H_4O_2)$

Compound no.	L	δ[c]	Δδ	ν(CO)		Δν(CO)[d]	ν(CO)(A_1) of $Ni(CO)_3L$[e]
				ν_1	ν_2		
I	$n\text{-}Bu_3P$[f]	4.36	1.66		1582[g]	75	
II	$n\text{-}Bu_3P$	5.64	0.48	1630	1613	44	2060.3
III	$(p\text{-}CH_3OC_6H_4)_3P$	5.61	0.41	1636[h]	1627	30	2066.1
IV	Ph_3P	5.41	0.61	1637[h]	1632	25	2068.9
V	$(p\text{-}ClC_6H_4)_3P$	5.38	0.64	1637[h]	1632	25	2072.8
VI	$(PhO)_3P$	4.82	1.20		1639	18	2085.3
	Free $p\text{-}C_6H_4O_2$	6.02		1670	1657		

[a] Measured in C_6D_6 solution at 34° under nitrogen. [b] Measured in THF solution using 0.1 mm liquid cell (NaCl). [c] In ppm relative to internal TMS. All complexes show multiplet due to coupling with two phosphorus atoms. [d] 1657 - ν_2. [e] Quoted from ref. 10, see also ref. 5. [f] This compound corresponds to $[(n\text{-}Bu_3P)_2Pd]_2(p\text{-}C_6H_4O_2)$. [g] Nujol mull. [h] (sh).

Results and discussion

$L_2Pd(p\text{-}C_6H_4O_2)$

All complexes of formula $L_2Pd(p\text{-}C_6H_4O_2)$ (L = tertiary phosphine, $C_6H_4O_2$ = benzoquinone) were prepared by the reaction [4] of p-benzoquinone with tris- or tetrakis-(tertiary phosphine)palladium(0) (see Experimental). IR and ^{1}H NMR data of these complexes are summarized in Table 1.

The ^{1}H NMR spectra of II-VI show that the chemical shifts due to the four protons of p-benzoquinone are equivalent in all complexes, and that the signal is split into a symmetrical multiplet by coupling with two phosphorus atoms ($AA'X_2X'_2$ spin system). This P—H coupling disappears on addition of the corresponding free phosphine, suggesting rapid exchange between the free and coordinated phosphine (Fig. 1). The addition of free p-benzoquinone, however, gives rise to no effect on chemical shift and coupling pattern of the coordinated quinone, which indicates no exchange. These data show that p-benzoquinone is coordinated rigidly to the palladium atom as bidentate ligand. The coordination geometry of these complexes would be, as discussed by Ugo et al. on the plati-

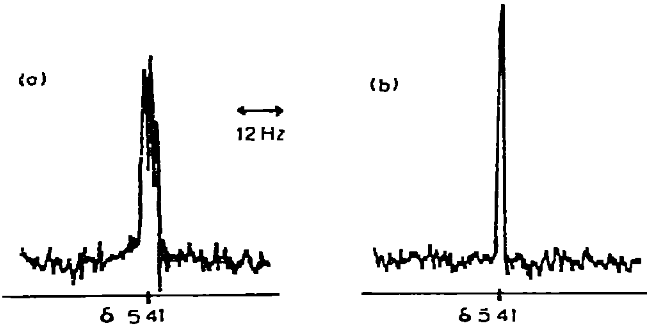
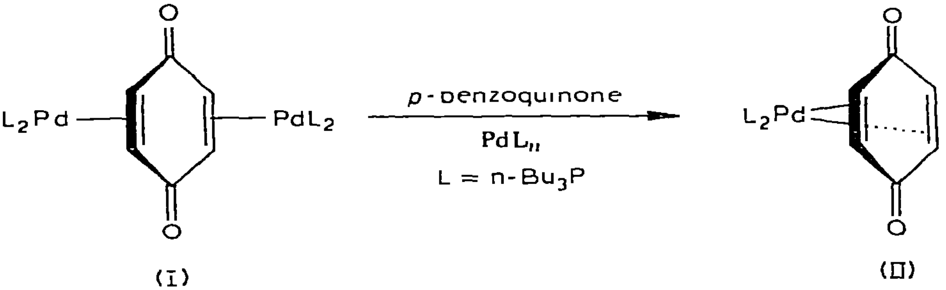


Fig. 1. (a) ^{1}H NMR spectrum of p-benzoquinone in $(Ph_3P)_2Pd(p\text{-}C_6H_4O_2)$ (IV). (b) (IV) + Ph_3P.

num(0)—quinone complexes [6], approximately tetrahedral with coordination number four.

In the case of L = n-Bu$_3$P we could obtain two types of *p*-benzoquinone complexes, I and II. The reaction between Pd(n-Bu$_3$P)$_n$ (which was prepared in situ by the reduction of *trans*-(n-Bu$_3$P)$_2$PdCl$_2$ with n-BuLi in the presence of n-Bu$_3$P) and *p*-benzoquinone (Pd/quinone molar ratio = 2/1) in hexane gave the yellow complex I in 75% yield. Complex I reacts readily with an additional equimolar amount of *p*-benzoquinone to afford the red complex II in 91% yield. II is found to be converted reversibly into I by addition of an equimolar quantity of Pd(n-Bu$_3$P)$_n$ (87% yield). This is the first example of interconvertibility between complexes with ligands of chelating and bridging types.



The coordination geometry around each palladium atom in I would be nearly planar with a coordination number three, as with complexes of formula (Ph$_3$P)$_2$Pt(monoolefin) [7]. Since the amount of π-back-donation from the zerovalent metal to the olefin becomes greatest when the coordination geometry is nearly planar [6,8], complex I can be expected to have a stronger bonding interaction than the tetrahedral complex II. This, indeed, is observed in the ^{1}H NMR, ^{13}C NMR and IR spectra.

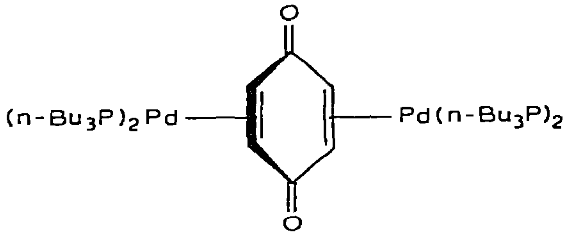
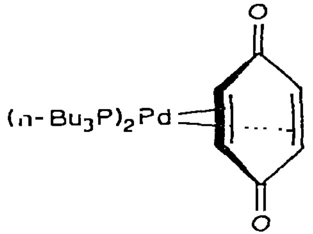
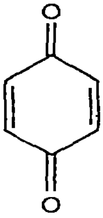
The ^{1}H chemical shift of quinone protons (δ 4.36 ppm, apparent d) for I is shifted considerably to higher field compared with II (δ 5.64 ppm, apparent t). ^{13}C NMR data (Table 2) are consistent with the ^{1}H NMR data. The ^{13}C NMR spectrum of free *p*-benzoquinone shows resonances at δ 135 due to the four olefinic carbons and at 189 ppm due to the two carbonyl carbons. The olefinic carbons in I are much more shielded (Δδ ^{13}C 70 ppm) than those in II (Δδ ^{13}C 31 ppm). The ^{13}C—H coupling constants show the expected decrease: free *p*-benzoquinone, 170 > II, 163 > I, 158 Hz, suggesting the decrease of olefinic character in this order. The ^{13}C—^{31}P coupling constants also provide the indirect evidence that the quinone in I has the stronger bonding interaction with palladium atoms.

It is interesting to note that the ^{13}C chemical shifts of carbonyl carbons are little influenced on complex formation. This could be presumably attributed to the polarization effect, $C^+—O^-$, of the carbonyl group [9]. In fact, the ν(CO) bands of I and II are shifted to lower wavenumbers by 75 and 44 cm^{-1}, respectively, compared with free *p*-benzoquinone.

We previously reported that the ^{1}H chemical shifts and the carbonyl stretching frequencies of the maleic anhydride ligand in L$_2$Pd(HCCO)$_2$O are linearly related to the basicities of the phosphorus ligand L [5]. *p*-Benzoquinone complexes studied here showed the same trend as maleic anhydride complexes

TABLE 2

^{13}C NMR DATA FOR FREE AND COORDINATED *p*-BENZOQUINONE[a]

Compound	δ (ppm)		J (Hz)	
	Olefinic	Carbonyl	$^{13}C-^{1}H$	$^{13}C-^{31}P$
I 	65	189	158	19
II 	104	183	163	5
	135	189	170	

[a] Measured in benzene-d_6 under nitrogen atmosphere; internal TMS standard.

(see Table 1). As the basicities of L increase, ν(CO) of *p*-benzoquinone moves to lower wavenumbers. This suggests that the $\Delta\nu$(CO) reflects the amount of π-back-donation from metal to quinone. On the other hand, the magnitude of high field shifts, $\Delta\delta$, becomes smaller as the basicities of L increase. The difference of $\Delta\delta$ in changing the L presumably arises, as we proposed [5], from the decreased deshielding due to consumption of π-electrons of olefinic systems for σ-bonding.

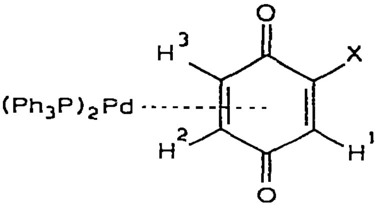
$(Ph_3P)_2Pd(p\text{-}C_6H_3O_2X)$

Whereas *p*-benzoquinone in II-VI coordinates to palladium via both double bonds (tetrahedral configuration) as mentioned above, monosubstituted *p*-quinones are found to coordinate via one double bond only, which corresponds to a trigonal planar configuration. The ^{1}H NMR and IR data for substituted *p*-quinone complexes are shown in Table 3.

The NMR spectra of the complexes, VII and VIII, show that both *p*-toluquinone and *p*-methoxyquinone, which have an electron-releasing substituent on

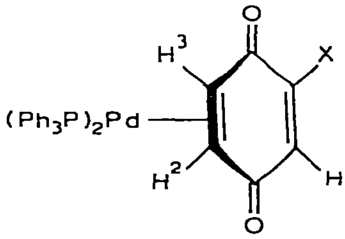
TABLE 3

^1H NMR[a] AND IR[b] DATA FOR FREE AND COORDINATED MONO- AND DI-SUBSTITUTED *p*-QUINONES

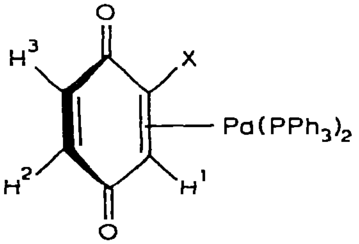
Compound no.			δ (ppm)			ν(CO)(cm^{-1})	
			Free	Complex		Free	Complex
	X	Proton assignments					
VII	CH_3	H^1	6.08	6.02	0.06	1660	1631
		H^2, H^3	6.10	4.85[f]	1.25		1606
		$-CH_3$	1.56	1.58	−0.02		
VIII	OCH_3	H^1	5.40	5.19	0.21	1672	1638
		H^2, H^3	6.05	4.73[g]	1.32	1640	1618
		$-OCH_3$	2.82	2.94	−0.12		
IX	$COCH_3$[c]	H^1	7.00	4.99[h]	2.01	1707[d]	1642[d]
		H^2, H^3	6.85	6.21	0.64	1657	1630
		$-COCH_3$	2.56	2.00	0.56		
X	$COOCH_3$	H^1	6.56	5.50[i]	1.06	1710[e]	1665[e]
		H^2, H^3	5.95	5.90	0.05	1657	1635
		$-COOCH_3$	3.40	3.32	0.08		
XI	CH_3 ($H^2 = CH_3$)	H^1, H^3	6.12	5.58	0.54	1660	1635
		2 $-CH_3$	1.60	1.64	−0.04	1637	1607

[a] In benzene-d_6 solution under nitrogen atmosphere; internal TMS standard. [b] Nujol mull. [c] In $CDCl_3$ solution (NMR). [d] Band due to $-COCH_3$. [e] Band due to $-COOCH_3$. [f] d, J(P—H) = 7 Hz. [g] d, J(P—H) = 7 Hz. [h] d, J(P—H) = 9 Hz. [i] d, J(P—H) = 8 Hz.

the quinone nucleus, coordinate to the palladium atom via the one double bond which bears no substituent. In Fig. 2 the NMR spectra of the olefinic region of free and coordinated toluquinone are shown. On complexation of *p*-toluquinone, the signals for H^2 and H^3 are shifted to high field (Δδ 1.25 ppm) and split into an apparent doublet (*J* = 7 Hz) by coupling with the phosphorus atoms, whereas the signal for H^1 remains at the essentially the same position (Δδ 0.06 ppm) as that of the free ligand. In contrast, *p*-quinones which have an electron-withdrawing substituent, such as acetyl or carbomethoxy, coordinate to palladium



(VII) X = CH_3
(VIII) X = OCH_3



(IX) X = $COCH_3$
(X) X = $COOCH_3$

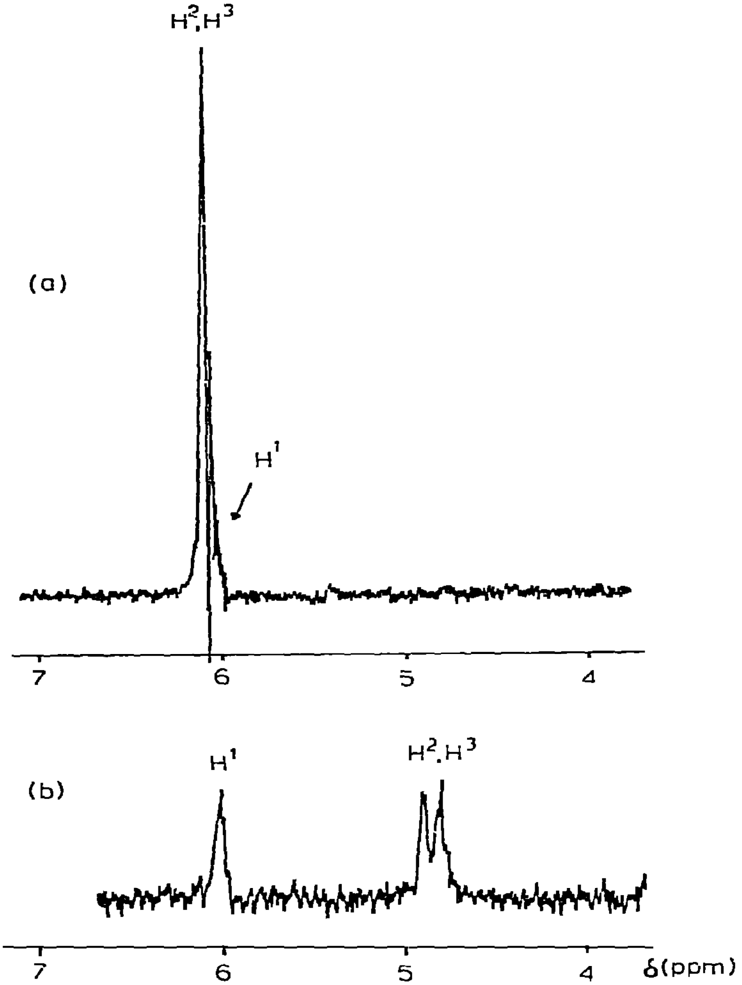


Fig. 2. ¹H NMR spectra (olefinic region) of *p*-toluquinone, (a) free (b) complex.

via the double bond which bears the substituent (Fig. 3). The high field shift for H^1 ($\Delta\delta$ 1.06 ppm) in *p*-carbomethoxyquinone is larger than those for H^2 and H^3 ($\Delta\delta$ 0.05 ppm), and the signal for H^1 is split into a doublet (J = 8 Hz) by coupling with the phosphorus atom.

In the case of the symmetrically substituted *p*-xyloquinone complex (XI), the chemical shifts of the two olefinic protons are equivalent to each other. This indicates coordination with both double bonds.

One may expect the coordination mode of substituted *p*-quinone to be influenced by both steric and electronic effects. However, the monosubstituted *p*-quinone complexes studied here indicate that the electronic effect of the substituents is the main factor which renders the quinone a monodentate ligand. It follows that the electronic effect of the substituent, which gives rise to an energy difference between two π^*-antibonding levels of olefinic systems, is the main factor which determines the coordination mode of the unsymmetrically substituted quinones. This phenomenon could reveal that the L_2Pd moiety favors energetic-

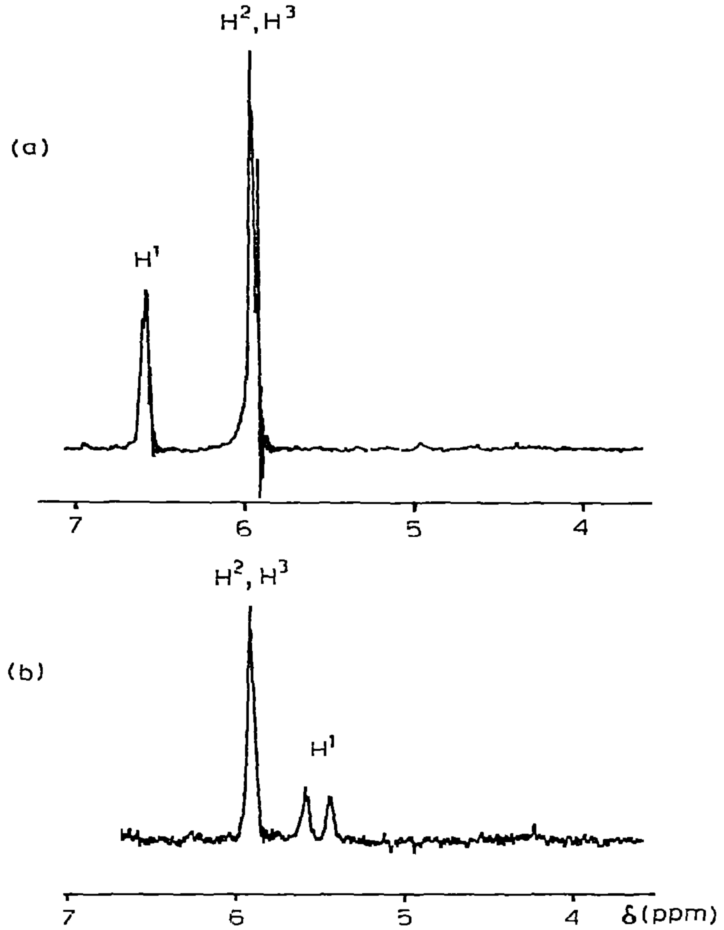


Fig. 3. ^1H NMR spectra (olefinic region) of p-carbomethoxyquinone, (a) free (b) complex.

ally planar configuration (NVE* 16) more than tetrahedral (NVE 18). In the complex of planar configuration, the bonding is formed via the olefinic system having the stronger π-acceptor property (lower π*-antibonding level) as shown above. This trend is consistent with the stability [4] of monoolefin complexes of L_2Pd(olefin).

Experimental

IR spectra were recorded on a Jasco Model DS-402G spectrophotometer. ^1H NMR spectra were obtained on a Hitachi—Perkin—Elmer R20 (60 MHz) spectrometer. ^{13}C NMR spectra were obtained on a Varian XL-100 Fourier transform spectrometer with proton decoupling. In addition, the off resonance decoupled method was adopted to obtain ^{13}C—H coupling constants. All reactions were carried out under a nitrogen atmosphere at ambient temperature unless otherwise stated.

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* NVE = number of valence electrons.

TABLE 4

PROPERTIES AND ANALYTICAL DATA FOR $L_2Pd(p\text{-}QUINONE)$

Compound no.	L	p-Quinone	Color	M.p. (°C) (dec.)	Analysis found (calcd.) (%)			
					C	H	P	Mol. wt.[a]
I	$n\text{-}Bu_3P$	$p\text{-}C_6H_4O_2$[b]	Yellow	92–93[c]	57.46	10.00	10.48	[d]
					(57.39)	(9.99)	(10.96)	(1130)
II	$n\text{-}Bu_3P$	$p\text{-}C_6H_4O_2$	Red	52–54[c]	58.18	9.54	9.97	605
					(58.20)	(9.44)	(10.01)	(619)
III	$(p\text{-}CH_3OC_6H_4)_3P$	$p\text{-}C_6H_4O_2$	Red	145–150	62.75	5.21	7.08	872
					(62.72)	(5.04)	(6.71)	(919)
V	$(p\text{-}ClC_6H_4)_3P$	$p\text{-}C_6H_4O_2 \cdot 0.5\ C_6H_6$[e]	Red	200–205	54.43	3.10	5.76	885
					(54.88)	(3.17)	(6.20)	(985)
VI	$(PhO)_3P$	$p\text{-}C_6H_4O_2$	Yellow	125–130	60.57	4.28	7.74	816
					(60.41)	(4.10)	(7.41)	(835)
VII	Ph_3P	$p\text{-}C_6H_3O_2CH_3$	Red	155–163	68.46	4.66	8.38	706
					(68.58)	(4.82)	(8.23)	(763)
VIII	Ph_3P	$p\text{-}C_6H_3O_2OCH_3 \cdot C_6H_6$	Orange	97–99[c]	69.98	5.09	7.79	
					(69.46)	(5.00)	(7.31)	(847)
IX	Ph_3P	$p\text{-}C_6H_3O_2COCH_3 \cdot 0.5\ Et_2O$	Dark red	148–150	67.44	4.64	7.41	735
					(67.53)	(5.05)	(7.57)	(818)
X	Ph_3P	$p\text{-}C_6H_3O_2COOCH_3 \cdot Et_2O$	Dark red	108–110[c]	66.53	4.75	7.50	784
					(66.17)	(5.32)	(7.11)	(871)
XI	Ph_3P	$p\text{-}C_6H_2O_2(CH_3)_2$	Red	109–113	68.96	4.88	7.85	
					(68.89)	(4.99)	(8.08)	(767)

[a] Measured by vapor pressure osmometry using dichloromethane solution. [b] This compound analyzes as $[(n\text{-}Bu_3P)_2Pd]_2(p\text{-}C_6H_4O_2)$. [c] Melt without decomposition. [d] Mol. wt. was not measured due to extensive dissociation in dichloromethane. [e] Found: Cl, 21.66. Calcd.: Cl, 21.60%.

Physical properties and analytical data of new complexes obtained here are shown in Table 4.

Materials

p-Benzoquinone, *p*-toluquinone, and *p*-xyloquinone were commercially available and purified by sublimation. *p*-Methoxyquinone [11], *p*-acetylquinone [12], and *p*-carbomethoxyquinone [13] were prepared according to literature methods. $Pd(Ph_3P)_4$ [1], $Pd[(p\text{-}CH_3OC_6H_4)_3P]_4$ [1] and $(Ph_3P)_2Pd(C_2H_4)$ [14] were prepared by methods described in the literature. The preparations of $Pd[(PhO)_3P]_4$ [5], $Pd[(p\text{-}ClC_6H_4)_3P]_3$ [5], and $(Ph_3P)_2Pd$(*p*-benzoquinone) [4] were reported in the literature.

Preparation of $[(n\text{-}Bu_3P)_2Pd]_2(p\text{-}C_6H_4O_2)$ *(I)*

n-Butyllithium (7.5 mmol) in 5 ml of hexane was added to a mixture of *trans*-$(n\text{-}Bu_3P)_2PdCl_2$ (1764 mg, 3.0 mmol) and tri-n-butylphosphine (1212 mg, 6.0 mmol) in 40 ml of hexane. After stirring the mixture for 3 h, the yellow solution was allowed to cool to 5° and washed three times with a mixture (1/1) of methanol/water. *p*-Benzoquinone (162 mg, 1.5 mmol) in 5 ml of benzene was added to this solution which was then stirred for 0.5 h. Evaporation of solvent gave an orange-yellow oil. This was dissolved in 20 ml of methanol, and then a mixture (3/1) of methanol/water was added until the solution became cloudy. Upon cooling to —20°, the solution yielded yellow needles of I, which were washed three times with a mixture (3/1) of methanol/water, and dried in vacuo (1270 mg, 75%).

Preparation of $(n\text{-}Bu_3P)_2Pd(p\text{-}C_6H_4O_2)$ *(II)*

p-Benzoquinone (216 mg, 2.0 mmol) and I (2260 mg, 2.0 mmol) were dissolved in 10 ml of dichloromethane. After removal of solvent, the resulting red oil was recrystallized from a mixture of ether (5 ml) and pentane (20 ml) at —78° to give red crystals of II (2250 mg, 91%).

Reaction of $(n\text{-}Bu_3P)_2Pd(p\text{-}C_6H_4O_2)$ *(II) with* $Pd(n\text{-}Bu_3P)_n$

To a solution of $Pd(n\text{-}Bu_3P)_n$ [prepared, as described above, from *trans*-$(n\text{-}Bu_3P)_2PdCl_2$ (2 mmol), $n\text{-}Bu_3P$ (4 mmol), and n-BuLi (5 mmol)], was added $(n\text{-}Bu_3P)_2Pd(p\text{-}C_6H_4O_2)$ (II) (2 mmol) in 10 ml of dichloromethane and the mixture stirred for 0.5 h. After removal of solvent, the resulting yellow oil was recrystallized from methanol/water to give complex I in 87% yield.

Preparation of $[(PhO)_3P]_2Pd(p\text{-}C_6H_4O_2)$ *(VI)*

To a solution of $Pd[(PhO)_3P]_4$ (675 mg, 0.50 mmol) in 20 ml of benzene, *p*-benzoquinone (108 mg, 1.0 mmol) in 20 ml of benzene was added, and the mixture was stirred for 1 h. The solution was then concentrated to about 7 ml and 25 ml of hexane added. On cooling to —20°, the solution yielded yellow crystals of VI (320 mg, 77%).

$[(p\text{-}CH_3OC_6H_4)_3P]_2Pd(p\text{-}C_6H_4O_2)$ (III) and $[(p\text{-}ClC_6H_4)_3P]_2Pd(p\text{-}C_6H_4O_2)\cdot 0.5C_6H_6$ (V) were prepared similarly in 82 and 86% yields, respectively.

Preparation of $(Ph_3P)_2Pd(p\text{-}C_6H_3O_2CH_3)$ *(VII)*

To a suspension of $Pd(Ph_3P)_4$ (3465 mg, 3.0 mmol) in 30 ml of benzene, *p*-toluquinone (440 mg, 3.6 mmol) in 10 ml of benzene was added, and the mixture was stirred until it became homogeneous. After the solution was concentrated to about 7 ml a mixture of 20 ml of ether and 10 ml of hexane was added to afford red crystals of VII (2100 mg, 93%).

Preparation of $(Ph_3P)_2Pd(p\text{-}C_6H_3O_2COCH_3) \cdot 0.5Et_2O$ *(IX)*

To a suspension of $Pd(Ph_3P)_4$ (578 mg, 0.5 mmol) in 5 ml of ether, *p*-acetylquinone (90 mg, 0.6 mmol) in 5 ml of ether was added. After stirring the mixture vigorously for 4 h dark red solid formed which was filtered off and washed with ether. This crude product, which contained a small amount of unreacted $Pd(Ph_3P)_4$, was allowed to react once again with 50 mg of *p*-acetylquinone in 5 ml of ether to complete the reaction. The dark red product was filtered off, washed with ether, and dried in a vacuo (250 mg, 61%).

$(Ph_3P)_2Pd(p\text{-}C_6H_3O_2COOCH_3) \cdot Et_2O$ (X) was prepared similarly in 73% yield.

Preparation of $(Ph_3P)_2Pd(p\text{-}C_6H_2O_2(CH_3)_2)$ *(XI)*

A solution of *p*-xyloquinone (178 mg, 1.31 mmol) in 20 ml of benzene was added to solid $(Ph_3P)_2Pd(C_2H_4)$ (576 mg, 0.874 mmol) and the mixture stirred for 1 h. The solution was filtered and the filtrate was concentrated to about 10 ml. On addition of 45 ml of hexane red crystals of XI were obtained (450 mg, 67%).

$(Ph_3P)_2Pd(p\text{-}C_6H_3O_2OCH_3) \cdot C_6H_6$ (VIII) was prepared similarly from the reaction of $(Ph_3P)_2Pd(C_2H_4)$ with *p*-methoxyquinone in 55% yield.

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