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A new approach to novel homobimetallic palladium complexes

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Abstract

Mononuclear *trans*-(PPh₃)₂Pd(I)(C₆H₄-4-I) (**3**), which is accessible by the oxidative addition of C₆H₄-1,4-I₂ (**2**) to (Ph₃P)₄Pd (**1**), reacts with [AgOTf] (**4**) in a 1:1 molar ratio to give *trans*-(PPh₃)₂Pd(C₆H₄-4-I)(OTf) (**5**). Complex **5** affords on treatment with 0.5 equivalents of 4,4'-dicyanobiphenyl (**6**) homobimetallic *trans*-[(PPh₃)₂(C₆H₄-4-I)Pd \leftarrow N=C-C₆H₄]₂(OTf)₂ (**7**). The latter species rearranges to give *trans*-[(PPh₃)₂(C₆H₄-4-PPh₃)Pd \leftarrow N=C-C₆H₄]₂(OTf)₄ (**8**) and [(PPh₃)(C₆H₄-4-PPh₃)Pd(µ-I)]₂(OTf)₂ (**9**), respectively. A possible mechanism for the formation of **8** and **9** will be presented. The solid-state structure of **8** is reported. In **8** two [*trans*-(PPh₃)(C₆H₄-4-PPh₃)Pd]²⁺ fragments are bridged by the 4,4'-dicyanobiphenyl unit. © 2004 Elsevier B.V. All rights reserved.

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Recently, homo- and heterobimetallic complexes in which the transition metal atoms are spanned by π -conjugated electron-transferring/-transmitting organic and/or inorganic building blocks, possessing metals of groups 8–10, were synthesized in order to use them as model compounds to study, for example, intraand/or intermolecular electron-transfer [1–5]. The electronic communication between the participating transition metals proceeds via the π -conjugated bridging units.

Monolayer assemblies provide excellent model systems for the study of interfacial processes. For example, electron-transfer benefits from the orderliness provided by self-assembling monolayers (SAMs) [6]. Self-assembled monolayers of redox-active (thiol-substituted) transition metal complexes/materials onto gold and other surfaces have been the topic of recent research [6a–b, 7], since the application of such systems and modified surfaces ranges from fundamental studies, concerning the structure of the layers and the thermodynamics and kinetics of adsorption, to applications, including sensors as well as molecular and electronic devices and catalysis [8]. It was found that, in the case of the metal complexes, they retain their redox-active responses at potentials very close to those of *non*-adsorbed analogs in homogeneous solutions [6a]. Although, the immobilization of transition metal complexes onto electrode surfaces has been partly studied.

In this respect, it would be of interest to study the interfacial electronic transfer between two surfaces which are bridged by homobimetallic organometallic species [9,10]. An entry into the area of molecular electronics would be given.

We here describe the synthesis of a rigid-rod structured homobimetallic palladium complex in which the transition metals are linked by a π -conjugated organic unit.

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A possibility to prepare a molecular wire type molecule is given by, for example, the oxidative addition of C_6H_4 -1,4-I₂ to Pd(PPh₃)₄, treatment of the obtained *trans*-(PPh₃)₂Pd(I)(C₆H₄-4-I) species with [AgOTf] and replacement of the weakly bound TfO⁻ in *trans*-(PPh₃)₂Pd(C₆H₄-4-I)(OTf) by stronger Lewis-bases, such as dicyano π -conjugated organic species. In this respect, we reacted Pd(PPh₃)₄ (1) with equimolar amounts of diiodobenzene (2) in toluene at 25 °C (Eq. (1))



Monometallic *trans*-(PPh₃)₂Pd(C₆H₄-I)(I) (3) precipitates during the course of the reaction. Complex 3 is obtained in 92% yield and in high purity as a colorless solid.

Treatment of **3** with [AgOTf] in a 1:1 molar ratio in dichloromethane/toluene mixtures led to the in situ formation of the corresponding palladium-triflate complex **5** (Eq. (2)). On addition of 0.5 equivalents of 4,4'-dicyanobiphenyl (6) to **5** homobimetallic *trans*-[(PPh₃)₂(C₆H₄-4-I)Pd $\leftarrow N \equiv C - C_6H_4$]₂(OTf)₂ (7) is produced (Eq. (2)). In this reaction the OTf⁻ is replaced by the better π -acid **6**



Complex 7 can be precipitated from the reaction medium by slow addition of n-hexane. An off-white, air-, moisture- and temperature-sensitive residue is formed. While solid 7 is stable in the dark for weeks, it appeared that on exposure to light it decomposes during hours to unknown materials.

In an attempt to grow single crystals of 7 from saturated dichloromethane solutions at 25 °C, we observed that the color of the solution changes to orange and palladium precipitates. After filtration through a pad of Celite and addition of *n*-hexane to the filtrate colorless crystals of **8** are produced as the major product (Eq. (3)). ¹ Concentration of the supernatant solution gives crystals of **9** (Eq. (3))



The formation of **8** and **9** can most probably be explained as follows. Complex **7** decomposes in solution by precipitation of palladium and formation of iodobenzene, triphenylphosphane and 4,4'-dicyanobiphenyl as detected by GC–MS studies. Presumably the Lewisbase PPh₃ undergoes a nucleophilic substitution reaction at the activated iodo-carbon atom of **7** to give **8**. The thus formed iodide can attack the square-planar coordinated palladium(II) ion in **8** to give **9**.

Complexes **3** and **7–9** were fully characterized by elemental analysis, IR and NMR (${}^{1}H$, ${}^{31}P{}^{1}H$) spectroscopy.

In the IR spectra of 7–9 the triflate counter-ion gives rise to one very characteristic absorption at 1265 cm⁻¹ (v_{SO}), which is consistent with the *non*-coordinating character of TfO⁻. The C=N stretching vibration of **6**, **7** and **8** is a most informative spectroscopic tool for monitoring the progress of the reaction of **3** with **6** and the rearrangement of 7–9 (vide supra). The $v_{C=N}$ band of **6** is thereby shifted to higher wavenumbers (**7**, 2260 cm⁻¹; **9**, 2280 cm⁻¹) as compared to that of *non*coordinated **6** ($v_{C=N} = 2228$ cm⁻¹). This indicates the dative bonding of the C=N groups to a palladium(II) ion. This observation resembles the data found for other

¹ Synthesis of **8**. Compound **7** is dissolved in 5 ml of dichloromethane. 30 ml of toluene are added as second layer. The two layers are mixed overnight whereby **8** crystallizes. The solvents are removed by filtration and the crystals are dried in oil-pump vacuum. Complex **8** is obtained in form of colorless crystals (0.08 g, 0.031 mmol, 27% based on **7**).

M.p.: 146 °C (dec.). Anal. Found: C, 58.69; H, 3.87; N, 0.92; C₁₃₈H₁₀₆F₁₂N₂O₁₂P₆Pd₂S₄ · CH₂Cl₂ (3027.24): Calc.: C, 59.11; H, 3.85; N, 0.99%. IR (KBr): 3065 (m), 2907 (s), 2255 (m), 1553 (m), 1432 (s), 1269 (vs), 1024 (s), 1154 (s), 1030 (s), 801 (s), 796 (s), 695 (s) cm⁻¹. ¹H NMR (250.123 MHz, 25 °C, CDCl₃): $\delta = 6.34$ (d, 2H, J = 7.5 Hz, ⁴ $J_{HP} = 3.7$ Hz, meta-H/C₆H₄PPh₃), 6.64 (d, 2H, J = 7.3 Hz, meta-H/C₆H₄CN), 6.73 (d, 2H, J = 7.5 Hz, ortho-H/C₆H₄PPh₃), 7.26–7.68 (m, 45H, PPh₃), 7.70 (d, 2H, J = 7.3 Hz, ortho-H/C₆H₄CN). ¹³C{¹H} NMR (62.860 MHz, 25 °C, CDCl₃): $\delta = 117.0$ (CN), 127.9–137 (Ph, C₆H₄). ³¹P{¹H} NMR (101.202 MHz, 25 °C, CDCl₃): $\delta = 21.86$ (s, PPh₃), 21.86 (s, C₆H₄PPh₃⁺).



Fig. 1. XP drawing of 8 at 50% probability level (the hydrogen atoms, the two toluene molecules and the four TfO⁻ ions are omitted for clarity). Symmetry generated atoms are indicated with the suffix A. Selected interatomic distances (Å): Pd1–N1 2.082(5), Pd1–P1 2.334(2), Pd1–P2 2.338(2), Pd1–C44 1.993(5), N1–C43 1.142(8), C62–P3 1.802(8); selected angles (°): P1–Pd1–P2 173.03(6), N1–Pd1–C44 173.5(3), Pd1–N1–C43 174.1(7), N1–C43–C37 176.1(9).

transition metal complexes, i.e., $\{[(dppp)Pd][C_6H_4-1,4-(CN)_2]_2[OTf]_2\}_4$ (2280 cm⁻¹) [11].

The ¹H NMR spectra of **3** and **7–9** show sharp and well-resolved resonance signals for the organic units C_6H_4I , $C_6H_4PPh_3$ and $C_6H_4-C_6H_4$.

In the ³¹P{¹H}NMR spectra of **3** and **7–9** one (**3**, **7**) or two (**8**, **9**) resonance signals can be detected at ca. 21 ppm for the PPh₃ groups datively bound to palladium and at ca. 27 ppm for the $C_6H_4PPh_3^+$ units.

Single crystals of 8 suitable for X-ray structure analysis could be obtained by diffusion of toluene into a dichloromethane solution containing 8 at 25 °C. ² The asymmetric unit of 8 contains half of the cationic part. two non-coordinated triflat ions and a solvent molecule of toluene. In between the two phenyl groups of the bridging 4,4'-dicyanobiphenyl molecule is a center of inversion. The palladium(II) ion possesses a square-planer environment, caused by the two trans situated phosphorous atoms P1 and P2 of PPh₃, C44 of $C_6H_4PPh_3^+$ and one nitrogen atom of the 4,4'-dicyanobiphenyl substituent (r.m.s.d.: 0.1271 Å). The phenylene unit of the $C_6H_4PPh_3^+$ group is perpendicular oriented to the transition metal coordination plane (87.1(2)°), while the biphenyl entity is almost in plane bound $(12.8(3)^{\circ})$. The Pd-N, Pd-P and Pd-C separations (Fig. 1) are in the typical range as reported elsewhere [12].

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² Crystallographic data for **8**: crystal data were collected from shock-cooled crystals on a BRUKER SMART CCD 1k diffractometer (Mo Kα radiation, $\lambda = 71.073$ pm) at 203(2) K [13]. The structure is solved by direct methods (SHELXS-97) and refined by full-matrix least-squares methods against F^2 (SHELXS-97) [14].

 $C_{152}H_{122}F_{12}N_2O_{12}P_6Pd_2S_4$, M = 2923.38 g/mol, monoclinic, space group $P2_1/n$, a = 17.630(2), b = 21.776(2), c = 18.791(3) Å, $\beta = 103.760(2)^\circ$, V = 7007.1(16) Å³, Z = 2, $\rho_{calc} = 1.386$ g/m³, $\mu = 0.462$ mm⁻¹, F(000) = 2996, 47,795 reflection measured, 14,794 unique, R(int) = 0.0827, wR_2 (all data) = 0.2254, $R_1(I > 2\sigma(I)) =$ 0.0847, 898 parameters and 207 restraints.

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