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PARAMAGNETIC π-ALLYL COMPLEXES OF PALLADIUM

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Summary

Paramagnetic π-allyl complexes of palladium with phenoxyl or *o*-semiquinolate ligands have been prepared and their ESR spectra studied. The stability of the resulting free radicals, the influence of various substituents attached to the palladium atom on the pattern of distribution of spin density of the unpaired electron and the nature of dynamic processes occurring in paramagnetic allyl complexes are discussed.

Introduction

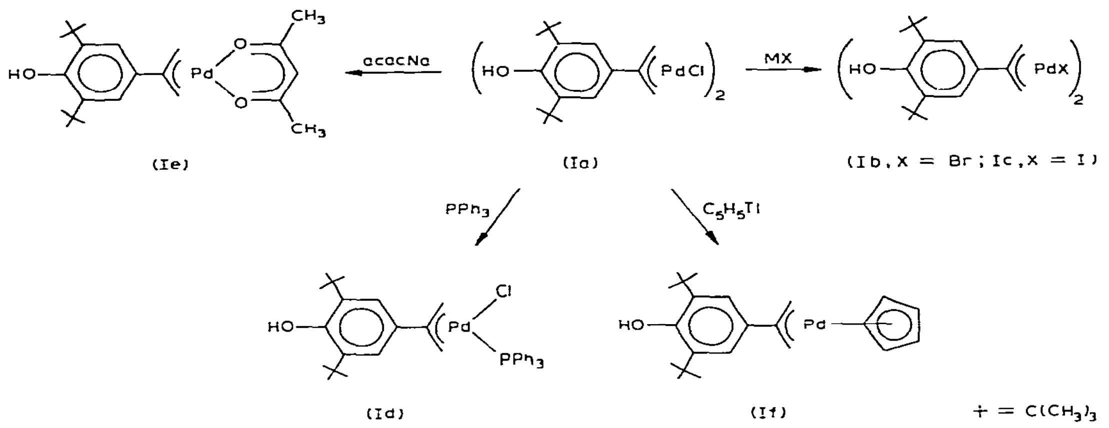
Complexes of transition metals with stable nitroxyl [1—3] and *o*-semiquinonyl [4—6] radicals as ligands are already known. In earlier studies we first prepared complexes of platinum ligands of azobenzene [7], π-allyl [8] and σ-phenyl [9] types containing a hindered phenoxyl radical. The fact of stabilization of free phenoxyl radicals by complexation was established; the highest effect was observed for σ-bonded derivatives of palladium and platinum containing an organometallic grouping in the *para*-position of the phenoxylring.

Results and discussion

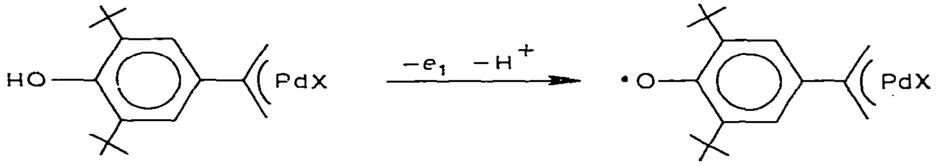
A number of π-allyl palladium complexes with a hindered phenol on the allyl ligand are reported in this paper.

Oxidation of the resulting phenols with lead dioxide in toluene results in the corresponding palladium-containing phenoxyl radicals. ESR spectra of these radicals are shown in Fig. 1, spectral characteristics are given in Table 1.

In an earlier paper [8], using complex 1a as an example, only hyper-fine interaction of the ring protons and protons of the terminal methylene groups of the π-allyl moiety (a(all-H) of about 1 G) was revealed. The more thorough study of ESR spectra reported here has shown that, in addition to the proton hyperfine interaction, the interaction with paramagnetic palladium isotope (^{105}Pd, SCHEME 1



natural abundance 22.6%) is observed. This results in satellite lines at the sides of the basic signal having intensities approximately 20 times less than that of the basic signal (Figs. 1a, b). Multiplicity of the satellite spectrum and its relative intensity fully correspond to the nuclear spin value of ^{105}Pd (I = 5/2) and its natural content. From the data shown in Table 1 it follows that in the series of radicals 1a—e under consideration there occurs a successive decrease in the hyperfine coupling constant of ^{105}Pd, the maximum effect being observed for the π-cyclopentadienyl ligand. In the square planar complexes 1a—e this value steadily decrease with increased volume of the substituent at the central atom (Cl, Br, I, PPh$_3$). In formally octahedral π-cyclopentadienyl derivatives a more pronounced decrease in the value of a(Pd) is observed.



The following fact should be emphasized: while in the case of diamagnetic

TABLE 1

PARAMETERS OF EPR SPECTRA OF π-ALLYL PALLADIUM-CONTAINING PHENOXYL RADICALS (TOLUENE, 25°C)

Initial complex	a(m—H)(G)	a(all—H)(G)	a(Pd)(G)	g-factor
1a	1.8	0.9	12.2	2.0051
1b	—[a]	—	11.5	2.0057
1c	—	—	10.3	2.0076
1d	—	—	9.2	2.0052
1e	—	—	—	2.0043
1f	1.6	0.8	5.4	2.0038

[a] Not observed in this case.

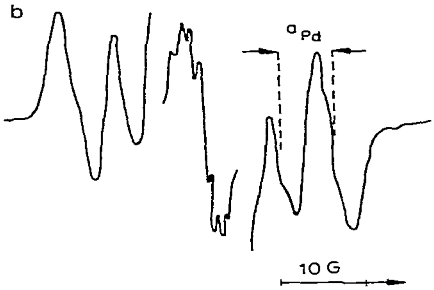


Fig. 1a. ESR spectrum of the radical produced upon oxidation of complex 1a (toluene, 25°C).

Fig. 1b. ESR spectrum of the radical produced upon oxidation of complex 1f (toluene, 25°C).

complexes 1a—f *syn*- and *anti*-protons absorb at different values of the field intensity (4.10 and 2.88 ppm) in the PMT spectrum, in the corresponding free radicals an average spectral pattern is observed indicating equivalence of all the four allyl protons (quintiplet, a(H) approx. 1 G). A *syn—anti* exchange resulting in the equivalence of all protons in most allyl complexes is observed in the NMR time scale either at higher temperatures or in the presence of a strong electron-donor ligand.

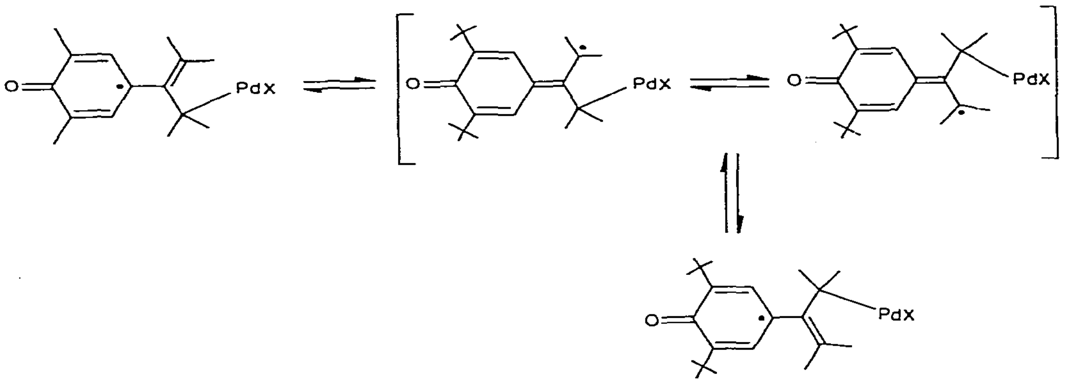
Three possible mechanisms for the averaging of methylene protons have been discussed [10—12]: 1) fast allyl rearrangement with the formation of a σ-bonded allyl compound; 2) fast rotation about C—C bonds in the structure with a delocalized allyl—metal bond; 3) ionization and similarly fast rotation about C—C bonds in the allyl anion. The dynamic state is typical for allyl complexes of non-transition metals at room temperature Li, Mg, Zn, Cd) [13—17].

The possibility of a fast allyl rearrangement as suggested above allows us to draw a direct analogy between allyl systems and synartetic ions. One of the current ideas on the structure of synartetic ions is that these ions should be regarded as a transition state between two rapidly interconverting classical ions [18]. Bartlet [19] suggested a simple physical explanation for this phenomenon: the rate of the transposition of the σ-bond is 4×10^{12} sec^{-1}, i.e. the rearrangement occurs substantially without activation energy and corresponds to the frequency of oscillations of the bond. This phenomenon corresponds substantially to Laar's ideas on tautomerism as an ultra fast translocation of nuclei and bonds [20].

As applied to the chemistry of π-allyl complexes, such an assumption would mean that a fast (probably at the frequency of valence oscillations) and reversible metallotropic rearrangement takes place between two structures, wherein the metal is bonded to the ligand by a σ-bond. In this case the π-allyl structure may be, at least formally, considered as a transition state between two σ-structures, provided that these structures are separated by a potential barrier.

The fact of the equivalence of the four allyl protons observed in the ESR time scale upon conversion from a diamagnetic to a paramagnetic system, gives rise to the idea that the activation barrier for intramolecular rearrangement in free radicals is substantially lower than in the corresponding diamagnetic compounds. This assumption means that in the case of paramagnetic complexes a fast reversible metallotropic rearrangement is readily performed (Scheme 2):

SCHEME 2



This system becomes, to a certain extent, similar to allyl compounds of non-transition metals for which the decisive role of metallotropy was shown in those dynamic processes which resulted in the equivalence of the terminal hydrogen atoms [21].

To investigate the influence of other factors (environments, temperature) on the processes occurring spectra have been determined in various solvents (Table 2) and for the temperature range of from —60 to 40°C (Table 3) for the paramagnetic complex 1a.

The above data demonstrate but a slight effect of temperature and environments on the hyper-fine coupling constant of ^{105}Pd in a paramagnetic system. In all cases the equivalence of the four protons of the allyl moiety and a(all—H) remain unchanged.

Therefore, the motivating force for fast dynamic processes occurring in paramagnetic allyl complexes is the delocalization of spin density of the unpaired electron over the entire molecule. The question is whether the dynamic state of the allyl system remains unchanged in the case where the paramagnetic moiety is not directly bonded with the allyl ligand.

In this connection, in the work reported here the interaction of π-allyl complexes of 1a—f with thallium 3,6-ditert. butyl-*ortho*-semiquinolate has been studied by the ESR method.

The ESR spectrum of complex II is shown in Fig. 2a.

The unpaired electron interacts with two equivalent protons of the *ortho*-

TABLE 2

RELATIONSHIP OF THE HYPER-FINE COUPLING CONSTANT OF ^{105}Pd VS. THE SOLVENT NATURE (20°C)

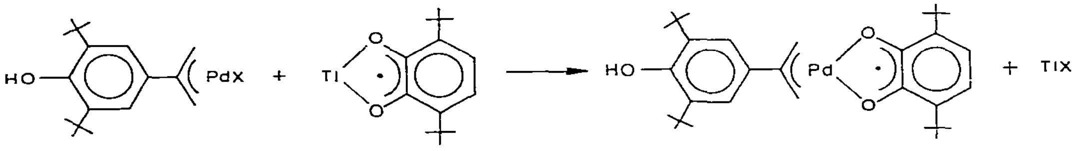
Solvent[a]	a (^{105}Pd) (G)
C_2H_5OH	14.6
$CH_3COC_2H_5$	13.6
$C_4H_8O_2$	13.2
$C_6H_5CH_3$	13.1

TABLE 3

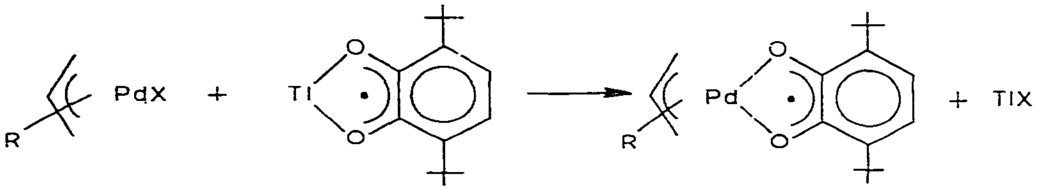
RELATIONSHIP OF THE HYPER-FINE COUPLING CONSTANT OF ^{105}Pd VS. TEMPERATURE (TOLUENE SOLVENT)

Temperature (°C)	$a(^{105}\mathrm{Pd})$ (G)
−60	13.7
−40	13.6
−20	13.4
0	13.2
20	13.1
40	13.0

semiquinolate ring (a(H) = 3.3 G), the paramagnetic isotope of ^{105}Pd (a(Pd) = 2.35 G) and two protons of the allyl moiety (a(all-H) = 0.97 G). A similar picture is observed for other substituted π-allyl complexes.

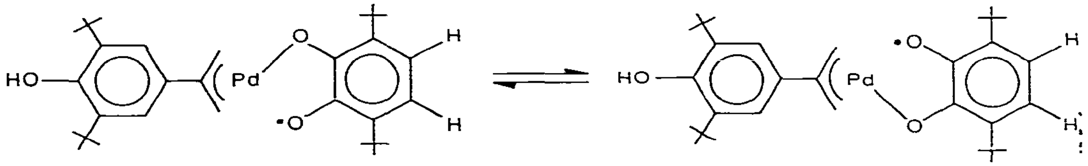


(I) (II)*



R = 2-CH_3, 2-C_6H_5 , 2-$CH_3OC_6H_4$, 1-FC_6H_4 .

In all cases a triplet is obtained from two protons of the paramagnetic ligand and two protons of the π-allyl ligand. The equivalence of two protons in the o-semiquinolate ligand is a consequence of a high-speed reversible migration of palladium atom [22] of the following type.



The appearance, in the ESR spectrum, of the triplet from two protons of the allyl ligand may be due to two reasons. Firstly, by the interaction of the un-

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* A similar compound to II, i.e. 3,5-ditert. butyl-4-hydroxyphenylallyl(3,5-ditert. butyl-*ortho*-semiquinolato)palladium was isolated by the authors and identified by elemental analysis, IR and ESR spectroscopy.

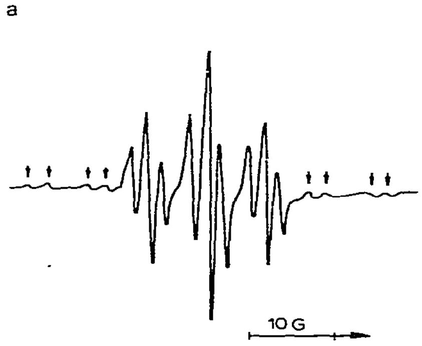


Fig. 2a. ESR specturm of complex II (toluene, 25°C).

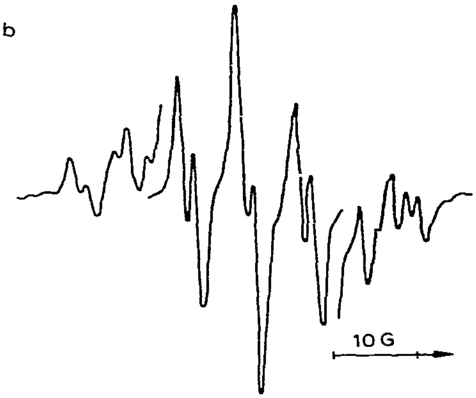
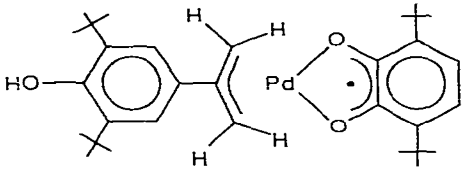
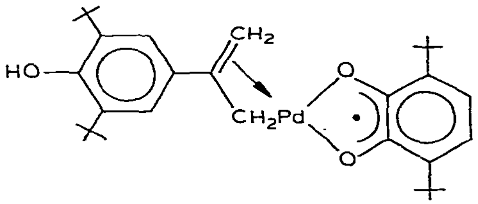


Fig. 2b. ESR specturm of complex IV (toluene, 25°C).

paired electron only with *anti*-protons while retaining the π-allyl structure (A) and, secondly, by the possibility of freezing the σ-structure (B).

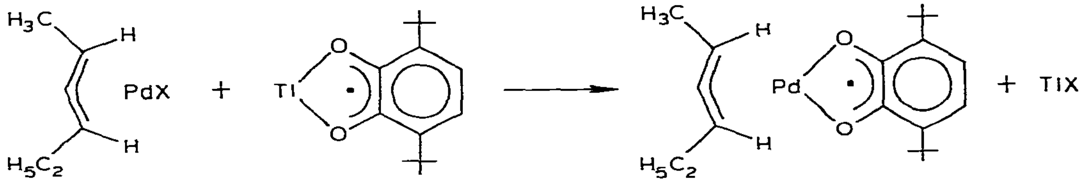


(A)



(B)

To solve this problem, a 1,3-disubstituted allyl complex was used (IIIa)



(IIIa)

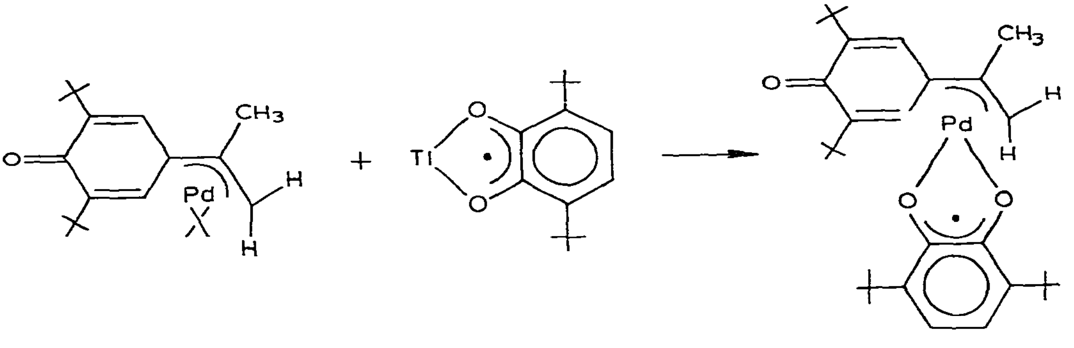
In the ESR spectrum of compound IIIa a triplet is present which in this case may be explained only by the interaction of spin of the unpaired electron with two *anti*-protons of the π-allyl ligand.

The same conclusion is drawn on the basis of ESR-investigation of the allyl complex with the quinoide system previously described by us [23].

In this case the unpaired electron interacts only with one *anti*-proton of the allyl, the hyper-fine coupling constant being about 0.5 G, i.e. about two times less than in all the above-described cases (Fig. 2b).

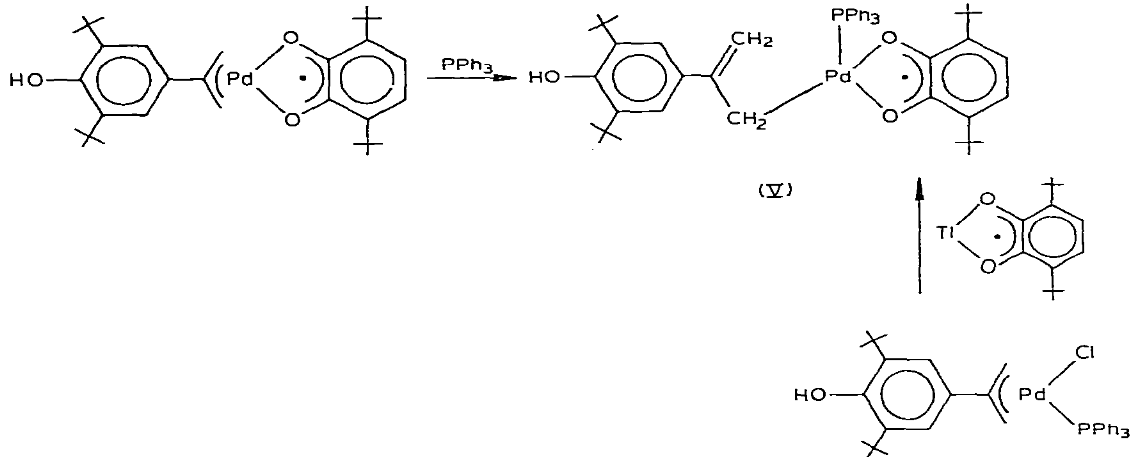
It was possible to observe the formation of σ-structure in the studied systems only in the presence of triphenylphosphine. Complex V was prepared and isolated and also produced by an independent synthesis.

A similar route resulting in a general rearrangement of the system of bonds



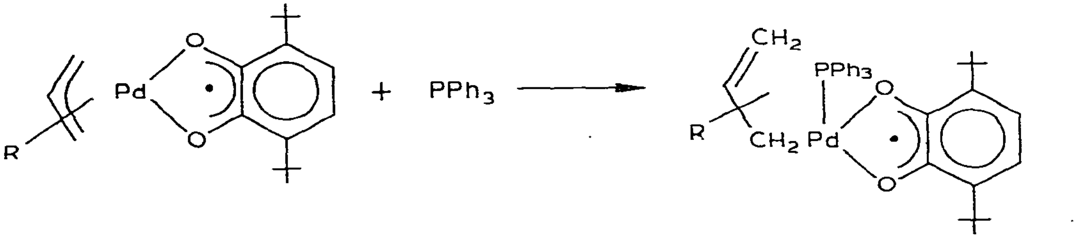
(IV)

has been studied spectroscopically for complexes with different substituents in



(V)

the π-allyl ligand (complexes VI).



(VI)

For compound VI, when R = 2-H, 2-C_6H_5, 2-$CH_3OC_6H_4$, 1-FC_6H_4, a triplet is observed from the two protons of the terminal carbon atom (a(H) = 0.4—0.6 G); furthermore, the electron interacts with the ^{31}P atom (a(P) = 2.55 G) (Fig. 3a). For the 1-methyl-3-ethylallylpalladium-o-semiquinolate, there is a doublet of one proton (a(H) = 0.5 G) in the EPR spectrum, while for the quinoide com-

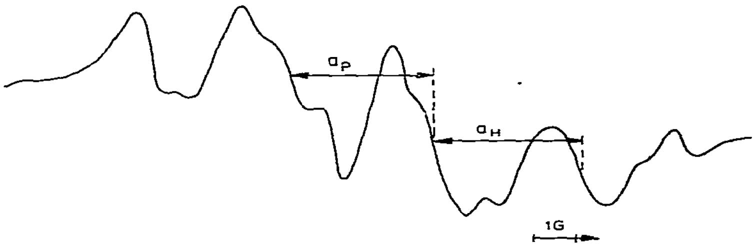


Fig. 3a. ESR spectrum of complex V (toluene, 25°C).

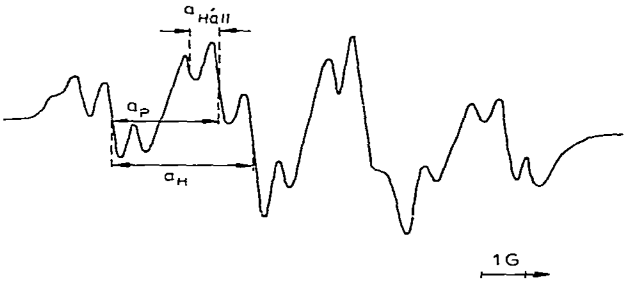
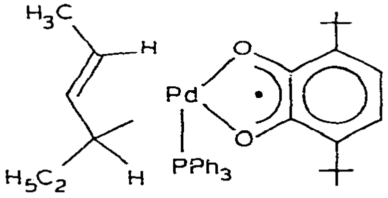
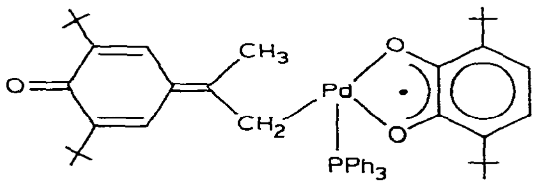


Fig. 3b. ESR spectrum of complex VIII (toluene, 25°C).

plex a triplet of two protons (a(H) = 0.6 G) is observed (Fig. 3b).



(VII)



(VIII)

Therefore, the character of the processes occurring in π-allyl complexes is defined, to a considerable extent, by the position of a free-radical substituent relative to the allyl grouping. In the case of the presence of an unpaired electron directly in the allyl ligand the system becomes dynamic, whereas for π-allyl complexes with other paramagnetic ligand the π-character of the allyl—metal bond is retained, though the π—σ transition is considerably facilitated as compared to diamagnetic allyl compounds.

Experimental

ESR spectra were recorded on a Varian E12A spectrometer in evacuated ampules. IR spectra were taken on a UR-10 instrument in KBr discs. PMR spectra were taken on a R-20 spectrometer with a working frequency of 60 MHz in deuterochloroform. All reactions were carried out in dry purified argon.

*Bis(2-(4-hydroxy-3,5-ditert. butylphenyl)allylpalladium chloride (**1a**)*

A solution of 0.0045 mole of 2,6-ditert. butyl-4-isopropenylphenol [24] in 10 ml of glacial acetic acid is added to a solution of 0.003 mole of palladium chloride in 55 ml of glacial acetic acid in the presence of 0.006 mole of sodium chloride and 0.003 mole of sodium acetate. The mixture is stirred at 80°C for 6 hours, broken down by an equal volume of water, and extracted with methylene chloride. The extract is dried over magnesium sulphate and the solvent is removed in vacuum. The residue is added with methanol; the insoluble portion is filtered-off, thoroughly washed with methanol and petroleum ether. The resulting product is recrystallized from a benzene-hexane mixture (1 : 1).

The yield is 72%, decomp. temp. 193—194°C. Found: C, 52.58; H, 6.20. $C_{34}H_{50}O_2Cl_2Pd_2$. Calcd.: C, 52.70; H, 6.43%. IR spectrum (ν, cm^{-1}): 3580.

*Bis(2-(4-hydroxy-3,5-ditert. butylphenyl)allylpalladium bromide) (**1b**)*

To a solution of 0.0003 mole of **1a** in 15 ml of acetone a 10% excess of anhydrous lithium bromide dissolved in acetone is added. The reaction mixture is stirred at room temperature for 8 hours and filtered. The filtrate is diluted with an equal volume of water and extracted with benzene. The extract is washed with water, dried over magnesium sulphate and evaporated to a small volume; then petroleum ether is added. The residue is recrystallized from a benzene-hexane mixture (1 : 1). The yield is 79%, decomp. temp. is 226—228°C. Found: C, 47.97; H, 5.67. $C_{34}H_{50}O_2Pd_2Br_2$ Calcd.: C, 47.80, H, 5.80%. IR spectrum (ν, cm^{-1}): 3585.

*Bis(2-(4-hydroxy-3,5-ditert. butylphenyl)allylpalladium iodide) (**1c**)*

The product is prepared in a similar manner from 0.0003 mole of **1a** and a 10% excess of anhydrous potassium iodide with recrystallization from a benzene-hexane mixture (1 : 1). The yield is 68%, decomp. temp. 251—252°C. Found: C, 42.54; H, 5.20. $C_{34}H_{50}O_2Pd_2I_2$. Calcd.: C, 42.60; H, 5.23%. IR spectrum (ν, cm^{-1}): 3580.

*2-(4-hydroxy-3,5-ditert. butylphenyl)allyl(triphenylphosphine)palladium chloride (**1d**)*

To a solution of 0.0003 mole of **1a** in 15 ml of acetone a 15% excess of dry triphenylphosphine is added. The reaction mixture is stirred at room temperature for 5 hours. The solvent is removed in vacuum. The residue is crystallized from petroleum ether-ether (1 : 1). The yield is 60%, decomp. temp. 189—192°C. Found: C, 64.75; H, 6.30. $C_{35}H_{40}OPdClP$ Calcd.: C, 64.75; H 6.16%. IR spectrum (ν, cm^{-1}): 3600.

*2-(4-hydroxy-3,5-ditert. butylphenyl)allyl(acetylacetonate)palladium (**1e**)*

To a solution of 0.0003 mole of **1a** in 15 ml of benzene there is added a solution of 0.0006 mole of sodium acetylacetonate dissolved in ethanol. The reaction mixture is stirred for 3 hours and filtered, then diluted with an equal volume of water. The benzene layer is separated, washed with water and dried over magnesium sulphate. The solvent is removed in vacuum. The residue is recrystallized from hexane. The yield is 74%, decomp. temp. 181.5—183°C. Found: C, 85.39; H, 7.00. $C_{32}H_{32}O_3Pd$ Calcd.: C, 85.38; H, 7.11%. IR spectrum (ν, cm^{-1}): 3610.

2-(4-hydroxy-3,5-ditert. butylphenyl)allyl(π-cyclopentadienyl)palladium (1f)

To a solution of 0.0003 mole of **1a** in 15 ml of methylene chloride a 10% excess of thallium cyclopentadienyl is added. The reaction mixture is stirred for 3 hours and filtered. The solvent is removed in vacuum. The resulting residue is dissolved in ether, filtered-off and the solvent is removed in vacuum. The product is recrystallized from petroleum ether. The yield is 70.8%, decomp. temp. 141°C. Found: C, 63.01; H, 7.20. $C_{22}H_{30}OPd$ Calcd.: C, 63.25; H, 7.21%. IR spectrum (ν, cm^{-1}) 3600.

2-(4-hydroxy-3,5-ditert. butylphenyl)allyl(3,5-ditert. butyl-ortho-semiquinolato)-palladium (II)

To a solution of 0.0005 mole of **1a** in 15 ml of abs. benzene is added a freshly prepared solution of thallium 3,5-ditert. butyl-*ortho*-semiquinolate in absolute benzene; the solution is prepared from thallium chloride and 3,5-ditert. butyl-*ortho*-quinone. The reaction mixture is stirred at room temperature for 2 hours, filtered in an inert atmosphere and the solvent removed in vacuum. The residue is dissolved in hexane, filtered-off from the insoluble portion and evaporated in vacuum to a small volume. The product precipitates upon cooling. The yield is 50.8%, decomp. temp. 138—139°C. Found: C, 62.09; H, 8.84. $C_{31}H_{45}O_3Pd$ Calcd.: C, 62.17; H, 8.89%. IR spectrum (ν, cm^{-1}): 3640.

2-(4-hydroxy-3,5-ditert. butylphenyl)propen-2-yl-1(triphenylphosphine)-3,5-di-tert. butyl-ortho-semiquinolate palladium (V)

To a solution of 0.0002 mole of II in 15 ml of acetone 0.0002 mole of dry triphenylphosphine is added. The reaction mixture is stirred for 3 hours at room temperature. The solvent is removed in vacuum. The residue is washed with a small amount of ether and reprecipitated from benzene with hexane. The yield is 44%, decomp. temp. 104—105° C. Found: C, 70.44; H, 7.20. $C_{49}H_{60}O_3PPd$ Calcd.: C, 70.62; H, 7.21. IR spectrum (ν, cm^{-1}): 3620.

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