and R_w are given in Table III. The atomic coordinates are reported in Tables IV and V, for compounds 3 and 5, respectively.

Acknowledgment. P.A., T.B., G.D., and A.M. thank the Progetto Finalizzato Chimica Fine II of the Italian CNR for financial support and for a grant to P.A.

Registry No. 1, 38887-05-7; **2**, 12130-66-4; **3**, 137546-76-0; **4a**, 126063-64-7; **4b**, 126186-21-8; **4c**, 126063-63-6; **5a**, 139495-14-0; **5b**, 139562-21-3; [$HRe(CO)_5$], 16457-30-0; [$Re_2Pt(CO)_{12}$], 91443-96-8; Pt, 7440-06-4; Re, 7440-15-5.

Supplementary Material Available: Tables of positional parameters for the hydrogen atoms, thermal parameters, and bond distances and angles for 3 and 5 (7 pages); final lists of observed and calculated structure factors moduli for 3 and 5 (44 pages). Ordering information is given on any current masthead page.

OM9106544

Electronic Structure of Catalytically Important Palladium Complexes Studied by Photoelectron Spectroscopy

F. Bökman,[†] A. Gogoll,*[,†] L. G. M. Pettersson,[‡] O. Bohman,[†] and H. O. G. Siegbahn[§]

Department of Organic Chemistry, University of Uppsala, P.O. Box 531, S-751 21 Uppsala, Sweden,
Department of Theoretical Physics, University of Stockholm, S-113 46 Stockholm, Sweden,
and Department of Physics, University of Uppsala, P.O. Box 530, S-751 21 Uppsala, Sweden

Received November 25, 1991

The Pd $3d_{5/2}$ core level binding energies have been measured by ESCA for a series of Pd(0) and Pd(II) compounds. Pd(0) complexes showed a considerable variation of these energies, depending on the ligands. In (π-allyl)Pd complexes, the energies were almost constant. This is explained by the donor–acceptor characteristics of the ligands. Differences in the reactivity of these complexes result from electron exchange between ligands via the metal atom, leaving its electron density unchanged.

Introduction

Complexes of palladium have become well-established tools in the synthesis of bulk chemicals as well as in elaborate synthetic strategies.[1] At the same time, the development of new reagents and methods relying on palladium is still one of the most productive fields in current organic chemistry. Usually, palladium compounds are assigned a formal oxidation number of 0, +I, +II, or +IV on the metal atom. If the formal oxidation number is kept constant, their reactivity and selectivity may be considerably altered by choice of the ligands on palladium.[2] For example, the addition of a quinone to the complexes **5–9** of the present work (cf. Figure 2), which substitutes one of the acetato or chloro ligands, results in an increased reactivity for nucleophilic substitution on the allyl moiety.[2c,3] However, apart from the observation that a chemical reaction occurs, there is no direct indication of an altered behavior of the metal atom. Oxidation numbers are of course a rather crude, formal model to describe the state of the metal atom. ^1H and ^{13}C NMR spectra of the organic ligands can provide some indirect indications,[3,4] but palladium itself is unfortunately not suitable for investigation by NMR spectroscopy,[5] which otherwise might reveal variations in its electronic state. For a limited number of palladium complexes, the redox potential of the metal atom has been determined.[6] The purpose of the present paper is to investigate a range of synthetically important complexes with ESCA (electron spectroscopy for chemical analysis) to provide information about the palladium state via the Pd 3d core level binding energies. This might be a possibility to probe directly the changes imposed on the metal atom by varying the ligands in palladium complexes with formally unaltered oxidation number. A variety of palladium(0) and palladium(II) complexes have been investigated.

The charge of the metal atom in a palladium complex results from the balance between donation and back-donation of electrons between the ligands and the metal atom.[1] The varying capacity of ligands to withdraw electrons from or to supply electrons to the metal atom emerges especially in mixed complexes. Thus, the oxidation potential of palladium in $Pd^0(quinone)(X)_2$ complexes has been shown to be independent of the quinone redox potential when the ligand X was a phosphine. When X was a diolefin, the oxidation potential increased with increasing redox potential of the quinone. This was explained by the higher capability of the phosphine ligand, as compared to an olefin, to supply electrons to the metal atom.[6]

ESCA has often been used as an experimental means of determining charges on the atoms in molecules and solids. The binding energy (E_B) of an electron in a certain core level of an atom in different chemical environments is in the first approximation directly proportional to the charge on the atom (q_{eff})[7]

[†] Department of Organic Chemistry, University of Uppsala.
[‡] Department of Theoretical Physics, University of Stockholm.
[§] Department of Physics, University of Uppsala.

(1) Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R.G. *Principles and Applications of Organotransition Metal Chemistry*; University Science Books: Mill Valley, CA, 1987.

(2) (a) Trost, B. M. *Tetrahedron* **1977**, *33*, 2615. (b) Tsuji, J. *Tetrahedron* **1986**, *42*, 4361. (c) Bäckvall, J. E.; Byström, S. E.; Nordberg, R. E. *J. Org. Chem.* **1984**, *49*, 4619. (d) Bäckvall, J. E.; Nordberg, R. E.; Wilhelm, D. *J. Am. Chem. Soc.* **1985**, *107*, 6892. (e) Goliaszewski, A.; Schwartz, J. *Organometallics* **1985**, *4*, 417.

(3) Bäckvall, J. E.; Gogoll, A. *Tetrahedron Lett.* **1988**, *29*, 2243.

(4) Åkermark, B.; Krakenberger, B.; Hansson, S.; Vitagliano, A. *Organometallics* **1987**, *6*, 620.

(5) Brevard, C.; Granger, P. *Handbook of High Resolution Multinuclear NMR*; J. Wiley & Sons: New York, 1981.

(6) (a) Hiramatsu, M.; Nakano, H.; Fujinami, T.; Sakai, S. *J. Organomet. Chem.* **1982**, *236*, 131. (b) Hiramatsu, M.; Shiozaki, K.; Fujinami, T.; Sakai, S. *J. Organomet. Chem.* **1983**, *246*, 203.

0276-7333/92/2311-1784$03.00/0

$$E_B = kq_{\text{eff}} + E_0 \quad (1)$$

where E_0 is the binding energy of the pure element. Although the binding energy depends not only on the local atomic charge but also on the charges on neighboring atoms as well as on the relaxation of electronic charge in the core-ionized species, these correlations proved valuable already in the first implementations of ESCA.

There are several ways to obtain the theoretical atomic charges to be used in the construction of the different correlation schemes, from Pauling charges to charges based on ab initio quantum chemical calculations, and many successful applications of these concepts have been made. For palladium compounds, Kumar et al.[8] could correlate the Pd $3d_{5/2}$ binding energies with the Pauling charges for different inorganic salts within groups of compounds having similar structures, e.g. $PdCl_2$, $PdBr_2$, and PdI_2, but not $Pd(CN)_2$ or $Pd(PPh_3)_2Cl_2$. Their data show a large spread (of totally 3 eV) in the Pd $3d_{5/2}$ binding energies for formal Pd(II) compounds, but their single Pd(IV) compound has a higher binding energy.

An example of a successful application of the oxidation state concept in ESCA studies of palladium compounds is the confirmation of the existence of the Pd(III) oxidation state in some inorganic palladium fluoride compounds by Tressaud et al.[9] This was achieved by showing the distinctive binding energies of Pd(II), Pd(III), and Pd(IV) in anions of the type $(PdF_x)^{y-}$. However, also this investigation shows the difficulties of a too straightforward use of formal oxidation numbers, since the binding energies for PdF_2 and $PdCl_2$ fell into the Pd(II) and Pd(III) ranges, respectively.

Nefedov et al.[10] have studied some formal Pd(0), Pd(I), and Pd(II) complexes containing triphenylphosphine ligands. They found no clear boundary in the Pd $3d_{5/2}$ binding energies between Pd(0) and Pd(I) compounds, but there was a step of 1 eV from Pd(I) to Pd(II).

Petrov et al.[11] have determined the Pd $3d_{5/2}$ binding energies of the (π-allyl)palladium chloride, bromide, and iodide dimers to be within 0.3 eV, and they conclude that the charge on the Pd atom is less in these complexes than in $PdCl_2$. These workers also showed that with an electron-withdrawing chloro substituent in the 2-position of the π-allyl ligand the binding energy increased by 0.6 eV.

Materials

Materials. $PdCl_2$ and $Pd(OAc)_2$ were purchased from Engelhard Industries. Palladium black was obtained by thermic decomposition of the (π-allyl)Pd complex **13** (vide infra). $Pd_2(dba)_3CHCl_3$ (**1**) (dba = dibenzylideneacetone),[12] Pd(*p*-benzoquinone) (**2**),[6b] Pd(naphthoquinone)$_2$ (**3**),[6b] bis[(1,3-η^3-allyl)palladium chloride] (**4**),[13] bis(μ-chloro)bis[η^2-8-*exo*-methoxytricyclo(5.2.1.0^{2,6})dec-3-en-9-*endo*-yl]palladium (**10**),[14] [tricyclo(5.2.1.0^{2,6})deca-3,8-diene]palladium chloride (**11**),[15] and $[PhCN]_2PdCl_2$[16] were prepared according to literature procedures.

Pd(*p*-benzoquinone) (2).[6b] Anal. Calcd for $C_6H_4O_2Pd$: C, 33.60; H, 1.88; Pd, 49.60. Found: C, 33.55; H, 2.01; Pd, 49.40.

Bis(4-acetoxy-1,3-η^3-cyclohexenyl)palladium Chloride (6).[3] Palladium acetate (400 mg, 1.79 mmol), lithium acetate dihydrate (1.52 g, 11.0 mmol), and lithium chloride (380 mg, 8.9 mmol) were dissolved in aqueous acetic acid (4.8 mL, 50% v/v) under gentle heating. After the solution was cooled to 0 °C and filtered, freshly distilled 1,3-cyclohexadiene (400 μL, 4.2 mmol) was added and the suspension vigorously shaken at the same temperature for 5 min. The yellow precipitate was filtrated out, washed with aqueous acetic acid (2 mL, 50% v/v), and dried in vacuo for 2 h at ambient temperature, yielding 406 mg (1.45 mmol, 81% from palladium acetate) of complex **6** as a bright yellow powder, mp 105–106 °C dec. ^{1}H NMR: δ 5.54 (app t, *J* = 6.2 Hz, 1 H, H-2), 5.28 (m, 1 H, H-1), 5.16 (ddd, *J* = 6.6, 5.5, 2.5 Hz, 1 H, H-4), 4.97 (ddd, 6.2, 2.5, 1.0 Hz, 1 H, H-3), 2.36 (m, *J* = 14.0, 6.2, 6.0, 5.5 Hz, H-5_{eq}), 2.05 (s, 3 H, OAc), 1.92 (m, 1 H, H-6_{ax}), 1.71 (m, 1 H, H-6_{eq}), 1.21 (m, *J* = 14.0, 7.9, 6.6, 6.0 Hz, H-5_{ax}). ^{13}C NMR: δ 170.2 (C=O), 101.6 (C-2), 82.0 (C-1), 74.6 (C-3), 69.3 (C-4), 26.8 (C-5), 24.7 (C-6), 21.4 (CH_3). IR (KBr): 3020, 2897, 1732, 1426, 1326, 1258, 1187, 1028, 986 cm^{-1}. Anal. Calcd for $C_{16}H_{22}Cl_2O_4Pd_2$: C, 34.19; H, 3.95; Cl, 12.62. Found: C, 34.6; H, 3.9; Cl, 12.3.

Bis(4-acetoxy-1,3-η^3-cyclohexenyl)palladium Acetate (13).[3] To a solution of **6** (100 mg, 0.36 mmol) in $CDCl_3$ (3 mL) at 0 °C was added AgOAc (60 mg, 0.36 mmol) and the solution stirred at this temperature for 15 min. The grayish precipitate was removed by centrifugation, leaving a solution of the acetato complex **13**, which is stable for several days but slowly decomposes upon removal of the solvent. ^{1}H NMR: 5.60 (m, 1 H, H-2), 5.30 (m, 1 H, H-4), 5.16 (m, 1 H, H-1), 4.86 (m, 1 H, H-3), 2.34 (m, 1 H, H-5_{eq}), 2.14 (s, 3 H, CH-O*Ac*), 2.13 (s, 3 H, acetato ligand), 1.99 (m, 2 H, H-6), 1.15 (m, 1 H, H-5_{ax}). ^{13}C NMR: δ 181.0 (C=O, acetato ligand) 170.4 (C=O, CHO*Ac*), 101.3 (C-2), 75.0 (C-1), 70.4 (C-4), 68.0 (C-3), 25.9 (C-5), 24.8 (C-6), 24.0 (CH_3, acetato ligand), 21.4 (CH_3, CHO*Ac*).

Tetrakis(μ-acetato)bis(4-acetoxy-1,3-η^3-cyclohexenyl)tripalladium (5).[3] Palladium acetate (200 mg, 0.89 mmol) and lithium acetate dihydrate (750 mg, 7.4 mmol) were dissolved in aqueous acetic acid (2.4 mL, 50% v/v) under gentle heating. After the solution was cooled to 0 °C and filtered, freshly distilled 1,3-cyclohexadiene (200 μL, 2.1 mmol) was added and the mixture vigorously shaken at this temperature for 5 min. After filtration, the yellow-gray solid residue was washed with aqueous acetic acid (2 mL, 50% v/v) and dried in vacuo at ambient temperature for 2 h, yielding 160 mg (0.19 mmol, 65% from palladium acetate) of **5** as a grayish-yellow powder, mp 130–140 °C dec. ^{1}H NMR: δ 6.25–6.05 (br m, 1 H, H-2), 5.44 (br m, 2 H, H-1, and H-4), 5.12 (br m, 1 H, H-3), 2.40 (br m, 1 H, H-5_{eq}), 2.04 (s, 3 H, CHO*Ac*), 1.90 (br m, 5 H, H-6 and acetato ligand), 1.20 (br m, H-5_{ax}). IR (KBr): 3000, 2925, 1735, 1578, 1413, 1378, 1352, 1248, 1024, 698 cm^{-1}. Molecular weight: calcd, 833.68; found, 795 (osmometrically in $CHCl_3$). Anal. Calcd for $C_{24}H_{34}O_{12}Pd_3$: C, 34.58; H, 4.11; Pd, 38.29. Found: C, 34.65; H, 3.87; Pd, 38.20.

Tetrakis(μ-acetato)bis[(5-acetoxy-2,4-η^3-hexenyl)]tripalladium (7) was prepared under the same conditions as described for **5**, but starting from (*E*,*E*)-2,4-hexadiene, yield 61% from palladium acetate, as a pale yellow powder. ^{1}H NMR: δ 6.0–3.5 (several br m, 6 H, π-allyl and CHOAc), 2.05 (m, 6 H, OAc), 1.90 (m, 12 H, OAc), 1.38 (m, 6 H, CH_3), 1.25 (m, 6 H, CH_3). IR (KBr): 2980, 1733, 1556, 1407, 1243, 1041, 699 cm^{-1}. Anal. Calcd for $C_{24}H_{38}O_{12}Pd_3$: C, 34.41; H, 4.57; Pd, 38.10. Found: C, 36.16; H, 4.61; Pd, 39.55.

***trans*-Bis[(5-acetoxy-2,4-η^3-hexenyl)palladium chloride] (8) and *cis*-bis[(5-acetoxy-2,4-η^3-hexenyl)palladium chloride] (9)** were prepared from (*E*,*E*)- and (*E*,*Z*)-2,4-hexadiene, respectively, under the conditions described for **6**; yield 50–60%.

8: mp 153 °C. ^{1}H NMR: δ 5.39 (dd, *J* = 11.0, 11.0 Hz, 1 H, H-3), 5.01 (dq, *J* = 6.5, 6.4 Hz, 1 H, H-5), 3.86 (ddq, *J* = 11.0, 6.4, 0.5 Hz, 1 H, H-2), 3.43 (dd, *J* = 6.5, 11.0 Hz, 1 H, H-4), 2.07 (s, 3 H, OAc), 1.45 (d, *J* = 6.4 Hz, 3 H, CH_3-6), 1.30 (d, *J* = 6.4

---

[7] Siegbahn, K.; Nordling, C.; Fahlman, A.; Nordberg, R.; Hamrin, K.; Hedman, J.; Johansson, G.; Bergmark, T.; Karlsson, S.-E.; Lindgren, I.; Lindberg, B. *ESCA-Atomic, Molecular and Solid State Structure Studied by Means of Electron Spectroscopy*; Nova Acta Regiae Soc. Sci. Upsaliensis: Uppsala, Sweden, 1967; Ser. IV, Vol. 20.

[8] Kumar, G.; Blackburn, J. R.; Albridge, R. G.; Moddeman, W. E.; Jones, M. M. *Inorg. Chem.* **1972**, *11*, 296.

[9] Tressaud, A.; Khairoun, S.; Touhara, H.; Watanabe, N. *Z. Anorg. Allg. Chem.* **1986**, *540/541*, 291.

[10] Nefedov, V. I.; Salyn, Ya. V.; Moiseev, I. I.; Sadovskii, A. P.; Berenbljum, A. S.; Knizhnik, A. G.; Mund, S. L. *Inorg. Chim. Acta* **1979**, *35*, 1343.

[11] Petrov, G. B.; Markovich, L. M.; Ryabtsev, A. V.; Belov, A. P. *Zh. Strukt. Khim.* **1983**, *24*, 113; **1984**, 915 (English).

[12] Ukai, T.; Kawazura, H.; Ishii, Y.; Bonnet, J. J.; Ibers, J. A. *J. Organomet. Chem.* **1974**, *65*, 253.

[13] Smidt, J.; Hafner, W. *Angew. Chem.* **1959**, *71*, 284.

[14] Wipke, W. T.; Goeke, G. L. *J. Am. Chem. Soc.* **1974**, *96*, 4244.

[15] Chatt, J.; Vallarino, L. M.; Venanzi, L. *J. Chem. Soc.* **1957**, 3413.

[16] Kharasch, M. S.; Seyler, R. C.; Mayo, F. R. *J. Am. Chem. Soc.* **1938**, *60*, 882.

Hz, 3 H, CH_3-1). ^{13}C NMR: δ 170.2 (C=O), 110.4 (C-3), 80.7 (C-2), 78.2 (C-4), 70.4 (C-5), 21.6 (CH_3C=O), 20.6 (C-6), 18.3 (C-1). IR (KBr): 2980, 1724, 1408, 1373, 1246, 1037 cm^{-1}. Anal. Calcd for $C_{16}H_{26}Cl_2O_4Pd_2$: C, 33.95; H, 4.63; Pd, 37.59. Found: C, 34.70; H, 4.69; Pd, 38.85.

9: mp 128 °C. ^1H NMR: δ 5.25 (app tt, J = 10.5, 0.75 Hz, 1 H, H-3), 5.06 (dq, J = 6.5, 4.75 Hz, 1 H, H-5), 3.88 (ddq, J = 10.5, 6.25, 0.75 Hz, 1 H, H-2), 3.59 (ddd, J = 10.5, 4.75, 0.75 Hz, 1 H, H-4), 2.07 (s, 3 H, OAc), 1.44 (d, J = 6.5 Hz, 3 H, CH_3-6), 1.31 (d, J = 6.25 Hz, 3 H, CH_3-1). ^{13}C NMR: δ 170.3 (C=O), 107.8 (C-3), 80.0 (C-2), 77.0 (C-4), 69.2 (C-5), 21.2 (CH_3C=O), 18.9 (C-6), 17.9 (C-1). IR (KBr): 2977, 2920, 1727, 1246, 1030 cm^{-1}. Anal. Calcd for $C_{16}H_{26}Cl_2O_4Pd_2$: C, 33.95; H, 4.63; Pd, 37.59. Found: C, 34.66; H, 4.64; Pd, 38.90.

Experimental Methods

NMR spectra were acquired on a Varian XL-300 NMR spectrometer for solutions in $CDCl_3$ at ambient temperature, at 300 MHz for ^1H and 75.4 MHz for ^{13}C. Chemical shifts were indirectly referenced to TMS via the solvent signals (^1H, $CHCl_3$ at 7.26 ppm; ^{13}C, $CDCl_3$ at 77.0 ppm). Signal assignments were obtained from COSY-45,[17] HETCOR,[18] and NOE difference spectra.[19] IR spectra were run on a Perkin-Elmer 1600 FTIR spectrometer. Elemental analyses were obtained from Mikrokemi AB, Uppsala, Sweden, and from Analytische Laboratorien, Engelskirchen, FRG, who also performed the molecular weight determination.

The ESCA spectra were recorded on an electron spectrometer with monochromatized Al Kα X-ray excitation and an electrostatic energy analyzer.[20] The sample probe is primarily designed for the study of liquid samples,[21] but this arrangement has proven to have significant advantages in studies of poorly conducting solids as well.

Common procedures in sample preparation of nonmetallic solids are to place the solid as a fine powder on a conducting adhesive tape, to evaporate a thin layer of gold on top of the sample or to dissolve the sample in a volatile liquid, and to drop it onto a metal backing and let the solvent evaporate, leaving only a thin film of sample on the conducting backing. Often these procedures are combined with the "showering" of the sample with low-energy electrons during the experiment, to compensate for any charge buildup.

In the present study we have benefited greatly from the fact that the sample backing consisted of a rotatable stainless steel disk. The solid sample was dissolved in chloroform or methanol and dropped onto the steel disk. We found it difficult to effectively control the thickness of the solid sample that remained when the solvent had evaporated, but given the possibility to rotate the disk from outside the sample compartment it was in most cases relatively easy to find spots suitable for analysis. In some cases we rotated the disk slowly and thus continuously renewed the spot under examination. The use of these two options gave good reproducible spectra for all complexes studied.

The binding energies are referenced to the C1s signal due to ambient hydrocarbons (e.g. from pump oil) at 285.0 eV. The position of this peak could be clearly defined in all cases as due to the most prominent feature in the C1s spectrum.

Results and Discussion

Figure 1 shows typical Pd 3d spectra obtained from two of the complexes in this study. The peaks are seen to be free of internal structure, and the spin-orbit splitting is the same for the two cases (~5.2 eV for all complexes in this study).

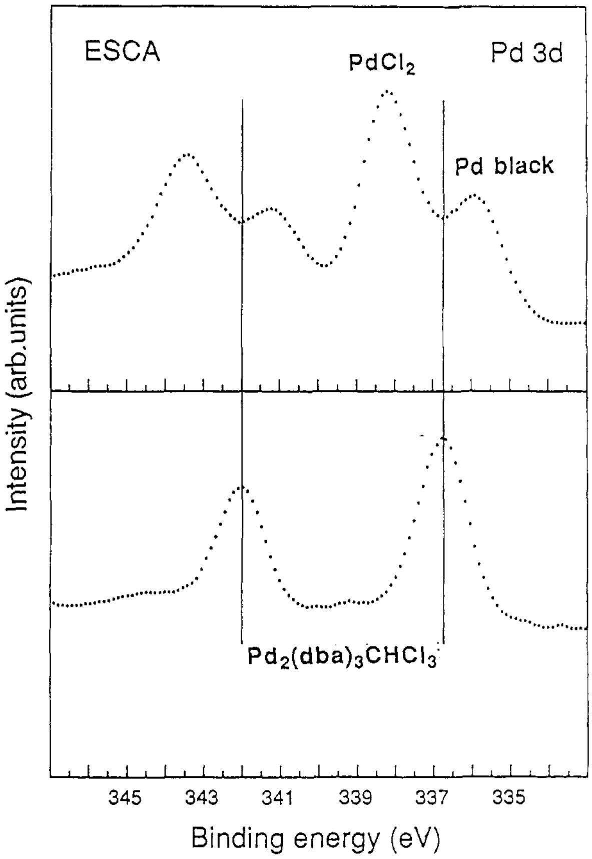


Figure 1. Pd 3d spectra of complex **1** (bottom) and $PdCl_2$ and Pd black (top).

Figure 2 summarizes the results in terms of Pd $3d_{5/2}$ binding energies for the present set of complexes, grouped according to type. The most prominent feature of the data is the near-constancy of the binding energies for all π-allyl complexes. Since the binding energy reflects both initial state and final state (relaxation) properties, this finding may of course be due to cancellation effects among these various properties for the present series of complexes. However, the most likely explanation is that the initial state charge distribution and dynamical polarization behavior around the different Pd atom sites are indeed very similar. Obviously, here the π-allyl ligand levels out the effect of the inorganic ligands on the metal atom. Thus, the palladium seems to be only a mediator for ligand effects, without changing its own charge. The observation of only one single value for complexes **5** and **7** is somewhat startling, since these contain two different sorts of palladium atoms. An even charge distribution between all metal atoms, as indicated by this result, is reminiscent of the polymeric palladium chloride,[22] where the arrangement of the $PdCl_2$ units in long chains is likely to cause a markedly different relaxation behavior upon ionization than observed e.g. for palladium acetate, which is trimeric.[23] It is thus conceivable that final state effects may take over and obscure any initial state differences that may pertain to the two palladium sites in these complexes. Complex **5** is also far less reactive toward *p*-benzoquinone than the dimeric acetato complex **13**,[3] which could not be investigated here due to its low stability.

The present findings for the group of π-allyl complexes can be related to the results of the previous investigations quoted above.[8,11] Thus, Kumar et al.[8] find that whereas a correlation between Pauling charge and Pd 3d binding

---

(17) Bax, A.; Freeman, R.; Morris, G. A. *J. Magn. Reson.* **1981**, *42*, 164.

(18) Wilde, J. A.; Bolton, P. H. *J. Magn. Reson.* **1984**, *59*, 343.

(19) Sanders, J. K. M.; Mersh, J. D. *Prog. NMR Spectrosc.* **1982**, *15*, 353.

(20) Siegbahn, H.; Svensson, S.; Lundholm, M. *J. Electron. Relat. Phenom.* **1981**, *24*, 205.

(21) Moberg, R.; Bökman, F.; Hagfeldt, A.; Lindqvist, S.-E.; Bohman, O.; Siegbahn, H.O.G. UUIP-1218. Uppsala, 1990.

(22) Wells, A. F. *Z. Kristallogr.* **1939**, *100*, 189.

(23) Skapski, A. C.; Smart, M. L. *J. Chem. Soc., Chem. Commun.* **1970**, 658.

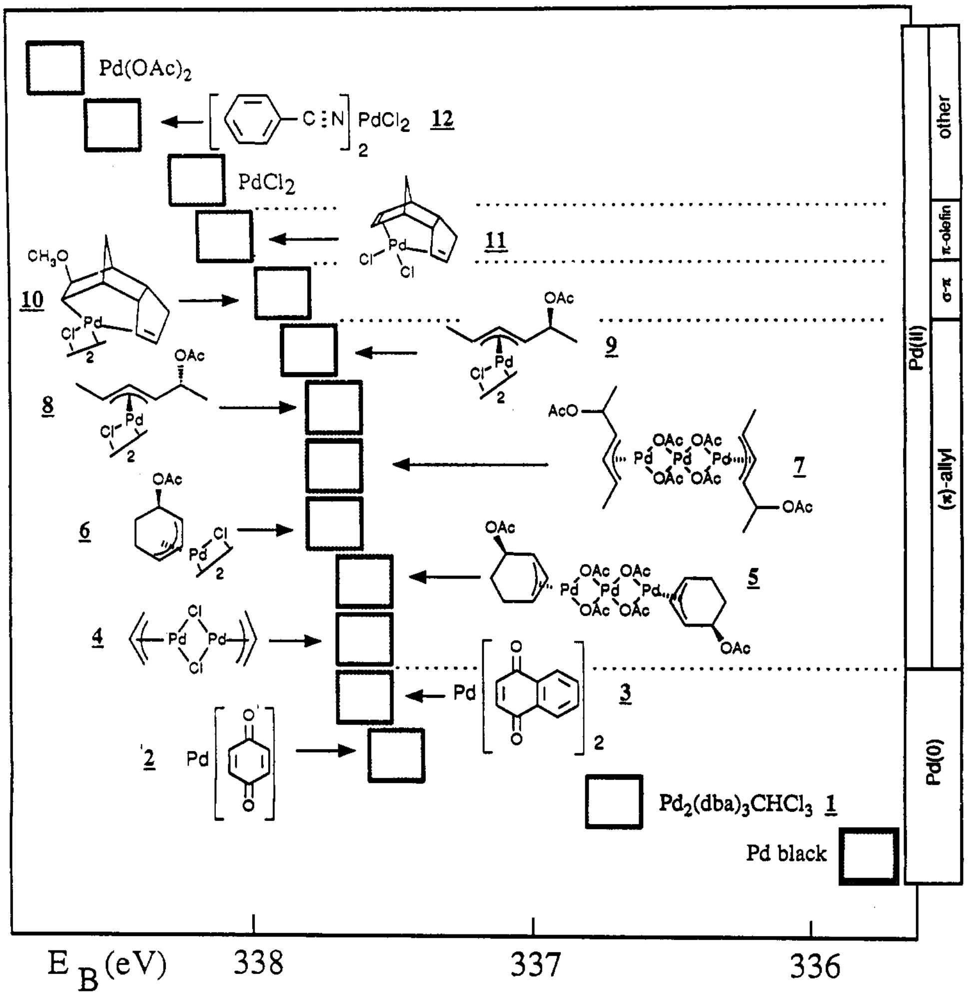
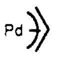
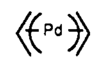
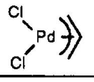


Figure 2. Pd $3d_{5/2}$ binding energies of the compounds investigated in this paper.

energy is obtained for the palladium halides, the Pd 3d binding energy is essentially constant in the phenylphosphine-substituted series, $Pd(PPh_3)_2X_2$ (X = Cl, Br, I). This is interpreted as due to a regulating mechanism where the increasing polarity of the metal–halide bond is counteracted by a change in the balance of the donor–acceptor character in the metal–phosphine bond. Thus, when the palladium–halide bond is more polarized, the palladium to phosphorus π-donation becomes less efficient and the phosphorus to palladium s-bonding more efficient. The net result is that any depletion of electron density around the palladium atom is averaged over both the palladium atom and the phosphine ligands. This leads to only small changes in the electron density on both the palladium and phosphorus atoms, which in turn results in only small core level shifts for these atoms. A similar explanation is likely to be applicable to the results of Petrov et al.[11] concerning the almost constant Pd 3d binding energies in the dimeric π-allyl halide complexes (of which the chloride is identical to our complex 4) and likewise to the set of π-allyl complexes studied here. In order to obtain some further insight concerning charge distributions in these types of complexes, we have also performed ab initio SCF calculations on some model species.[24] Results are shown in Table I for (π-allyl)Pd, bis(π-allyl)Pd, and $(\pi\text{-allyl})PdCl_2$ species with respect to the gross atomic charges obtained. Although absolute significance should not be attached to these figures, it is a striking observation that the charge on Pd is almost identical in these different species, in sharp contrast to the charge alteration of the π-allyl subunit. This again confirms the view of a regulating mechanism via the donor–acceptor character of the bonding.

Table I. Gross Atomic Charges of Model (π-Allyl)palladium Species As Obtained from ab Initio SCF Calculations[24]

			
Pd	+0.12	+0.11	+0.20
π-allyl	−0.12	−0.06	+0.35
Cl			−0.28

For the remaining compounds the present investigation shows that the formal oxidation number of palladium is only loosely related to the actual charge on the metal atom, which depends predominantly on the type of ligand, i.e. its donor–acceptor properties. In the group of Pd(0) complexes, the binding energy E_B increases with increasing ability of the ligand to withdraw electrons from the metal atom (quinones vs dibenzylideneacetone), corresponding to a higher positive charge. Thus, the strongly electron-attracting quinones, which are known to activate (π-allyl)palladium complexes for nucleophilic attack by coordination to the metal atom,[2c,3] have Pd 3d binding energies almost coincident with the formal Pd(II) complexes. The reaction rate differs for various quinones. Therefore, one would expect the two types of quinone ligands to lead to somewhat different Pd 3d binding energies. However, the naphthoquinone complex (3) has about the same Pd 3d

---

[24] Bökman, F.; Pettersson, L. G. M.; Gogoll, A.; Bohman, O.; Siegbahn, H. O. G. To be published.

binding energy as the benzoquinone complex (**2**), although the free naphthoquinone has a considerably lower redox potential than benzoquinone (0.484 vs 0.711 V).[25] Similarly, comparing the electrochemically determined redox potentials of palladium in Pd^0(quinone)(cyclooctadiene) complexes, the benzoquinone complex is found to have a more positive value.[6b] It cannot be excluded, however, that different structure characteristics might influence the relative Pd 3d binding energies.[6b]

The only σ–π complex studied here (**10**) shows as expected a slightly higher binding energy, indicating the lower electron-donating capability of this ligand, as compared to π-allyl. When complexes **11** and **12** are compared, the electron-donating effect of the olefin in **11** is apparent in the lower binding energy, whereas nitriles are known to be only moderate σ-donors as well as very weak π-acceptors.[1] The higher binding energies of **12** compared to palladium chloride is most likely due to the polymeric character of the latter.[22]

It is not straightforward to assign charges to the Pd atoms in the present set of complexes on the basis of the ESCA data alone. Judging from Figure 2, the charges may be estimated on a scale ranging from complex **1** to $Pd(OAc)_2$, the former representing probably most truly (within the present series) a neutral palladium atom and the latter a typical divalent species. The actual charges on palladium at these extremes cannot, however, be stated without resort to some theoretical framework (e.g. ab initio quantum chemical calculations) in which the charge concept is defined. What can be said, on the other hand, is that relative to the two extremes defined above, in e.g. the π-allyl complexes, the palladium atom has an intermediate charge more resembling Pd(I) than the formal Pd(II).

It should be noted that for particular cases final state effects, which depend on the electronic and geometrical structure, must also be taken into consideration. These factors may influence the comparison of the present series of complexes with other types of compounds. One case mentioned above is that of $PdCl_2$, where the polymeric form probably leads to a different relaxation behavior than in the other cases. Likewise, Pd black cannot reliably be associated with a neutrally charged palladium on the same scale as the present complexes on account of the different relaxation anticipated due to metallic conductance.

In conclusion, ESCA is capable of providing information about the state of the metal atom in synthetically important palladium complexes. This is particularly so in complexes containing only one type of ligand. Thus, quinones, which are applied as oxidants in reactions with (π-allyl)palladium species as intermediates, withdraw charge from the metal atom in formal Pd(0) complexes, resulting in a metal atom charge resembling that in the formal Pd(II) complexes **4**–**9**. When, on the other hand, ligands with different donor–acceptor properties interact via the metal atom, this might effect a charge shift between the ligands which leaves the metal atom itself unchanged. This behavior was observed for the π-allyl complexes, resulting in very similar binding energies for all examined species of this type. ^{13}C NMR chemical shift differences have been surveyed as a possible indicator for the metal atom charge and reactivity of such complexes, concluding that a correlation between these parameters exists.[4] Our present results show that it is not the metal atom charge that changes but the flow of electrons between ligands via the metal atom. In complexes with different ligands, but without a strong donor (**10**–**12**), variations of the metal atom charge are again observed. In interpretation of the ESCA data attention should however be paid to structural effects.

The electronic properties of the palladium complexes are not always reflected by the binding energies of palladium. Therefore, a measurement of the binding energies of the adjacent centers is likely to provide a more complete picture. Further research, which also will include palladium complexes with phospine ligands and bis(π-allyl)-palladium complexes, are scheduled with a new spectrometer which is under construction in this laboratory.

Acknowledgment. This work was supported by the Swedish Natural Science Research Council (NFR) and the Bank of Sweden Tercentenary Foundation. We are grateful to Prof. J. E. Bäckvall for stimulating discussions.

Registry No. **1**, 51364-51-3; **2**, 140175-31-1; **3**, 86228-60-6; **4**, 12012-95-2; **5**, 140201-40-7; **6**, 118212-05-8; **7**, 140386-63-6; **8**, 140384-75-4; **9**, 140384-76-5; **10**, 33218-61-0; **11**, 12294-98-3; **12**, 14220-64-5; **13**, 135619-93-1; $Pd(OAc)_2$, 3375-31-3; $PdCl_2$, 7647-10-1; Pd, 7440-05-3; 1,3-cyclohexadiene, 592-57-4; (*E*,*E*)-2,4-hexadiene, 5194-51-4; (*E*,*Z*)-2,4-hexadiene, 5194-50-3.

OM910728B

---

(25) Laird, T. In *Comprehensive Organic Chemistry*; Stoddart, J. F., Ed.; Pergamon Press: Oxford, England, 1979; Vol. 1, p 1213.