diffuse into the solvent. The ferryl species is also formed in the gas-phase simulation (being the thermodynamically favored end product), but in this case by migration of an H^+ ion to the second OH^- ligand. As mentioned before, the solvent involvement was already indicated by the introduction of a single water molecule into the second coordination sphere in the gas-phase study. This water molecule aided migration of the H^+ ion to form $[Fe^{IV}O(H_2O)_5]^{2+}$, but the present complete picture could only be obtained by the explicit introduction of the solvent at finite temperature.

In conclusion, the simulations in water solution confirm our gas-phase calculations of the formation of the iron(IV)–oxo complex from the Fenton reagents. We have assumed the formation of the pentaaquairon–hydrogen peroxide complex as the initial necessary step. Our results demonstrate the importance of full incorporation of the water as both a solvent and reagent in the initial reaction steps. The oxo complex is found to be the important oxidative intermediate in the Fenton reaction. How it acts as the reactive species in, for example, hydroxylation of aliphatic and aromatic substrates,[23–25] oxidation of alcohols, and in other reactions will be the subject of further study.

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Insights into the Aryl–Aryl Exchange between Palladium and Phosphane Ligands in Pd^{II} Complexes: Preparation of Phthalocyanine-Containing Phosphonium Salts**

Gema de la Torre, Andreas Gouloumis,
Purificación Vázquez, and Tomás Torres*

The employment of modern synthetic methods in the phthalocyanines (Pc) field[1] can provide a large variety of functionalized derivatives and complex structures based on these macrocycles which may have interesting applications in materials science. In the last few years many scientists, ourselves included, have concentrated on the preparation of unsymmetrically functionalized phthalocyanines[2, 3] and binuclear Pc derivatives in which the macrocyclic units are fused to each other[4, 5] or bridged through different kinds of spacers.[6–8] Our interest in noncentrosymmetric and octupolar[9] systems for nonlinear optical (NLO) applications[10] as well as in the preparation of molecular materials with multiple functions led us to the synthesis of phosphonium salts containing one phthalocyanine unit (Figure 1). Pc-containing phosphonium cations are targets of choice for the preparation of hybrid materials that combine magnetism with NLO properties.[11]

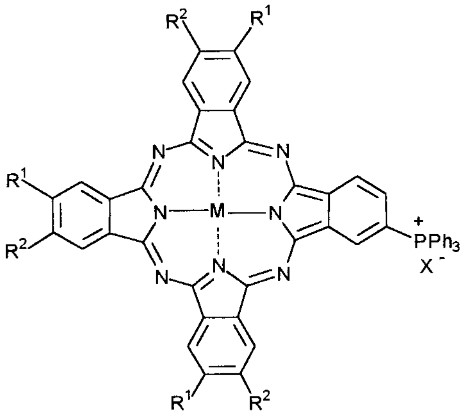

Figure 1. Phthalocyanine-phosphonium salts.

Tetraarylphosphonium salts can be formed by a palladium-catalyzed reaction between triphenylphosphane and an aryl bromide or iodide.[12] The mechanism of the quaternization reaction seems to involve oxidative addition of the aryl halide (ArI) to a palladium(0)–phosphane complex, followed by the reductive elimination of the phosphonium ion and a loss of the halide ion from the metal center (Scheme 1).

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[*] Prof. T. Torres, Prof. P. Vázquez, Dr. G. de la Torre, A. Gouloumis
Departamento de Química Orgánica
Universidad Autónoma de Madrid
Cantoblanco, 28049-Madrid (Spain)
Fax: (+34) 91-397-3966
E-mail: tomas.torres@uam.es

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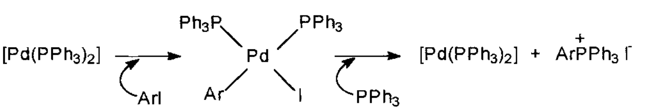
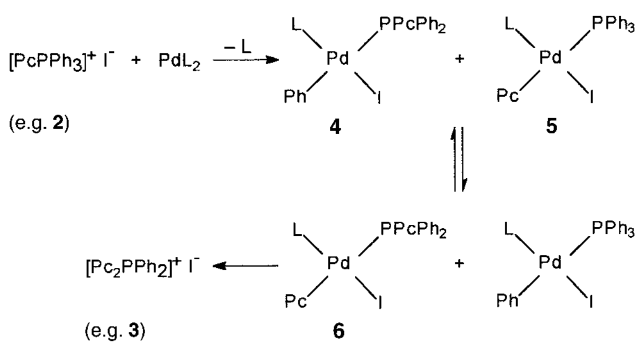


Scheme 1. Mechanism of formation of tetraarylphosphonium salts.

Considering this mechanism and that iodophthalocyanines give rise to oxidative-addition complexes,[6] we undertook the synthesis of these phosphonium derivatives by treating tri(*tert*-butyl)iodophthalocyaninate zinc(II) (**1**; ZnPcI)[6a] with PPh_3 in the presence of catalytic amounts of $[PdCl_2(PPh_3)_2]$ in DMF as solvent at 100 °C. Under these conditions, we observed the formation of the desired product $[(ZnPc)PPh_3]^+I^-$ (**2**) in 15 % yield, in addition to another compound which was identified as a phosphonium salt containing two Pc-based units $[(ZnPc)_2PPh_2]^+I^-$ (**3**), isolated in 50 % yield (Scheme 2).

The presence of **3** in the reaction mixture suggests that an exchange occurs between the phenyl groups on the phosphane ligand and the phthalocyanine-based unit in the oxidative-addition intermediate. Scrambling of aryl groups in Pd^{II} complexes with the triphenylposphane ligand has been observed by other authors.[13, 14] The nature of this interchange is explained[14–16] by the formation of an aryltriphenylphosphonium salt (e.g. **2**), followed by an oxidative addition to the palladium center as shown by the formation of **4** and **5** in Scheme 3.

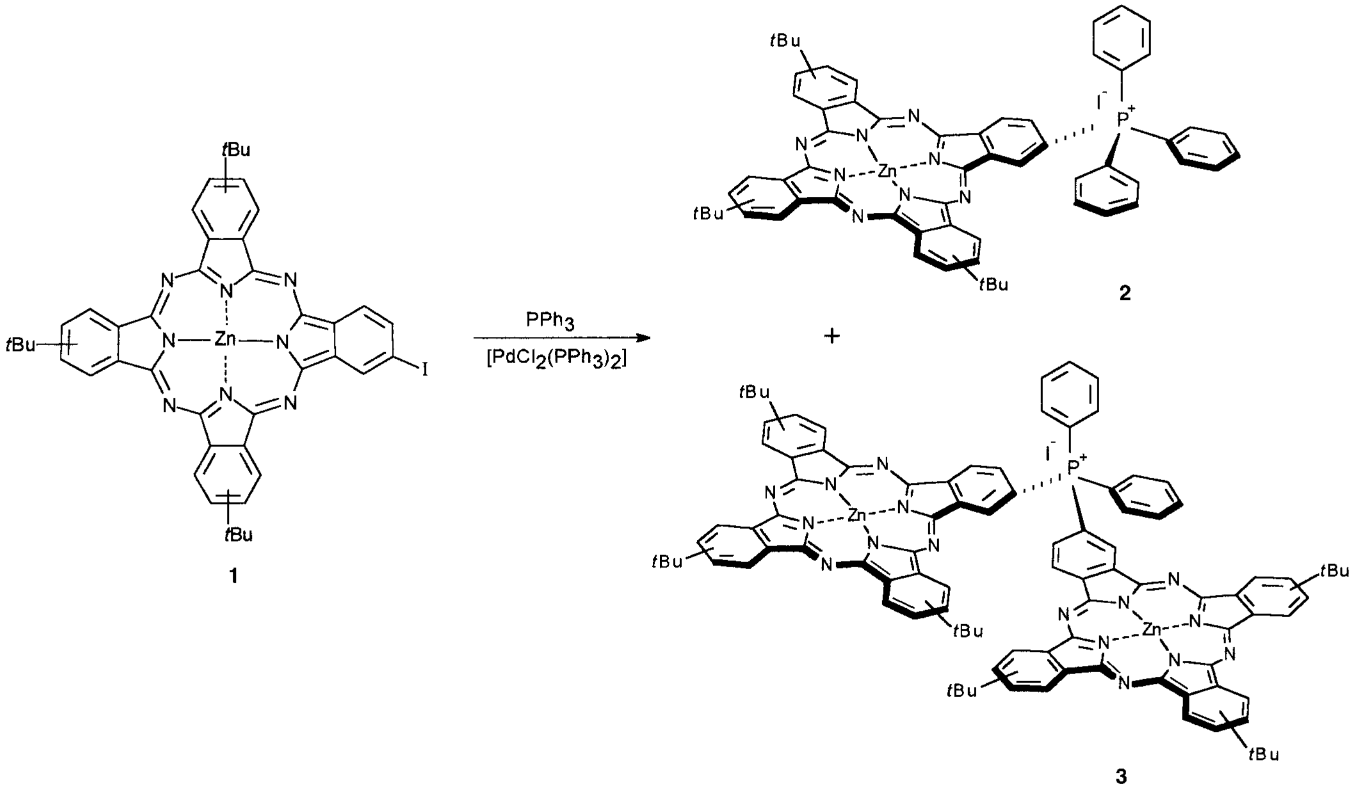
Following these precedents, a phosphonium salt such as **2**, easily formed under these conditions, can undergo oxidative addition to give a mixture of compounds analogous to **4** and **5** (Scheme 3). Many $[(PPh_3)_2Pd(R)X]$ complexes can exchange phosphane ligands rapidly,[17] and such a process can generate



Scheme 3. Proposed mechanism for the formation of phthalocyanine-phosphonium salts **2** and **3**.

complex **6**, which in turn gives rise to a new phosphonium salt, such as **3**, by reductive elimination. The treatment of the isolated phosphonium salt **2** with a palladium complex without phosphane ligands furnishes a mixture of **2** and **3**, supporting the proposed mechanism.

The binuclear Pc-based system **3** is also of interest because of potential interactions between the two macrocyclic units. We have tested different palladium complexes and reaction conditions to obtain either **2** or **3** as the major product. First, the ratio of PPh_3 was increased in the hope of to obtaining exclusively the monophthalocyanine-based **2**.[16] Even on adding 5 equivalents of PPh_3, a mixture of **2** and **3** was isolated when using a catalytic amount of $[PdCl_2(PPh_3)_2]$. However, the reaction of **1** with equimolar amounts of $[PdCl_2(PPh_3)_2]$ either in the presence or absence of PPh_3 afforded **2** in 35 % yield without traces of **3**. Longer reaction times do not result in an increase of the yield but to the



Scheme 2. Synthesis of phosphonium salts **2** and **3**.

deposition of black palladium metal. A great amount of iodophthalocyanine **1** remains, but can be recovered after column chromatography of the crude reaction mixture.

When the reaction was carried out with [$Pd_2(dba)_3$] (dba = *trans*, *trans*-dibenzylideneacetone) in a 1:1 ratio with **1** and in the presence of two equivalents of PPh_3, the only phosphonium salt isolated after 24 h was compound **3**, even though a mixture of **2** and **3** was detected by thin layer chromatography (TLC) early in the reaction. Under these conditions, oxidative addition of the phosphonium salt **2** to the Pd center seems to take place easily. The main difficulty is that undesired coupling reactions between **1** and dba also take place, so that the yield of **3** is around 40% lower than that obtained with the initial conditions employing a catalytic amount of [$PdCl_2(PPh_3)_2$]. Note that some of the trinuclear compound [$(ZnPc)_3PPh]^+I^-$ (**7**, Figure 2) is also detected in the crude mixture. The use of other palladium complexes, such as [$Pd(OAc)_2$] (OAc = acetate) or [$PdCl_2(CH_3CN)_2$], without phosphane ligands does not give an improvement in the yield of compound **3**.

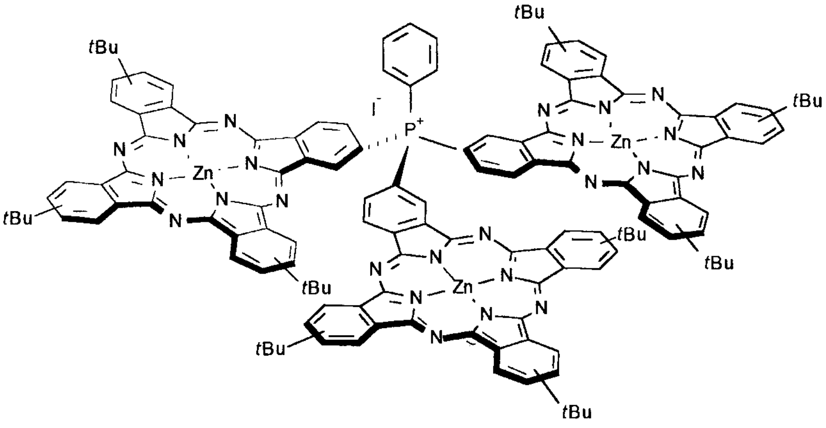


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Figure 2. Aryltrisphthalocyanine-phosphonium salt [$(ZnPc)_3PPh]^+I^-$.

To obtain the derivative with three Pc-based units, we have also treated phosphonium salt **3** with [$Pd(OAc)_2$] in a 1:1 ratio without adding **1**, thus affording **7** in a 3% yield. When phthalocyanine **1** is added to the mixture, the yield of **7** increases to around 10%.

We have confirmed that tetraarylphosphonium salts can undergo oxidative addition to palladium centers and may be responsible for the scrambling phenomenon. The relatively easy formation of these phthalocyanine-containing phosphonium salts may be related to the electron richness of the Pc core,[16] which stabilizes the developing positive charge as the phosphonium salt is generated. Trisphthalocyanine-based phosphonium salt **7** seems to be more hindered and difficult to form. Nevertheless, efforts will be made to improve the yield of this derivative and even to obtain the tetraphthalocyanine-phosphonium salt, already detected in trace amounts in the mass spectra of some reaction mixtures.

The second-order NLO responses at the molecular level for the dipolar compound **2** and octupolar phthalocyanine **7** have been determined through HyperRayleigh Light Scattering (HRS). The measured β_{HRS} values at $\lambda = 1.06\,\mu m$ in THF solution were 20.5×10^{-30} esu and 189×10^{-30} esu, respectively, for **2** and **7**. No multiphoton-induced luminescence has been detected at this wavelength. The high first-order hyperpolarizability value measured for compound **7** is comparable to those reported for subphthalocyanines, core-modified Pcs with octupolar character,[9a] and clearly superior to those available for related unsymmetrically substituted phthalocyanines with dipolar characteristics.[9b] This fact points out the role of "central acceptor" played by the positively charged phosphorus atom in tailoring the multipolar character of the hyperpolarizability.[10] A more detailed study on the NLO properties of this new family of compounds has been undertaken.

Experimental Section

All reactions were performed under an argon atmosphere. DMF was dried over CaH_2, distilled, and degassed before use. Mass spectra were obtained from a Bruker Reflex III matrix-assisted laser desorption/ionization time of flight (MALDI-TOF) spectrometer. UV/Vis spectra were recorded on a Hewlett Packard 8453 spectrometer. Analytical data were performed on the corresponding hexafluorophosphate (PF_6^-) salts prepared by standard ion exchange.

2: A mixture of iodophthalocyanine **1** (100 mg, 0.115 mmol) and [$PdCl_2(PPh_3)_2$] (81 mg, 0.115 mmol) was heated at 100 °C for 24 h in DMF. After removal of the solvent under reduced pressure, column chromatography of the crude product(eluting with CH_2Cl_2/2-propanol 15/1) afforded compound **2** (20 mg, 15%); elemental analysis calcd (%) for $C_{62}H_{54}N_8F_6P_2Zn \cdot 2H_2O$ (1188.50): C 62.66, H 4.92, N 9.43; found C 61.93, H 4.85, N 9.17; MALDI-TOF (dithranol): *m*/*z*: 1005–1010 $[M - I^-]^+$; UV/Vis ($CHCl_3$): λ_{max} (ε) = 707 (375000), 665 (235000), 642 (135000), 602 (61000), 358 nm (152000).

3: Following the same procedure as for **2**, treatment of **1** (100 mg, 0.115 mmol) with [$PdCl_2(PPh_3)_2$] (8 mg, 0.011 mmol) afforded compound **3** (52 mg, 50%) after column chromatography (THF/hexane 1/1; THF); elemental analysis calcd (%) for $C_{100}H_{88}N_{16}F_6P_2Zn_2 \cdot 2H_2O$ (1856.62): C 64.69, H 4.99, N 12.07; found C 63.80, H 5.27, N 11.75; MALDI-TOF (dithranol): *m*/*z*: 1671–1678 $[M - I^-]^+$; UV/Vis (THF): λ_{max} (ε) = 678 (172000), 666 (83000), 643 (51000), 603 (13000), 358 nm (63000).

7: A mixture of **3** (50 mg, 0.028 mmol), phthalocyanine **1** (24 mg, 0.028 mmol), and $Pd(OAc)_2$ was heated at 100 °C for 24 h. The green solution was evaporated under reduced pressure, the solid was purified by chromatography on silica gel (THF/hexane 1/1; THF; THF/MeOH 2/1), and washed with methanol, furnishing **7** (6 mg, 9%); elemental analysis calcd (%) for $C_{138}H_{122}N_{24}F_6P_2Zn_3 \cdot H_2O$ (2488.62): C 66.60, H 5.02, N 13.51; found C 66.10, H 5.36, N 13.18; MALDI-TOF (dithranol): *m*/*z*: 2338–2346 $[M - I^-]^+$; UV/Vis (THF): λ_{max} (ε) = 678 (229000), 348 nm (178000).

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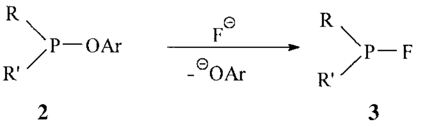
Synthesis of Tri- and Tetracoordinate Phosphorus Compounds Containing a PCF_3 Group by Nucleophilic Trifluoromethylation of the Corresponding PF Compounds

Izabela Tworowska, Wojciech Dąbkowski, and
Jan Michalski*

Dedicated to Professor Marianne Baudler
on the occasion of her 80th birthday

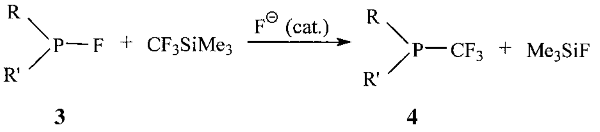
The introduction of a trifluoromethyl group into an organic compound can bring about remarkable changes in physical, chemical, and biological properties.[1] Therefore, the importance of fluorinated compounds in life sciences is rapidly increasing. Modification of the backbone of biophosphates by replacement of the anionic phosphodiester group with the neutral trifluoromethylphosphonato group should have steric, polar, and electronic effects similar to those of a hydroxyl group. Additionally, the lipophilicity should be enhanced.[2] Tricoordinate P^{III}–CF_3 compounds may act as useful ligands in organometallic chemistry.[3] Among the variety of methods for introducing a CF_3 group into organic compounds, the application of (trifluoromethyl)trimethylsilane CF_3SiMe_3 (**1**) as nucleophilic trifluoromethylating reagent is rapidly becoming the method of choice. CF_3SiMe_3 was first synthesized by Ruppert et al. in 1984[4] and is commercially available. In contrast to organic compounds containing a CF_3 group, little is known about P^{III}–CF_3 compounds. P^V–F compounds, which are apparent candidates for nucleophilic trifluoromethylation by **1**, have been used for this purpose in only two cases.[5] So far no reaction of this kind has been described for P^{III}–F compounds.

Our interest in P–CF_3 compounds is related to our recent studies on phosphorus–fluorine compounds derived from alcohols of biological interest. The method of choice for preparing P^{III}–F groups is based on nucleophilic displacement of OAr^- from a P^{III}–OAr group by a fluoride ion [Eq. (1)].[6] Both types of P^{III} compounds, **2** and **3**, are available in excellent yield and exhibit a high degree of chemical and stereochemical stability.[7]



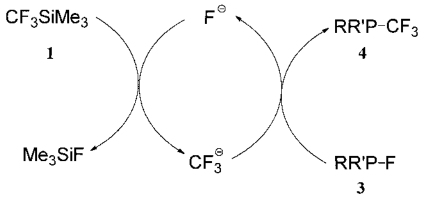
2 **3** (1)

We found that P^{III}–F compounds react with the Ruppert reagent **1** at 20 °C in THF or acetonitrile in almost quantitative yield [Eq. (2)].[8] The reaction is catalyzed by fluoride ions.



3 **4** (2)

Cesium fluoride is a convenient fluoride donor, but other donors such as tetrabutylammonium fluoride (TBAF) can also be used. As the fluoride ion is used in catalytic amounts, the catalytic cycle shown in Scheme 1 is proposed.



Scheme 1. Proposed cycle for the nucleophilic trifluoromethylation of P^{III}–F compounds by **1**.

The strength of the P–F bond is compensated by the high affinity of fluorine for the silicon center. An analogous mechanism should operate in the case of tetracoordinate phosphorus–fluorine compounds RR′P(X)F (X = O, S). The optimized protocol for this reaction was applied to a variety of

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[*] Prof. Dr. J. Michalski, I. Tworowska, W. Dąbkowski
Centre of Molecular and Macromolecular Studies
Polish Academy of Sciences
90-363 Łódź, Sienkiewicza 112 (Poland)
Fax: (+48) 42 684-71-26
E-mail: jmich@bilbo.cbmm.lodz.pl