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# OXIDATIVE ADDITION OF ARYLHYDRAZONOYL AND BENZYLSULPHONYL CHLORIDES TO TRANSITION METAL COMPLEXES

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## Summary

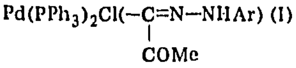
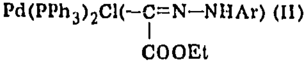
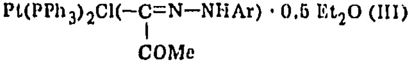
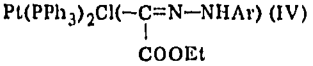
The complexes $M(PPh_3)_2Cl(-\underset{R^1}{\underset{|}{C}}=N-NHR^2)$ (M = Pd, Pt; $R^1 = COCH_3$, $COOC_2H_5$; $R^2 = p\text{-}CH_3OC_6H_4$) have been obtained by reaction of arylhydrazonoyl chlorides with $Pd(PPh_3)_4$ and $Pt(PPh_3)_3$. In the presence of excess $PPh_3$, $Pt(PPh_3)_3$ acts as a base and allows the formation of the arylazomethylentriphenylphosphoranes, $R^2-N=N-\underset{R^1}{\underset{|}{C}}=PPh_3$. Sulphinato-S complexes, $M(PPh_3)_2Cl(SO_2CH_2R^3)$, $Rh(PPh_3)_2Cl_2(SO_2CH_2R^3)$ and $Ir(PPh_3)_2COCl_2(SO_2CH_2R^3)$ (M = Pd; Pt; $R^3 = H$, $p\text{-}CH_3C_6H_4$, $p\text{-}NO_2C_6H_4$) are formed by reaction of the appropriate sulphonyl chlorides with $Pd(PPh_3)_4$, $Pt(PPh_3)_3$, $Rh(PPh_3)_3Cl$ and *trans*-$IrCl(CO)(PPh_3)_2$, respectively. The reactions of the new complexes with various bases have been studied, but in no case was a clean dehydrohalogenation observed.

## Introduction

Recent reports on the synthesis of the complexes containing the iminoacyl ligand, $-\underset{R'}{\underset{|}{C}}=N-R''$, have pointed out the potential utility of these derivatives in organic synthesis [1]. Of similar interest is the hydrazonoyl ligand, $-\underset{R'}{\underset{|}{C}}=N-NH-R''$, whose organometallic complexes are unknown. Benzyl sulphinato-S complexes also appear to be unknown, although the corresponding arene sulphinato-S complexes are well known [2]. The hydrazonoyl chlorides

TABLE 1

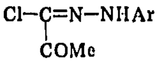
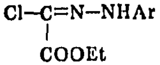
ANALYTICAL DATA [a] FOR ARYLHYDRAZONOYL DERIVATIVES [b]

| Compound | Colour | m.p. (°C) | C (%) | H (%) | N (%) |
|---|---|---|---|---|---|
|  $\mathrm{Pd(PPh_3)_2Cl(-}\underset{\substack{\mid\\ \mathrm{COMe}}}{\mathrm{C}}\mathrm{{=}N{-}NHAr)}$ (I) | yellow | 215 | 64.1(64.5) | 4.7(4.8) | 3.0(3.3) |
|  $\mathrm{Pd(PPh_3)_2Cl(-}\underset{\substack{\mid\\ \mathrm{COOEt}}}{\mathrm{C}}\mathrm{{=}N{-}NHAr)}$ (II) | yellow | 195 | 63.6(63.6) | 5.0(4.9) | 2.9(3.2) |
|  $\mathrm{Pt(PPh_3)_2Cl(-}\underset{\substack{\mid\\ \mathrm{COMe}}}{\mathrm{C}}\mathrm{{=}N{-}NHAr)\cdot 0.5\ Et_2O}$ (III) | yellow | 175 | 58.2(58.6) | 4.3(4.7) | 2.7(2.9) |
|  $\mathrm{Pt(PPh_3)_2Cl(-}\underset{\substack{\mid\\ \mathrm{COOEt}}}{\mathrm{C}}\mathrm{{=}N{-}NHAr)}$ (IV) | yellow | 190 | 57.5(57.8) | 4.4(4.4) | 2.7(2.8) |

[a] Required values in parentheses; [b] Ar = $p$-MeOC$_6$H$_4$.

TABLE 2

IR (cm$^{-1}$) AND $^1$H NMR (in CDCl$_3$) DATA FOR ARYLHYDRAZONOYL DERIVATIVES [a]

| Compound | $\nu$(C=O) [b] | $\nu$(C=N) [c] | $\nu$(M—Cl) [c] | $\tau$(NH) [d] | $\tau$(OMe) | $\tau$(COMe) | $\tau$(COOEt) |
|---|---|---|---|---|---|---|---|
|  $\mathrm{Cl{-}}\underset{\substack{\mid\\ \mathrm{COMe}}}{\mathrm{C}}\mathrm{{=}N{-}NHAr}$ | 1685 | 1535 | — | 1.52 | 6.22 | 7.48 | — |
|  $\mathrm{Cl{-}}\underset{\substack{\mid\\ \mathrm{COOEt}}}{\mathrm{C}}\mathrm{{=}N{-}NHAr}$ | 1720 | 1555 | — | 1.7 | 6.22 | — | 5.63(q)—8.62(t) |
| I | 1640 | 1510 | — | 0.9 | 6.28 | 8.8 | — |
| II | 1675 [c] | 1515 | — | 1.07 | 6.30 | — | 6.38(q)—9.03(t) |
| III [e] | 1640 | 1510 | 290 | 0.68 | 6.25 | 8.14 | — |
| IV | 1665 | 1505 | 290 | —1.25 | 6.30 | — | 6.57(q)—8.88(t) |

[a] Ar = $p$-MeOC$_6$H$_4$; [b] In CHCl$_3$; [c] In Nujol; [d] These signals disappeared by treatment with D$_2$O; [e] The presence of ethyl ether was confirmed in the $^1$H NMR spectrum.

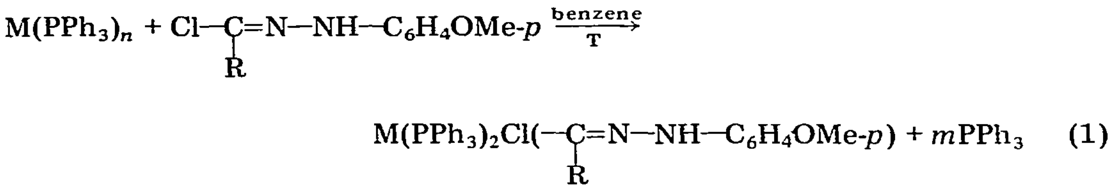
$Cl-\underset{R'}{C}=N-NH-R''$, and alkyl or arylalkyl sulphonyl chlorides were the obvious precursor of the above organometallic complexes. Both of the starting materials had another interesting feature: their reaction with bases to give labile but important organic intermediates; namely nitrilimines $R'-\overset{+}{C}=N-\overset{-}{N}-R''$ [3] from hydrazonoyl chlorides and sulphenes ($R'R''C{=}SO_2$) [4] from the sulphonyl chlorides.

We have studied the synthesis of complexes of the general structure $L_nMClL'$ (where $L' = -\underset{R'}{C}=N-NHR''$ or $-CH_2-SO_2R''$) and have examined their reactions with bases, but in no case was there a clean dehydrohalogenation.

## Results and discussion

### *i) Arylhydrazonoyl derivatives*

Arylhydrazonoyl chlorides readily react with zerovalent triphenylphosphine palladium and platinum complexes, to give the expected metal(II) derivatives [5] (eq. 1) (Table 1).



$$M(PPh_3)_n + Cl-\underset{R}{C}=N-NH-C_6H_4OMe\text{-}p \xrightarrow[T]{\text{benzene}} M(PPh_3)_2Cl(-\underset{R}{C}=N-NH-C_6H_4OMe\text{-}p) + mPPh_3 \quad (1)$$

[$M = Pd$, $n = 4$, $m = 2$, $R = COCH_3$ (I), $R = COOC_2H_5$ (II);
$M = Pt$, $n = 3$, $m = 1$, $R = COCH_3$ (III), $R = COOC_2H_5$ (IV)]

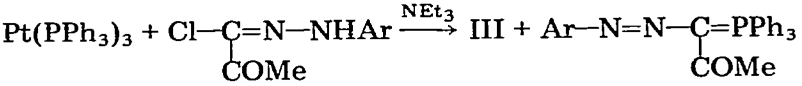
In these complexes, which probably have a *trans* square planar configuration [1] $\nu(C{=}O)$ and $\nu(C{=}N)$ of the organic ligands are shifted of about 40 $cm^{-1}$ to lower frequencies with respect to the arylhydrazonoyl chlorides (Table 2). In their IR spectra no bands were observed attributable to the N—H groups; however, in their $^1H$ NMR spectra the corresponding signal was always observed at low fields and disappeared upon treatment with $D_2O$. The other absorptions of the organic ligands in the IR and $^1H$ NMR spectra were observed in the expected positions, with a remarkable high field shift of the resonances due to the —COMe and —COOEt groups.

The $^{31}P$ NMR spectrum in $CDCl_3$ of compound III has confirmed the *trans* configuration for this derivative ($\delta = 20.3$ ppm downfield from external 85% $H_3PO_4$, singlet with $^{195}Pt$ satellites, $J(Pt-P) = 2901.6$ Hz).

However, when reaction 1 was conducted at room temperature (see Experimental section), a mixture of the *cis* with small amounts of the *trans* isomer and other impurities was obtained. The $^{31}P$ NMR spectrum of this material in $CDCl_3$ also showed two triplets, each line being split by P — P coupling ($\delta = 16.164$ ppm, $J(Pt-P) = 4236.5$ Hz, for P *trans* to chlorine; $\delta = 20.376$,

$J(\mathrm{Pt{-}P}) = 1767.6$ Hz, for P *trans* to carbon; $J(\mathrm{P_1{-}P_2}) = 15.876$ Hz) *. The formation of the *cis* isomer was confirmed by the IR spectrum, which showed $\nu(\mathrm{Pt{-}Cl}) = 310\ \mathrm{cm^{-1}}$. Compound III did not react with bases such as $NEt_3$ or with t-BuOK in benzene at room temperature.

We then attempted to generate the nitrilimine "in situ" with $NEt_3$ in the presence of the complexing agent $Pt(PPh_3)_3$ (eq. 2):



$$\mathrm{Pt(PPh_3)_3 + Cl{-}\underset{\displaystyle COMe}{C}{=}N{-}NHAr \xrightarrow{NEt_3} III + Ar{-}N{=}N{-}\underset{\displaystyle COMe}{C}{=}PPh_3} \qquad (2)$$

Compound III was again obtained but in low yield; in this case the corresponding arylazomethylentriphenylphosphorane was also formed in large amount (80% based on the added chloride). The phosphorane was also present as a by-product in reaction 1, but in low quantities (20% based on the added chloride). Moreover even the reaction between the hydrazonoyl chloride and $Pt(PPh_3)_3$ conducted in the presence of free $PPh_3$ gave the phosphorane in significant amounts (67% based on the added chloride). It is noteworthy that the hydrazonoyl chlorides do not react at all with triphenylphosphine in the absence of a base **.

On the other hand compound III did not show any reaction with triphenylphosphine. On the basis of these results it can be concluded that: i) in the absence of the base the formation of the oxidative addition products is the faster reaction, possibly involving the coordinatively unsaturated intermediate $Pt(PPh_3)_2$ [8]; ii) in the presence of a base such as $NEt_3$, the reaction leading to arylazomethylentriphenylphosphorane proceeds more favorably, presumably by reaction of the free phosphine always present in solution with the nitrilimine generated by reaction of the base with the hydrazonoyl chloride; and iii) $Pt(PPh_3)_3$, the predominant species in solution in the presence of added phosphine, can act as a base like $NEt_3$, again leading to the formation of the nitrilimine.

Very recently it was reported that these species, formed by reaction of $NEt_3$ with the arylhydrazonoyl chlorides in the presence of palladium(II)-isocyanide complexes, react with the bound isocyanide ligand leading to cyclic carbene-palladium(II) complexes [9]. Thus under the conditions of ii) and iii), the nitrilimine might also react with the phosphine bound to platinum, but to give a product which is not able to remain in the coordination sphere of the metal.

Compounds I and III could probably also act as N,O-donor chelate ligands (A) towards metals M′, as has been observed for 1,2-bis(arylimino)propyl palladium(II) complexes (B) which behave as N-donor chelate ligands towards metals of the first transition series [10]:

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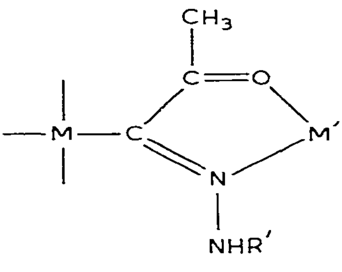
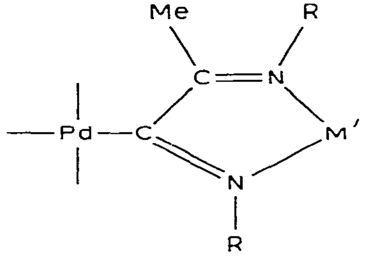
* See ref. 15 for $^{31}P$ NMR data for *cis* and *trans* platinum(II) derivatives.

** A number of stabilized arylazomethylentriphenylphosphoranes have been synthesized by some of us [6] and by other authors [7].



(A)



(B)

Preliminary results have shown that III reacts with $ZnBr_2$, but the product has not been further investigated.

*ii) Sulphinato-S complexes*

Sulphinato-S complexes can be obtained by the usual oxidative addition of benzylsulphonyl chlorides to the appropriate low oxidation state metal complex [5] (eq. 3—6) (Table 3):

$$Pt(PPh_3)_3 + RCH_2SO_2Cl \rightarrow Pt(PPh_3)_2Cl(SO_2CH_2R) + PPh_3 \qquad (3)$$

$$Pd(PPh_3)_4 + RCH_2SO_2Cl \rightarrow Pd(PPh_3)_2Cl(SO_2CH_2R) + 2\ PPh_3 \qquad (4)$$

$$Rh(PPh_3)_3Cl + RCH_2SO_2Cl \rightarrow Rh(PPh_3)_2Cl_2(SO_2CH_2R) + PPh_3 \qquad (5)$$

$$IrCl(CO)(PPh_3)_2 + RCH_2SO_2Cl \rightarrow Ir(CO)(PPh_3)_2Cl_2(SO_2CH_2R) \qquad (6)$$

$(R = p\text{-}MeC_6H_4, p\text{-}NO_2C_6H_4, H)$

Analogous products were obtained with methanesulphonyl chloride (R = H). Of these the iridium complex (XV) has been already briefly reported [11]. All these complexes show two absorptions in their i.r. spectra at ca. 1250 and 1050 $cm^{-1}$ (Table 4), attributable to the asymmetric and symmetric vibrations of the S-bonded sulphonyl group [2]. On the basis of the spectroscopic data

TABLE 3

ANALYTICAL DATA [a] FOR SULPHINATO-S COMPLEXES

| Compound | Colour | m.p. (°C) | C (%) | H (%) | N (%) |
|---|---|---|---|---|---|
| $Pt(PPh_3)_2Cl(SO_2CH_2R^1)$ (V) | pale-yellow | 195—200 | 53.0(54.0) | 3.7(3.8) | 1.4(1.5) |
| $Pd(PPh_3)_2Cl(SO_2CH_2R^1)$ (VI) | lemon-yellow | 141—145 | 59.0(59.6) | 4.0(4.2) | 1.7(1.6) |
| $Rh(PPh_3)_2Cl_2(SO_2CH_2R^1)$ (VII) [c] | brown | 200 | 58.4(57.5) | 3.8(4.1) | 1.5(1.6) |
| $Ir(CO)(PPh_3)_2Cl_2(SO_2CH_2R^1)$ (VIII) | white | 246 | 51.8(52.1) | 3.7(3.5) | 1.2(1.4) |
| $Pt(PPh_3)_2Cl(SO_2CH_2R^2)$ (IX) | pale-yellow | 210—213 | 58.0(57.2) | 4.1(4.2) | — |
| $Pd(PPh_3)_2Cl(SO_2CH_2R^2)$ (X) | lemon-yellow | 120 | 63.8(63.4) | 4.3(4.7) | — |
| $Rh(PPh_3)_2Cl_2(SO_2CH_2R^2)$ (XI) | brown | 190 | 62.3(60.9) | 4.7(4.5) | — |
| $Ir(CO)(PPh_3)_2Cl_2(SO_2CH_2R^2)$ (XII) | white | 183—185 | 54.6(54.8) | 4.0(4.0) | — |
| $Pd(PPh_3)_2Cl(SO_2CH_2R^3)$ (XIII) | yellow | 190—195 | 60.2(59.8) | 4.7(4.4) | — |
| $Rh(PPh_3)_2Cl_2(SO_2CH_2R^3)$ (XIV) | salmon-pink | 160—162 | 58.0(57.1) | 4.3(4.3) | — |
| $Ir(CO)(PPh_3)_2Cl_2(SO_2CH_2R^3)$ (XV) | white | 230 | 50.2(50.4) | 3.8(3.7) | — |

[a] Required values in parentheses; [b] $R^1 = p\text{-}NO_2C_6H_4$, $R^2 = p\text{-}MeC_6H_4$. $R^3$ = H; [c] chlorine; 7.5(7.9).

TABLE 4

IR (cm$^{-1}$, IN NUJOL) AND $^1$H NMR (in CDCl$_3$) DATA FOR SULPHINATO-S COMPLEXES

| Compound | $\nu(SO_2)_{asym}$ | $\nu(SO_2)_{sym}$ | $\nu$(M—Cl) | $\tau(CH_2)$ | $\tau(p\text{-}CH_3)$ | $\tau(SO_2CH$ |
|---|---|---|---|---|---|---|
| $p$-$NO_2C_6H_4CH_2SO_2Cl$ | 1370 | 1165 | — | 5.05 | — | — |
| V | 1225 | 1060 | 310 | — | — | — |
| VI | 1220 | 1070 | 315 | 6.64 | — | — |
| VII | 1260 | 1060 | 365(350sh) | 5.85 | — | — |
| VIII [a] | 1230 | 1080 | 320—275 | 6.1 | — | — |
| $p$-$CH_3C_6H_4CH_2SO_2Cl$ | 1365 | 1150 | — | 5.19 | 7.61 | — |
| IX | 1220 | 1055 | 310 | — | — | — |
| X | 1220 | 1070 | 310 | 6.71 | 7.78 | — |
| XI | 1255 | 1085 | 365(355sh) | 5.9 | 7.84 | — |
| XII [b] | 1225 | 1065 | 320—270 | 5.8 [d] | 8.01 [d] | — |
| $CH_3SO_2Cl$ | 1405 [e] | 1165 [e] | — | — | — | 6.33 [f] |
| XIII | 1220 | 1070 | 310 | — | — | 8.09 |
| XIV | 1255 | 1090 | 365 | — | — | 7.25 |
| XV [c] | 1225 | 1075 | 305—255 | — | — | 7.74 |

[a] $\nu$(CO) = 2100 cm$^{-1}$, in Nujol; [b] $\nu$(CO) = 2090 cm$^{-1}$, in Nujol; [c] $\nu$(CO) = 2110 cm$^{-1}$, in Nujol; [d] in $C_6D_6$; [e] film liquid; [f] in $CCl_4$.

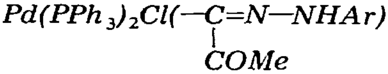
shown in Table 4, the stereochemistry of these complexes can be tentatively assigned. The iridium complexes appear to have always a *cis* arrangement of the chlorine atoms, as it has already been suggested for XV [11] but this seems not to be the case for the rhodium complexes, where sometimes only a shoulder of the main absorption due to $\nu$(Rh—Cl) was observed.

The $^1$H NMR spectra of these complexes generally show a marked high field shift of the resonances due to the —$CH_2$— and —$SO_2CH_3$ groups (Table 4), indicative of a high charge delocalisation from the metal to the ligand, while the signals due to the R substituents lie in the expected positions. However compound IX showed a complex number of bands in the $^1$H NMR spectrum in the 6—9 $\tau$ region, probably due to some decomposition of this complex in solution. This has also been observed for $Pt(PPh_3)_2Cl(SO_2CH_3)$ [12], which has been obtained by us via the reaction of $Pt(PPh_3)_3$ with $CH_3SO_2Cl$. However even the $^1$H NMR spectra registered at variable temperature did not clarify this behaviour, which is probably related to the tendency of these complexes to loose the $SO_2$ group when in solution or to give dimeric products by loss of phosphine. As for the aryl-hydrazonoyl derivatives, the reactions of the sulphinato-S complexes with bases such as $NEt_3$ or t-BuOK were in general unsuccessful, although in some cases we found some evidence that a dehydrohalogenation occurred, but we could not obtain reproducible results. Most of our effort was directed towards the reaction of $Pt(PPh_3)_2Cl(SO_2CH_2C_6H_4NO_2$-$p)$ (V) with t-BuOK in benzene at various temperatures. In some cases an ochre-yellow material was obtained, having new bands in the IR spectrum attributable to the sulphonyl group. The elemental analyses, including oxygen and sulphur were satisfactory for $Pt(PPh_3)_2(SO_2CHC_6H_4NO_2$-$p)$ but variable amounts of chlorine were also found in the products arising from different reactions. Reaction of this material with hydrogen chloride gave the white *cis*-$Pt(PPh_3)_2Cl_2$ while the organic ligand was recovered as $p$-$NO_2C_6H_4CH_2Cl$, as confirmed by thin layer chromatography. In an attempt to prepare platinum-sulphene complexes by a different route we also tried adding $RCH_2SO_2Cl$ (R = H, $p$-$NO_2C_6H_4$) to a chilled suspension of $Pt(PPh_3)_3$ and $NEt_3$ in diethyl ether. However for R = H, $Pt(PPh_3)_2Cl(SO_2CH_3)$ was again isolated, while for R = $p$-$NO_2C_6H_4$, a material different from V was obtained. This was shown to be a derivative of the corresponding sulphonic acid by comparison of its IR spectrum with that of a material obtained by reaction of $Pt(PPh_3)_3$ with $p$-$NO_2C_6H_4CH_2SO_3H$ in diethyl ether. It seems thus that in this case the intermediate $p$-$NO_2C_6H_4CH{=}SO_2$ reacts with adventitious moisture instead of being trapped and stabilised by coordination to the metal.

Sulphenes appear to be thus elusive ligands for transition metal complexes as was indicated when a sulphene-triethylamine adduct [14] was used as reagent for low oxidation state transition metal complexes [13] *.

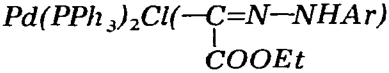
## Experimental

All the reactions were carried out under nitrogen, with stirring. Dried solvents were used. Infrared spectra were recorded with a Perkin-Elmer 457 and a Beckman 4210 instruments, and $^1$H NMR spectra with a Varian NV-14 instrument operating at 60 MHz and $SiMe_4$ as internal standard. Melting points were determined on a Leitz Heiztischmikroskop, and are not corrected. Elemental analyses were carried out by the Analytical Laboratories of Milan University. The starting complexes and organic reagents were prepared as described in the literature.



### $Pd(PPh_3)_2Cl(-\underset{COMe}{C}=N-NHAr)$ (I)

To $Pd(PPh_3)_4$ (0.3 g) and  $Cl-\underset{COMe}{C}=N-NHAr$ (0.059 g) benzene (15 ml) was added. The solution was maintained at ca. 75°C for 8 h and then left to cool overnight. Upon evaporation to a small volume and addition of n-hexane a yellow compound precipitated. It was filtered off, washed with diethyl ether, crystallized from benzene-ligroin under nitrogen, and dried in vacuo.



### $Pd(PPh_3)_2Cl(-\underset{COOEt}{C}=N-NHAr)$ (II)

To $Pd(PPh_3)_4$ (0.32 g) and  $Cl-\underset{COOEt}{C}=N-NHAr$ (0.082 g) benzene (20 ml) was added. The solution was maintained at ca. 75°C for 7—8 h. The resulting yellow-brown solution was filtered under nitrogen to remove some insoluble impurities and evaporated to a small volume. Upon adding n-hexane a yellow-green precipitate was obtained, and this was filtered off, washed with n-hexane, crystallized under nitrogen from benzene-ligroin, and dried in vacuo.

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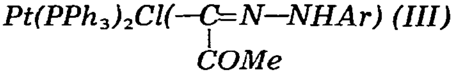
* We have also examined some reactions of this adduct with complexes such as $Pt(PPh_3)_3$ and $Rh(PPh_3)_3Cl$ obtaining negative results. We thank Prof. G. Opitz and K. Rieth for a gift of the sulphene-triethylamine adduct.

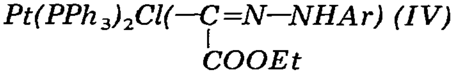


### $\mathrm{Pt(PPh_3)_2Cl(-\underset{\displaystyle COMe}{C}{=}N{-}NHAr)}$ (III)

(a) To $\mathrm{Pt(PPh_3)_3}$ (0.35 g) and $\mathrm{Cl{-}\underset{\displaystyle COMe}{C}{=}N{-}NHAr}$ (0.103 g) benzene (20 ml) was added. The solution was maintained at ca. 75°C for 6—7 h. Insoluble impurities were occasionally present; they were filtered off under nitrogen. The solution was evaporated to small volume and n-hexane was added to give a yellow precipitate. This was filtered off, washed repeatedly with diethyl ether with magnetic stirring, filtered off, and dried in vacuo.

(b) The same reaction was conducted at room temperature using $\mathrm{Pt(PPh_3)_3}$ (1.02 mmol), hydrazonoyl chloride (1.02 mmol) and benzene (35 ml), for 12 h. After isolation of the complex as above described the corresponding phosphorane was recovered from a mixture of the mother liquor and of the diethyl ether washings (20% yield based on the added chloride); m.p. 188—89°C [6].

In a different experiment $\mathrm{Pt(PPh_3)_3}$ was treated with the hydrazonoyl chloride i) in the presence of free $\mathrm{PPh_3}$, ii) in the presence of $\mathrm{NEt_3}$. i) $\mathrm{Pt(PPh_3)_3}$ (0.38 mmol) was added to a solution of $\mathrm{PPh_3}$ (0.76 mmol) and hydrazonoyl chloride (0.76 mmol) and the mixture was left at room temperature for 24 h. After isolation of complex III in very low quantities, the phosphorane (67.2% yield based on the added chloride) was isolated as decribed above, m.p. 188—189°C [6]; ii) to $\mathrm{Pt(PPh_3)_3}$ (0.61 mmol) and $\mathrm{NEt_3}$ (0.66 mmol) in acetonitrile (50 ml) at 40°C, a solution of the hydrazonoyl chloride (0.61 mmol) in acetonitrile (20 ml) was added dropwise during 30 min. When the starting chloride had disappeared (TLC) the solution was evaporated to dryness in vacuo. The residue was crystallized from ethanol to give the pure phosphorane (80% yield based on the added chloride).



### $\mathrm{Pt(PPh_3)_2Cl(-\underset{\displaystyle COOEt}{C}{=}N{-}NHAr)}$ (IV)

This compound was prepared as described for III by using $\mathrm{Pt(PPh_3)_3}$ (0.25 g), $\mathrm{Cl{-}\underset{\displaystyle COOEt}{C}{=}N{-}NHAr}$ (0.075 g), and benzene (15 ml).

### $\mathrm{Pt(PPh_3)_2Cl(SO_2CH_2C_6H_4NO_2\text{-}}p\mathrm{)}$ (V)

To $\mathrm{Pt(PPh_3)_3}$ (0.25 g) in diethyl ether (15 ml), $p\text{-}\mathrm{NO_2C_6H_4CH_2SO_2Cl}$ (0.068 g) was added. After 2 h the pale yellow product was filtered off and crystallized from chloroform-diethyl ether.

### $\mathrm{Pd(PPh_3)_2Cl(SO_2CH_2C_6H_4NO_2\text{-}}p\mathrm{)}$ (VI)

To $\mathrm{Pd(PPh_3)_4}$ (0.278 g) and $p\text{-}\mathrm{NO_2C_6H_4CH_2SO_2Cl}$ (0.074 g) benzene (25 ml) was added. After 2 h the solution (filtered under nitrogen if insoluble impurities were present) was evaporated to a small volume. Addition of n-hexane gave a yellow precipitate. This was filtered off, washed with diethyl ether, and dried in vacuo.

### $\mathrm{Rh(PPh_3)_2Cl_2(SO_2CH_2C_6H_4NO_2\text{-}}p\mathrm{)}$ (VII)

To $\mathrm{Rh(PPh_3)_3Cl}$ (0.3 g) and $p\text{-}\mathrm{NO_2C_6H_4CH_2SO_2Cl}$ (0.088 g), diethyl ether

(20 ml) was added. The initial red-violet suspension turned brown. After 1.5 h the brown precipitate was filtered off, washed with diethyl ether and dried in vacuo.

### $Ir(CO)(PPh_3)_2Cl_2(SO_2CH_2C_6H_4NO_2\text{-}p)$ (VIII)

To *trans*-$IrCl(CO)(PPh_3)_2$ (0.3 g) and *p*-$NO_2C_6H_4CH_2SO_2Cl$ (0.105 g) benzene (20 ml) was added. The solution was stirred overnight. The white precipitate was filtered off, washed with diethyl ether and dried in vacuo.

### $Pt(PPh_3)_2Cl(SO_2CH_2C_6H_4Me\text{-}p)$ (IX)

To $Pt(PPh_3)_3$ (0.35 g) and p-$MeC_6H_4CH_2SO_2Cl$ (0.08 g) diethyl ether (20 ml) was added. The yellow-orange suspension immediately became pale yellow. After 2 h the compound was filtered off, washed with diethyl ether and dried in vacuo.

### $Pd(PPh_3)_2Cl(SO_2CH_2C_6H_4Me\text{-}p)$ (X)

To $Pd(PPh_3)_4$ (0.39 g) and *p*-$MeC_6H_4CH_2SO_2Cl$ (0.07 g) benzene (20 ml) was added. The suspension was maintained at ca. 5—10° C for 4 h. Some insoluble material was filtered off under nitrogen, and the solution was evaporated to a small volume under vacuum without heating. By adding n-hexane the yellow product precipitated; it was filtered off, washed with diethyl ether and dried in vacuo.

### $Rh(PPh_3)_2Cl_2(SO_2CH_2C_6H_4Me\text{-}p)$ (XI)

To $Rh(PPh_3)_3Cl$ (0.25 g) and *p*-$MeC_6H_4CH_2SO_2Cl$ (0.063 g) diethyl ether (20 ml) was added. The red-violet suspension became brown. After 1 h the product was filtered off, washed with diethyl ether and dried in vacuo.

### $Ir(CO)(PPh_3)_2Cl_2(SO_2CH_2C_6H_4Me\text{-}p)$ (XII)

To *trans*-$IrCl(CO)(PPh_3)_2$ (0.3 g) and *p*-$MeC_6H_4CH_2SO_2Cl$ (0.09 g) benzene (20 ml) was added. After 8 h the solution was evaporated to a small volume; addition of n-hexane gave a white precipitate. This was crystallized from benzene-n-hexane to remove some unchanged starting material and dried in vacuo.

### $Pd(PPh_3)_2Cl(SO_2CH_3)$ (XIII)

To $Pd(PPh_3)_4$ (0.3 g) suspended in ethyl ether (10 ml) a solution of $CH_3SO_2Cl$ (0.036 g) in diethyl ether (10 ml) was added. After 2 h the yellow precipitate was filtered off, washed with diethyl ether and dried in vacuo.

### $Rh(PPh_3)_2Cl_2(SO_2CH_3)$ (XIV)

This compound was prepared as described for XIII by using $Rh(PPh_3)_3Cl$ (0.166 g), $CH_3SO_2Cl$ (0.041 g), diethyl ether (20 ml) and by allowing the reaction to proceed for 3.5 h.

### $Ir(CO)(PPh_3)_2Cl_2(SO_2CH_3)$ (XV)

To *trans*-$IrCl(CO)(PPh_3)_2$ (0.3 g), a solution of $CH_3SO_2Cl$ (0.053 g) in benzene (13 ml) was added. The solution formed after 4 h was stirred overnight. The solution was evaporated to a small volume, and addition of n-hexane gave a white solid. This was filtered off, washed with n-hexane, and dried in vacuo.

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