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On the Surface Reactivity of Functionalized Phosphinines on Inorganic Supports

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Abstract. Phosphinines with pendant phenol or catechol functionalities and their gold(I) complexes were synthesised and characterised by spectroscopic data and in one case by a single-crystal X-ray diffraction study. Reactions of ligands or complexes with TiO_2 or chloropropyl modified hexagonal mesoporous silica were then studied with the aim to immobilise ligands or complexes on the carrier by covalent tethering. ^{31}P MAS NMR studies revealed that immobilisation on TiO_2 was accompanied by complete degradation of the phosphinine moiety. Base induced coupling with chloropropyl modified silica produced a material that contained a mixture of several surface-bound phosphorus compounds. ^{31}P MAS NMR studies revealed that approx. 40 % of the ligand had retained its integrity whereas the remaining fraction had been converted into further, not unambiguously identified structures.

Introduction

Phosphinines (phosphabenzenes) were first prepared about 40 years ago [1] and have since then developed from laboratory curiosities into useful ligands that have found application in coordination chemistry and catalysis [2, 3], or for the stabilisation of metal nanoparticles [4]. Catalytic reactions with participation of phosphinine ligands include hydroformylation, amination, CC-coupling, with the diversity suggesting that phosphinines may also belong to a set of privileged ligands that can support a wide range of catalytic reactions. To the best of our knowledge, all catalytic applications reported so far are based on homogeneous reactions, and although attempts to immobilise the catalysts in order to improve their separation and recycling receive currently great attention [5, 6], no such attempts with phosphinine ligands or their complexes have been reported.

Owing to the stabilisation by π-aromaticity, phosphinines are less prone to hydrolyse than other low coordinate phosphorus compounds. Having recently elaborated *Märkl*'s original approach [1] into a modular synthesis of functional phosphinines, *Vogt* and *Müller* showed that the phosphinine core tolerates a variety of functional groups, including phenol and carboxylic acid moieties [7]. The fact that catechol moieties have recently been employed as anchoring group for the immobilisation of phosphine complexes on inorganic supports [8, 9] stimulated us to explore if the same approach allows also the anchoring of phosphinines or their complexes, respectively. We report here on the synthesis of tailored phosphinines with pendant phenol and catechol moieties, and their reactions with TiO_2 nanoparticles and surface modified mesoporous silica, respectively.

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Results and Discussion

Considering that the previously reported immobilisation protocols [8, 9] require substrates with one or two adjacent freely accessible phenolic OH-groups, we regarded 2,4,6-trisubstituted phosphinines like **1a**–**c** as viable and readily accessible target compounds (Scheme 1). As precursors, we prepared first methoxy-substituted derivatives **2a**–**c** from appropriately substituted chalcone and acetophenone building blocks by following the protocol of *Vogt* and *Müller* [7]. Deprotection of the phenolic OH-functionalities was accomplished by reaction with BBr_3 in CH_2Cl_2 [7] to give **1a**–**c** as air sensitive, yellowish powders in near quantitative yields. All phosphinines prepared were sufficiently characterised by analytical and spectroscopic (^1H, ^{13}C, ^{31}P NMR, MS) data.

In order to demonstrate the efficacy of phosphinines **1a**–**c** and **2a**–**c** as ligands, we prepared gold complexes from the free ligands and an equimolar amount of AuCl(tht) (tht = tetrahydrothiophene) in CH_2Cl_2 or thf, respectively. Gold(I) was chosen since phosphinines form stable complexes with this metal that are distinguished by a 1:1 metal-to-ligand ratio and are not supported by additional ligands [10] and thus possibly minimise the chance of decomposition during subsequent immobilisation. Model complexes **3a**/**b** and **4a** were isolated as pale yellow solids in 90–95 % yield after precipitation with hexane and identified by spectroscopic data and a single-crystal X-ray diffraction study of **4a**. The ^{31}P NMR spectra are distinguished by showing moderate negative coordination shifts ($\Delta\delta$ = –30

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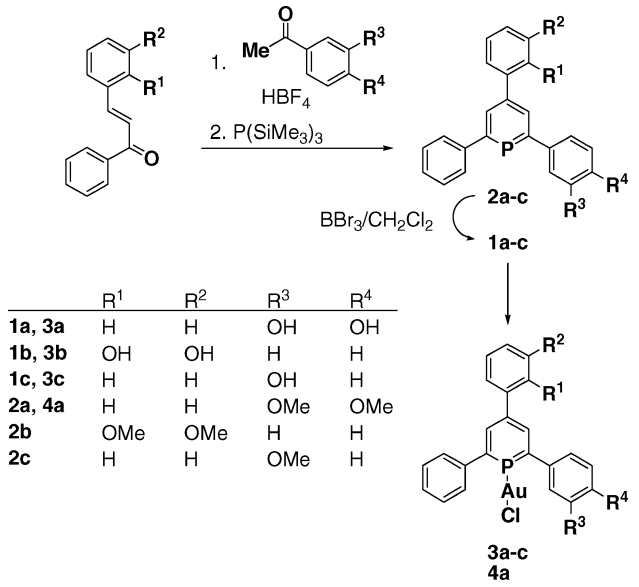

	R^1	R^2	R^3	R^4
1a, 3a	H	H	OH	OH
1b, 3b	OH	OH	H	H
1c, 3c	H	H	OH	H
2a, 4a	H	H	OMe	OMe
2b	OMe	OMe	H	H
2c	H	H	OMe	H

Scheme 1.

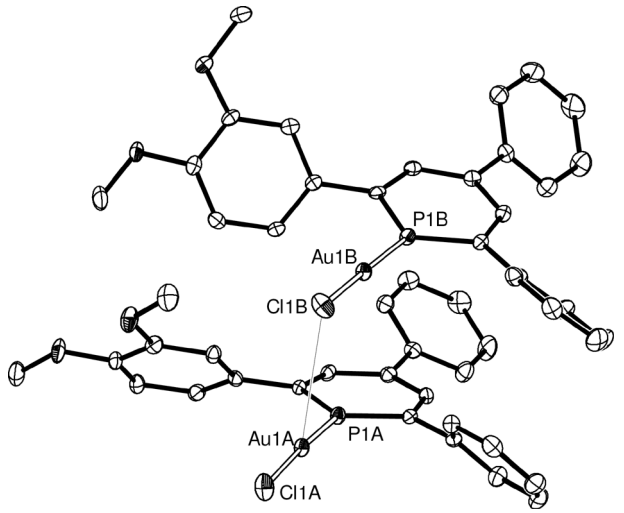

Figure 1. ORTEP-style representation showing two of the three crystallographically independent molecules of **4a** in the crystal (hydrogen atoms omitted for clarity; displacement parameters drawn at 50 % probability level). Selected bond lengths /Å and angles /° (values for the second and third molecule given in brackets): P1A–Au1A 2.206(1) [2.207(1), 2.212(1)], Au1A–Cl1A 2.277(1) [2.273(1), 2.278(1)], P1A–Au1A–Cl1A 175.9(1) [177.0(1), 176.0(1)].

to –33) which are indicative of η^1(P)-coordination of the phosphinine. The absence of splitting or line broadening effects arising from $^1J(^{197}Au,^{31}P)$ coupling is attributable to the high quadrupole moment of the metal nucleus which induces effective decoupling of both nuclei [10].

The single-crystal X-ray diffraction study reveals that crystals of **4a** contain three crystallographically independent molecular complexes of composition LAuCl two of which are connected by a weak Au···Cl interaction (Au1A–Cl1B 3.387 Å) that is hardly shorter than the sum of van-der-Waals radii (Figure 1). The individual bond lengths and bond angles in all three specimens show no significant deviations. The metal atoms exhibit quasi-linear coordination (P–Au–Cl 175.9–177.0°). The Au–Cl (2.273–2.278 Å) and Au–P (2.206–2.212 Å) bond lengths match those in bis(trimethylsilyl) phosphinine gold(I) chloride (Au–Cl 2.281(2) Å, Au–P 2.211(2) Å [10]) and lie at the lower end of the ranges found for tertiary phosphane complexes (Au–Cl 2.30 ± 0.03 Å, Au–P 2.24 ± 0.03 Å [11]; the short Au–P bond length is in accord with the different formal hybridisation of the phosphorus atom in phosphinines and phosphanes) [2].

Attempts towards immobilisation of the phosphinine **1a** and the gold complexes **3a**/**b** on TiO_2 nanoparticles (NP-TiO_2) were carried out as described previously [8, 9] by stirring a suspension of the substrates and preheated NP-TiO_2 in THF for 24 h at ambient temperature, filtering off the supernatant liquid, washing the solid residue with several portions of THF, and drying in vacuo. The materials were then characterised by elemental analyses and solid-state ^{31}P NMR spectroscopy.

The ^{31}P CP-MAS NMR spectra of all materials displayed each a single broad resonance ($\Delta\nu_{1/2}$ = 0.8–3.1 kHz, Figure 2 a,c) which suggested the presence of a single surface species with a marked chemical shift dispersion. The isotropic chemical shifts in the two immobilised complexes **3a**/NP-TiO_2 (δ = 28) and **3b**/NP-TiO_2 (δ = 27) were essentially identical and somewhat larger than in the case of **1a**/NP-TiO_2 (δ = –10), and comparison of the lineshapes observed in spectra of non rotating samples (Figure 2 b,d) revealed that the deshielding was accompanied by a larger shielding anisotropy (although the line widths prevented the specific evaluation of individual principal components of the shielding tensor, the observed spectra allowed to estimate the overall shielding anisotropy $\Omega = \delta_{11}-\delta_{33}$ as < 55 ppm for **1a**/NP-TiO_2 and ≈170 ppm for **3a**/NP-TiO_2). The amount of organic material deposited on the support corresponds on the basis of the analytical data to 23 μmol·g^{-1} NP-TiO_2 for the phosphinine **1a**, or 53 and 48 μmol·g^{-1} NP-TiO_2 for the complexes **3a**/**b**, respectively (The given loadings were derived from the analytically determined carbon content and were computed under the assumption that the intact ligand or complex had been deposited. Although this is obviously not the case we reckon that the given figures allow at least a rough estimation of the amount of material deposited.). Even though the available data do not allow to decide if the phosphane ligands is bound to the surface by a covalent bond or otherwise, the higher loading of the complex is significant and points possibly to the presence of additional interaction of the chloride ligands with Lewis acidic sites on the surface.

The observation of a single ^{31}P NMR signal from the surface-bound species indicates that the immobilisation is clean and produces no side products. However, comparison of the spectroscopic data with those of authentic samples of the phosphinine **2a** and complex **4a** (Figure 3) indicates clearly that the surface-bound species feature significantly lower isotropic chemical shifts and chemical shielding anisotropies [12] and exhibit thus no longer a phosphinine structure.

Although unambiguous structure elucidation was unfeasible, the ^{31}P chemical shift and shielding anisotropy of **1a**/NP-TiO_2

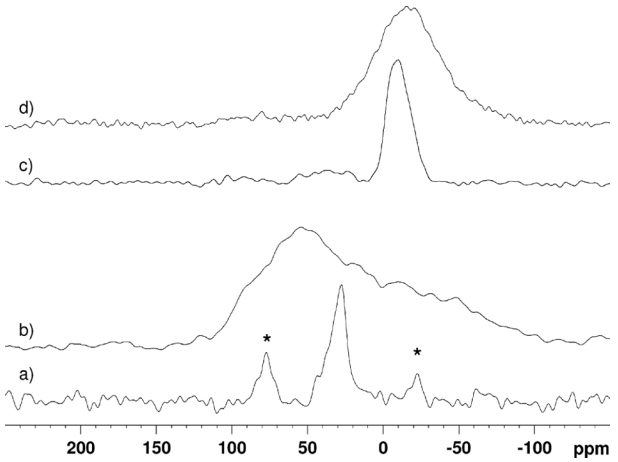

Figure 2. Solid state ^{31}P NMR spectra of **3a**/NP-TiO_2 (a,b) and **1a**/NP-TiO_2 (c, d) recorded with cross polarisation for signal enhancement. Spectra in traces (a) and (c) were recorded under MAS (ν_{rot} = 8 kHz, spinning sidebands labelled with an asterisk) whereas traces (b) and (d) show spectra of non-spinning samples.

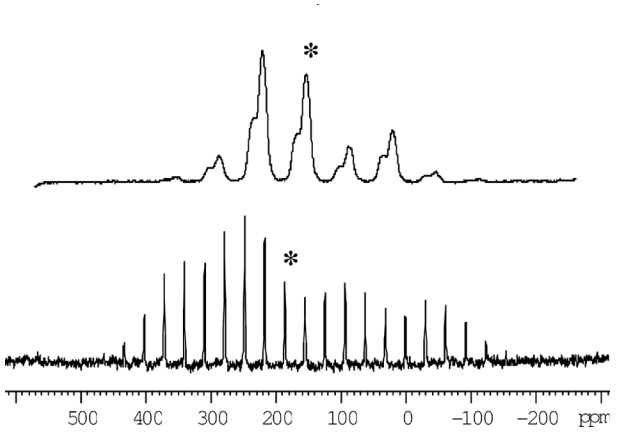

Figure 3. ^{31}P CP MAS NMR spectra of **4a** (top trace, ν_{rot} = 8 kHz, δ_{iso} = 155) and **2a** (bottom trace, ν_{rot} = 5 kHz, δ_{iso} = 188.0). Isotropic chemical shifts are marked by asterisks. The fine structure of the lines in the spectrum of **4a** results from scalar and residual dipolar coupling with the ^{197}Au nucleus (I = 3/2).

are typical for a tertiary phosphane with a three coordinate phosphorus atom. Regarding that phosphane derivatives are easily accessible, e.g. via nucleophilic attack of the electrophilic phosphorus centre in a phosphinine, or addition of various XH-acidic compounds to the 6π-system [2], we consider it likely that the phosphinine moiety cannot tolerate the acidic environment on the TiO_2 surface (the pH of a 4 % aqueous dispersion is 3.5–4.5) and reacts during the immobilisation process under uptake of a further ligand at the phosphorus atom. Starting from this assumption, we assign the surface-bound species in **3a**/NP-TiO_2 and **3b**/NP-TiO_2 to gold complexes of the same phosphane species. This hypothesis is in line with the observed increase in isotropic chemical shift and shielding anisotropy that is characteristic for many phosphane complexes, and also with the results of an XPS analysis of **3a**/NP-TiO_2 which disclosed that the solid material contains both phosphorus and gold with an atomic ratio P:Au of 0.92:1 that comes quite close to the ideal value of 1:1.

Since the preceding experiments proved TiO_2 to be not suitable for the immobilisation of phosphinines, we decided to explore the use of alternative carrier materials. Silica seemed a good choice as it provides a less acidic surface, and a number of techniques allowing covalent tethering of a variety of functional molecules, including phosphanes and their complexes, under mild reaction conditions have been reported [5]. As the synthesis of **1a**–**c** had shown the feasibility of selective transformations at the phenolic functionality under retention of the phosphinine core, we reckoned that alkylation of the hydroxyl group by a surface-bound haloalkyl moiety to give a phenol ether should offer a viable approach to immobilise **1c**. Hexagonal mesoporous silica (HMS) [13] was selected as carrier material as its preparation is straightforward and does not require strongly acidic conditions, the material can be readily functionalized by treatment with chloropropyl triethoxysilane, and incorporation of the phosphinine into the porous material might provide some additional protection against degradation of the ligand during the immobilisation process.

Following the outlined scheme, HMS was first derivatised by reaction with chloropropyl(triethoxy)silane in toluene. The specific functionalisation was proven by ^{13}C and ^{29}Si CP-MAS NMR studies. The ^{13}C NMR spectrum (Figure 4) contains beside signals of the carbon atoms of the propyl chain at 6.1, 23.6 and 44.0 ppm two resonances (13.0, 56.6 ppm) arising from an ethoxy group. The ^{29}Si NMR spectrum (Figure 5) displays in addition to the signals of Q^4, Q^3 and Q^2 groups in the carrier material at –112.2, –102.8 and –93.5 ppm a resonance at –53.2 ppm for the grafted organosilane species. These findings suggest the predominance of a single surface species with a constitution as shown in Figure 3, although the presence of an additional unassigned ^{13}C signal around 20 ppm indicates the presence of another (minor) species of unknown structure. Surface bound organosilane moieties which still contain residual OEt moieties were also found in other modified silica materials that had been prepared from triethoxysilane precursors [14] whereas materials made from chloropropyl(trimethoxy)silane were reported to contain only T^3 and T^2-type silicon atoms that carry no more alkoxy groups [15]. The observation that the intensity of the signal of T^2-groups relative to that of the Q^n-moieties in the bulk support is much lower than in other modified silica materials [14, 15] suggests a rather low loading of functional groups on the surface.

Coupling of the phosphinine to the surface was carried out by dropwise addition of a CH_2Cl_2 solution of **1c** to a cooled (–78 °C) suspension of the silica in a mixture of CH_2Cl_2/triethylamine. The mixture was then stirred overnight while warming to room temperature was allowed, and the modified silica was isolated after work-up (see Experimental Section). Attempts to characterise the isolated material by ^{31}P CP-MAS NMR gave spectra with unsatisfactory signal-to-noise ratios whereas much better results were obtained when the spectra were recorded without cross polarisation under direct excitation of ^{31}P nuclei (Figure 6). Large effects on signal intensities

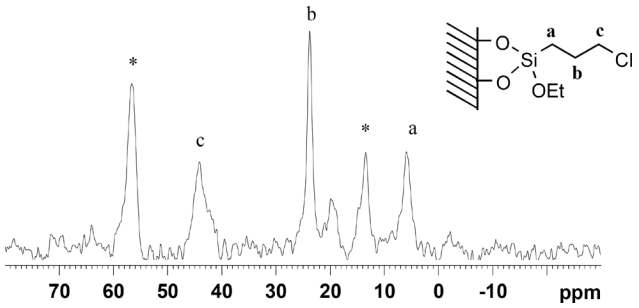

Figure 4. ^{13}C CP MAS NMR spectrum and molecular constitution of the predominant surface species in chloropropyl modified HMS (ν_{rot} = 8 kHz, contact time: 1.8 ms). The signals labelled a–c are attributable to the carbon atoms in the propyl chain, and signals arising from the ethoxy group are labelled with an askerisk.

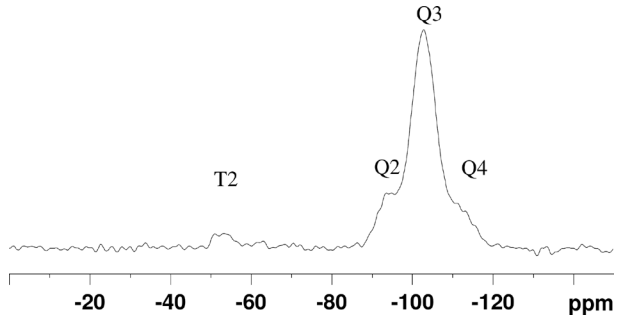

Figure 5. ^{29}Si CP MAS NMR spectrum of chloropropyl modified HMS (ν_{rot}: 9 kHz, contact time: 4 ms). Signals labelled Q2–Q4 arise from the silicon nuclei in bulk HMS and the signal labelled T2 from the surface bound organosilicon species.

in CP-MAS NMR spectra had also been detected for other surface bound phosphane species, and arise presumably from subtle differences in residual mobility or relaxation parameters of the tethered ligands [16].

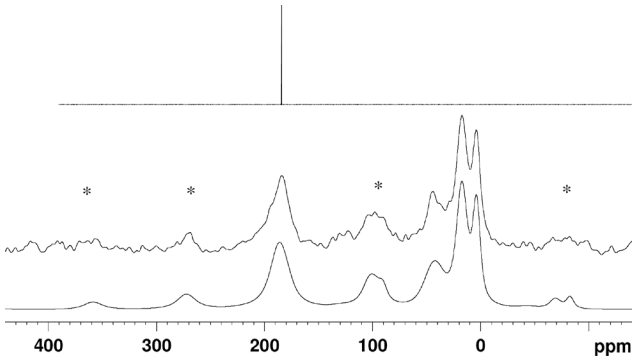

Figure 6. Solution $^{31}P\{^1H\}$ NMR spectrum of **1c** (top trace) and experimental (middle trace) and simulated (bottom trace) solid state $^{31}P\{^1H\}$ MAS NMR spectrum (ν_{rot} = 14 kHz) of **1c** immobilised on chloropropyl modified HMS. Spinning sidebands are denoted by asterisks.

Deconvolution of the measured spectrum reveals the presence of four distinguishable surface species. The main product (41 % of the total spectral intensity) gives rise to a spinning sideband system with the same isotropic chemical shift as **1c** (δ =185.2) and a large shielding anisotropy and is assigned to the desired covalently tethered phosphinine. The large linewidth ($\Delta\nu_{1/2} \approx 4$ kHz) as compared to solid **2a** (Figure 3, $\Delta\nu_{1/2} = 0.3$ kHz) is attributed to the inhomogeneity of surface environments. The remaining signals (δ = 43.0, 17.4, 3.8) exhibit again smaller chemical shifts and shielding anisotropies and are assigned to unidentified, presumably phosphine-type side-products. Characterisation of the material by ^{13}C MAS NMR was unfeasible as the strong overlap of signals from different surface species rendered the spectra uninterpretable but ^{29}Si MAS spectra gave no evidence that the material had changed during the attachment process. As ^{31}P NMR spectra of the supernatant solution contained only the signal of unreacted **1c**, it is clear that the degradation of the phosphinine moiety occurs in the surface reaction; the available data do not allow, however, to decide whether the reaction proceeds via direct attack of surface functionalities on the electrophilic phosphorus atom, or through a surface-induced intramolecular attack by phenol or catechol functional groups.

Conclusions

The synthesis of phosphinines **1a**–**1c** illustrates the stability of the delocalised π-system against acidic phenol and redox active catechol functional groups and thus emphasises the functional group tolerance of this class of compounds. The results of immobilisation studies show that the reactivity and stability of these molecules is in principle sufficient to allow their immobilisation by covalent tethering to an inorganic carrier. However, the observed degradation of ligands or complexes during these reactions demonstrates also that immobilisation reaction imposes a great challenge to the stability of the delocalised π-system which is not always met. Further efforts to find a suitable carrier material and suitable reaction conditions are therefore necessary in order to prepare well defined materials that contain no decomposition products. It may be envisaged that a similar degradation of the phosphinine moiety as observed here may also affect other reactions (e.g. transformations with phosphinine-based catalysts) and may thus have some impact on the mechanistic interpretation of these reactions.

Experimental Section

General Remarks

All manipulations were carried out under argon using Schlenk techniques. Solvents were dried prior to use by common procedures. Chalcone derivatives [17] and AuCl(tht) [18] were prepared as described. Pyrogenic TiO_2 nanoparticles (Degussa AEROXIDE TiO_2 P25, pH of 4 % dispersion in $H_2O \approx 3.5$–4.5, specific surface 50 ± 15 $m^2 \cdot g^{-1}$, avg. particle size 21 nm) was commercially available and dried at 90 °C for about 4 h prior to use. Solution NMR spectra were recorded with a Bruker Avance 250 spectrometer (^1H: 250.1 MHz, ^{13}C: 62.8 MHz, ^{31}P: 101.2 MHz) at 303 K and solid-state NMR spectra with a Bruker Avance 400 spectrometer (^{13}C: 100.5 MHz, ^{29}Si: 79.49 MHz, ^{31}P: 161.9 MHz) equipped with a 4 mm MAS probe. MAS experiments were performed using Standard ZrO_2 rotors and spinning speeds be-

tween 5 and 14 KHz. Cross polarization was applied using a ramp-shaped contact pulse and mixing times between 1.5 and 5ms unless noted. Chemical shifts were referenced to ext. TMS (^{1}H,^{13}C) or 85 % H_3PO_4 (Ξ = 40.480747, ^{31}P). EI-MS: Varian MAT 711, 70eV. ESI-MS: Bruker Daltonics-microOTOF-Q. Elemental analysis: Perkin–Elmer 24000 CHN/O Analyser. Melting points were determined in sealed capillaries.

General Procedure for the Synthesis of Pyrylium Salts

Tetrafluoroboric acid (52 % ethereal solution, 2 equiv.) was added dropwise at 70 °C to a solution of the corresponding chalcone (2 equiv.) and acetyl component (1 equiv.) in 1,2-dichloroethane (50 mL). The reaction mixture was heated under reflux for 6 h, allowed to cool to room temp. Addition of Et_2O (approx. 150 mL) produced a precipitate, which was collected by filtration, washed with Et_2O, and dried in vacuo.

2-(3,4-Dimethoxyphenyl)-4,6-diphenyl-pyrylium tetrafluoroborate: Orange solid from benzylidene acetophenone (12.96 g, 62.3 mmol), 3,4-dimethoxyacetophenone (5.61 g, 31.2 mmol) and ethereal HBF_4 (10.2 g of 52 % solution, 62.3 mmol). Yield: 8.2 g (58 %); m.p. 248 °C. $C_{25}H_{21}O_3B_1F_4$ (456.25): calcd. C 65.81, H 4.64; found C 65.81, H 4.32. **^{1}H NMR** (250 MHz, CD_3COCD_3): δ = 4.03 (s, 3 H, OCH_3), 4.04 (s, 3 H, OCH_3), 7.35 (d, J_{HH} = 8.7 Hz, 1 H), 7.72–7.86 (m, 5 H), 8.06 (d, J_{HH} = 2.1 Hz, 1 H), 8.32 (dd, J_{HH} = 8.5 Hz, 2.3 Hz, 1 H), 8.44–8.48 (m, 2 H), 8.54–8.58 (m, 2 H), 8.97 (d, J_{HH} = 1.6 Hz, 1 H), 9.00 (d, J_{HH} = 1.6 Hz, 1 H). **^{13}C{^{1}H} NMR** (250 MHz, CD_3COCD_3): δ = 56.76, 56.81, 111.9, 113.4, 115.0, 115.6, 122.3, 125.5, 129.3 (2 C), 130.4 (2 C), 130.4, 130.8 (2 C), 130.) (2 C), 134.2, 135.6 (2 C), 151.4, 157.4, 166.1, 170.5, 172.2. **MS** (ESI): m/e (%) = 369.15 (100) [M^+–BF_4].

2,6-Diphenyl-4-(2,3-dimethoxyphenyl)-pyrylium tetrafluoroborate: Dark orange solid from 2,3-dimethoxybenzylidene acetophenone (10.53 g, 38.8 mmol), acetophenone (2.33 g, 19.4 mmol) and ethereal HBF_4 (6.37 g of 52 % solution, 38.8 mmol). Yield: 4.9 g (55 %); m.p. 183 °C. $C_{25}H_{21}O_3B_1F_4$ (456.25): calcd. C 65.81, H 4.64; found C 64.42, H 4.52. **^{1}H NMR** (250 MHz, CD_3COCD_3): δ = 3.95 (s, 3 H, OCH_3), 4.02 (s, 3 H, OCH_3), 7.40 (d, J_{HH} = 8.0 Hz, 1 H), 7.49 (dd, J_{HH} = 8.1 Hz, 1.4 Hz, 1 H), 7.62 (dd, J_{HH} = 7.8 Hz, 1.6 Hz, 1 H), 7.78–7.93 (m, 7 H), 8.56–8.61 (m, 5 H). **^{13}C{^{1}H} NMR** (250 MHz, CD_3COCD_3): δ = 56.9, 62.3, 119.51 (2 C), 119.54 (2 C), 123.4, 126.1, 129.1, 129.6 (4 C), 130.3, 131.0 (4 C), 136.1 (2 C), 149.7, 154.5, 167.0, 171.7 (2 C). **MS** (ESI): m/e (%) = 369.15 (100) [M^+–BF_4].

2-(3-Methoxyphenyl)-4,6-diphenyl-pyrylium tetrafluoroborate: Yellow solid from benzylidene acetophenone (9.09 g, 43.7 mmol), 3-methoxyacetophenone (3.27 g, 21.8 mmol) and tetrafluroboric acid (7.17 g of 52 % ethereal solution, 43.7 mmol). Yield: 5.6 g (60 %); m.p. 182 °C. Spectroscopic data are identical with those reported in the literature [13].

General Procedure for the Synthesis of Methoxy-Functionalized Phosphinines 2a–2c

The pyrylium salt (1 equiv.) was dissolved in acetonitrile, and tris(trimethylsilyl)phosphine (2 equiv.) was added dropwise at room temp. The dark coloured solution was heated to 80 °C for 5 h. Formation of the product was confirmed by ^{31}P NMR spectroscopy. After cooling to room temperature, the solvent was removed under vacuum. The residue was dissolved in CH_2Cl_2 and an appropriate amount of silica gel was added. The solvent was evaporated and the residue subjected to flash chromatography with petroleum ether/ethyl acetate (18.5:1.5) to give the phosphinine as pale yellow solid.

2-(3,4-Dimethoxyphenyl)-4,6-diphenylphosphinine 2a: Pale yellow solid from the appropriate pyrylium salt (3.38 g, 7.2 mmol) and tris(trimethylsilyl)phosphine (4.42 g, 18.1 mmol) in acetonitrile (25 mL). Yield: 0.87 g (32 %); m.p. 147 °C. $C_{25}H_{21}O_2P_1$ (384.41): calcd. C 78.11, H 5.51; found C 78.11, H 5.62. **^{31}P{^{1}H} NMR** (C_6D_6): δ = 182.3. **^{1}H NMR** (C_6D_6): δ = 3.41 (s, 3 H, OCH_3), 3.44 (s, 3 H, OCH_3), 6.60 (d, $^{3}J_{HH}$ = 8.2 Hz, 1 H), 7.18–7.36 (m, 8 H), 7.45–7.50 (m, 2 H), 7.71–7.74 (m, 2 H), 8.11 (dd, $^{3}J_{HP}$ = 5.9, $^{4}J_{HH}$ = 1.1 Hz, 1 H), 8.21 (dd, $^{3}J_{HP}$ = 5.8, $^{4}J_{HH}$ = 1.21 Hz, 1 H). **^{13}C{^{1}H} NMR** (C_6D_6): δ = 55.47 (OCH_3), 55.50 (OCH_3), 112.0 (d, $^{3}J_{CP}$ = 13.4 Hz), 112.6, 120.1 (d, $^{3}J_{CP}$ = 13.4 Hz), 125.5, 127.9, 127.97, 128.05, 128.13, 128.3, 129.02 (2 C), 129.05 (2 C), 129.1, 131.4 (d, $^{2}J_{CP}$ = 11.3 Hz, C3/5), 131.6 (d, $^{2}J_{CP}$ = 11.3 Hz, C3/5), 136.5 (d, $^{2}J_{CP}$ = 24.7 Hz, C-*i* of Ph), 142.7 (d, $^{3}J_{CP}$ = 3.2 Hz, C4), 143.7 (d, $^{2}J_{CP}$ = 24.5 Hz, C-*i* of Ph), 144.3 (d, $^{3}J_{CP}$ = 13.9 Hz), 150.5, 171.9 (d, $^{1}J_{CP}$ = 52.5 Hz, C2/C6), 172.1 (d, $^{1}J_{CP}$ = 52.1, C2/C6). **MS** (EI, 70eV): m/e (%) = 384.1 (100) [M^+].

4-(2,3-Dimethoxyphenyl)-2,6-diphenylphosphinine 2b: Pale yellow solid from the appropriate pyrylium salt (4.98 g, 10.92 mmol) and tris(trimethylsilyl)phosphine (5.47 g, 21.84 mmol). Yield: 0.9 g (22 %); m.p. 112 °C. $C_{25}H_{21}O_2P_1$ (384.41): calcd. C 78.11, H 5.51; found C 77.12, H 5.76. **^{31}P{^{1}H} NMR** (C_6D_6): δ = 184.3. **^{1}H NMR** (C_6D_6): δ = 3.36 (s, 3 H, OCH_3), 3.53 (s, 3 H, OCH_3), 6.61 (m, 1 H), 6.97 (d, J_{HH} = 5.0 Hz, 2 H), 7.10–7.24 (m, 6 H), 7.71–7.73 (m, 4 H), 8.25 (d, $^{3}J_{HP}$ = 5.9 Hz, 2 H). **^{13}C{^{1}H} NMR** (C_6D_6): δ = 55.6, 60.1, 112.8, 123.0 (d, $^{4}J_{CP}$ = 2.0, 124.1, 127.7, 127.96, 128.01 (3 C), 128.1, 129.0 (4 C), 133.7 (d, $^{2}J_{CP}$ = 12.1 Hz, C3/C5, 2 C), 137.1 (d, $^{3}J_{CP}$ = 2.7 Hz, C4), 141.4 (d, $^{3}J_{CP}$ = 14.3 Hz), 143.6 (d, $^{2}J_{CP}$ = 24.3 Hz, C-α of Ph, 2 C), 147.4 (d, $^{4}J_{CP}$ = 1.6 Hz), 153.7, 170.9 (d, $^{1}J_{CP}$ = 52.4 Hz, C2/C6, 2 C). **MS** (EI = 70eV): m/e (%) = 384.1 (100) [M^+].

2-(3-Methoxyphenyl)-4,6-diphenylphosphinine 2c: Pale yellow solid from the appropriate pyrylium salt (4.05 g, 9.5 mmol) and tris(trimethylsilyl)phosphine (4.75 g, 19.0 mmol). Yield: 1.2 g (35 %); m.p. 121 °C. Spectroscopic data were identical with those reported in the literature [7].

General Procedure for the Synthesis of Hydroxy-Functionalized Phosphinines

The appropriate methoxy phosphinine (1 equiv.) was dissolved in dichloromethane. BBr_3 in CH_2Cl_2 (5 equiv.) was added dropwise at –78 °C. The reaction mixture was warmed to room temp. and stirred for about 24 h. Afterwards, it was poured into cooled degassed water and stirred for 30 min. The organic layer was separated and dried with $MgSO_4$. The crude mixture was then subjected to flash chromatography (silica gel, hexane/ethyl acetate 50:50) to obtain the desired product.

2-(3,4-Dihydroxyphenyl)-4,6-diphenylphosphine 1a: from **2a** (0.84 g, 2.2 mmol) and BBr_3 (11 mL 1 M soln in CH_2Cl_2, 11 mmol). Yield: 500 mg (63 %); m.p. 192 °C. $C_{23}H_{17}O_2P_1$ (356.36): calcd. C 77.52, H 4.81; found C 77.70, H 5.55. **^{31}P{^{1}H} NMR** (CD_2Cl_2): δ = 181.1. **^{1}H NMR**(CD_2Cl_2): δ = 5.85 (br. s, 2 H, OH), 6.85 (d, J_{HH} = 8.3 Hz, 1 H), 7.21 (m, 1 H), 7.32 (m, 1 H), 7.44–7.56 (m, 6 H), 7.71–7.78 (m, 4 H), 8.16 (dd, $^{4}J_{HH}$ = 1.2, $^{3}J_{HP}$ = 9.1 Hz, 1 H), 8.02 (m, 1 H). **^{13}C{^{1}H} NMR** (CD_2Cl_2): δ = 114.9 (d, $^{3}J_{CP}$ = 13.1 Hz), 116.2 (2C), 120.5 (d, $^{3}J_{CP}$ = 13.1 Hz), 127.9, 128.1 (2 C), 128.1, 128.3, 129.3

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(2 C), 129.4, 131.4 (d, $^2J_{CP}$ = 11.9 Hz, C3/C5), 131.6 (d, $^2J_{CP}$ = 12.2 Hz, C3/C5), 136.7 (d, $^2J_{CP}$ = 24.8 Hz, C-α of Ph), 142.5 (d, $^3J_{CP}$ = 3.3 Hz, C4), 143.6 (d, $^2J_{CP}$ = 24.4 Hz, C-α of Ph), 144.4, 144.6 (2 C), 144.8 (d, $^4J_{CP}$ = 2.1 Hz), 171.2 (d, $^1J_{CP}$ = 51.7 Hz, C2/C6), 171.6 (d, $^1J_{CP}$ = 51.2 Hz, C2/C6). **MS** (EI, 70eV): m/e (%) = 356.1 (100) [M^+].

4-(2,3-dihydroxyphenyl)-2,6-diphenylphosphinine 1b: from **2b** (700 mg, 1.8 mmol) and BBr_3 (9 mL 1 M soln in CH_2Cl_2, 9 mmol). Yield: 400 mg (62 %); m.p. 165 °C. $C_{23}H_{17}O_2P_1$ (356.36) with ethyl acetate: C 72.96, H 5.67; found C 72.43, H 5.00. **$^{31}P\{^1H\}$ NMR** (CD_2Cl_2): δ = 185.3. **^1H NMR**(CD_2Cl_2): δ = 4.85 (br., 2 H, OH), 6.58–6.81 (m, 4 H), 7.18–7.23 (m, 5 H), 7.65–7.68 (m, 4 H), 8.08 (d, $^3J_{HP}$ = 5.7 Hz, 2 H). **$^{13}C\{^1H\}$ NMR** (CD_2Cl_2): δ = 115.1, 121.0 (2 C), 122.4, 127.5 (2 C), 127.9 (2 C), 128.1 (2 C), 128.7, 129.2 (2 C), 133.4 (d, $^3J_{CP}$ = 12.1 Hz, C3/C5, 2 C), 140.3 (d, $^3J_{CP}$ = 13.9 Hz), 141.5 (d, $^3J_{CP}$ = 1.8 Hz, C4), 143.6 (d, $^2J_{CP}$ = 24.1 Hz, C-α of Ph, 2 C), 144.7 (2 C), 171.9 (d, $^1J_{CP}$ = 52.8 Hz, C2/C6, 2 C). **MS** (EI, 70eV): m/e (%) = 356.1 (100) [M^+].

2-(3-Hydroxyphenyl)-4,6-diphenylphosphinine 1c: from **2c** (700 mg, 2.0 mmol) and BBr_3 (9.9 mL 1 M soln in CH_2Cl_2, 9.9 mmol). Yield: 410 mg (61 %); m.p. 183 °C. $C_{23}H_{17}O_1P_1$ (340.36): calcd. C 81.17, H 5.46; found C 81.33, H 5.32. **$^{31}P\{^1H\}$ NMR** (CD_2Cl_2): δ = 184.2. **^1H NMR** (CD_2Cl_2): δ = 3.96 (br., 1 H, OH), 6.58 (m, 1 H), 6.98 (m, 1 H), 7.05 (m, 1 H), 7.12–7.28 (m, 7 H), 7.39–7.45 (m, 2 H), 7.64–7.69 (m, 2 H), 8.08 (d, $^3J_{HP}$ = 5.8 Hz, 2 H). **$^{13}C\{^1H\}$ NMR** (CD_2Cl_2): δ = 114.7 (d, $^3J_{CP}$ = 12.7 Hz), 115.0 (d, $^4J_{CP}$ = 2.1 Hz), 120.1 (d, $^3J_{CP}$ = 13.3 Hz), 127.91, 127.94, 128.0 (2 C), 128.1, 129.0 (4 C), 130.0, 131.8 (d, $^3J_{CP}$ = 10.2 Hz, C3/C5), 132.0 (d, $^3J_{CP}$ = 10.2 Hz, C3/C5), 142.4 (d, $^3J_{CP}$ = 3.2 Hz, C4), 143.6 (d, $^2J_{CP}$ = 24.1 Hz, C-α of Ph), 144.2 (d, $^3J_{CP}$ = 13.6 Hz), 145.0 (d, $^2J_{CP}$ = 24.6 Hz, C-α of Ph), 156.7 (2C), 171.6 (d, $^1J_{CP}$ = 52.3 Hz, C2/C6), 171.9 (d, $^1J_{CP}$ = 52.5 Hz, C2/C6). **MS** (EI, 70eV): m/e (%) = 339.09 (100) [M^+–H].

General Procedure for the Synthesis of Phosphinine Complexes

The phosphinine (1 equiv.) and AuCl(tht) (1 equiv.) were weighed inside a glove box. Freshly distilled CH_2Cl_2 (for **4a**) or thf (for **3a**/**b**) was then added and the mixture stirred for 15 min. Completion of the reaction was checked by ^{31}P NMR spectroscopy. Reduction of the volume in vacuo followed by hexane precipitation afforded the complexes as pale yellow solids.

4a: from **2a** (110 mg, 0.36 mmol) and AuCl(tht) (110 mg, 0.36 mmol) in CH_2Cl_2 (5 mL). Yield: 110 mg (96 %); m.p. 142 °C. $C_{25}H_{21}O_2P_1Cl_1Au_1$ (616.83): calcd. C 44.50, H 3.30; found C 44.47, H 3.21. **$^{31}P\{^1H\}$ NMR** (CD_2Cl_2): δ = 152.39. **^1H NMR** (CD_2Cl_2): δ = 3.93 (s, 3 H), 3.99 (s, 3 H), 7.05 (d, $^4J_{HP}$ = 8.0 Hz, 1 H), 7.36 (dt, $^4J_{HP}$ = 8.2, $^3J_{HH}$ = 2.1 Hz, 1 H), 7.41–7.42 (m, 1 H), 7.49–7.59 (m, 6 H), 7.70–7.74 (m, 2 H), 7.78–7.83 (m, 2 H), 8.40 (dd, $^3J_{HP}$ = 22.7, $^4J_{HH}$ = 1.7 Hz, H at C3/C5, 1 H), 8.49 (dd, $^3J_{HP}$ = 22.7, $^4J_{HH}$ = 1.7 Hz, H at C3/C5, 1 H). **$^{13}C\{^1H\}$ NMR** (CD_2Cl_2): δ = 55.1, 55.3, 111.07, 111.10, 111.13, 120.1 (d, $^3J_{CP}$ = 12.7 Hz), 126.9 (d, $^4J_{CP}$ = 3.3 Hz), 127.6 (d, $^3J_{CP}$ = 11.6 Hz), 128.0 (d, $^4J_{CP}$ = 1.1 Hz), 128.4 (4 C), 128.5 (d, $^4J_{CP}$ = 2.1 Hz), 130.4 (d, $^3J_{CP}$ = 12.3 Hz), 135.0 (d, $^2J_{CP}$ = 10.1 Hz, C3/C5), 135.2 (d, $^2J_{CP}$ = 10.6 Hz, C3/C5), 138.0 (d, $^2J_{CP}$ = 12.0 Hz), 139.8 (d, $^2J_{CP}$ = 5.7 Hz), 142.8 (d, $^3J_{CP}$ = 26.2 Hz, C4), 149.0, 149.9 (d, $^4J_{CP}$ = 2.2 Hz), 158.8 (d, $^1J_{CP}$ = 36.1 Hz, C2/C6), 158.8 (d, $^1J_{CP}$ = 36.1 Hz, C2/C6). **MS** (EI, 70eV): m/e (%) = 616.0 (100) [M^+], 384.1 (50) [M^+–AuCl].

3a: from **1a** (100 mg, 0.28 mmol) and AuCl(tht) (90 mg, 0.28 mmol). Yield: 150 mg (91 %); m.p. 202 °C. $C_{23}H_{17}O_2P_1Cl_1Au_1$ (588.78): calcd. C 46.92, H 2.91; found C 47.84, H 3.53. **$^{31}P\{^1H\}$ NMR** (CD_2Cl_2): δ = 152.40. **^1H NMR** (CD_2Cl_2): δ = 6.88 (dd, $^3J_{HH}$ = 0.8, $^4J_{HP}$ = 8.2 Hz, 1 H), 7.18 (dt, $^4J_{HH}$ = 2.2, $^3J_{HP}$ = 8.1 Hz, 1 H), 7.28–7.35 (m, 1 H), 7.41–7.57 (m, 6 H), 7.77–7.88 (m, 4 H), 8.44 (dd, $^4J_{HH}$ = 1.6, $^3J_{HP}$ = 22.4 Hz, 1 H, H at C3/C5), 8.52 (dd, $^4J_{HH}$ = 1.6, $^3J_{HP}$ = 22.4 Hz, 1 H, H at C3/C5).

3b: from **1b** (100 mg, 0.28 mmol) and AuCl(tht) (90 mg, 0.28 mmol). Yield: 0.16 g (97 %); m.p. 208 °C. $C_{23}H_{17}O_2P_1Cl_1Au_1$ (588.78): calcd. C 46.92, H 2.91; found C 47.97, H 3.43. **$^{31}P\{^1H\}$ NMR** (CD_2Cl_2): δ = 153.17. **^1H NMR** (CD_2Cl_2): δ = 6.74–6.86 (m, 2 H), 6.93 (dd, $^3J_{HH}$ = 1.6, $^4J_{HP}$ = 7.2 Hz, 1 H), 7.45–7.57 (m, 6 H), 7.84–7.88 (m, 4 H), 8.57 (d, $^3J_{HP}$ = 22.7 Hz, 2 H, H at C3/C5). **MS** (ESI): m/e (%) = 587.02 (100) [M^+–H].

1a/NP-TiO_2: Phosphinine **1a** (150 mg, 0.25 mmol) was dissolved in CH_2Cl_2 (20 mL). The solution was added to a suspension of TiO_2 (1.00 g) in CH_2Cl_2. The suspension was stirred for 24 h. Afterwards the solid was filtered off, washed with CH_2Cl_2 (3 × 20mL), and dried under vacuum.

3a/NP-TiO_2 and 3b/NP-TiO_2): A solution of the phosphinine complex **3a** (or **3b**) (150 mg, 0.25 mmol) in thf (20 mL) was added to TiO_2 (1.00 g). The suspension was stirred for 24 h. Afterwards the solid was filtered off, washed with thf (3 × 20 mL), and dried under vacuum for 8 h.

Chloropropyl-modified HMS: A mixture of calcined HMS (3.00 g) in anhydrous toluene (50 mL) and (3-chloropropyl)triethoxysilane (2.16 g, 9.0 mmol) was heated under reflux for 24 h. The solid was filtered off, washed with toluene (3 × 50 mL), and dried under vacuum at 80 °C for 8 h.

Immobilisation of 1c on chloropropyl-HMS: Triethylamine (0.89 g, 8.8 mmol) was added to a suspension of chloropropyl-HMS (0.85 g) in toluene (7 mL). The mixture was cooled to –78 °C, and a solution of **1c** (300 mg, 0.88 mmol) in CH_2Cl_2 (5 mL) was added dropwise. The suspension was allowed to warm slowly to room temp. while stirring was continued for 24 h. Afterwards the solid was filtered off, washed successively with toluene (3 × 20 mL) and CH_2Cl_2 (3 × 20 mL), and dried under vacuum for about 8 h.

Single Crystal X-ray Diffraction Study of 4a

Bruker-Nonius Kappa-CCD diffractometer at 123(2) K using Mo-K_α radiation (λ = 0.71073 Å). Direct Methods (SHELXS-97 [19]) were used for structure solution and full-matrix least-squares refinement on F^2 (SHELXL-97 [19]). Hydrogen atoms were localised by difference Fourier synthesis and refined using a riding model.

4a: yellow-orange crystals, $C_{25}H_{21}AuClO_2P$, M = 616.80, crystal size 0.30 × 0.20 × 0.15 mm, triclinic, space group $P\bar{1}$ (No. 2): a = 11.376(1) Å, b = 14.232(2) Å, c = 21.024(2) Å, α = 101.68(1) °, β = 98.86(1) °, γ = 92.83(1)°, V = 3282.2(6) Å^3, Z = 6, ρ(calcd) = 1.872 Mg·m^{-3}, F(000) = 1788, μ = 6.94 mm^{-1}, 63463 reflexes ($2\theta_{max}$ = 55°), 14992 unique [R_{int} = 0.035], semiempirical absorption correction from equivalents, max. and min. transmission 0.4305 and 0.2368, 817 parameters, 0 restraints, $R1$ [$I > 2\sigma(I)$] = 0.023, $wR2$ (*all data*) = 0.046, GooF = 1.07, largest diff. peak and hole 0.777 and –1.230 e·Å^{-3}.

Crystallographic data (excluding structure factors) for the structure reported in this work have been deposited with the Cambridge Crystallo-

graphic Data Centre as supplementary publication no. CCDC-756491. Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge DB2 1EZ, UK (Fax: +44-1223-336-033; E-Mail: deposit@ccdc.cam.ac.uk).

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