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OXIDATIVE ADDITION OF ARYLHYDRAZONOYL AND BENZYL SULPHONYL CHLORIDES TO TRANSITION METAL COMPLEXES

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Summary

The complexes $M(PPh_3)_2Cl(-\overset{\overset{R^1}{|}}{C}=N-NHR^2)$ ($M = Pd, Pt$; $R^1 = COCH_3$, $COOC_2H_5$; $R^2 = p-CH_3OC_6H_4$) 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 arylazomethylenetriphenylphosphoranes, $R^2-N=N-\overset{\overset{R^1}{|}}{C}=PPh_3$. Sulphinato-S complexes, $M(PPh_3)_2Cl-(SO_2CH_2R^3)$, $Rh(PPh_3)_2Cl_2(SO_2CH_2R^3)$ and $Ir(PPh_3)_2COCl_2(SO_2CH_2R^3)$ ($M = Pd; Pt$; $R^3 = H, p-CH_3C_6H_4, p-NO_2C_6H_4$) 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, $-\overset{\overset{R'}{|}}{C}=N-R''$, have pointed out the potential utility of these derivatives

in organic synthesis [1]. Of similar interest is the hydrazonoyl ligand, $-\overset{\overset{R'}{|}}{C}=N-NH-R''$, 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 (%)
$\text{Pd}(\text{PPh}_3)_2\text{Cl}(-\text{C}(\text{N}=\text{N}(\text{HAr}))\text{Cl})$ (I)	yellow	215 ^c	64.1 (64.5)	4.7 (4.8)	3.0 (3.3)
$\text{Pd}(\text{PPh}_3)_2\text{Cl}(-\text{C}(\text{N}=\text{N}(\text{HAr}))\text{Cl})$ (II)	yellow	195	63.6 (63.6)	5.0 (4.9)	2.9 (3.2)
$\text{Pt}(\text{PPh}_3)_2\text{Cl}(-\text{C}(\text{N}=\text{N}(\text{HAr}))\text{Cl}) \cdot 0.5 \text{Et}_2\text{O}$ (III)	yellow	175	58.2 (58.6)	4.3 (4.7)	2.7 (2.9)
$\text{Pt}(\text{PPh}_3)_2\text{Cl}(-\text{C}(\text{N}=\text{N}(\text{HAr}))\text{Cl})$ (IV)	yellow	190	57.5 (57.8)	4.4 (4.4)	2.7 (2.8)

^a Required values in parentheses; ^b Ar = *p*-MeOC₆H₄.

TABLE 2

IR (cm⁻¹) AND ¹H NMR (in CDCl₃) DATA FOR ARYLHYDRAZONOYL DERIVATIVES ^a

Compound	$\nu(\text{C}=\text{O})$ ^b	$\nu(\text{C}=\text{N})$ ^c	$\nu(\text{M}-\text{Cl})$ ^c	$\tau(\text{NH})$ ^d	$\tau(\text{OMe})$	$\tau(\text{COMe})$	$\tau(\text{COOEt})$
$\text{Cl}-\text{C}(\text{N}=\text{N}(\text{HAr}))\text{Cl}$	1685	1535	—	1.52	6.22	7.48	—
$\text{Cl}-\text{C}(\text{N}=\text{N}(\text{HAr}))\text{Cl}$	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*-MeOC₆H₄; ^b In CHCl₃; ^c In Nujol; ^d These signals disappeared by treatment with D₂O; ^e The presence of ethyl ether was confirmed in the ¹H NMR spectrum.

$\text{Cl}-\underset{\text{R}'}{\text{C}}=\text{N}-\text{NH}-\text{R}''$, 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 $\text{R}'-\dot{\text{C}}=\text{N}-\ddot{\text{N}}-\text{R}''$ [3] from hydrazonoyl chlorides and sulphenes ($\text{R}'\text{R}''\text{C}=\text{SO}_2$) [4] from the sulphonyl chlorides.

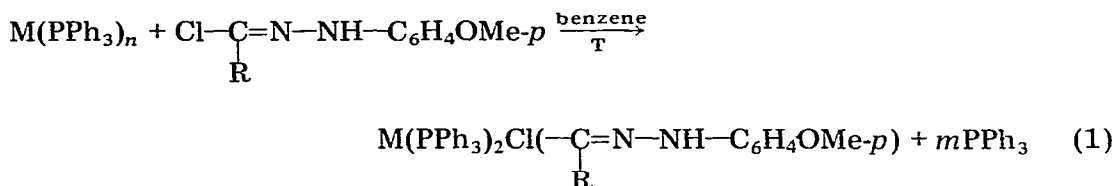
We have studied the synthesis of complexes of the general structure $\text{L}_n\text{MCIL}'$ (where $\text{L}' = \underset{\text{R}'}{\text{C}}=\text{N}-\text{NHR}''$ or $-\text{CH}_2-\text{SO}_2\text{R}''$) and have examined their reactions

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 = Pd, $n = 4$, $m = 2$, R = COCH₃ (I), R = COOC₂H₅ (II);
M = Pt, $n = 3$, $m = 1$, R = COCH₃ (III), R = COOC₂H₅ (IV)]

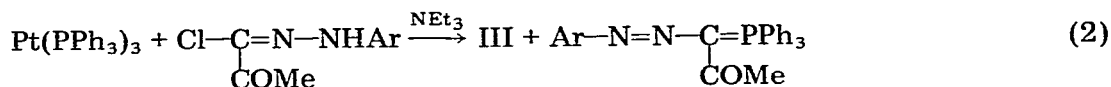
In these complexes, which probably have a *trans* square planar configuration [1] $\nu(\text{C}=\text{O})$ and $\nu(\text{C}=\text{N})$ of the organic ligands are shifted of about 40 cm⁻¹ to lower frequencies with respect to the arylhydrazonoyl chlorides (Table 2). In their IR spectra no bands were observed 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 D₂O. 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 ³¹P NMR spectrum in CDCl₃ of compound III has confirmed the *trans* configuration for this derivative ($\delta = 20.3$ ppm downfield from external 85% H₃PO₄, singlet with ¹⁹⁵Pt satellites, $J(\text{Pt}-\text{P}) = 2901.6$ 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 ³¹P NMR spectrum of this material in CDCl₃ also showed two triplets, each line being split by P — P coupling ($\delta = 16.164$ ppm, $J(\text{Pt}-\text{P}) = 4236.5$ Hz, for P *trans* to chlorine; $\delta = 20.376$,

$J(\text{Pt}-\text{P}) = 1767.6 \text{ Hz}$, for P *trans* to carbon; $J(\text{P}_1-\text{P}_2) = 15.876 \text{ Hz}$ *. The formation of the *cis* isomer was confirmed by the IR spectrum, which showed $\nu(\text{Pt}-\text{Cl}) = 310 \text{ cm}^{-1}$. 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 $\text{Pt}(\text{PPh}_3)_3$ (eq. 2):



Compound III was again obtained but in low yield; in this case the corresponding arylazomethyltriphenylphosphorane 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 $\text{Pt}(\text{PPh}_3)_3$ 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 **.

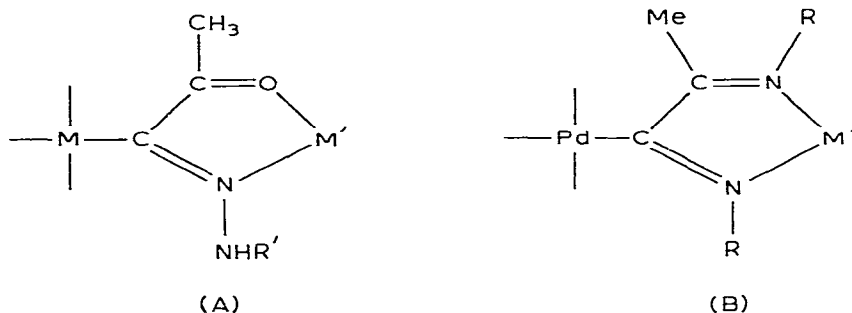
On the other hand compound III did not show any reaction with triphenylphosphine. On the basis of these results it can be concluded that: i) in the absence of the base the formation of the oxidative addition products is the faster reaction, possibly involving the coordinatively unsaturated intermediate $\text{Pt}(\text{PPh}_3)_2$ [8]; ii) in the presence of a base such as NEt_3 , the reaction leading to arylazomethyltriphenylphosphorane 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) $\text{Pt}(\text{PPh}_3)_3$, 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]:

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

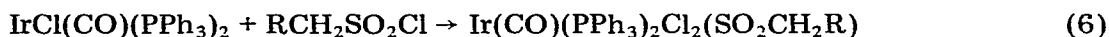
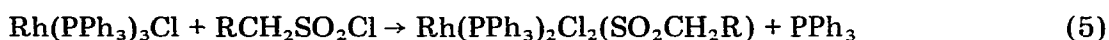
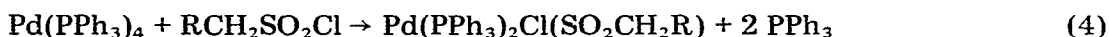
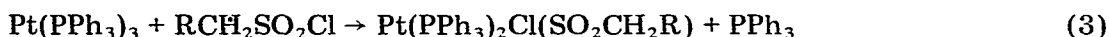
** A number of stabilized arylazomethyltriphenylphosphoranes have been synthesized by some of us [6] and by other authors [7].



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):



(R = *p*- MeC_6H_4 , *p*- $\text{NO}_2\text{C}_6\text{H}_4$, 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 (%)
$\text{Pt}(\text{PPh}_3)_2\text{Cl}(\text{SO}_2\text{CH}_2\text{R}^1)$ (V)	pale-yellow	195–200	53.0(54.0)	3.7(3.8)	1.4(1.5)
$\text{Pd}(\text{PPh}_3)_2\text{Cl}(\text{SO}_2\text{CH}_2\text{R}^1)$ (VI)	lemon-yellow	141–145	59.0(59.6)	4.0(4.2)	1.7(1.6)
$\text{Rh}(\text{PPh}_3)_2\text{Cl}_2(\text{SO}_2\text{CH}_2\text{R}^1)$ (VII) ^c	brown	200	58.4(57.5)	3.8(4.1)	1.5(1.6)
$\text{Ir}(\text{CO})(\text{PPh}_3)_2\text{Cl}_2(\text{SO}_2\text{CH}_2\text{R}^1)$ (VIII)	white	246	51.8(52.1)	3.7(3.5)	1.2(1.4)
$\text{Pt}(\text{PPh}_3)_2\text{Cl}(\text{SO}_2\text{CH}_2\text{R}^2)$ (IX)	pale-yellow	210–213	58.0(57.2)	4.1(4.2)	—
$\text{Pd}(\text{PPh}_3)_2\text{Cl}(\text{SO}_2\text{CH}_2\text{R}^2)$ (X)	lemon-yellow	120	63.8(63.4)	4.3(4.7)	—
$\text{Rh}(\text{PPh}_3)_2\text{Cl}_2(\text{SO}_2\text{CH}_2\text{R}^2)$ (XI)	brown	190	62.3(60.9)	4.7(4.5)	—
$\text{Ir}(\text{CO})(\text{PPh}_3)_2\text{Cl}_2(\text{SO}_2\text{CH}_2\text{R}^2)$ (XII)	white	183–185	54.6(54.8)	4.0(4.0)	—
$\text{Pd}(\text{PPh}_3)_2\text{Cl}(\text{SO}_2\text{CH}_2\text{R}^3)$ (XIII)	yellow	190–195	60.2(59.8)	4.7(4.4)	—
$\text{Rh}(\text{PPh}_3)_2\text{Cl}_2(\text{SO}_2\text{CH}_2\text{R}^3)$ (XIV)	salmon-pink	160–162	58.0(57.1)	4.3(4.3)	—
$\text{Ir}(\text{CO})(\text{PPh}_3)_2\text{Cl}_2(\text{SO}_2\text{CH}_2\text{R}^3)$ (XV)	white	230	50.2(50.4)	3.8(3.7)	—

^a Required values in parentheses; ^b $\text{R}^1 = p\text{-NO}_2\text{C}_6\text{H}_4$, $\text{R}^2 = p\text{-MeC}_6\text{H}_4$, $\text{R}^3 = \text{H}$; ^c chlorine; 7.5(7.9).

TABLE 4

IR (cm^{-1} , IN NUJOL) AND ^1H NMR (in CDCl_3) DATA FOR SULPHINATO-S COMPLEXES

Compound	$\nu(\text{SO}_2)_{\text{asym}}$	$\nu(\text{SO}_2)_{\text{sym}}$	$\nu(\text{M}-\text{Cl})$	$\tau(\text{CH}_2)$	$\tau(p\text{-CH}_3)$	$\tau(\text{SO}_2\text{CH})$
<i>p</i> -NO ₂ C ₆ H ₄ CH ₂ SO ₂ Cl	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	—	—
<i>p</i> -CH ₃ C ₆ H ₄ CH ₂ SO ₂ Cl	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 ₃ SO ₂ Cl	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 $\nu(\text{CO}) = 2100 \text{ cm}^{-1}$, in Nujol; ^b $\nu(\text{CO}) = 2090 \text{ cm}^{-1}$, in Nujol; ^c $\nu(\text{CO}) = 2110 \text{ cm}^{-1}$, in Nujol; ^d in C₆D₆;^e film liquid; ^f in CCl₄.

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 $\nu(\text{Rh}-\text{Cl})$ was observed.

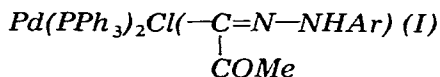
The ^1H NMR spectra of these complexes generally show a marked high field shift of the resonances due to the $-\text{CH}_2-$ and $-\text{SO}_2\text{CH}_3$ groups (Table 4), indicative of a high charge delocalisation from the metal to the ligand, while the signals due to the R substituents lie in the expected positions. However compound IX showed a complex number of bands in the ^1H NMR spectrum in the 6–9 τ region, probably due to some decomposition of this complex in solution. This has also been observed for $\text{Pt}(\text{PPh}_3)_2\text{Cl}(\text{SO}_2\text{CH}_3)$ [12], which has been obtained by us via the reaction of $\text{Pt}(\text{PPh}_3)_3$ with $\text{CH}_3\text{SO}_2\text{Cl}$. However even the ^1H NMR spectra registered at variable temperature did not clarify this behaviour, which is probably related to the tendency of these complexes to lose 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 $\text{Pt}(\text{PPh}_3)_2\text{Cl}(\text{SO}_2\text{CH}_2\text{C}_6\text{H}_4\text{NO}_2\text{-}p)$ (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 $\text{Pt}(\text{PPh}_3)_2(\text{SO}_2\text{CHC}_6\text{H}_4\text{NO}_2\text{-}p)$ 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*- $\text{Pt}(\text{PPh}_3)_2\text{Cl}_2$ while the organic ligand was recovered as *p*-NO₂C₆H₄CH₂Cl, as confirmed by thin layer chromatography. In an attempt to prepare platinum-sulphene complexes by a

different route we also tried adding $\text{RCH}_2\text{SO}_2\text{Cl}$ ($\text{R} = \text{H}$, $p\text{-NO}_2\text{C}_6\text{H}_4$) to a chilled suspension of $\text{Pt}(\text{PPh}_3)_3$ and NEt_3 in diethyl ether. However for $\text{R} = \text{H}$, $\text{Pt}(\text{PPh}_3)_2\text{Cl}(\text{SO}_2\text{CH}_3)$ was again isolated, while for $\text{R} = p\text{-NO}_2\text{C}_6\text{H}_4$, 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 $\text{Pt}(\text{PPh}_3)_3$ with $p\text{-NO}_2\text{C}_6\text{H}_4\text{CH}_2\text{SO}_3\text{H}$ in diethyl ether. It seems thus that in this case the intermediate $p\text{-NO}_2\text{C}_6\text{H}_4\text{CH}=\text{SO}_2$ 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] *.

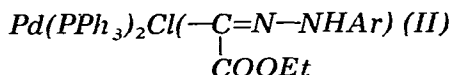
Experimental

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 ^1H 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 Heitzschmikroskop, 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.



To $\text{Pd}(\text{PPh}_3)_4$ (0.3 g) and $\text{Cl---}\underset{\substack{| \\ \text{COMe}}}{\text{C}}=\text{N---NHAr}$ (0.059 g) benzene (15 ml) was added.

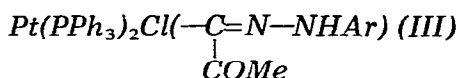
The solution was maintained at ca. 75°C for 8 h and then left to cool overnight. Upon evaporation to a small volume and addition of n-hexane a yellow compound precipitated. It was filtered off, washed with diethyl ether, crystallized from benzene-ligroin under nitrogen, and dried in vacuo.



To $\text{Pd}(\text{PPh}_3)_4$ (0.32 g) and $\text{Cl---}\underset{\substack{| \\ \text{COOEt}}}{\text{C}}=\text{N---NHAr}$ (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.

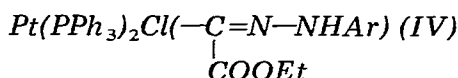
* We have also examined some reactions of this adduct with complexes such as $\text{Pt}(\text{PPh}_3)_3$ and $\text{Rh}(\text{PPh}_3)_3\text{Cl}$ obtaining negative results. We thank Prof. G. Opitz and K. Rieth for a gift of the sulphene-triethylamine adduct.



(a) To $\text{Pt}(\text{PPh}_3)_3$ (0.35 g) and $\text{Cl---}\underset{\text{COMe}}{\text{C}}=\text{N---NHAr}$ (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 $\text{Pt}(\text{PPh}_3)_3$ (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 $\text{Pt}(\text{PPh}_3)_3$ was treated with the hydrazonoyl chloride i) in the presence of free PPh_3 , ii) in the presence of NEt_3 . i) $\text{Pt}(\text{PPh}_3)_3$ (0.38 mmol) was added to a solution of 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 described above, m.p. 188–189°C [6]; ii) to $\text{Pt}(\text{PPh}_3)_3$ (0.61 mmol) and 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).



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



To $\text{Pt}(\text{PPh}_3)_3$ (0.25 g) in diethyl ether (15 ml), $p\text{-NO}_2\text{C}_6\text{H}_4\text{CH}_2\text{SO}_2\text{Cl}$ (0.068 g) was added. After 2 h the pale yellow product was filtered off and crystallized from chloroform-diethyl ether.



To $\text{Pd}(\text{PPh}_3)_4$ (0.278 g) and $p\text{-NO}_2\text{C}_6\text{H}_4\text{CH}_2\text{SO}_2\text{Cl}$ (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.



To $\text{Rh}(\text{PPh}_3)_3\text{Cl}$ (0.3 g) and $p\text{-NO}_2\text{C}_6\text{H}_4\text{CH}_2\text{SO}_2\text{Cl}$ (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)(PPh₃)₂Cl₂(SO₂CH₂C₆H₄NO₂-p) (VIII)

To *trans*-IrCl(CO)(PPh₃)₂ (0.3 g) and *p*-NO₂C₆H₄CH₂SO₂Cl (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(PPh₃)₂Cl(SO₂CH₂C₆H₄Me-p) (IX)

To Pt(PPh₃)₃ (0.35 g) and *p*-MeC₆H₄CH₂SO₂Cl (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(PPh₃)₂Cl(SO₂CH₂C₆H₄Me-p) (X)

To Pd(PPh₃)₄ (0.39 g) and *p*-MeC₆H₄CH₂SO₂Cl (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(PPh₃)₂Cl₂(SO₂CH₂C₆H₄Me-p) (XI)

To Rh(PPh₃)₃Cl (0.25 g) and *p*-MeC₆H₄CH₂SO₂Cl (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)(PPh₃)₂Cl₂(SO₂CH₂C₆H₄Me-p) (XII)

To *trans*-IrCl(CO)(PPh₃)₂ (0.3 g) and *p*-MeC₆H₄CH₂SO₂Cl (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(PPh₃)₂Cl(SO₂CH₃) (XIII)

To Pd(PPh₃)₄ (0.3 g) suspended in ethyl ether (10 ml) a solution of CH₃SO₂Cl (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(PPh₃)₂Cl₂(SO₂CH₃) (XIV)

This compound was prepared as described for XIII by using Rh(PPh₃)₃Cl (0.166 g), CH₃SO₂Cl (0.041 g), diethyl ether (20 ml) and by allowing the reaction to proceed for 3.5 h.

Ir(CO)(PPh₃)₂Cl₂(SO₂CH₃) (XV)

To *trans*-IrCl(CO)(PPh₃)₂ (0.3 g), a solution of CH₃SO₂Cl (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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