The First Structurally Characterized Example of a η^5-Coordinate Mesitylato Palladium Complex

Axel Klein*,† and Akbey Dogan

Institut für Anorganische Chemie, Universität Stuttgart, Pfaffenwaldring 55, D-70550 Stuttgart, Germany

Received October 22, 2001

Summary: The red complex [(COD)Pd(OMes)](SbF$_6$) (OMes = 2,4,6-trimethylphenolate = mesitylate) was prepared and structurally characterized. The molecular structure reveals that the palladium atom coordinates η^5 to the aryl π system and not to the negatively charged oxygen atom on the mesitylate ligand.

Introduction

The use of organometallic palladium(II) complexes in catalysis spans a wide range from small-scale applications, e.g., in olefin polymerization,[1,2] or C−C coupling reactions,[3−5] which have developed enormously in recent years, to well-established industrial processes such as the Wacker process.[4−8] The latter has motivated us to explore the chemistry of olefin palladium(II) complexes especially the reactivity of organometallic palladium(II) complexes of the type [(COD)Pd(CH$_3$)(OR)] (COD = 1,5-cyclooctadiene, R = alkyl or aryl).[9] In the presence of mild proton donators (carbonic acids, phenols) these compounds undergo loss of methane to give cationic species [(COD)Pd(OR)]$^+$ which turned out to be highly reactive and could not be isolated or characterized in cases where R = alkyl, whereas the species with R = aryl seemed to be more stable. In this contribution we would like to report the preparation and structural characterization of one example (R = 2,4,6-trimethylphenol) of this series.

Results and Discussion

Reaction of the complex [(COD)Pd(CH$_3$)(OR)] (COD = 1,5-cyclooctadiene, R = Mes) with HBF$_4$ gave a red air-sensitive material. First ^{1}H NMR investigations showed the product to be a complex species containing only COD and the OMes ligand.

Further trials showed that the best way to obtain good results is to start from a solvento complex [(COD)Pd(CH$_3$)(Solv)]$^+$ as shown in Scheme 1 and reacting it in situ with trimethylphenol (HOMes). By this procedure we obtained a red air-sensitive compound in appreciable yield (66% isolated yield), which turned out to be [(COD)Pd(OMes)](SbF$_6$).

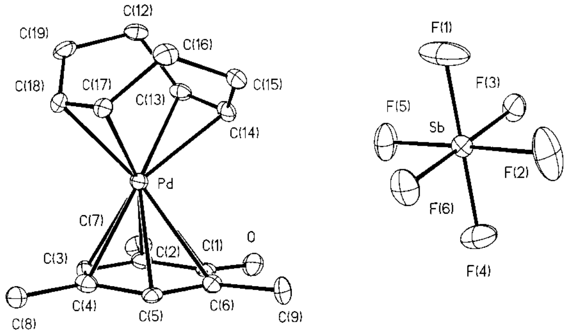

Figure 1. Molecular structure of [(COD)Pd(OMes)](SbF$_6$) (30% probability ellipsoids; hydrogen atoms are omitted for clarity).

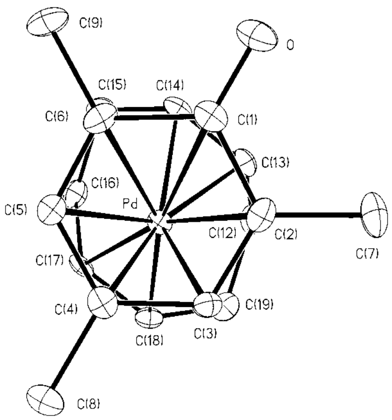

Figure 2. Perspective view of [(COD)Pd(OMes)]$^+$ (30% probability ellipsoids; hydrogen atoms are omitted for clarity).

Suitable deep red crystals for X-ray crystallography were obtained from a concentrated THF solution. Representations of the molecular structure are shown in Figures 1 and 2.

The crystal structure does not reveal any intermolecular interactions other than van der Waals contacts. In the molecule the COD ligand is coordinated in a chelating way by both olefinic groups. Taking the centroids for the olefinic C=C bonds, the distances to the palladium atom are 2.113 Å for X1A (C13=C14) and 2.128 Å for X1B (C17=C18), respectively (Table 1). They are slightly longer than the corresponding distances of 2.092 or 2.097 Å, respectively, found in the dichloro complex [(COD)Pd(Cl)$_2$].[10] The chelate bite angle of the COD ligand is 86.7°. This lies within the typical range of 85−87° for this angle in such complexes[9] and close

---

[†] E-mail: aklein@iac.uni-stuttgart.de.

(1) Mecking, S. *Angew. Chem.* **2001**, *113*, 550.

(2) Britovsek, G. J. P.; Gibson, V. C.; Wass, D. F. *Angew. Chem.* **1999**, *111*, 448.

(3) Grasa, G. A.; Hillier, A. C.; Nolan, S. P. *Org. Lett.* **2001**, *3*, 1077.

(4) Tsuji, J. *Pure Appl. Chem.* **1999**, *71*, 1539.

(5) Tsuji, J. *New J. Chem.* **2000**, *24*, 127.

(6) Jira, R. Oxidation of olefins to carbonyl compounds (Wackerprocess). In *Appl. Homogeneous Catal. Organomet. Compd.*; Cornils, B.. Herrmann, W. A., Eds.; VCH: Weinheim, 1996; Vol. 1, p 374.

(7) Baeckvall, J. E.; Akermark, B.; Ljunggren, S. O. *J. Am. Chem. Soc.* **1979**, *101*, 2411.

(8) Siegbahn, P. E. M. *Struct. Chem.* **1995**, *6*, 271.

(9) Klein, A.; Dogan, A.; Feth, M.; Bertagnolli, H. *Inorg. Chim. Acta*, submitted.

(10) Benchekroun, L.; Herpin, P.; Julia, M.; Saussine, L. *J. Organomet. Chem.* **1977**, *128*, 275.

10.1021/om010922q CCC: $22.00

Scheme 1. Preparation of [(COD)Pd(OMes)](SbF_6)

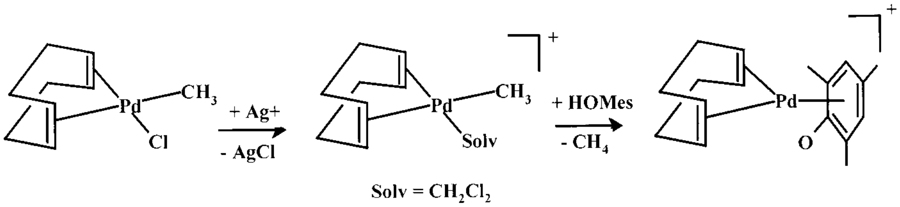

Table 1. Selected Structural Parameters in [(COD)Pd(OMes)](SbF_6)

Distances (Å)

Pd−C1	2.588(8)	Pd−C13	2.234(7)	Pd−O	3.534(8)
Pd−C2	2.447(8)	Pd−C14	2.213(7)	C1−O	1.230(9)
Pd−C3	2.345(8)	Pd−X1A	2.113(7)	C1−C2	1.467(10)
Pd−C4	2.219(8)	Pd−C17	2.238(7)	C2−C3	1.394(10)
Pd−C5	2.353(7)	Pd−C18	2.234(7)	C3−C4	1.428(10)
Pd−C6	2.468(8)	Pd−X1B	2.128(7)	C4−C5	1.422(10)
C12−C13	1.517(11)	C16−C17	1.535(10)	C5−C6	1.378(10)
C13−C14	1.382(10)	C17−C18	1.373(10)	C6−C1	1.499(10)
C14−C15	1.529(10)	C18−C19	1.512(10)	$C_{Ar}−C_{Ar}$ (av)[a]	1.431(10)
C15−C16	1.531(10)	C19−C12	1.547(11)		

Angles (deg)

C17−Pd−C18	35.8(3)	C18−C17−C16	125.6(7)
C13−Pd−C14	36.2(3)	C14−C13−C12	126.1(8)
C17−Pd−C14	82.6(3)	C17−C18−C19	125.6(7)
C18−Pd−C13	80.8(3)	X1A−Pd−X1B	86.7
C15−C14−C13	125.1(7)		

[a] Averaged values within the mesitylato ligand.

to the value of 86.3° found in the dichloro derivative.[10] The palladium(II) atom is further bound to the six C atoms of the mesitylate ligand with the Pd−C distances ranging between 2.219(8) and 2.588(8) Å with an average value of 2.402(8) Å. C3, C4, and C5 are closer to the palladium atom than C1, C2, and C6 as can be seen in Figure 1. Nevertheless the coordination mode of the palladium atom can be described as nearly regular η^6 to the aryl π system of the mesitylate since the deviation from the average distance is smaller than 0.19 Å and the largest value is still in the range of the sum of the van der Waals radii.[11] The mesitylate ligand is entirely planar showing no Pd−O interaction. The C1−O distance (1.23 Å) is markedly shorter than expected for a single bond in phenolates (1.35−1.37 Å) and approximately in the same range as the C=O double bond in free benzoquinone (1.22 Å) or coordinated benzoquinone in complexes such as [(bpy)Pd(η^2-$C_6H_4O_2$] where the C−O distance is 1.224(5) Å.[12] Furthermore the C1 atom bound to the oxygen exhibits the longest distance to the palladium atom and also the C1−C6 and C1−C2 bonds are elongated. In this view the coordination mode can also be regarded as η^5 in agreement with work by Wilkinson and co-workers, who have reported spectroscopic and structural evidence for similar binding of phenolate (OPh) to ruthenium(II) and rhodium(I).[13] Their IR data as well as the crystal structure of [$(PPh_3)_2$(H)Ru(η^6-OPh)]·MeOH (C−O 1.277 Å) suggest a large contribution from a η^5-oxacyclohexadienyl resonance structure of the phenoxo ligand. Similar η^5-arene coordination has also been concluded from spectroscopic data for cyclopentadienyl ruthenium(II) complexes with phenol or benzoic acid ligands,[14] and from structural data of [(COD)Rh(OPh*)]·HOPh* (Ph* = 2,6-*t*-Bu-4-MeC_6H_2; C−O 1.258 Å),[15] or [$(PPh_3)_2$Rh(OPh)]·3HOPh (C−O 1.278 Å).[16] The very short C−O distance in [(COD)Pd(OMes)](SbF_6) probably reflects the good electron accepting ability of the formal $[(COD)Pd]^{2+}$ unit. Note that, e.g., the C−O distance in pentachlorophenolate is reduced to 1.285 Å.[17] A simple electron count for the η^5-coordination gives 18 valence electrons, which is unusual for palladium(II) complexes.[18]

There are only few examples of phenolato complexes of palladium. One is the dimeric complex [{$(R_2HP)_2Pd_2$(μ-$P(R)_2$)}(μ-η^2;η^2-C_6H_5O)]·$3HOC_6H_5$ (R = *t*-Bu), where a phenolate ligand bridges two palladium(I) atoms both η^2.[19] In agreement with our findings the phenolate oxygen does not show interaction with the palladium centers, but is involved in aggregation of three hydrogen-bonded phenol molecules. π-Arene coordination is also reported in a related Pd(I)−Pd(I) dimeric complex [$(AlCl_4)_2Pd_2$(μ-η^2:η^2-$C_6H_6)_2$], where two benzene molecules coordinate in the same way.[20] Recently Campora et al. reported the crystal structure (at 223(2) K) of the homoleptic complex [$(Pd(OR)_2$] (R = 2,6-*t*-$Bu_2C_6H_3$) in which both aryloxo ligands show a η^3 coordination to palladium.[21] From NMR investigations the authors assume a very fast exchange of the metal center between the two possible η^3-allylic sites. We assume that at lower temperatures the coordination might approach a η^5 coordination like we found for $[(COD)Pd(OMes)]^+$.

Phenolate ligands are however in principle able to bind to 4d elements in complexes through their oxygen atom as shown in palladium(II) complexes of the type [$(PR_3)_2$Pd(H)(OAr)] (R = cyclohexyl, Ar = C_6H_5 or C_6F_5)[22] or [$(PR_3)_2$Pd(Me)(OAr)] (R = CH_3 or C_6H_5, Ar = C_6H_5),[23] and also in the rhodium(I) complex [$(PMe_3)_3$Rh(OTol)]·(HOTol).[24] As a conclusion from these results it seems that η-arene coordination is favored in cases where the number of valence electrons and the coordi-

---

[11] The distance d(A−B) between two atoms is bonding if $r(A) + r(B) - 0.4$ Å < d(A−B) < $r(A) + r(B) + 0.4$ Å. For further information, see: http://www.ccdc.cam.ac.uk.

[12] Milani, B.; Anzilutti, A.; Vicentini, L.; Sessanta o Santi, A.; Zangrando, E.; Geremia S.; Mestroni, G. *Organometallics* **1997**, *16*, 5064.

[13] Cole-Hamilton, D. J.; Young, R. J.; Wilkinson, G. *J. Chem. Soc., Dalton Trans.* **1976**, 1995.

[14] Chaudret, B.; He, X.; Huang, Y. *J. Chem. Soc., Chem. Commun.* **1989**, 1844.

[15] Dahlenburg, L.; Hock, N. *J. Organomet. Chem.* **1985**, *284*, 129.

[16] Kuznetsov, V. F.; Yap, G. P. A.; Bensimon, C.; Alper, H. *Inorg. Chim. Acta* **1998**, *280*, 172.

[17] Majerz, J.; Malarski, Z.; Lis, T. *Pol. J. Chem.* **1998**, *72*, 325.

[18] A preliminary geometry optimization on the HF/3-21G* (C_1 symmetry) level yields a η^3-coordination for the mesitylato ligand with the Pd atom bound to C3, C4, and C5 with a 16 valence electron configuration. Further work is in progress.

[19] Sommovigo, M.; Pasquali, M.; Leoni, P.; Braga, D.; Sabatino, P. *Chem. Ber.* **1991**, *124*, 97.

[20] Allegra, G.; Tettamanti Casagrande, G.; Immirzi, A.; Porri, I.; Vitulli, G. *J. Am. Chem. Soc.* **1970**, *92*, 289.

[21] Campora, J.; Reyes, M. L.; Mereiter, K. *Organometallics* **2002**, *21*, 1014.

[22] Di Bugno, C.; Pasquali, M.; Leoni, P.; Sabatino, P.; Braga, D. *Inorg. Chem.* **1989**, *28*, 1390.

[23] Kim, Y.-J.; Osakada, K.; Takenaka, A.; Yamamoto, A. *J. Am. Chem. Soc.* **1990**, *112*, 1096.

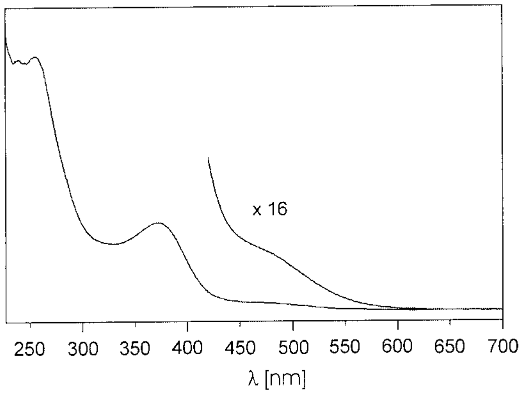

Figure 3. Absorption spectrum of [(COD)Pd(OMes)](SbF_6) in CH_2Cl_2.

nation number are low. In the cases of the 12-electron fragments [(COD)Pd]$^+$, $[(PPh_3)_2Rh]^+$, $[(PR_3)_2(H)Ru]^+$, and [Cp*Ru]$^+$ the η-arene coordination formally adds three ligands and 6 electrons to yield 18 valence electron species and a complete coordination sphere. In cases where the metal fragment contains already 14 valence electrons such as in $[(PCy_3)_2Pd(H)]^+$ or $[(PMe_3)_3Rh]^+$ the aryloxo ligands need only to coordinate via their O-donor atom to yield fully coordinated square planar 16 valence electron species, which is satisfying for the d^8-configured metals.

The red color exhibited by the complex is due to an absorption at 475 nm (in CH_2Cl_2) that appears only as a weak shoulder in the absorption spectrum (Figure 3). A strong broad band at 372 nm dominates the spectrum. Further intense absorption maxima are found at 258 and 249 nm. In $[(COD)Pd(Cl)_2]$, which exhibits a similar spectrum, the weak lowest electronic transition is assigned to a ligand-field (LF) transition, followed by a ligand-to-metal charge transfer (LMCT).[25] The lowest absorption of [(COD)Pd(OMes)]$^+$ is found at lower energies, which might be due to reduced ligand-field strength compared to $[(COD)Pd(Cl)_2]$. On the other hand the lowest transition might also be assigned to a ligand-(mesitylate)-to-ligand(COD) charge transfer (L'LCT).[26,27] Both assignments would imply photochemical reactivity, what remains to be investigated in the near future.

Conclusion

Making use of the stabilizing effect of the mesityl substituent we were able to stabilize the species [(COD)-Pd(OMes)]$^+$, isolate it as a red SbF_6 salt in good yields, and determine the crystal and molecular structure of the compound [(COD)Pd(OMes)](SbF_6). The mesitylato ligand coordinates in a η^5 fashion with no Pd···O interaction. Further investigations will comprise other bulky phenolate ligands to stabilize such cationic species. Since we expect these complexes to show fluxional behavior at ambient temperature, we intend to study their spectroscopy (NMR or IR) in detail in the near future and also add some calculations of the molecular geometry.

Experimental Section

Instrumentation. ^{1}H NMR spectra were recorded on a Bruker AC 250 spectrometer. UV/vis absorption spectra were recorded on a Bruins Instruments Omega 10 spectrophotometer.

Preparation of [(COD)Pd(OMes)](SbF_6). To a solution of 370 mg of [(COD)PdMeCl] (1.39 mmol) in 50 mL of CH_2Cl_2 was added 481 mg of $AgSbF_6$ (1.4 mmol), whereupon AgCl precipitated. The reaction mixture was stirred for 30 min at ambient temperature and filtered carefully. To this solution was added 190 mg of 2,4,6-trimethylphenol (1.4 mmol), and the color of the solution slowly turned orange. After 30 min of stirring, all volatiles were removed. The brown sticky residue was recrystallized from CH_2Cl_2/*n*-heptane (1:5) several times to yield 537 mg (0.92 mmol, or 66%) of orange microcrystalline material. Elemental anal. Calcd for $C_{17}H_{23}O_1Pd_1Sb_1F_6$: C, 34.87; H, 3.96. Found: C, 34.51; H, 3.91. ^{1}H NMR (CD_2Cl_2): δ 6.92 (s, 2H, HMes), 6.18 (m, br, 4H, HC=), 2.81−2.42 (m, 8H, $-CH_2-$), 2.31 (s, 6H, *o*-CH_3), 2.24 (s, 3H, *p*-CH_3). UV/vis (CH_2Cl_2): 475sh, 372, 282 sh, 258 nm.

Crystallography. Crystal data for [(COD)Pd(OMes)](SbF_6): $C_{17}H_{23}O_1Pd_1Sb_1F_6$ (585.5), red cubes, 0.3 × 0.2 × 0.2 mm; Siemens P4 diffractometer, Mo Kα, $\lambda = 71.073$ pm; monoclinic, $P2(1)/c$; cell dimensions $a = 14.7109(5)$, $b = 11.018(3)$, $c = 12.064(3)$, $\beta = 102.50(3)$; $V = 1908.8(10)$ Å^3; $Z = 4$; $\delta_{calcd} = 2.037$ mg/m^3; $\mu = 2.416$ mm^{-1}; $F(000) = 1136$; 5044 reflections were collected (21.33−27.49°), 4123 independent reflections were used for refinement ($R_{int} = 0.0063$), final R indices [$I > 2\sigma(I)$] were R1 = 0.0510 and wR2 = 0.0876; GOF on $F^2 = 0.988$ with 260 parameters and 0 restraints; largest difference peak and hole 0.897 and −0.693 e·Å^{-3}.

Acknowledgment. Mark Niemeyer (IAC Stuttgart) is thanked for assistance on the XRD refinement and for the HF/3-21G* calculations. We are also grateful to Johnson Matthey for a loan of K_2PdCl_4.

Supporting Information Available: Two figures representing crystal packing of [(COD)Pd(OMes)](SbF_6) in the unit cell and five tables (S1−S5) containing full structural information.This material is available free of charge via the Internet at http://pubs.acs.org.

OM010922Q

---

(24) Kegley, S. E.; Schaverien, C. J.; Freudenberger, J. H.; Bergman, R. G.; Nolan, S. P.; Hoff, C. D. *J. Am. Chem. Soc.* **1987**, *109*, 6563.

(25) Kunkely, H.; Vogler, A. *J. Organomet. Chem.* **1998**, *559*, 223.

(26) Vogler, A.; Kunkely, H. *Comments Inorg. Chem.* **1990**, *9*, 201.

(27) Vogler, A.; Kunkely, H. *Coord. Chem. Rev.* **2001**, *211*, 223.