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Synthesis of triarylphosphines having *para* –SH and –SMe groups. Preparation of their complexes and formation of a monolayer on a gold surface

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Abstract

The phosphines $P(C_6H_4\text{-}4\text{-}SR)_3$ (R = H, Me, 2-C_5H_9O) and $(C_6H_4\text{-}4\text{-}SR)_2PCH_2CH_2P(C_6H_4\text{-}4\text{-}SR)_2$ (R = H, Me) have been synthesized. The phosphines with –SMe groups can be prepared by reaction of 4-BrC_6H_4SMe with either BuLi or magnesium (to generate the corresponding Grignard compound) followed by reaction with PCl_3 or $Cl_2PCH_2CH_2PCl_2$, respectively. The methyl group can be eliminated by reaction with sodium in liquid NH_3. Other methods of protection/deprotection of the thiol group failed to afford the desired compounds. Reaction of 4-BrC_6H_4SH with dihydropyrane afforded the protected thiol 4-BrC_6H_4S-2-C_5H_9O from which the corresponding phosphine was successfully synthesized. However, attempts to remove the tetrahydropyranyl group by reaction with $AgNO_3$–HCl, gave an insoluble polymer as product. Reaction of $P(C_6H_4SR)_3$ (R = H, Me) with $Ni(CO)_4$ affords the corresponding mono phosphine complex quantitatively. The complex with the unprotected thiol group can be absorbed on a gold surface and the corresponding ν_{CO} bands were detected by grazing angle Fourier transform infrared reflection absorption spectroscopy (grazing angle FTIR-RAS). Reaction of $Rh(acac)(CO)_2$ with $P(C_6H_4SR)_3$ (R = Me) affords the complex Rh(acac)(CO)($P(C_6H_4SR)_3$) (R = Me), but if R = H a polymer insoluble in any solvent was obtained. The same occurs in the case of $PtCl_2$(CO)(DMSO). Apparently, once $P(C_6H_4SH)_3$ is coordinated to a metal not in the zero oxidation state, oxidation of the thiol group to disulphide becomes very easy even in a dinitrogen atmosphere.

Keywords: Phosphines; Thiols; Gold; Monolayers; Transition metal complexes

1. Introduction

Studies of monolayers on different substrates are an important research field. Among the most important features of monolayers is the modification they induce on both the chemical and electrochemical reactivity of the surface on which they are deposited. Many studies have been devoted to the electrochemical behavior of gold surfaces modified by thiol-terminated organic molecules [1]. In a few cases, metal complexes were linked to a gold surface by means of a thiol group, the anchoring ligand being for example 4-thiopyridine [2] or a porphyrin bearing a thiol-terminated side chain [3]. Although most catalytic studies are related to the influence of the monolayer on electrochemical reactions, the specific organization brought by a monolayer can by itself modify the chemical reactivity of a bound catalyst, as has been shown in at least one case by Milstein and co-workers [4].

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Monolayers of catalytically active metal complexes on a metal surface may display interesting properties, because, apart from the specific organization of the complexes on the surface, the bulk metal may act as an electron reservoir, smoothing energy differences during the catalytic cycle and thus accelerating the reaction. In order for electronic effects of this kind to be possibly observable, it is expected that the distance between the metal surface and the metal complex should be short and the "linker" be a conjugate molecule. The long alkyl chains commonly employed as spacers are expected to strongly decrease the electronic communication between the metal surface and the complex. In this light, the previously reported monolayers based on 4-thiopyridine as linker are good candidates for further studies, but it is also clear that most homogeneous catalysts reported to date employ phosphines as ligands. The mode of absorption of a thiol-containing phosphine on a gold surface is not obvious, because it is well known that phosphines can directly interact with metallic gold through the phosphorus atom, independent of the presence of a thiol group [5]. Several phosphines having a pendant thiol group have been synthesized to be employed as hemilabile ligands, including tris(2-thiophenyl)phosphine [6] and some of its complexes [7]. However, the thiol group in these molecules is most often not in the correct position to bind to a metal surface and usually chelates to the metal. A few phosphines having the sulfur atom remote from the phosphorus one have been reported [8] but their behavior with respect to a metal surface was not reported. To the best of our knowledge, in only one case was a thiol-containing phosphine, $Ph_2PCH_2CH_2SH$, anchored on a metal surface up to now [9]. The possible interaction of the phosphorus atom with the metal surface was not discussed and reaction of the absorbed phosphine with $Rh_2(\mu\text{-}Cl)_2(CO)_4$ afforded several compounds depending on the reagents concentrations.

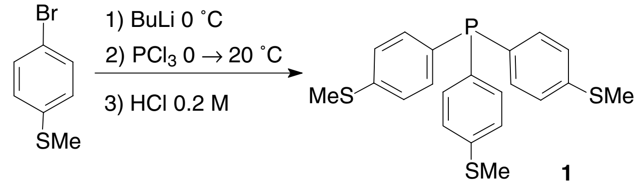
In this paper, we report the synthesis of new phosphines having –SH or –SMe groups and of some of their complexes, and the successful formation of a monolayer of one of them on a gold surface.

2. Results and discussion

*2.1. Synthesis of tri-(4-methylthio)phosphine (**1**)*

Since initial attempts to prepare $P(4\text{-}HSC_6H_4)_3$ by reaction of $4\text{-}HSC_6H_4Br$ with BuLi, followed by reaction with PCl_3 afforded a mixture of products, we decided to first synthesize the methyl protected analogue $P(4\text{-}MeSC_6H_4)_3$ (**1**). The synthesis of this phosphine has not been described in the literature previously. Its ^{31}P NMR spectrum was reported in a paper [10] and the compound was said to have been prepared by a Grignard reaction, but no detail was given.

Tri-(4-methylthio)phosphine (**1**) was synthesized by treating $4\text{-}MeSC_6H_4Br$ with BuLi, followed by reaction with PCl_3, similarly to what reported in the literature for its *ortho* analogue [6].



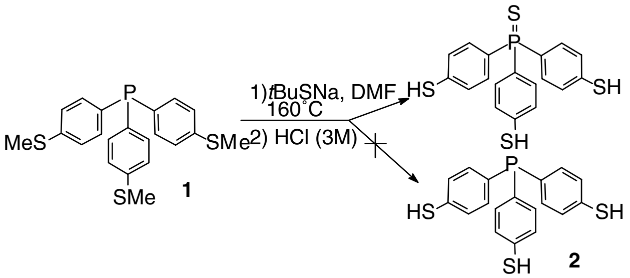
(1)

The crude product can be recrystallized to afford pure **1**, in a 40.7% isolated yield. The ^{31}P NMR spectrum of **1** shows a single peak consistent with the reported value [10].

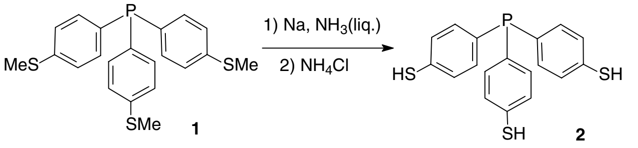
*2.2. Deprotection of **1** and synthesis of tri-(4-thiophenyl)phosphine (**2**)*

In the literature, it has been reported that deprotection of a methylthio group to afford the corresponding thiol can be achieved by reaction of the former with sodium *t*-butylthiolate in DMF, followed by aqueous HCl [11]. Application of the published protocol to **1**, however, afforded a mixture of products in which, according to mass spectral and NMR data, the predominant product is the deprotected phosphinsulfide $(4\text{-}HSC_6H_4)_3P{=}S$ (Scheme 1). Only trace amounts of **2** were present and attempts to eliminate the undesired sulfur atom from the phosphinsulfide failed.

Transformation of **1** into **2** could be effectively achieved by the use of sodium in liquid ammonia, followed by treatment with aqueous NH_4Cl (Eq. (2)) [12,13]. Pure **2** was isolated in a 87% yield, provided care is taken to exclude air from the manipulation of the reaction solution even at the neutralization step with NH_4Cl. Failure to do so sharply decreased the yield to a mere 11%.



Scheme 1.



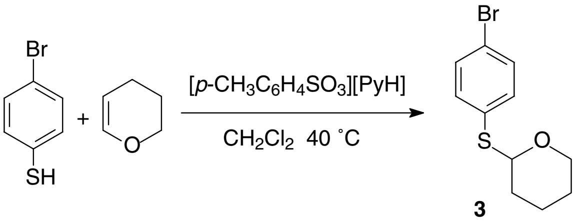
(2)

2.3. Other protection strategies and synthesis of (4-tetrahydropyranylthiophenyl)phosphine (**4**)

In order to find a more user friendly synthetic method which may allow not to use liquid ammonia, other protection–deprotection strategies were investigated.

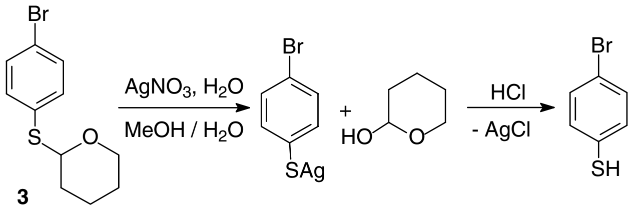
Protection of the thiol group with the $–SiMe_3$ group was first performed, but the same rearrangement problems reported in the literature [14] were observed upon treatment of the protected product with butyllithium.

Another protection strategy for the –SH group reported in the literature consists in the reaction with dihydropyrane to afford the tetrahydropyranil protected thiol. When we applied the reaction protocol described for thiophenol [15] to 4-bromo-thiophenol, the protected derivative **3** was obtained in only a 15% isolated yield. The main product was $4\text{-Br-}C_6H_4S–CH_2\text{-}SC_6H_4Br\text{-}4$, as identified by GC–MS analysis. Since the reaction protocol requires treating the solution after reaction with NaOH, followed by extraction with CH_2Cl_2, the observed byproduct clearly derives from a condensation reaction of CH_2Cl_2 with the thiolate generated from unreacted bromothiol. Simply by refluxing the solution for several hours, instead of working at room temperature, increased the yield to 86%.



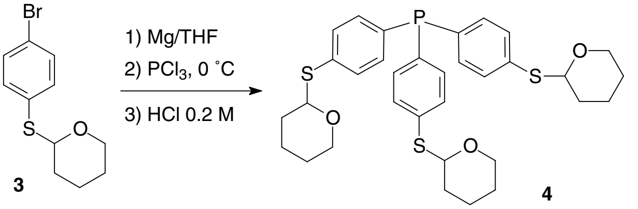
(3)

Before proceeding to the synthesis of the phosphine, the deprotection strategy was investigated. Despite some compounds of this kind have been reported to be sensitive to acidic hydrolysis [16], **3** was not hydrolyzed to any detectable extent even by hot concentrated HCl. It has been reported that tetrahydropyrane protected thiols resistant to acidic hydrolysis can be deprotected in a two steps procedure by treating them with $AgNO_3$, followed by HCl [15,17]. During the first step, a silver thiolate is formed, which precipitates out the solution and is collected by filtration. In the second step, HCl precipitates silver as its chloride and protonates the thiolate group. Application of this protocol to **3** gave excellent results and 4-bromothiophenol was regenerated in almost quantitative yields (Scheme 2).



Scheme 2.

Reaction of **3** with BuLi and PCl_3 following the same protocol employed for the synthesis of **2** afforded a mixture of difficult to separate products. However, generating the Grignard reagent instead of the lithiated arene afforded sufficient amounts of the phosphine **4** to allow purification by column chromatography (Eq. (4), 12% isolated yields of the pure product).



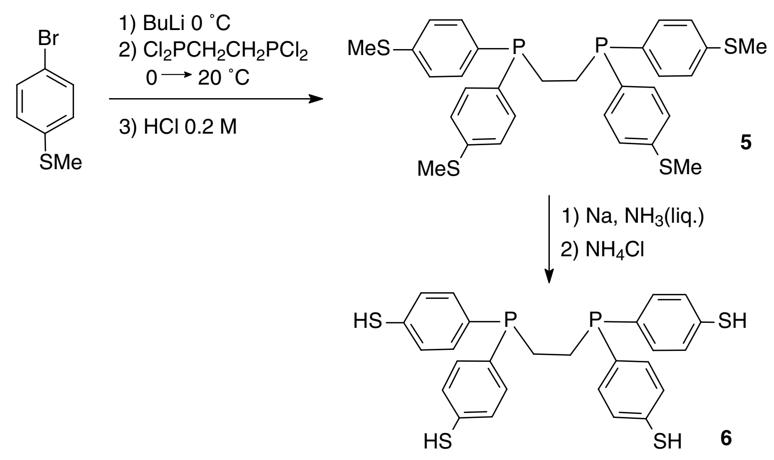
(4)

However, when deprotection was attempted by the same protocol employed for the parent bromide (Scheme 2), a solid yellow product was obtained upon treatment with $AgNO_3$, which did not redissolve upon addition of HCl and was completely insoluble in any solvent. The formation of this apparently polymeric compound is related to the one of similar materials obtained during attempts to generate some complexes of **2** and will be further discussed later. In any case, this unwanted reaction prevents the synthetic route via **4** to be employed for the synthesis of **2** and the strategy via **1** remains the only viable at the moment.

2.4. Synthesis of bis(di-(4-thiophenyl)phosphino)ethane (**6**)

The same synthetic strategy described in Eqs. (1) and (2) was next applied to the synthesis of a chelating phosphine, by employing $Cl_2PCH_2CH_2PCl_2$ in place of PCl_3 (Scheme 3).

The aromatic region of the phosphorus-coupled ^1H NMR spectrum of both **5** and **6** was quite complex, but simulation of the spectrum of **6** allowed the complete identification of all coupling constants. The signal for the central CH_2 groups was expected to be a doublet of doublets, but is observed as a triplet because of the almost coincident $J_{P–H}$ coupling constants, despite the

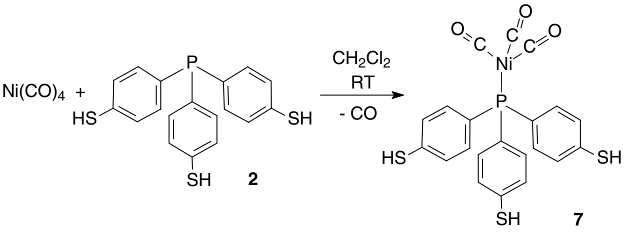


Scheme 3.

fact that the two phosphorus atoms are not equivalent with respect to each CH_2 group.

2.5. Synthesis of complexes of **1** and **2**

Interaction of **2** with excess $Ni(CO)_4$ in CH_2Cl_2 at room temperature generates the complex $Ni(CO)_3(P(4\text{-}C_6H_4SH)_3)$ (**7**), which can be isolated in a pure form by evaporating the solvent and excess $Ni(CO)_4$ in vacuo (Eq. (5)).



(5)

The IR spectrum of **7** in CH_2Cl_2 shows the expected two absorptions at 2066.4 (m) and 1993.2 (vs) cm^{-1}. The first value is slightly lower than that reported by Tolman in his famous review [18] for the analogous complex with triphenylphosphine (2068.9 cm^{-1}) and is intermediate between the values reported for tri-(*p*-tolyl)phosphine (2066.7 cm^{-1}) and tri-(*p*-methoxyphenyl)phosphine (2066.1 cm^{-1}) complexes. This indicates that the thiol group in **6** has a slight donating character.

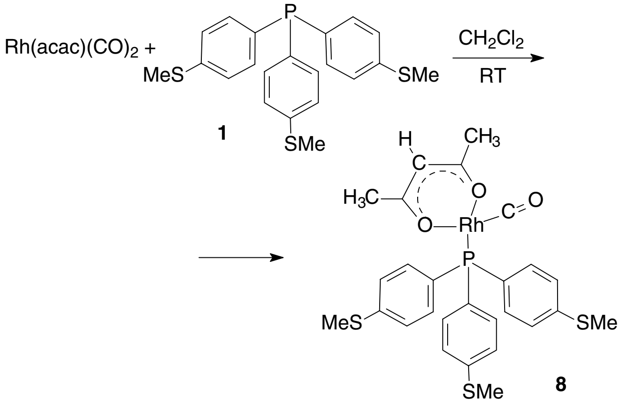
Complex **7** is extremely air sensitive. Handling its solutions with a standard nitrogen line and Schlenk apparatus was not sufficient to prevent partial decomposition within a few hours to afford an insoluble species showing in the IR spectrum (in nujol) absorptions at 2067 (m), 2000 (s), and 1943 (s) cm^{-1}. This decomposition is extremely noxious from the point of view of the characterization of monolayers (see next paragraph), since two of the absorptions are almost coincident with the ones of **7**.

In search for more oxidation stable complexes, we investigated the complexes Rh(acac)(CO)(L) (L = **1** or **2**, acacH = acetylacetone). Several phosphine complexes of this kind are known and were obtained by reaction of $Rh(acac)(CO)_2$ with the corresponding phosphine [19]. The starting $Rh(acac)(CO)_2$ was first reported by Bonati and Wilkinson [20], but the original synthesis is quite long. A much more straightforward synthesis has been reported later, which employs dimethylformamide as both the solvent and the reducing agent (Eq. (6)) [21].

$$\mathrm{RhCl_3\cdot 3H_2O + acacH} + n\mathrm{DMF} \rightarrow \mathrm{Rh(acac)(CO)_2} \qquad (6)$$

We succeeded in reproducing the reaction in Eq. (6), although in our hands the yield was quite low (23%). Performing the reaction under a CO atmosphere did not improve the yield.

Reaction of $Rh(acac)(CO)_2$ with **1** in CH_2Cl_2 cleanly afforded $Rh(acac)(CO)(P(4\text{-}C_6H_4SMe)_3)$ (**8**), as indicated by IR and elemental analysis.



(7)

However, when the same reaction was repeated by employing **2**, an insoluble product, **9**, was immediately formed, which did not dissolve in any solvent. Both complexes showed in the IR spectrum a single absorption for the CO group at 1975 cm^{-1} for **8** (in CH_2Cl_2) and 1979 cm^{-1} for **9** (in nujol), in complete agreement with what expected from the spectra of other Rh(acac)(CO)(phosphine) complexes [19].

The same problem encountered with **9** was observed when $PtCl_2(DMSO)_2$ was treated with **2** under a CO atmosphere. An insoluble product, **10**, immediately formed again, despite the fact that the analogous reaction with triphenylphosphine cleanly afforded the known and soluble $PtCl_2(CO)(PPh_3)$ [22]. The IR spectrum of **10** (in nujol) shows a single absorption in the carbonyl region at 2103 cm^{-1}, close to the one observed by us for the triphenylphosphine complex (2110 cm^{-1}, in CH_2Cl_2).

The complete insolubility of **9** and **10** seems to indicate a polymeric nature. However, the similarity of their IR spectra with those of monomeric compounds of known composition strongly suggests that the coordination sphere of the metal has not been involved in the polymerization. Given the high tendency of thiol groups to be oxidized to disulphide and the presence of three such groups on each complex molecule, the best explanation for the observed behavior is that oxidation of at least two thiol groups per molecule leads to disulphide-linked polymeric products. The role of the metal in this process is however unclear and, to the best of our knowledge, unprecedented. Since the reactions are very fast even under a dinitrogen atmosphere and with freshly purified solvents, even the nature of the oxidant is obscure and it cannot be excluded that other pathways for the polymerization (e.g. one involving other positions of the phosphine aryl rings) are operating.

2.6. Interaction of phosphine complexes with a gold surface

To study the absorption of metal complexes on a metal surface, a gold polycrystalline lamina was made mechanically flat by polishing it with abrasive paper of decreasing grain (up to *n* 2000). The surface was then further smoothed with alumina powder of decreasing size (1, 0.3, 0.03 μm). Between every polishing cycle with alumina and after the last, the lamina was irradiated with ultrasounds for 10 min in an ultrasound bath to remove any residue of the alumina employed. Chemical cleaning was then effected by immersing the lamina in a 1:1 vol/vol concentrated H_2SO_4/35% H_2O_2 solution for 30 min, followed by extensive washings with HPLC grade water and methanol. When the lamina was reused, only the treatment with 0.03 μm alumina and the following chemical cleanings were performed. Some experiments were also performed with gold surfaces obtained by sputtering a gold layer on freshly cut mica surfaces, but the IR spectra recorded were invariably of poorer quality and will not be discussed here. It has already been noted by others that the mica surface is very flat on a small domain level (such as that investigated by STM), but is quite rough on the much larger extension required to record an IR spectrum in the reflection–absorption mode [23].

When the gold lamina was immersed for 5 min in a solution of $Ni(CO)_3(P(4\text{-}C_6H_4SH)_3)$ (**7**) in THF, rinsed with more THF in a nitrogen stream and immediately placed in the nitrogen purged sample compartment of the IR spectrophotometer, the IR spectrum showed the presence of two absorptions at 2070 and 2001 cm^{-1} (Fig. 1(b)), close to the positions of the bands of **7** in CH_2Cl_2 solution (Fig. 1(a)). The spectra were recorded with the grazing angle FTIR-RAS technique. This technique has already been used successfully for the characterization of monolayers on gold [24]. It is important to note that the degeneracy of the lower frequency carbonyl stretching of the $Ni(CO)_3$ moiety is not removed by the coordination to the gold surface. This indicates that the complex is interacting with the

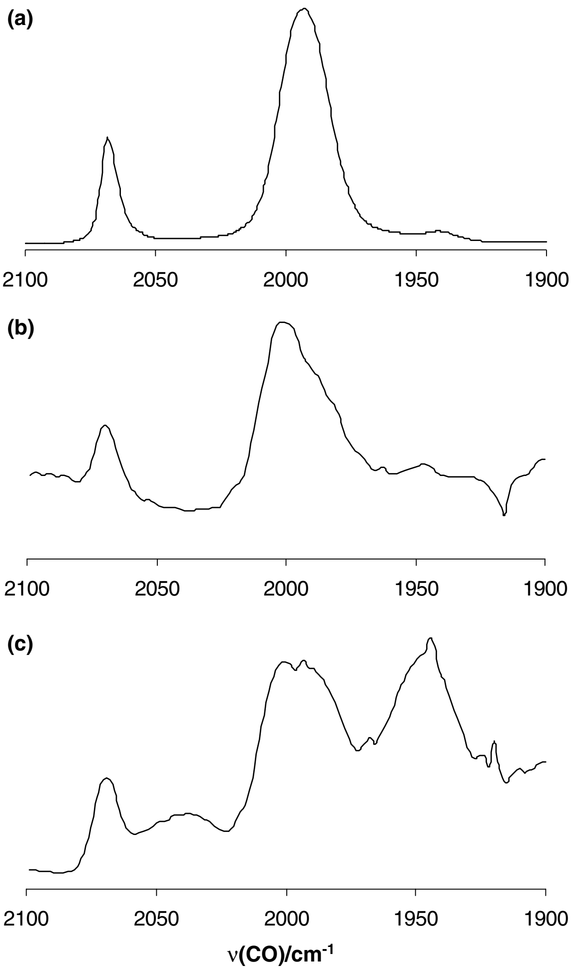


Fig. 1. (a) IR absorption spectrum of $Ni(CO)_3(P(4\text{-}C_6H_4SH)_3)$ (**7**) in CH_2Cl_2. (b) Grazing angle FTIR-RAS spectrum of a gold lamina which had been immersed in a solution of **7** for 5 min. (c) Grazing angle FTIR-RAS spectrum of a gold lamina which had been immersed in a solution of **7** for 4 h.

surface by all the three thiolate groups. If only one or two of the sulfur atoms were interacting with gold, the C_{3v} symmetry axis of the $Ni(CO)_3$ moiety would be tilted with respect to the metal surface and splitting of the lower frequency band should be observed. Due to the very small amount of complex deposited on the surface, it must be acknowledged that if a small fraction of the complex molecules were interacting with the gold lamina through only one or two sulfur atoms, the corresponding IR absorptions may not be distinguishable from the background noise. However, in case this type of coordination is indeed occurring, it appears to be the exception rather than the rule.

To the best of our knowledge only one precedent, mentioned in Section 1 [9], has been reported in the literature for a monolayer of a phosphine metal complex on a metal surface, although metal phosphine complexes anchored to oxide surfaces are quite common. The known tendency of phosphines to interact with bulk metals through the phosphorus atom has surely been a conceptual and experimental obstacle to this goal, but the successful formation of a monolayer of **7** on a gold surface indicates that preforming the complex can be an effective way of circumventing the problem.

Unfortunately, the afore mentioned absorptions disappeared in a few minutes. If the lamina was kept in the solution of **7** for several hours, a more persistent spectrum was obtained (Fig. 1(c)), which also shows an additional band at 1943 cm^{-1}. However, as previously mentioned, this band indicates that **7** has been oxidized and even the two other bands must be ascribed to the decomposition product and not to **7**.

Although disappointing, it should be noted that instability of thiol monolayers on gold is very common. Pyridinethiolate monolayers start to decompose after a few minutes in solution [25] and other short chain thiol monolayers also do the same [25,26]. The monolayers formed by pyridinethiolate complexes are somewhat more stable, but they also decompose with time [2]. The decomposition has been identified as arising from S–C bond breaking, with formation of surface oligomeric sulfur species [25,26]. The instability of the monolayer of **7** may be due to the same kind of process. However, given the high sensitivity of **7** to oxygen and the fact that exposure of the gold lamina to air is unavoidable when mounting it on the sample holder of the IR spectrophotometer, we consider it also likely that oxidation of the complex is responsible for the decomposition of the monolayer.

Complexes **9** and **10** were too insoluble and no IR absorptions were detected on the gold lamina after immersion in a THF suspension of these complexes. Even **8**, having –SMe groups on the phosphine, did not absorb onto the gold surface, supporting the conclusion that interaction of **7** with gold must be driven by a reaction of the –SH bonds and is not just a physical absorption. An attempt was also made to absorb the free phosphine first and then react the functionalized lamina with $Rh(CO)_2(acac)$, but with no success. As previously mentioned, phosphines can interact with gold even through the phosphorus atom. Unfortunately, IR absorptions due to residual water vapor in the instrument chamber prevented us from characterizing the phosphine-only monolayer in a reliable way to asses if phosphorus absorption is indeed the cause for this failure.

3. Conclusions

In this paper, we have reported the synthesis of the new phosphines **1**, **2**, **5**, and **6**, having –SH or –SMe groups in the *para* positions of the aryl rings, and of three of their complexes. An unexpected easy polymerization was observed when the thiol-containing phosphine **2** was contacted with a rhodium(I) or a platinum(II) complex and the same apparently occurs in the presence of silver(I) salts. This polymerization strongly limits the range of metal fragments that can give stable, soluble, complexes with these phosphines. The nickel complex $Ni(CO)_3(P(4\text{-}C_6H_4SH)_3)$ (**7**) could be successfully anchored onto a gold surface to yield a monolayer. The latter was unstable, likely due to the high oxygen sensitivity of the complex. Based on the accumulated experience, a more stable monolayer will probably require the preparation of an air-stable complex of a metal in a zero oxidation state. Attempts in this direction will be made in the future.

4. Experimental

4.1. General procedure

Unless otherwise specified, all reactions and manipulations were performed under a N_2 atmosphere using standard Schlenk apparatus and magnetic stirring. All glassware was kept in an oven at 125 °C for at least 2 h and evacuated while still hot before use. Solvents were dried and distilled by standard procedures and stored under dinitrogen. $Rh(CO)_2(acac)$ [21] and $PtCl_2(DMSO)_2$ [27] were synthesized by methods reported in the literature. All other starting materials were commercial products and were used as received. NMR spectra were recorded on a Bruker AC 300 FT (working at 300 MHz for ^1H NMR spectra and at 121 MHz for ^{31}P NMR spectra) at RT. Simulation of the ^1H NMR spectrum of **6** was performed with the gNMR 4 program. Transmission IR spectra were recorded on a Bio Rad FTS-7 FT-IR. Grazing angle FTIR-RAS spectra were recorded on a Digilab FTS-40 FT-IR spectrophotometers, equipped with a Specac variable angle specular reflectance accessory. Elemental analyses and mass spectra were recorded in the analytical laboratories of Milan University.

4.2. Synthesis of $P(4\text{-}C_6H_4SMe)_3$ (1)

To a 100 ml Schlenk flask were added 4-bromothioanisole (5.77 g, 28.4 mmol) and diethyl ether (30 ml). To the obtained solution was added during 2 h BuLi (18 ml of a 1.6 M solution in hexanes, 28.8 mmol). During the addition, the temperature was maintained at 0 °C by an ice bath. After the addition was over, the solution was stirred at the same temperature for an additional hour and a PCl_3 (1.31 g, 9.56 mmol) solution in diethyl ether (20 ml) was slowly added at 0 °C in 2.5 h. A yellow precipitate formed during this addition. When the addition was over, 0.2 M HCl (18.8 ml) was added at room temperature. The yellow solid immediately dissolved upon addition of HCl and a colorless one formed instead. After stirring the suspension at room temperature overnight, the solid was collected by filtration in the air, washed with water (3×30 ml), methanol (3×10 ml), and diisopropyl ether (3×10 ml). Recrystallization from *n*-butanol (35 ml) afforded the analytically pure product. 1.54 g, 40.7% yield. Anal. Found: C, 62.99; H, 5.20. Calc. for $C_{21}H_{21}PS_3$: C, 62.97; H, 5.28. ^1H NMR (300 MHz, $CDCl_3$, 298 K): $\delta = 7.21–7.22$ (m, 12H, Ar–H), 2.49 (s, 9H, CH_3). ^{31}P NMR (121 MHz, 298 K, $CDCl_3$): $\delta = -7.55$, m.p. 135–137 °C.

4.3. Synthesis of $P(4\text{-}C_6H_4SH)_3$ (2)

A three necked flask was connected to a dinitrogen line and a NH_3 line, leaving the third neck free for the additions. In a dinitrogen atmosphere was added **1** (1.00 g, 2.5 mmol). The flask was cooled down to −78 °C by a dry ice-acetone bath and about 20 ml of liquid NH_3 were condensed into the flask. Small pieces of metallic sodium were then added in about 1 h, until a blue color persisted for 15 min. During this time, it was necessary to add more NH_3 to compensate for the evaporated one. The blue suspension was stirred for an additional 30 min, after which solid NH_4Cl was added until a clear solution was obtained, which was left at room temperature up to complete evaporation of NH_3. The so obtained solid was treated with a degassed 1 M NaOH aqueous solution (100 ml). The solid dissolved almost completely. The solution was filtered through filter paper mounted on a Teflon cannula and taken to pH 3 by the addition of a degassed HCl solution (20 ml 37% HCl and 40 ml H_2O). The precipitated solid was separated by filtration, washed with water and dried in vacuo. Then it was dissolved in diethyl ether (a small amount of impurities remained undissolved) and the solution was dried with Na_2SO_4. After separating sodium sulfate and the impurities by filtration, the solution was evaporated to afford the analytically pure product. 780 mg, 87% yield. Anal. Found: C, 59.94, H, 4.21. Calc. for $C_{18}H_{15}PS_3$: C, 60.33; H, 4.22. ^1H NMR (300 MHz, $CDCl_3$, 298 K): $\delta = 7.23$ (dd, $J_{ortho} = 8.4$, $J_{H–P} = 1.5$ Hz, 6H, $H_{meta\ to\ P}$), 7.14 (dd, $J_{ortho} = 8.4$, $J_{P–H} = 7.4$ Hz, 6H, $H_{ortho\ to\ P}$), 3.50 (s, 3H, SH). ^{31}P NMR (121 MHz, 298 K, $CDCl_3$): $\delta = -7.39$.

4.4. Synthesis of $(4\text{-}C_6H_4SMe)_2PCH_2CH_2P(4\text{-}C_6H_4SMe)_2$ (5)

The synthesis was performed as described for **1**, employing the following reagents amounts: 4-bromothioanisole (4.071 g, 20.04 mmol), diethyl ether (25 ml), BuLi (13.75 ml of a 1.6 M solution in hexanes, 22 mmol), $Cl_2PCH_2CH_2PCl_2$ (811.3 mg, 3.5 mmol) dissolved in diethyl ether (10 ml), 0.2 M HCl (14 ml). The product was recrystallized twice from *n*-butanol. 579.6 mg, 28.5% yield. Anal. Found: C, 61.65; H, 5.47. Calc. for $C_{30}H_{32}P_2S_4$: C, 61.83; H, 5.53. $\{^{31}P\}^1H$ NMR (300 MHz, $CDCl_3$, 298 K): $\delta = 7.23$ (d, $J = 8.5$ Hz, 8H, Ar–H), 7.17 (d, $J = 8.5$ Hz, 8H, Ar–H), 2.49 (s, 12H, CH_3), 2.03 (s, 4H, CH_2). ^{31}P NMR (121 MHz, $CDCl_3$, 298 K): $\delta = -13.98$, m.p. 143–146 °C.

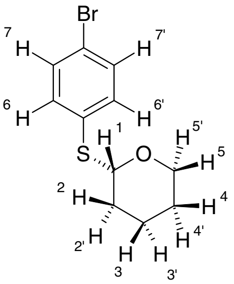
4.5. Synthesis of $(4\text{-}C_6H_4SH)_2PCH_2CH_2P(4\text{-}C_6H_4SH)_2$ (6)

The synthesis was performed as described for **2**, employing the following reagents amounts: $(4\text{-}MeSC_6H_4)_2PCH_2CH_2P(4\text{-}C_6H_4SMe)_2$ (**5**) (410.6 mg, 0.706 mmol), NH_4Cl (302 mg, 5.65 mmol), NaOH 1 M (50 ml). 263.8 mg, 71.0% yield. Anal. Found: C, 59.32; H, 4.70. Calc. for $C_{26}H_{24}P_2S_4$: C, 59.30; H, 4.59. ^1H NMR (300 MHz, $CDCl_3$, 298 K, *J* values resulting from $\{^{31}P\}^1H$ NMR spectrum and computer simulation): $\delta = 7.21$ (m, $J_{ortho} = 8.4$, $J_{H–P} = 0.6$ Hz, 8H, H_{meta}), 7.16 (m, $J_{ortho} = 8.4$, $J_{H–P} = 4.1$ Hz, 8H, H_{ortho}), 3.48 (s, 4H, SH), 1.98 (pt, $J_{H\alpha–P} = 4.4$, $J_{H\beta–P} = 4.2$ Hz, 4H, CH_2). ^{31}P NMR (121 MHz, $CDCl_3$, 298 K): $\delta = -13.88$.

4.6. Synthesis of S-(2-tetrahydropyranil)-4-bromothiophenol (3)

The procedure is adapted from the one reported in the literature for thiophenol [15]. To a 50 ml Schlenk flask were added 4-bromothioanisole (4.52 g, 23.9 mmol), pyridinium *p*-toluensulfonate (597 mg, 2.34 mmol), tetrahydropyrane (previously distilled over sodium and stored under N_2, 3.5 ml, 38.4 mmol), and CH_2Cl_2 (12 ml). The solution was stirred at room temperature for 2 h, then refluxed for 4 h. After cooling, it was extracted with 10% aqueous NaOH (4×20 ml) and saturated aqueous NaCl (2×20 ml). The organic phase was dried with Na_2SO_4 and the solvent evaporated in vacuo. The yellow oil was analyzed by GC–MS and found to contain the desired product, contaminated by small amounts (∼4% overall) of the starting thiol and of the disulphide $4\text{-}BrC_6H_4SSC_6H_4Br\text{-}4$.

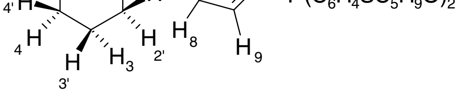
No further purification was attempted and the product was employed as such in the following reaction.



^{1}H NMR (300 MHz, $CDCl_3$, 298 K): $\delta = 7.42$ (d, $J = 8.6$ Hz, 2H, H^7 and $H^{7'}$), 7.35 (d, $J = 8.6$ Hz, 2H, H^6 and $H^{6'}$), 5.20 (dd, $J_1 = 5.5$, $J_2 = 3.9$ Hz, 1H, H^1), 4.14–4.19 (m, 1H, H^5 or $H^{5'}$), 3.58–3.62 (m, 1H, $H^{5'}$ or H^5), 1.88–2.05 (m, 1H), 1.80–1.87 (m, 2H), 1.62–1.65 (m, 3H).

*4.7. Synthesis of tri-(S-(2-tetrahydropyranil)-4-thiophenyl)phosphine (**4**)*

To a 100 ml Schlenk flask was added magnesium (450 mg, 17.49 mmol, previously washed with diethyl ether), and THF (7 ml). A solution of **3** (2.580 mg, 9.44 mmol) in THF (13 ml) was placed in a dropping funnel and about 1/3 of the solution was quickly added to the flask, followed by a few crystals of I_2. The rest of the solution was added during 2 h, after which the flask was stirred at RT for an additional hour and then cooled to 0 °C. At this temperature, a solution of PCl_3 (0.28 ml, 3.15 mmol) in THF (15 ml) was slowly added by the same dropping funnel over 2 h. After the addition was over, 0.2 M HCl (10 ml) was added at once and the biphasic solution stirred at RT overnight. Solid NaCl (about 1 g) was added in order to improve separation between the two phases and the organic phase was separated. The aqueous phase was extracted with more THF (2×7 ml) and the combined organic phases washed with water (15 ml) and dried with Na_2SO_4. The oil after evaporation of the solvent was separated by flash chromatography on silica (CH_2Cl_2 as eluent) to give pure **4** (251 mg, 13% yield) as a pale yellow oil. Anal. Found: C, 65.01; H, 6.60. Calc. for $C_{33}H_{39}O_3PS_3$: C, 64.89; H, 6.44%.



{^{31}P}^{1}H NMR (300 MHz, $CDCl_3$, 298 K): $\delta = 7.42$ (d, $J = 7.6$ Hz, 2H, H^7 and H^9), 7.19 (d, $J = 7.6$ Hz, 2H, H^6 and H^8), 5.28 (m, 1H, H^1), 4.15–4.19 (m, 1H, H^5 or $H^{5'}$), 3.59–3.63 (m, 1H, $H^{5'}$ or H^5), 2.01–2.06 (m, 1H), 1.81–1.88 (m, 2H), 1.62–1.68 (m, 3H). ^{31}P NMR (121 MHz, $CDCl_3$, 298 K): $\delta = -6.74$.

4.8. Synthesis of Ni(CO)$_3$(P(4-C$_6$H$_4$SH)$_3$) (7)

To a Schlenk tube were added $P(4\text{-}C_6H_4SH)_3$ (**2**) (100 mg, 0.28 mmol) and CH_2Cl_2 (5 ml) and the tube was cooled to 0 °C. Another Schlenk tube under dinitrogen was connected to a $Ni(CO)_4$ bottle and cooled to −78 °C by a dry ice-acetone bath. About 0.3 ml of $Ni(CO)_4$ were condensed into the tube. From this tube, liquid $Ni(CO)_4$ (100 μL, 136 mg, 0.80 mmol) was withdrawn with a microsyringe and added to the Schlenk tube containing the phosphine. The solution was stirred at 0 °C for a few minutes and then brought to RT. At this stage, an IR spectrum of the solution showed the presence of absorptions at 2066 (m), 1993 (vs) (ν_{CO}), and 1579, 1548, 1480, 1390, 1190 (phosphine absorptions) cm^{-1}, due to **7**. In addition, an absorption was also present at 2040 cm^{-1} due to excess $Ni(CO)_4$. The solution was immediately evaporated in vacuo, thus eliminating the excess $Ni(CO)_4$ with the solvent. Redissolution of part of the obtained pale yellow solid in CH_2Cl_2 gave a solution showing in the IR spectrum the same signals mentioned above, with the exception of the band at 2040 cm^{-1}. Anal. Found: C, 50.09, H, 3.41. Calc. For $C_{21}H_{15}O_3NiPS_3$: C, 50.33; H, 3.02. The compound is very air sensitive even in the solid state and slowly darkened during several weeks even if kept in a dinitrogen atmosphere. If the reaction solution was not evaporated after a few minutes, but stirred at room temperature overnight, the solution darkened and a small amount of a brown solid deposited on the walls of the tube. The IR spectrum of the solution showed, apart from the absorption at 2040 cm^{-1} due to excess $Ni(CO)_4$, three absorptions in the carbonyl region at 2066 (m), 1993 (s), and 1942 (s), the first two of which virtually coincident with the ones of **7**. However, all three absorptions were also present in the IR spectrum (in nujol) of the brown residue [2067 (m), 2000 (s), 1943 (s)], indicating that all of them are due to the decomposition product.

*4.9. Synthesis of Rh(acac)(CO)(P(4-C$_6$H$_4$SMe)$_3$) (**8**)*

To a Schlenk tube were added Rh(acac)$(CO)_2$ (18.0 mg, 0.070 mmol), $P(4\text{-}C_6H_4SMe)_3$ (30.9 mg, 0.077 mmol), and toluene (10 ml). The solution was stirred at RT for 2 days, after which an IR spectrum showed complete disappearance of the starting complex. The solution was concentrated in vacuo to about half volume and hexane (10 ml) was added to precipitate the product. Anal. Found: C, 51.73; H, 4.51. Calc. for $C_{27}H_{28}O_3RhS_3$: C, 51.43; H, 4.48. IR (CH_2Cl_2): 1977 cm^{-1} (ν_{CO}).

4.10. Synthesis of **9**

The same procedure was followed as for **8**, but employing **2** in place of **1**. However, a yellow-green precipitate started to form immediately. After 3 h, the solid was separated by filtration and washed with methanol. It was insoluble in all common solvents. IR (nujol): 1975 cm^{-1} (ν_{CO}).

4.11. Preparation of the monolayer of **7** on gold

A 1 mM solution of **7** in THF was prepared in a Schlenk tube having a 3.5 cm wide mouth and a gold lamina smoothed and cleaned as described in the text was immersed into the solution. After the decided time (from a few minutes to several hours, see also Fig. 1(a)–(c)) the lamina was taken out of the solution and extensively washed with THF while still in the Schlenk tube. The lamina was then quickly transferred to another Schlenk tube and the residual solvent evaporated in vacuo. The tube was placed under a dinitrogen atmosphere and an IR spectrum recorded as soon as possible. Despite the sample compartment of the IR spectrophotometer was nitrogen purged, oxygen cannot be eliminated as efficiently from this compartment as from a Schlenk tube and, moreover, brief exposure to air during the mounting of the lamina on the sample holder was unavoidable.

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