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# Chemistry of chelate-stabilized aryloxopalladium(II) complexes: syntheses, X-ray crystal structures and formation of C—H···O hydrogen-bonds*

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**Abstract**—In this paper the synthesis, characterization and properties of various Pd(II) complexes with 2-acylphenolates as chelating ligands are reported. The compounds are easily accessible by stirring 2-acylphenoles with Pd(II) complexes in the presence of potassium *tert*-butoxide. Cyclometallated tri(*o*-tolyl)phosphine derivatives and allyl palladium complexes were chosen as palladium precursor. The solid state structures of the complexes 2-acetylphenolato-[*o*-(di-*o*-tolylphosphino)benzyl]palladium(II) (**2**), 2-benzoylphenolato-[*o*-(di-*o*-tolylphosphino)benzyl]palladium(II) (**4**) and 2-acetyl-1-naphtholato-[*o*-(di-*o*-tolylphosphino)benzyl] palladium(II) (**6**) were further studied by X-ray diffraction analyses. In all complexes the palladium center is coordinated in a square planar fashion. Interestingly, coordination of the 2-acylphenolates to palladium results in a significant perturbation of the delocalization within the aromatic ring. The strong hydrogen-bond acceptor behavior of the phenolic oxygen as well as the *cis*/*trans*-isomerisation is discussed in terms of the solid structure (**2, 4** and **6**) and the NMR shifts observed in various solvents. 

*Keywords*: palladacycles; π-allylpalladium complexes; hydrogen bonds

The chemistry of late transition metal alkoxide complexes has recently attracted much attention [1]. Such complexes are important intermediates in various transition metal-catalyzed reactions [2], including the palladium-catalyzed formation of carbon-oxygen bonds [3] and the rhodium and palladium mediated activation of C—O single bonds [4]. During the last few years important aspects of the chemistry of palladium(II) alkoxide and aryloxide complexes were established elegantly by van Koten *et al.* and others [5–8]. However, there are only few reports of palladium alkoxide complexes containing an additional donor group (usually nitrogen or phosphorus) [7,8]. Pd(II)-complexes with easily accessible 2-acylphenolates and related ligands are surprisingly rare in the literature and, to the best of our knowledge, there is no structural characterization of such compounds [9]. An interesting feature of palladium and other late transition metal alkoxides is the formation of intermolecular O—H···O hydrogen bonds to an aditional alcohol [10]. The formation of O—H···O hydrogen bonding has important effects on the properties and self organization of the corresponding metal complexes [11]. In addition to an O—H···O interaction there are few examples known with C—H···O hydrogen bonds [6,8,12]. Here the carbon atom participating in the C—H···O hydrogen bond is attached to a heteroatom (O,N), which coordinates to a metal center. Thus, this interaction is a model of the initial stage of a base-assisted β-hydride elimination.

In cooperation with Herrmann *et al.* we have been engaged in the synthesis of cyclometallated palladium complexes of tri(*o*-tolyl)phosphine, e.g. **1**, as efficient catalysts or catalyst-precursors for important C—C coupling reactions [13]. Recently, we have shown that cyclometallated palladium complexes are also suitable

* Dedicated to Prof. Dr. Drs. h. c. W. A. Herrmann on the occasion of his 50th birthday.

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for C—N coupling processes [14]. In order to synthesize model complexes for similar C—O coupling reactions, as well as to study the behavior of 2-acylphenolates as ligand, we were interested in the preparation of cyclometallated palladium complexes containing the 2-acylphenolate ligand.

Herein, we report for the first time on the synthesis and properties of this class of complexes. The synthesis and characterisation of $\pi$-allylpalladium complexes containing 2-acylphenolate ligands is presented. These $\pi$-allylpalladium complexes with additional coordination of a phenoxide ligand are interesting as model compounds for the palladium-catalyzed *O*-arylation and phenoxycarbonylation of allylic substrates leading to allyl–aryl ethers and unsaturated esters, respectively [15].

## RESULTS AND DISCUSSION

### *Preparation of the aryloxopalladium(II) complexes*

The palladium phenolate complexes **2–6** were readily prepared by stirring a solution of the palladacycle **1** [13] and 2 equiv. of the corresponding 2-acylphenol together with 2 equiv. of potassium *tert*-butoxide in toluene at room temperature (Scheme 1). Good to very good yields (76%–92%) were obtained after crystallization from toluene/pentane.

The addition of a strong base is crucial for the success of the reaction. Only starting material was isolated from the reaction mixture of **1** and 2-acylphenol if sodium acetate was used as base. Using 2-hydroxybenzophenone as ligand, the synthesis is succesful if performed under reflux conditions. However, in case of 2-hydroxyacetophenone as ligand, palladium black is formed under such reaction conditions. This may be due to formation of enolates from the acetophenone.

The palladium(II) phenolate complexes **9–12**, which contain an $\eta^3$-allyl unit, were prepared in a similar way to compounds **2–6**. Addition of 2 equiv. of the 2-acylphenol and 2 equiv. of potassium *tert*-butoxide to a toluene solution of the corresponding $\pi$-allylpalladium chloride dimer and stirring the mixture for approximately 7 h at ambient temperature yielded the desired products (Scheme 2). When weak bases, such as sodium acetate, were employed, starting material was recovered unchanged. Though precipitation of palladium black seems to be inevitable during the course of the reaction, the allylic complexes **9–12** were isolated in reasonable yields of 73–88% as yellow solids.

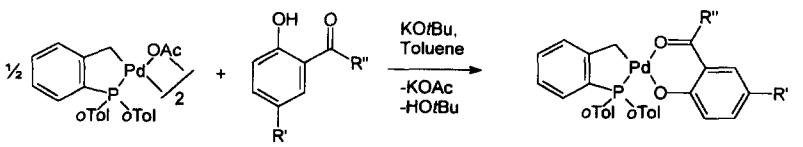
The allylic complexes **9–12** are less stable than the corresponding phosphapalladacycles **2–6**. Toluene solutions of **9–12** decomposed slowly with metal deposition at room temperature. In the solid state (room temperature) their yellow color darkens within a few days due to formation of elemental palladium. In the case of **9**, the *O*-allylated ligand could be detected ($^1$H NMR) as a decomposition product resulting from reductive elimination.

### *Molecular structures of the complexes* **2**, **4** *and* **6**

Compounds **2**, **4** and **6** were characterized by X-ray diffraction analysis. Selected bond distances and angles are given in Table 1.

The molecular structure of **2** is depicted in Fig. 1. The structure consists of a palladium atom which is coordinated in a square planar fashion by a cyclometallated tri(*o*-tolyl)phosphine and a chelating 2-acetyl phenolate ligand. Two geometric isomers are possible with the phenolic oxygen located *cis* or *trans* to the phosphorus atom and both were observed in solution (*vide infra*). In complex **2** O31, the phenolic oxygen and O11, the carbonyl oxygen of the parent 2-acetyl phenol ligand, are located *trans* to the phosphorus atom P and C27 of the phosphine ligand, respectively. The principal coordination sphere is close to planar, the maximum deviation being 0.047(2) Å. The distances Pd—P = 2.223(1) Å and Pd—C27 = 2.010(4) Å compare favorably with those observed in **1** (2.216(1) Å and 2.021(5) Å, respectively) [16].

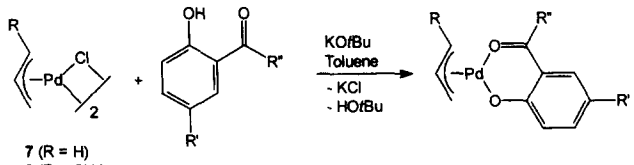
The phenolic oxygen palladium bond Pd—O31 = 2.042(2) Å was significantly shorter than




**1**

| | R' | R'' | yield |
|---|---|---|---|
| **2** | H | $CH_3$ | 86 % |
| **3** | F | $CH_3$ | 92 % |
| **4** | H | $C_6H_5$ | 77 % |
| **5** | $CH_3$ | $C_6H_5$ | 76 % |
| **6** | 2-Acetyl-1-naphtholate | | 79 % |

Scheme 1.




7 (R = H)
8 (R = $CH_3$)

| | R | R' | R'' | yield |
|---|---|---|---|---|
| **9** | H | H | $C_6H_5$ | 88 % |
| **10** | $CH_3$ | F | $CH_3$ | 74 % |
| **11** | $CH_3$ | H | $C_6H_5$ | 73 % |
| **12** | $CH_3$ | 2-Acetyl-1-naphtholate | | 81 % |

Scheme 2.

the carbonyl oxygen palladium bond Pd—O11 = 2.110(2) Å and associated with this effect are different C—O bond distances (C3—O31 = 1.302(4) Å, C1—O11 = 1.254(4) Å). However, the difference is not as much as one would expect for a purely phenolic C—O single and a C=O double bond. The distances for C1—C2 = 1.427(5) Å and C2—C3 = 1.427(5) Å are equal, which is surprising as these are an aromatic and a single bond in the parent ligand, respectively, and should therefore differ more. Distances within the fused benzene ring deviate from the normal sixfold symmetry with short bonds for C6—C7 and C4—C5 (1.335(8) Å and 1.356(7) Å, respectively). The significant differences in the two Pd—O and the two C—O bond lengths indicate that the presence of the fused benzene ring has attenuated the resonance system in the chelate ring, of the type found in most metal complexes with $\beta$-diketones, such as acylacetonato complexes.

The interpretation of these results in terms of resonance structures is in line with the assumption that the delocalisation within the aromatic ring (Scheme 3, A) is less significant and that the acac-type delocalization (Scheme 3, B) makes an important contribution to the overall structure and reactivity of this molecule. Analogous effects have been observed in the complexes $Ni(C_9H_9O_2)_2$ [17], $C_9H_9O_2$ = 2-acetyl-4-methyl-phenol and $Cu(C_8H_7O_2)_2py$ [18], $C_8H_7O_2$ = 2-aceto-phenol, py = pyridine.

Regarding hydrogen bonds of the coordinated oxygen atoms there is a short contact between O11 and the methyl group C47. The non-bonded distance O11 · · · C47 = 3.13 Å is considerably shorter than the sum of the van-der-Waals radii of oxygen and an averaged radius for the methyl group indicating a weak hydrogen bond between C47—H · · · O11. Recent studies of such C—H · · · O contacts show their importance as secondary interactions and in determining the crystal packing [11].

The molecular structure of complex **4** is similar to the structure of complex **2** except that in **4** the carbonyl oxygen O11 is located *trans* to the phosphorus atom and the phenolic oxygen O31 is *trans* to C27 (Fig. 2). This geometry avoids steric conflict between the phenyl group attached to C1 and the *o*-tolyl groups attached to the phosphorus atom. The distances Pd—P = 2.198(1) Å, Pd—C27 = 2.022(2) Å in **4** are comparable to those observed in **2**. However, the distances of palladium to the oxygen atoms are different with Pd—O31 = 2.092(1)Å longer and Pd—O11 = 2.087(1) Å slightly shorter than in compound **2**, probably reflecting the different *trans*-influence of phosphorus and carbon. As expected, the phenolic C3—O31 bond (1.290(3) Å) is longer than the C1—O11 bond (1.244(2) Å), but again the difference is less pronounced compared to a localized C—O single and a C=O double bond. The asymmetry in the aromatic ring is more pronounced than in complex **2** with C4—C5 and C6—C7 being short (1.361(3) Å and 1.367(3) Å, respectively) and C2—C3 being long (1.441(3) Å). Again, this effect can be explained in terms of resonance structure B. The phenyl ring attached to C1 is not conjugated with the chelate ring being twisted by 52° to the plane defined by Pd, O31, O11, C1, C2, C3.

There are short contacts between O31 and the methyl groups of the *o*-tolyl rings. The non-bonded distances C · · · O are longer than those observed in **2**, however, there are two weak contacts with methyl groups (O31 · · · C37 = 3.31Å; O31 · · · C47 = 3.40 Å). The hydrogen atoms of the methyl groups were clearly located in the difference map and allow to further characterize the geometry around O31. The distance of H37a to O31 is 2.40 Å (H37a—C37 = 0.91 Å) and the angle O31 · · · H37a—C37 is 176°. The distance of H47b to O31 is 2.59 Å (H47b—C47 = 0.86 Å) and the angle O31 · · · H47b—C47 is 155°. The oxygen atom is in a pseudotetrahedral environment with an angle H37a · · · O31 · · · H47b = 98°. This arrangement is clearly indicative of C—H · · · O interactions.

The X-ray structure of the complex **6** is shown in Fig. 3. The overall geometry of **6** is very similar to that observed in **2** (Fig. 1). The steric requirement of the naphthyl group favors the position of the phenolic oxygen *trans* to phosphorus. Bond distances to palladium (Pd—P = 2.221(1) Å, Pd—C27 = 2.017(2) Å,

Table 1. Selected bond lengths (Å) and angles (°)

| Complex | **2** | Complex | **4** | Complex | **6** |
|---|---|---|---|---|---|
| Pd—C(27) | 2.010(4) | Pd—C(27) | 2.022(2) | Pd—C(27) | 2.017(2) |
| Pd—O(11) | 2.110(2) | Pd—O(11) | 2.0871(13) | Pd—O(11) | 2.104(2) |
| Pd—O(31) | 2.042(2) | Pd—O(31) | 2.0915(13) | Pd—O(31) | 2.057(2) |
| Pd—P | 2.2225(9) | Pd—P | 2.1982(5) | Pd—P | 2.2209(6) |
| P—C(21) | 1.811(3) | C(1)—O(11) | 1.244(2) | P—C(21) | 1.811(2) |
| P—C(31) | 1.822(3) | C(1)—C(2) | 1.451(2) | P—C(31) | 1.832(2) |
| P—C(41) | 1.824(3) | C(1)—C(11) | 1.495(3) | P—C(41) | 1.835(2) |
| C(1)—O(11) | 1.254(4) | C(2)—C(7) | 1.412(3) | C(1)—O(11) | 1.254(3) |
| C(1)—C(2) | 1.427(5) | C(2)—C(3) | 1.441(3) | C(1)—C(2) | 1.435(3) |
| C(1)—C(11) | 1.513(6) | C(3)—O(31) | 1.290(3) | C(1)—C(11) | 1.515(3) |
| C(2)—C(7) | 1.423(5) | C(3)—C(4) | 1.428(3) | C(2)—C(3) | 1.423(3) |
| C(2)—C(3) | 1.427(5) | C(4)—C(5) | 1.361(3) | C(2)—C(7) | 1.443(3) |
| C(3)—O(31) | 1.302(4) | C(5)—C(6) | 1.403(3) | C(3)—O(31) | 1.293(3) |
| C(3)—C(4) | 1.413(5) | C(6)—C(7) | 1.367(3) | C(3)—C(4) | 1.457(3) |
| C(4)—C(5) | 1.356(7) | P—C(21) | 1.816(2) | C(4)—C(5) | 1.409(3) |
| C(5)—C(6) | 1.374(8) | P—C(41) | 1.820(2) | C(4)—C(4A) | 1.414(4) |
| C(6)—C(7) | 1.335(8) | P—C(31) | 1.831(2) | C(4A)—C(4B) | 1.375(4) |
| | | | | C(4B)—C(5B) | 1.394(5) |
| | | | | C(5)—C(5A) | 1.417(4) |
| | | | | C(5)—C(6) | 1.425(4) |
| | | | | C(5A)—C(5B) | 1.358(5) |
| | | | | C(6)—C(7) | 1.336(4) |
| O(31)—Pd—O(11) | 86.59(9) | O(11)—Pd—O(31) | 86.95(5) | O(31)—Pd—O(11) | 86.00(6) |
| C(27)—Pd—P | 83.87(13) | C(27)—Pd—P | 82.85(7) | C(27)—Pd—P | 83.94(7) |
| C(21)—P—Pd | 104.26(13) | O(11)—C(1)—C(2) | 125.2(2) | C(21)—P—Pd | 104.82(8) |
| C(31)—P—Pd | 121.85(11) | O(11)—C(1)—C(11) | 114.7(2) | C(31)—P—Pd | 123.55(7) |
| C(41)—P—Pd | 113.25(11) | C(2)—C(1)—C(11) | 120.1(2) | C(41)—P—Pd | 112.27(7) |
| O(11)—C(1)—C(2) | 124.8(3) | C(1)—O(11)—Pd | 128.18(12) | O(11)—C(1)—C(2) | 124.9(2) |
| O(11)—C(1)—C(11) | 114.9(4) | C(7)—C(2)—C(3) | 119.0(2) | O(11)—C(1)—C(11) | 114.8(2) |
| C(2)—C(1)—C(11) | 120.4(4) | C(7)—C(2)—C(1) | 118.4(2) | C(2)—C(1)—C(11) | 120.3(2) |
| C(1)—O(11)—Pd | 129.7(3) | C(3)—C(2)—C(1) | 122.6(2) | C(1)—O(11)—Pd | 129.7(2) |
| C(7)—C(2)—C(1) | 118.7(4) | O(31)—C(3)—C(4) | 117.9(2) | C(3)—C(2)—C(1) | 123.7(2) |
| C(7)—C(2)—C(3) | 117.2(4) | O(31)—C(3)—C(2) | 125.6(2) | C(3)—C(2)—C(7) | 117.7(2) |
| C(1)—C(2)—C(3) | 124.0(3) | C(4)—C(3)—C(2) | 116.5(2) | C(1)—C(2)—C(7) | 118.6(2) |
| O(31)—C(3)—C(4) | 116.9(4) | C(3)—O(31)—Pd | 123.31(12) | O(31)—C(3)—C(2) | 125.7(2) |
| O(31)—C(3)—C(2) | 125.8(3) | C(5)—C(4)—C(3) | 122.4(2) | O(31)—C(3)—C(4) | 115.8(2) |
| C(4)—C(3)—C(2) | 117.3(4) | C(4)—C(5)—C(6) | 120.8(2) | C(2)—C(3)—C(4) | 118.5(2) |
| C(3)—O(31)—Pd | 129.0(2) | C(7)—C(6)—C(5) | 119.0(2) | C(3)—O(31)—Pd | 129.2(2) |
| C(5)—C(4)—C(3) | 122.0(5) | C(6)—C(7)—C(2) | 122.4(2) | C(5)—C(4)—C(3) | 120.8(2) |
| C(4)—C(5)—C(6) | 120.9(5) | C(21)—P—Pd | 105.08(6) | C(4)—C(5)—C(6) | 119.0(2) |
| C(7)—C(6)—C(5) | 119.4(5) | C(41)—P—Pd | 121.51(6) | C(7)—C(6)—C(5) | 120.6(2) |
| C(6)—C(7)—C(2) | 123.2(5) | C(31)—P—Pd | 113.74(6) | C(6)—C(7)—C(2) | 123.4(2) |
| C(26)—C(27)—Pd | 118.8(3) | C(26)—C(27)—Pd | 118.42(13) | C(26)—C(27)—Pd | 119.3(2) |

Pd—O31 = 2.057(2) Å and Pd—O11 = 2.104(2) Å) as well as the carbon-oxygen distances (C3—O31 = 1.293(3) Å and C1—O11 = 1.254(3) Å) are nearly identical to those observed in **2**. The naphthyl ring has a short bond C6—C7 = 1.336(4) Å, relatively short bonds for C5a—C5b = 1.358(5) Å and C4a—C4b = 1.375(4) Å and long bonds for C2—C7 = 1.443(3) Å and C3—C4 = 1.457(3) Å indicating partially localized double bonds. A similar asymmetry of the naphthyl ring has been detected in the complex $Cd(C_{12}H_8O_2)_2bpy$, $C_{12}H_8O_2$ = 2-acetyl-1-hydroxy-naphthalene, bpy = 2,2′-bipyridine [25]. As observed in **2**, there is a short contact between O11 and the protons of the methyl group C47 with a non-bonded distance O11 ··· C47 = 3.17 Å.

*Solution studies*

Obviously, the complexes **2–6** can exist as two isomers, with the phenolic oxygen *cis* or *trans* towards

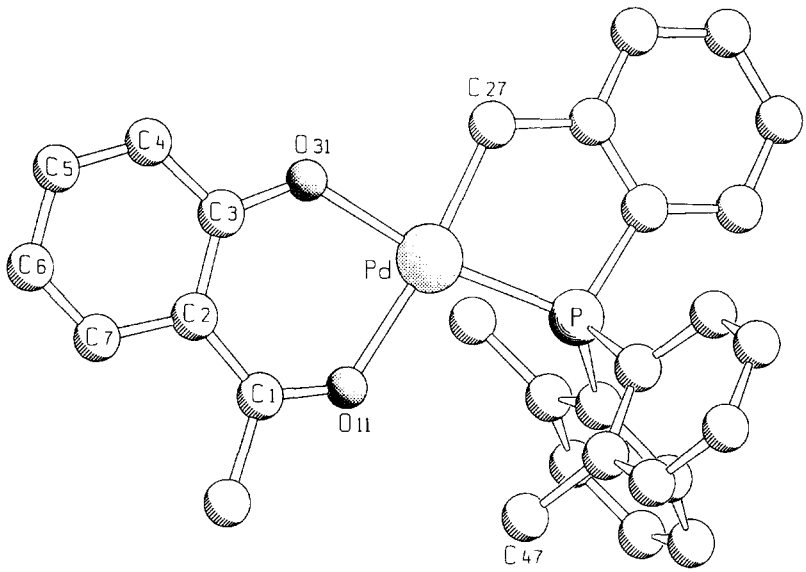
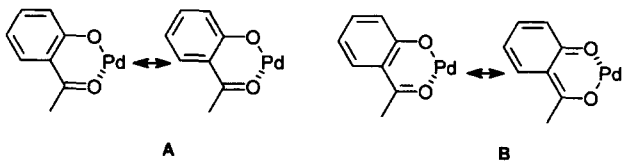



Fig. 1.




Scheme 3.

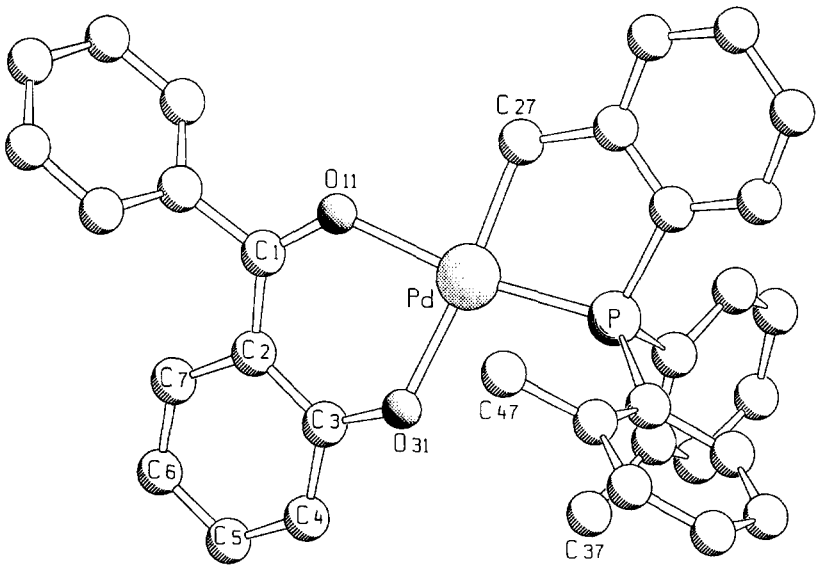



Fig. 2.

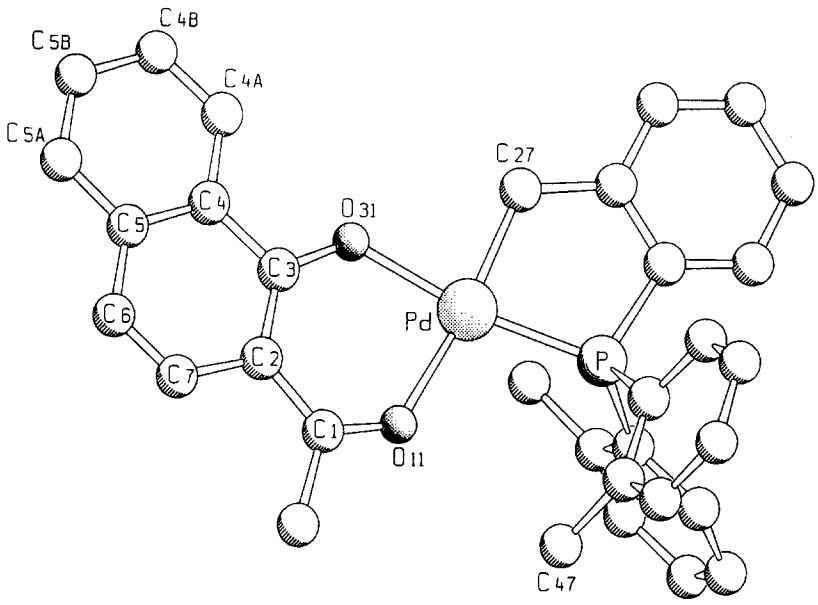



Fig. 3.

the phosphorus atom (Scheme 4). Depending on the substituent R″ the *cis*- or *trans*-isomer can be preferred. This was exemplified by the geometry of complexes **2, 4,** and **6** in the solid state. To further investigate isomerization processes and the ratio between the two isomers, NMR experiments were performed in various solvents. For each of the two geometric isomers of **2–6** distinct $^{31}P\{^1H\}$NMR signals were observed.

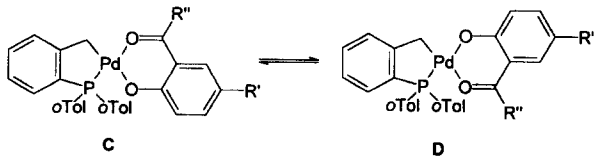
We provisionally assign the high field $^{31}P\{^1H\}$NMR signal to **D** and the low field signal to **C**. The intensity of the high field signal is always higher than that of the low field signal for each of the compounds **2–6**.

Taking into account the ability of the oxygen atoms in **2–6** to participate in hydrogen bonding, the *cis*-/*trans*-isomerization should be affected by the solvent. To study the isomerization phenomenon in further detail, the $^{31}P\{^1H\}$NMR spectrum of **2** was recorded in 10 different solvents. In $CDCl_3$, two signals were observed at 35.7 ppm and 34.2 ppm. The ratio of the intensities of the two signals ($K$) changed slightly upon warming. It changes from 0.11 (25°C) to 0.14 (50°C) reversibly. A similar effect was observed in toluene-$d_8$ as solvent: $K$ changes from 0.44 (25°C) to 0.50 (50°C). As expected, the nature of the solvent has a dramatic effect on $K$ (Table 2).

As shown in Table 2, $K$ can vary from 0 to 0.5. There seems to be no correlation between $K$ and either

Table 2. $K$ values of **2** in different solvents ($K$ = intensity of the $^{31}P$ NMR low field signal to the intensity of the high field signal)

| Solvent | Ratio of $^{31}P$ NMR intensities | $K$ |
|---|---|---|
| MeOD/2-BuOH | 0:100 | 0 |
| $CDCl_3$ | 10:90 | 0.11 |
| $CD_2Cl_2$ | 14:86 | 0.16 |
| DMSO-$d_6$ | 17:83 | 0.21 |
| $C_6H_5Cl$ | 22:78 | 0.29 |
| Sulfolane | 22:78 | 0.29 |
| thf-$d_8$ | 27:73 | 0.37 |
| Benzene-$d_6$ | 29:71 | 0.40 |
| Toluene-$d_8$ | 31:69 | 0.44 |
| $CCl_4$ | 33:67 | 0.48 |




Scheme 4.

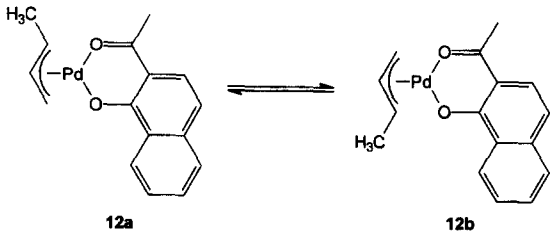
the $E_T^N$-values as empirical parameter of solvent polarity [20] or the $\pi^*$-scale of solvent dipolarity/polarity [21]. Obviously, $K$ is affected by other properties of the solvent. As mentioned earlier, phenolate complexes usually behave as strong hydrogen bond acceptors (HBA). In the solid state even hydrogen bonds from the benzylic protons of the *o*-tolyl substituents are formed (stabilizing **C**). An interaction of the phenolic oxygen with the solvent would be easier in form **D** because of minor sterical hindrance. Since hydrogen bond acceptors usually are also electron-pair donors, $K$ should be affected by both the ability of the solvent to act as hydrogen bond donor (HBD) $\alpha$ and the solvent acceptor number $AN$ [22].

This argumentation is in good agreement with the observed data. Alcohols and chloroform are good HBD solvents and therefore $K$ is low, leading to **D** as the predominant species in solution. On the other hand, tetrachloromethane or toluene are not able to form hydrogen bonds. Thus high values are observed for $K$. The same tendency is observed if correlating $K$ with the acceptor number $A$ [22].

The $^1$H and $^{13}$C NMR spectra of the allylic complexes exhibit some interesting features concerning the dynamic solution behavior of the $\eta^3$-allyl unit. In the case of **9** the $^{13}$C NMR (room temperature) shows a broad signal at 55.2 ppm similar to a doublet which is assigned to C1/C3 of the $\eta^3$-allyl ligand. Apparently, the absorptions for these carbon atoms almost coalescence, indicating a rotation of the allyl group. The $^1$H NMR of **9** exhibits only one absorption each for the *syn* and *anti* hydrogens.

In contrast, in the $^{13}$C NMR spectrum of **12** each of the signals for C1, C3 of the crotyl moiety and $CH_3$ of the phenolate ligand consists of two sharp peaks (C1: 51.39 ppm, 50.35 ppm; C3: 72.60 ppm, 71.48 ppm; $CH_3$: 27.71 ppm, 27.16 ppm), arising from the stereoisomers **12a** and **12b** (Scheme 5). Therefore the rotation of the allyl unit is slow compared to the NMR time scale. The resonances of the aromatic carbon atoms of the 2-acylphenolate-ligand are not influenced by the orientation of the crotyl ligand; only one peak per carbon atom is observed for both stereoisomers.

The ratio of the *cis*/*trans* isomers of **12** can be determined from the $^1$H NMR spectrum (25°C, $CDCl_3$; 63:37).




**12a** **12b**

Scheme 5.

In the $^1$H and $^{13}$C NMR spectra of compounds **10** and **11** there is no evidence for a hindered rotation of the allyl moiety as only one absorption appears for each atom. However, this may be due to very similar chemical environments in both stereoisomers.

## EXPERIMENTAL

### *General comments*

NMR spectra ($^1$H, $^{13}$C, $^{31}$P) were recorded on a Jeol JMX-GX 400 instrument. FAB-MS spectra were recorded on a Varian MAT 311a. Elemental analyses were carried out by the Microanalytical Laboratory at the TU München. IR spectra were recorded on a Perkin–Elmer 1600.

The palladacycle **1** was prepared as reported previously [13]. Bis($\eta^3$-allyl)di($\mu$-chloro)dipalladium(II) (**7**) and bis[(1,2,3-$\eta$)-2-butenyl]di($\mu$-chloro)palladium (II) (**8**) were prepared from the corresponding allylic chlorides according to the literature [23].

The substituted phenoles and 2-acetyl-1-naphthole were obtained from Aldrich and were used without further purification. All operations were carried out under an atmosphere of argon using standard Schlenk techniques. All solvents were dried according to standard procedures.

### *X-ray crystal structure determination*

Suitable single crystals of **2** and **4** for the X-ray diffraction studies were grown by slow diffusion of pentane into the sample solution in toluene. Suitable crystals of **6** were obtained by recrystallization of the compound from chloroform. The structures were solved by a combination of direct methods, difference-Fourier syntheses and least-squares methods. Neutral atom scattering factors for all atoms and anomalous dispersion corrections for the non-hydrogen atoms were taken from the *International Tables for X-Ray Crystallography* [24]. All calculations were performed on a DEC 3000 AXP workstation with the STRUX-V [25] system, including the programs PLATON-92 [26], PLUTON-92 [26], SIR-92 [27] and SHELXL-93 [28].

### *Data collection*

A summary of the crystal and experimental data is reported in Table 3. Preliminary examination and data collection were carried out on an imaging plate diffraction system (IPDS; STOE&CIE) (**2**, **4**) or a CCD system (KappaCCD; NONIUS) equipped with a rotating anode (NONIUS FR591; 50 kV; 80 (**2**, **4**)/60 (**6**) mA) and graphite monochromated Mo–$K_\alpha$ radiation. Data collection were performed at 293 (193 and 293) K within the $\theta$-range of $3.1° < 2\theta < 50.2°$ ($4.1° < 2\theta < 51.2°$; $6.8° < 2\theta < 61.7°$) with an

Table 3. Crystallographic data for **2, 4** and **6**

| Complex | **2** | **4** | **6** |
|---|---|---|---|
| Formula | $C_{29}H_{27}O_2PPd \cdot 0.5C_7H_8$ | $C_{34}H_{29}O_2PPd$ | $C_{33}H_{29}O_2PPd \cdot CHCl_3$ |
| $Fw$ | 590.94 | 606.94 | 714.30 |
| $T$ (K) | 293(1) | 193(1) | 293(1) |
| Wavelength | 0.71073 Å | 0.71073 Å | 0.71073 Å |
| Crystal system | Triclinic | Triclinic | Triclinic |
| Space group | $P\bar{1}$ | $P\bar{1}$ | $P\bar{1}$ |
| $a$ (Å) | 8.8819(4) | 9.9178(6) | 9.0148(1) |
| $b$ (Å) | 9.7722(6) | 10.2461(6) | 12.5287(3) |
| $c$ (Å) | 17.2956(10) | 14.5783(9) | 14.5763(4) |
| $\alpha$ (°) | 99.535(7) | 78.342(6) | 100.7739(9) |
| $\beta$ (°) | 101.262(6) | 70.273(6) | 102.641(2) |
| $\gamma$ (°) | 101.511(6) | 78.925(6) | 91.721(2) |
| $V$ (Å$^3$) | 1409.58(13) | 1353.33(14) | 1573.75(6) |
| $Z$ | 2 | 2 | 2 |
| $d_c$ (g cm$^{-3}$) | 1.392 | 1.489 | 1.507 |
| $\mu$ (mm$^{-1}$) | 0.742 | 0.775 | 0.925 |
| $F(000)$ | 606 | 620 | 724 |
| Crystal size (mm) | $0.125 \times 0.125 \times 0.1$ | $0.30 \times 0.24 \times 0.13$ | $0.25 \times 0.20 \times 0.20$ |
| Theta range (°) | 1.5 to 25.1 | 2.05 to 25.61 | 3.4 to 30.85 |
| Index ranges | $-10 \leqslant h \leqslant 10$, $-11 \leqslant k \leqslant 11$, $-20 \leqslant l \leqslant 20$ | $-1 \leqslant h \leqslant 12$, $-12 \leqslant k \leqslant 12$, $-17 \leqslant l \leqslant 17$ | $0 \leqslant h \leqslant 9$, $-16 \leqslant k \leqslant 16$, $-19 \leqslant l \leqslant 18$ |
| Total data collected | 14,253 | 11,358 | 19,521 |
| Total unique data | 4487 | 4724 | 7528 |
| No. of data used | 4335 | 4721 | 7526 |
| Parameters | 408 | 459 | 398 |
| G.O.F | 0.910 | 1.027 | 1.087 |
| $R_1$[a] | 0.0295 | 0.0234 | 0.0345 |
| $wR_2$[b] | 0.0634 | 0.0581 | 0.0938 |
| Largest diff. peak and hole (e Å$^{-3}$) | 0.354 and −0.412 | 0.360 and −0.398 | 0.367 and −0.574 |

[a] $(R_1 = \Sigma(\|F_o\| - \|F_c\|)/\Sigma|F_o|)$, for $F^2 > 2\sigma(F^2)$.
[b] $wR_2 = [\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]]^{1/2}$.

exposure time of 5.0 min (5.0 min; 25 s) per image (rotation scan modus from $\phi = 0.0°$ (75°; 0°) to 290° (293°; 360°) with $\Delta\phi = 1°$). A total number of 14,253 (11,358; 19,521) reflections were collected. After merging a sum of 4487 (4724; 7528) independent reflections remained and were used for all calculations (2, 3, 2 reflections were suppressed during refinements on compounds **2, 4, 6,** respectively). Data were corrected for Lorentz and polarization effects. The unit cell parameters were obtained by full-matrix least-squares refinements of 4813 (4815; 15,927) reflections with the program Cell [29a] (DENZO-SMN [29b]).

The structures were solved using the heavy atom method. In **2** additional toluene as solvent is disordered over two positions which are related by a center of symmetry. In **6** the $CHCl_3$ is disordered over two positions which are related by a rotation around the C—H axis. For **4** all hydrogen atoms were located, for **2** all hydrogen atoms with exception of the toluene hydrogen atoms were located and refined. The hydrogen atoms of toluene in **2** and the hydrogen atoms in **6** were generated geometrically and allowed to ride on their respective parent carbon atoms. In **2** and **6** the hydrogen atoms were assigned fixed isotropic temperature factors (1.2 $U_{equiv.}$ and 1.5 $U_{equiv.}$ of the parent carbon atom for aromatic and other CH groups, respectively). Full matrix least squares refinement of all non-hydrogen atoms with anisotropic temperature factors led to convergence. Owing to the high disorder of $CHCl_3$ in **6,** the $R$ values are higher.

*General procedure for the synthesis of complexes* **2–6**

0.10 g (0.21 mmol) of the palladacycle **1** is stirred together with 2.0 equiv. of the corresponding 2-acylphenole and 47 mg (0.42 mmol) potassium *tert*-butoxide in 10 ml toluene. After approximately 12 h the reaction mixture is filtered and the solvent is removed *in vacuo*. Analytically pure samples of the phenolate complexes are obtained by crystallization from toluene/pentane.

2-Acetylphenolato-[*o*-(di-*o*-tolylphosphino)benzyl] palladium(II) (**2**) (*yellow needles, 86% yield*)

$^1$H NMR ($CDCl_3$, 20°C, 400 MHz): $\delta$ = 7.58–6.82 (15H, m, $H_{Ar}$); 6.44 (1H, m, $H_{Ar}$); 3.65 (2H, s, broad, $CH_2$); 2.85 (3H, s, broad, $CH_{3\,(Benzyl)}$); 2.50 (3H, s, broad, $CH_{3\,(Benzyl)}$); 2.42 (3H, s, $CH_{3\,(Acetyl)}$). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 20°C, 161.85 MHz, with integral *I*): $\delta$ = 35.7 (s, *I* = 10%); 34.2 (s, *I* = 90%). IR ($cm^{-1}$, KBr): 3054 m, 3005 m, 2953 m, 2910 m, 2869 m, 1593 s, 1523 s, 1469 m, 1431 s, 1374 m, 1354 m, 1338 m, 1283 w, 1250 w, 1219 s, 1157 w, 1135 m, 1085 w, 966 m, 861 m, 804 w, 760 s, 755 s, 714 m, 585 m, 561 m, 472 m. MS (FAB): *m/z* = 544 [$M^+$], 409 [$M^+$ – phenolate ligand]. $C_{29}H_{27}O_2PPd$ (544.93): calc. (+0.5 toluene) C 66.05, H 5.28, P 5.24; found C 65.82, H 5.60, P 5.27.

2-Acetyl-4-fluorophenolato-[*o*-(di-*o*-tolylphosphino) benzyl]palladium(II) (**3**) (*yellow needles, 92% yield*)

$^1$H NMR ($CDCl_3$, 20°C, 400 MHz): $\delta$ = 7.44–6.83 (15H, m, $H_{Ar}$); 3.66 (2H, s, broad, $CH_2$); 2.85 (3H, s, broad, $CH_{3\,(Benzyl)}$); 2.49 (3H, s, broad, $CH_{3\,(Benzyl)}$); 2.37 (3H, s, $CH_{3\,(Acetyl)}$). $^{31}P\{^1H\}$ NMR ($CDC_{l3}$, 20°C, 161.85 MHz, with integral *I*): $\delta$ = 35.8 (s, *I* = 12%); 34.3 (s, *I* = 88%). IR ($cm^{-1}$, KBr): 3056 m, 3011 w, 2967 w, 2889 w, 1602 s, 1523 s, 1469 m, 1444 s, 1375 m, 1324 s, 1284 w, 1241 w, 1201 s, 1186 m, 1119 w, 967 m, 914 m, 811 s, 749 s, 560 m, 527 w, 479 m. MS (FAB): *m/z* = 562 [$M^+$], 409 [$M^+$ – phenolate ligand]. $C_{29}H_{26}FO_2PPd$ (562.91): calc. C 61.88, H 4.65, P 5.50; found C 61.84, H 4.87, P 5.50.

2-Benzoylphenolato-[*o*-(di-*o*-tolylphosphino)benzyl] palladium(II) (**4**) (*yellow needles, 77% yield*)

$^1$H NMR ($CDCl_3$, 20°C, 400 MHz): $\delta$ = 7.66–6.85 (20H, m, $H_{Ar}$); 6.37 (1H, m, $H_{Ar}$); 3.72 (2H, s, broad, $CH_2$); 2.80 (3H, s, broad, $CH_{3\,(Benzyl)}$); 2.47 (3H, s, broad, $CH_{3\,(Benzyl)}$). $^{31}P\{^1H\}$ NMR (toluene-$d_8$, 20°C, 161.85 MHz, with integral *I*): $\delta$ = 35.6 (s, *I* = 34%); 33.9 (s, *I* = 66%). IR ($cm^{-1}$, KBr): 3047 w, 2962 w, 2868 w, 1613 s, 1579 s, 1561 s, 1515 s, 1466 m, 1452 m, 1442 m, 1415 s, 1351 s, 1261 m, 1228 m, 1203 w, 1177 w, 1141 m, 1078 s, 1025 m, 939 m, 913 w, 854 m, 802 s, 751 s, 713 m, 751 s, 699 s, 674 w, 643 m, 586 m, 559 m, 521 m. MS (FAB): *m/z* = 605 [$M^+$ – H], 409 [$M^+$ – phenolate ligand]. $C_{34}H_{29}O_2PPd$ (606.99): calc. C 67.28, H 4.82, P 5.10; found C 66.78, H 4.81, P 4.99.

2-Benzoyl-4-methylphenolato-[*o*-(di-*o*-tolylphosphino)benzyl]palladium(II) (**5**) (*orange needles, 76% yield*)

$^1$H NMR ($CDCl_3$, 20°C, 400 MHz): $\delta$ = 7.58–6.88 (20H, m, $H_{Ar}$); 3.73 (2H, s, broad, $CH_2$); 2.82 (3H, s, broad, $CH_{3(P\text{-}Benzyl)}$); 2.49 (3H, s, broad, $CH_{3(P\text{-}Benzyl)}$); 2.12 (3H, s, $CH_{3(Benzyl)}$). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 20°C, 161.85 MHz, with integral *I*): $\delta$ = 35.6 (s, *I* = 10%); 34.5 (s, *I* = 90%). IR ($cm^{-1}$, KBr): 3054 w, 2920 w, 2855 w, 1624 m, 1581 s, 1557 s, 1508 s, 1445 s, 1401 m, 1374 m, 1336 m, 1284 w, 1233 s, 1199 m, 1143 m, 1073 w, 953 w, 824 m, 814 m, 756 s, 733 m, 707 m, 561 w, 521 w. MS (FAB): *m/z* = 620 [$M^+$ – H], 409 [$M^+$ – phenolate ligand]. $C_{35}H_{31}O_2PPd$ (621.02): calc. (+0.5 toluene) C 69.32, H 5.29, P 4.79; found C 69.06, H 5.44, P 4.40.

2-Acetyl-1-naphtholato-[*o*-(di-*o*-tolylphosphino) benzyl]palladium(II) (**6**) (*yellow needles, 79% yield*)

$^1$H NMR ($CDCl_3$, 20°C, 400 MHz): $\delta$ = 7.66–6.70 (22H, m, $H_{Ar}$); 3.82 (2H, s, broad, $CH_2$); 2.90 (3H, s, broad, $CH_{3\,(P\text{-}Benzyl)}$); 2.55 (3H, s, broad, $CH_{3(P\text{-}Benzyl)}$); 2.45 (3H, s, $CH_{3\,(Acetyl)}$). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 20°C, 161.85 MHz, with integral *I*): $\delta$ = 35.6 (s, *I* = 38%); 34.5 (s, *I* = 62%). IR ($cm^{-1}$, KBr): 3052 w, 2989 w, 2933 w, 2878 w, 1616 m, 1578 s, 1528 s, 1490 w, 1454 w, 1424 w, 1387 s, 1280 w, 1248 m, 1238 m, 1203 m, 1160 m, 1128 m, 1080 w, 1023 w, 989 w, 896 w, 787 m, 765 s, 749 m, 737 m, 713 m, 688 w, 585 w, 560 w, 527 w, 479 w, 471 m. MS (FAB): *m/z* = 594 [$M^+$], 409 [$M^+$ – naphtholate ligand]. $C_{33}H_{29}O_2PPd$ (594.98): calc. C 66.62, H 4.91; found C 66.81, H 4.88.

*General procedure for the synthesis of complexes* **9**–**12**

0.30 g (0.82 mmol) of the $\pi$-allylpalladium chloride complex (**7**) (0.32 g (0.82 mmol) of the $\pi$-(1-methylallyl)palladium chloride complex (**8**)) are stirred together with 2.0 equiv. of the protonated ligand and 184 mg (1.64 mmol) potassium *tert*-butoxide in 13 ml toluene at ambient temperature. After some hours the initially orange solution turns black due to precipitated palladium-metal which is removed by filtration (celite) to obtain a yellow solution. The solvent is removed *in vacuo* and the yellow residue is washed with two 15 ml portions of pentane. The allyl complexes can be recrystallized from toluene/pentane at −78°C. The numeration of the atoms of the ligands are similar to the X-ray studies of the aforementioned compounds.

$\eta^3$-Allyl-(2-benzoylphenolato)palladium(II) (**9**) (*yellow needles, 88% yield*)

$^1$H NMR ($CDCl_3$, 25°C, 300 MHz): $\delta$ = 7.50 (1H, m, $H_{Ar\text{-}2'}$); 7.44 (1H, m, $H_{Ar\text{-}4'}$); 7.35 (1H, m, $H_{Ar\text{-}3'}$); 7.27 (1H, ddd, $^3J_1$(H,H) = 6.4 Hz, $^3J_2$(H,H) = 8.6 Hz, $^4J$(H,H) = 2.0 Hz, $H_{Ar\text{-}5}$); 7.20 (1H, dd, $^3J$(H,H) = 8.2 Hz, $^4J$(H,H) = 1.8 Hz, $H_{Ar\text{-}7}$); 6.89 (1H, dd, $^3J$(H,H) = 8.4 Hz, $^4J$(H,H) = 1.4 Hz, $H_{Ar\text{-}4}$); 6.34 (1H, ddd, $^3J_1$(H,H) = 8.0 Hz, $^3J_2$(H,H) = 6.6

Hz, $^4J$(H,H) = 1.4 Hz, $H_{Ar\text{-}6}$); 5.48 (1H, m, $H_{Allyl\text{-}2}$); 3.91 (2H, d, $^3J$(H,H) = 6.8 Hz, $H_{Allyl\text{-}syn}$); 2.90 (2H, d, $^3J$(H,H) = 12.0 Hz, $H_{Allyl\text{-}anti}$). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 25°C, 75 MHz): $\delta$ = 196.02 (C=O); 171.55 ($C_{Ar\text{-}3}$); 139.21 ($C_{Ar\text{-}1'}$); 135.63 ($C_{Ar\text{-}5}$); 135.21 ($C_{Ar\text{-}7}$); 129.94 ($C_{Ar\text{-}4'}$); 128.53 ($C_{Ar\text{-}2'}$); 127.00 ($C_{Ar\text{-}3'}$); 123.64 ($C_{Ar\text{-}4}$); 120.01 ($C_{Ar\text{-}2}$); 112.64 ($C_{Ar\text{-}6}$); 110.95 ($C_{Allyl\text{-}2}$); 55.2 ($C_{Allyl\text{-}1,3}$, broad). IR ($cm^{-1}$, KBr): 3053 w, 1605 s, 1582 s, 1560 s, 1518 s, 1456 m, 1421 m, 1385 w, 1365 m, 1351 m, 1254 w, 1235 m, 1201 w, 1169 w, 1142 m, 1117 w, 1033 w, 999 w, 944 w, 933 w, 838 w, 761 m, 718 w, 705 m, 644 w, 596 w, 522 w. MS (FAB): $m/z$ = 344 [$M^+$], 302 [$M^+$ − allyl − H]. $C_{16}H_{14}O_2Pd$ (344.71): calc. C 55.7, H 4.1, O 9.3; found C 54.2, H 4.1, O 8.9.

2-Acetyl-4-fluorophenolato-[(1,2,3-$\eta$)-2-butenyl]palladium(II) (**10**) (*yellow crystals, 74% yield*)

$^1H$ NMR ($CDCl_3$, 25°C, 300 MHz): $\delta$ = 7.13 (1H, dd, $^3J$(H,F) = 10.2 Hz, $^4J$(H,H) = 3.0 Hz, $H_{Ar\text{-}7}$); 7.01 (1H, ddd, $^3J$(H,F) = 9.6 Hz, $^3J$(H,H) = 7.4 Hz, $^4J$(H,H) = 3.4 Hz, $H_{Ar\text{-}5}$); 6.75 (1H, dd, broad, $^3J$(H,H) = 9.0 Hz, $^4J$(H,F) = 5.0 Hz, $H_{Ar\text{-}4}$); 5.23 (1H, m, $H_{Allyl\text{-}2}$); 3.66 (1H, d, $^3J$(H,H) = 6.4 Hz, $H_{Allyl\text{-}1,syn}$); 3.65 (1H, m, broad, $H_{Allyl\text{-}3}$); 2.63 (1H, d, $^3J$(H,H) = 11.4 Hz, $H_{Allyl\text{-}1,anti}$); 2.46 (3H, s, $CH_{3\,(Acetyl)}$); 1.28 (3H, d, $^3J$(H,H) = 6.2 Hz, $CH_{3\,(Allyl)}$). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 25°C, 75 MHz): $\delta$ = 197.00 (C=O); 167.00 ($C_{Ar\text{-}3}$); 150.34 (d, $^1J$(CF) = 232 Hz, $C_{Ar\text{-}6}$); 126.04 ($C_{Ar\text{-}4}$); 124.57 (d, $^2J$(CF) = 25 Hz, $C_{Ar\text{-}5/7}$); 118.17 ($C_{Ar\text{-}2}$); 114.21 (d, $^2J$(CF) = 22 Hz, $C_{Ar\text{-}5/7}$); 110.66 ($C_{Allyl\text{-}2}$); 73.85 ($C_{Allyl\text{-}3}$); 49.76 ($C_{Allyl\text{-}1}$); 27.29 ($CH_{3\,(Acetyl)}$); 15.92 ($CH_{3\,(Allyl)}$). IR ($cm^{-1}$, KBr): 2958 w, 2918 w, 1649 m, 1628 m, 1605 s, 1526 s, 1486 m, 1447 s, 1429 s, 1374 m, 1324 s, 1281 m, 1243 m, 1206 s, 1181 s, 1124 m, 1059 w, 1026 w, 970 m, 913 m, 864 m, 832 w, 807 s, 782 m, 698 w, 667 w, 638 w, 581 w, 523 w. MS (FAB): $m/z$ = 314 [$M^+$]. $C_{12}H_{13}FO_2Pd$ (314.65): calc. C 45.8, H 4.2, O 10.2; found C 45.2, H 4.2, O 9.9.

2-Benzoylphenolato-[(1,2,3-$\eta$)-2-butenyl]palladium(II) (**11**) (*yellow crystals, 73% yield*)

$^1H$ NMR ($CDCl_3$, 25°C, 300 MHz): $\delta$ = 7.58–7.18 (7H, m, $H_{Ar}$); 6.89 (1H, m, $H_{Ar\text{-}4}$); 6.33 (1H, m, $H_{Ar\text{-}6}$); 5.26 (1H, m, $H_{Allyl\text{-}2}$); 3.73 (1H, d, $^3$J(H,H) = 6.6 Hz, $H_{Allyl\text{-}1,syn}$); 3.72 (1H, m, $H_{Allyl\text{-}3}$); 2.68 (1H, d, $^3J$(H,H) = 11.0 Hz, $H_{Allyl\text{-}1,anti}$); 1.33 (3H, d, $^3J$(H,H) = 6.0 Hz, $CH_{3\,(Allyl)}$). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 25°C, 75 MHz): $\delta$ = 196.07 (C=O); 172.06 ($C_{Ar\text{-}3}$); 139.40 ($C_{Ar\text{-}1'}$); 135.40 ($C_{Ar\text{-}5}$); 135.12 ($C_{Ar\text{-}7}$); 129.93 ($C_{Ar\text{-}4l}$); 128.66 ($C_{Ar\text{-}2'}$); 126.94 ($C_{Ar\text{-}3'}$); 123.94 ($C_{Ar\text{-}4}$); 120.33 ($C_{Ar\text{-}2}$); 112.14 ($C_{Ar\text{-}6}$); 110.52 ($C_{Allyl\text{-}2}$); 74 ($C_{Allyl\text{-}3}$, broad); 50 ($C_{Allyl\text{-}1}$, broad); 16.05 ($CH_{3\,(Allyl)}$). IR ($cm^{-1}$, KBr): 3051 w, 2945 w, 1603 s, 1581 m, 1552 s, 1517 s, 1454 m, 1446 m, 1413 s, 1348 s, 1249 m, 1228 s, 1180 m, 1164 w, 1141 s, 1114 m, 1077 w, 1028 m, 997 w, 976 w, 945 m, 928 w, 854 w, 836 m, 803 w, 764 m, 757 m, 718 w, 702 s, 642 m, 598 w, 533 w, 520 w, 457 w. MS (FAB): $m/z$ = 358 [$M^+$], 304 [$M^+$ − crotyl + H]. $C_{17}H_{16}O_2Pd$ (358.73): calc. C 56.9, H 4.5, O 8.9; found C 55.6, H 4.6, O 8.2.

2-Acetyl-1-naphtholato-[(1,2,3-$\eta$)-2-butenyl]palladium(II) (**12**) (*yellow powder, 81% yield*)

$^1H$ NMR ($CDCl_3$, 25°C, 300 MHz): $\delta$ = 8.48 (1H, d, $^3J$(H,H) = 8.0 Hz, $H_{Ar\text{-}4}$); 7.52–7.26 (4H, m, $H_{Ar}$); 6.72 (1H, d, $^3J$(H,H) = 9.0 Hz, $H_{Ar\text{-}8}$); 5.29 (1H, m, $H_{Allyl\text{-}2}$); 3.75–3.62 (2H, m, $H_{Allyl\text{-}1,syn}$ and $H_{Allyl\text{-}3}$); 2.69 (1H, d, $^3J$(H,H) = 12.0 Hz, $H_{Allyl\text{-}1,anti}$); 2.53 (3H, s, $CH_{3\,(Acetyl)}$); 1.42 (d, $^3J$(H,H) = 6.2 Hz, $I$ = 63%, $CH_{3\,(Allyl)}$); 1.33 (d, $^3J$(H,H) = 6.2 Hz, $I$ = 37%, $CH_{3\,(Allyl)}$). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 25°C, 75 MHz): $\delta$ = 194.69 (C=O); 170.27 ($C_{Ar\text{-}3}$); 136,73, 130.10 ($C_{Ar\text{-}3a/7a}$); 128.75; 127.23; 125.82; 125.60; 123.76 (all $C_{Ar}$); 113.36 ($C_{Ar\text{-}2}$); 112.56 ($C_{Ar\text{-}8}$); 110.82 ($C_{Allyl\text{-}2}$); 72.60, 71.48 (both $C_{Allyl\text{-}3}$); 51.39, 50.35 (both $C_{Allyl\text{-}1}$); 27.71, 27.16 (both $CH_{3\,(Acetyl)}$); 16.00 ($CH_{3\,(Allyl)}$). IR ($cm^{-1}$, KBr): 2962 w, 1614 m, 1602 w, 1576 s, 1527 s, 1489 m, 1449 m, 1427 m, 1408 w, 1388 m, 1349 w, 1279 w, 1240 m, 1205 w, 1151 w, 1130 w, 1023 w, 992 w, 937 w, 895 w, 856 w, 806 w, 792 m, 756 w, 735 w, 690 w, 609 w, 579 w, 532 w, 513 w, 447 w. MS (FAB): $m/z$ = 346 [$M^+$], 289 [$M^+$ − crotyl − 2H]. $C_{16}H_{16}O_2Pd$ (346.72): calc. C 55.4, H 4.7; found C 54.9, H 4.7.

## CONCLUSION

Pd(II)-complexes with chelating 2-acylphenolate ligands and cyclometallated tri(*o*-tolyl)phosphine or allyl units, respectively, are easily available in good yields by treatment of an appropriate Pd(II)-precursor with the corresponding 2-acylphenole and a strong base such as potassium *tert*-butoxide. X-ray diffraction analyses of **2, 4** and **6** show that the coordination sphere of palladium is close to square planar. The conjugated aromatic system of the free ligands is partially disrupted through coordination to the metal. The different *cis*-/*trans*-stereochemistry observed for compounds **2, 6** and **4** can be correlated with the steric requirement of the 2-acylphenolate ligand. All structures exhibit short $CH_3 \cdots O$ distances which is indicative of C—H···O interactions. This phenomena was further studied in solution using complex **2**. The ratio of **C** to **D** depends on the ability of the solvent to act as a hydrogen donor, replacing a $CH_3 \cdots O$ by a H-solvent···O interaction. The NMR spectra of the allyl and crotyl complexes displayed that the former one is highly dynamic at room temperature while the latter ones exist as two stable isomers in solution.

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