Reaction of Trithiazyl Trichloride, $(NSCl)_3$, with Triphenylphosphine or Triphenylphosphine Metal Complexes. *X*-Ray Crystal Structure† of Aminotriphenylphosphonium Chloride–Dichloromethane (1/1), $[Ph_3PNH_2]Cl{\cdot}CH_2Cl_2$

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The reaction between $(NSCl)_3$ and $[RuCl_2(PPh_3)_3]$ gives $[RuCl_3(NS)(PPh_3)_2]$ together with $[Ph_3PNH_2]Cl{\cdot}CH_2Cl_2$ (**2**) (characterised by *X*-ray crystallography, ^{31}P n.m.r. and i.r. spectroscopy) and Ph_3PNH (**4**). Reaction between $(NSCl)_3$ and PPh_3 also gives (**2**) and (**4**); a mechanism for this reaction is proposed. Reactions of $(NSCl)_3$ with $[RhCl(PPh_3)_3]$, *trans*-$[Rh(CO)Cl(PPh_3)_2]$, or $[Rh(NO)(PPh_3)_3]$ were investigated by ^{31}P n.m.r. and contrary to several previous reports do not give thionitrosyl complexes but rather result in the formation of (**2**) and (**4**) or in the oxidation of the material to $[Rh(CO)Cl_3(PPh_3)_2]$. The existence of any rhodium phosphine thionitrosyls is thus cast into doubt.

In 1978 Kolthammer and Legzdins[1] successfully used trithiazyl trichloride (1,3,5-trichlorocyclotriaza-λ^4-thiene), $(NSCl)_3$, in the preparation of $[Cr(CO)_2(\eta^5\text{-}C_5H_5)(NS)]$ from $Na[Cr(CO)_3(\eta^5\text{-}C_5H_5)]$ in tetrahydrofuran (thf), the reactive sulphur–nitrogen species being assumed to be the solvated monomer NSCl·thf. Since this report there has been a wide range of reactions carried out along the same lines. In particular, Pandey and co-workers[2–6] have reported numerous preparations of metal complexes containing phosphine and thionitrosyl ligands, including a recent crystal structure determination[7] for $[OsCl_3(NS)(PPh_3)_2]$. It is the publication of this latter paper and a review[6] which prompts us to report the results of our studies, which cast doubt on many of the currently accepted formulations.

Although a large number of compounds apparently containing thionitrosyl ligands have been claimed very few of them have been fully characterised, with many of the structures relying on i.r. evidence only.[4–7] Table 1 summarises the salient data for compounds whose structures are fully established; of note is the large variation in ν(NS) which is not obviously correlated with the M–N–S angle. Contrary to this evidence Pandey *et al.*[3–5] have made use of what they believe to be the ν(NS) frequency in a number of publications on rhodium complexes (Table 2) to postulate the existence of 'bent' thionitrosyl groups. Remarkably all of the compounds in Table 2 have ν(NS) = 1 118 ± 3 cm^{-1}, a very narrow range which is probably within experimental error. For comparison[8] changing the phosphine (L) (which is *cis* to the thionitrosyl group) in compounds of the type $[ReCl_3(NS)(L)_2]$ gave a range for ν(NS) from 1 214 cm^{-1} (L = PPh_3) to 1 230 cm^{-1} (L = PEt_2Ph).

We have been investigating the reactions between $(NSCl)_3$ and ruthenium and rhodium phosphine complexes and wish to report our results which are at variance with those mentioned above. In particular many of the reactions studied by us result in the formation of $[Ph_3PNH_2]Cl$ which has a very strong absorption in its i.r. spectrum at 1 118 cm^{-1}. We believe that impurities of this compound may be responsible for erroneously reported preparations of rhodium thionitrosyl complexes.

Table 1. Reported M–N–S angles from *X*-ray crystallography and ν(NS) frequencies for metal thionitrosyls

Compound	M–N–S/°	ν(NS)/cm^{-1}	Ref.
$[Cr(CO)_2(\eta\text{-}C_5H_5)(NS)]$	176.8	1 180	1
$[Mo(S_2CNMe_2)_3(NS)]$	172.0	1 100	8, *a*
$[OsCl_3(NS)(PPh_3)_3]$	177.9	1 310	7
$[AsPh_4][OsCl_4\{(NS)_2Cl\}]$	170.0	1 298, 1 215	*b*

[a] J. Chatt and J. R. Dilworth, *J. Chem. Soc., Chem. Commun.*, 1979, 1; M. B. Hursthouse and M. Motevalli, *J. Chem. Soc., Dalton Trans.*, 1979, 1362. [b] R. Weber, U. Muller, and K. Dehnicke, *Z. Anorg. Allg. Chem.*, 1983, **504**, 13.

Table 2. Reported ν(NS) frequencies for rhodium phosphine thionitrosyl complexes (see text for discussion)

Compound	ν(NS)/cm^{-1}	Ref.
$[RhCl_2(NS)(PPh_3)_2]$	1 120	3
$[RhCl_2(NS)(AsPh_3)_2]$	1 120	3
$[RhCl_2(NS)(AsPh_3)(PPh_3)]$	1 116—1 120	4
$[RhBrCl(NS)(PPh_3)_2]$	1 120	3
trans-$[Rh(CO)Cl_2(NS)(PPh_3)_2]$	1 118	3
trans-$[Rh(CO)Cl_2(NS)(AsPh_3)_2]$	1 115	3
$[\{Rh(CO)Cl_2(NS)(PPh_3)_2\}_2]$	1 118	5
$[Rh(CO)(NS)(PPh_3)_2]$	1 122	5

Results and Discussion

We have attempted the preparation of a number of thionitrosyl metal phosphines and in all but one case have been unsuccessful. Reaction of $[RuCl_2(PPh_3)_3]$ with $(NSCl)_3$ does proceed essentially as described by Pandey and co-workers[7] [equation (1)] with the solution changing to dark brown and the

$$[RuCl_2(PPh_3)_3] + NSCl{\cdot}thf \longrightarrow [RuCl_3(NS)(PPh_3)_2] \quad (1)$$

formation of a brown precipitate of $[RuCl_3(NS)(PPh_3)_2]$ (**1**), which can be isolated in *ca.* 25% yield. This compound was characterised by microanalysis, i.r. [ν(NS) = 1 316 cm^{-1}], and ^{31}P n.m.r. (δ 13.30). However, with such a low yield it is of some consequence to establish the identities of the other products and

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† *Supplementary data available* (No. SUP 56194, 3 pp.): H-atom co-ordinates, thermal parameters. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1985, Issue 1, pp. xvii—xix. Structure factors are available from the editorial office.

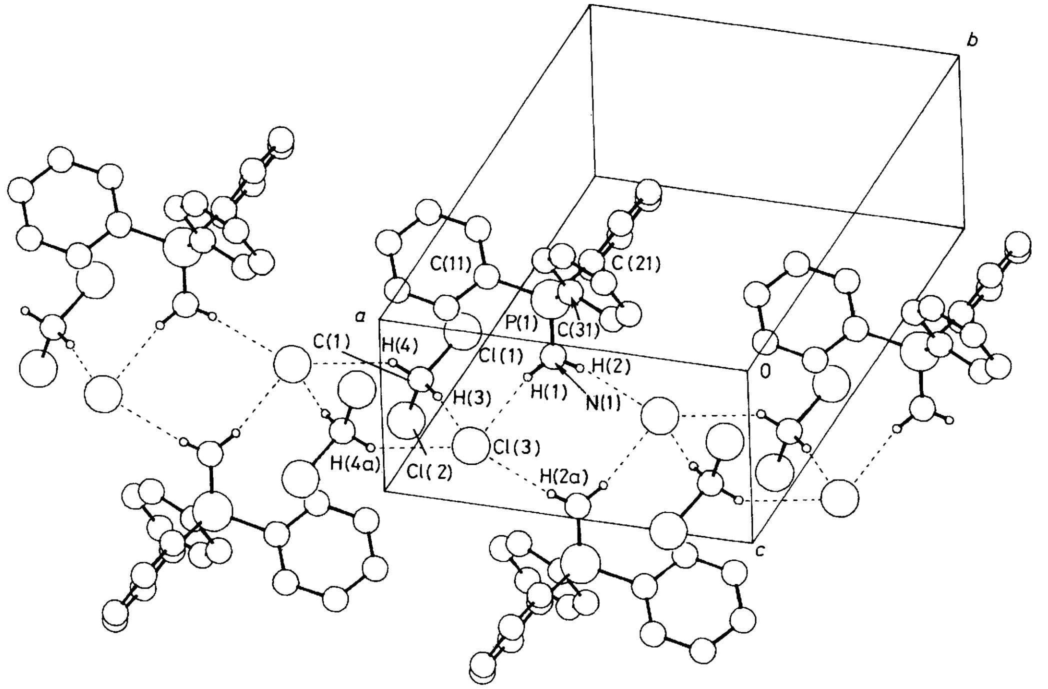

Figure Packing diagram of the X-ray crystal structure of $[Ph_3PNH_2]Cl{\cdot}CH_2Cl_2$, (**2**) to show the H-bonding scheme (E. K. Davies, SNOOPI Program for drawing Crystal Structures, University of Oxford, 1983)

in this regard ^{31}P n.m.r. has been particularly useful. Thus, when the above reaction was carried out in thf with a molar ratio of 1:1 we observed formation of Ph_3PS (δ 43.2) and Ph_3PO (δ 28.2) together with (**1**). However, on increasing the ratio of NSCl•thf to $[RuCl_2(PPh_3)_3]$ to a ten-fold excess of the former (conditions which may mimic those reported by Pandey[3] who used 'solutions'), no Ph_3PS was observed but new bands at δ 35.5 and 25.2 which accounted for a large proportion (60%) of the phosphorus in the ^{31}P n.m.r. were observed. Similarly if the reaction was carried out in thf–CH_2Cl_2 mixtures we observed a strong band at δ 35.5 and a weaker band at δ 25.2. Longer reaction times result in increasing intensity for the low-field (δ 35.5) band at the expense of the high-field band. When a mixture of $RuCl_3{\cdot}3H_2O$ and PPh_3 (1:4) in ethanol was treated with NSCl•thf (molar ratio 1:10), Ph_3PS (25%), Ph_3PO (65%), and a species giving a band at δ 35.5 (10%) accounted for all the phosphorus observed. It thus becomes of importance to establish the identity of the compound responsible for the band at δ 35.5. Pure samples of this compound were obtained from the reaction mixture but the i.r. spectrum and microanalysis data were difficult to fit to any simply predicted structure. However, an X-ray crystal structure determination has enabled the product to be identified as $[Ph_3PNH_2]Cl{\cdot}CH_2Cl_2$ (**2**), shown in the Figure, with selected bond distances and angles in Table 3. This is the first example of a crystal structure of an aminophosphonium salt containing a primary amine. The distances and angles are generally as expected; one interesting feature is the hydrogen bonding to the CH_2Cl_2. Selected 'non-bonding' distances are also given in Table 3.

As a further check of our ^{31}P n.m.r. and i.r. data a sample of $[Ph_3PNH_2]Cl$ (**3**) was prepared by the literature method[9] and found to have identical (except for vibrations due to CH_2Cl_2) properties to the product obtained *via* $(NSCl)_3$. The n.m.r. and i.r. data for (**2**) and (**3**) are consistent with the X-ray analysis, with δ(^{31}P) in a reasonable region (35.5) for phosphorus(v); in the i.r. in addition to the bands due to triphenylphosphine we observed ν(NH) = 3 100, δ(NH) = 1 551, and ν(PN) = 970 cm^{-1} together with a very strong band at 1 118 cm^{-1} as expected for a phosphonium compound.[10]

Table 3. Selected bond distances (Å) and angles (°) in (**2**)

(*a*) Bond lengths			
N(1)–P(1)	1.615(6)	C(11)–P(1)	1.803(6)
C(21)–P(1)	1.788(6)	C(31)–P(1)	1.796(6)
H(1)–N(1)	0.883(50)	H(2)–N(1)	0.760(44)
Cl(1)–C(1)	1.754(9)	Cl(2)–C(1)	1.751(8)
H(3)–C(1)	0.970(68)	H(4)–C(1)	0.883(54)
(*b*) 'Non-bonding' distances			
Cl(3)–N(1)	3.244	Cl(3)–H(1)	2.375
Cl(3)–N(1a)	3.239	Cl(3)–H(2a)	2.490
Cl(3)–H(3)	2.685	Cl(3)–H(4b)	2.923
(*c*) Bond angles			
C(11)–P(1)–N(1)	108.5(3)	C(21)–P(1)–N(1)	108.1(3)
C(21)–P(1)–C(11)	108.6(3)	C(31)–P(1)–N(1)	114.7(3)
C(31)–P(1)–C(11)	109.1(3)	C(31)–P(1)–C(21)	107.7(3)
H(1)–N(1)–P(1)	119.4(32)	H(2)–N(1)–P(1)	114.9(34)
H(2)–N(1)–H(1)	116.7(47)		

Key to symmetry operators relating designated atoms to reference atoms at (x,y,z): atoms a, 1.0 − x, −y, 1.0 − z; atoms b, 2.0 − x, −y, 1.0 − z.

Since the band at δ 35.5 was attributed to an aminophosphonium salt it seemed possible that the compound responsible for the higher field resonance might be the equivalent iminophosphorane. Reduction of (**3**) with $NaNH_2$ in benzene gave Ph_3PNH (**4**) which has δ(^{31}P) 25.2 p.p.m. and ν(PN) = 1 190 cm^{-1}, *i.e.* the same as the second product from reaction (1).

So as to ascertain if the metal centre is involved in the formation of (**3**) or if the NSCl•thf simply reacts with free phosphine, we reacted NSCl•thf with triphenylphosphine and found that the major phosphorus-containing products are **(3)** and **(4)** together with small amounts of an as yet, unidentified compound having δ 24.7; also obtained, as a precipitate, was S_4N_3Cl and a trace of S_4N_4 (both identified by i.r. spectroscopy). Once again longer reaction times favoured **(3)** at the expense of **(4)**. Mechanistically it is possible to write a (somewhat speculative) Scheme for the reaction. The major difficulty encountered in explaining both the reaction and the mechanism is the apparent availability of protons. All of the solvents employed were thoroughly dried and the $(NSCl)_3$ was checked by i.r. spectroscopy for the absence of ammonium chloride. It seems that either $(NSCl)_3$ or one of the intermediates themselves are either particularly strong hydrogen scavengers or capable of cleaving the C–H bond in the solvent. This bond cleavage would, of course, not be necessary in the case of reactions carried out in ethanol. Some support for our proposed mechanism is the evidence of longer reaction times favouring **(3)** over **(4)**.

$$\mathrm{NSCl} \xrightarrow{\mathrm{PPh_3}} \mathrm{Ph_3PNSCl} \xrightarrow{\mathrm{H+}} \mathrm{Ph_3P(NH)SCl} \xrightarrow{\mathrm{Cl}}$$
$$\mathrm{Ph_3PNH} + \mathrm{SCl_2} \longrightarrow [\mathrm{Ph_3PNH_2}]\mathrm{Cl}$$

Scheme.

Turning now to the rhodium reactions, we found that treatment of *trans*-$[Rh(CO)Cl(PPh_3)_2]$ with 1 mol equiv. of NSCl·thf gave Ph_3PS (20%), **(3)** (5%), **(4)** (18%), and $[Rh(CO)Cl_3(PPh_3)_2]$ **(5)** (40%). This last compound was identified by comparison with an authentic sample prepared[11] by chlorination of $[Rh(CO)Cl(PPh_3)_2]$ [^{31}P n.m.r., δ 12.87 p.p.m., $^1J(Rh-P) = 76$ Hz; ν(CO) = 2 104, ν(Rh–Cl) = 352 cm^{-1}]. Also obtained from the reaction of $(NSCl)_3$ and $[Rh(CO)Cl(PPh_3)_2]$ was a trace of Ph_3PO together with some (10%) unreacted starting material. The powerful oxidising ability of $(NSCl)_3$ has already been reported,[12] for example, treatment of $[M(CO)_3(\eta^5-C_5H_5)]^-$ (M = Mo or W) with NSCl·thf gives $[\{M(CO)_3(\eta^5-C_5H_5)\}_2]$ and $[M(CO)_3Cl(\eta^5-C_5H_5)]$. The oxidation of Rh^I to Rh^{III} observed here is thus not surprising. Pandey *et al.*[5] report bands at 2 110 and 1 118 cm^{-1} in the preparation of $[Rh(CO)Cl_2(NS)(PPh_3)]$, and at 2 105 and 1 118 cm^{-1} in the preparation of $[Rh(CO)Cl_2(NS)(PPh_3)_2]$, these bands being interpreted as ν(CO) of Rh^{III}(CO) and ν(NS). In our view the bands are probably due to ν(CO) in **(5)** and the phosphonium band of **(3)**. We did consider that the product reported by Pandey[5] might be formed from the action of $(NSCl)_3$ on $[Rh(CO)Cl_3(PPh_3)_3]$ but we found no reaction between these two materials.

Reaction[3] between $[RhCl(PPh_3)_3]$ and NSCl·thf has been reported to result in the formation of $[RhCl_2(NS)(PPh_3)_2]$ but we were unable to obtain any compounds that contain phosphorus bound to rhodium, as judged by the presence of Rh–P couplings in the ^{31}P n.m.r. Thus when the reaction is carried out in a 1 : 1 molar ratio Ph_3PS (25%), Ph_3PO (10%), **(3)** (35%), and **(4)** (25%) account for the majority of the phosphorus observed, a situation which is also evident when an excess of $(NSCl)_3$ is used or when the reaction is carried out in the presence of zinc.[6] Finally, reaction of $[Rh(NO)(PPh_3)_3]$ with $(NSCl)_3$ is reported[4] as resulting in an NS-bridged [ν(NS) = 840 cm^{-1}] species, $[\{RhCl_2(NS)(PPh_3)\}_2]$, but once again in our hands only Ph_3PO and **(3)** were obtained.

Overall our results suggest that in many of the reported examples thionitrosyl complexes may not have been prepared. Other workers have also noticed difficulties in the preparation of ruthenium[13] and rhodium[14] complexes. As mentioned above we believe that the band assigned as ν(NS) at 1 118 ± 3 cm^{-1} for the rhodium complexes in Table 2 is erroneous and probably due to impurities of $[Ph_3PNH_2]Cl$ which has a very strong band in its i.r. at 1 118 cm^{-1}. It seems likely that some of this compound would coprecipitate from thf in which it is only moderately soluble and since in many of the reactions no further purifications were carried out any final product would thus be contaminated with **(3)**. It is difficult to rationalise the microanalysis results obtained by previous workers but in this regard we note that the same compound (prepared by the same workers) often has quite large variations in melting point: *e.g.*, $[Rh(CO)Cl_2(NS)(PPh_3)_2]$, m.p. 128—130 (ref. 3), 165 °C (ref. 5); $[RuCl_3(NS)(PPh_3)_2]$, m.p. 220—222 (ref. 2), 197—198 (ref. 15), 192—194 °C (ref. 7). Indeed these and many other inconsistencies in melting point and spectroscopic data are often evident and lend support to the belief that many of the claimed thionitrosyl complexes do not exist. This underlines the necessity for full spectroscopic characterisation of new compounds whenever possible.

Experimental

All reactions were carried out under an atmosphere of argon. All solvents were dried before use; thf was dried and then distilled from sodium and benzophenone and thoroughly degassed before use. The $^{31}P-\{^1H\}$ n.m.r. spectra were recorded on a JEOL FX90Q F.T. n.m.r. spectrometer at 36.21 MHz and are referred to external 85% H_3PO_4. The i.r. spectra were recorded as KBr discs on a Perkin-Elmer 683 spectrophotometer. Elemental analyses were performed by the microanalytical department of the chemistry department of Imperial College.

The compounds $(NSCl)_3$,[16] $[RuCl_2(PPh_3)_3]$,[17] $[RhCl(PPh_3)_3]$,[18] $[Rh(NO)(PPh_3)_3]$,[19] $[Rh(CO)Cl(PPh_3)_2]$,[20] and $[Rh(CO)Cl_3(PPh_3)_2]$[11] were prepared by standard methods.

Aminotriphenylphosphonium Chloride.—This was prepared according to ref. 9. $^{31}P-\{^1H\}$ N.m.r. spectrum (CH_2Cl_2), δ 35.5 p.p.m.(s). I.r.: in addition to bands due to PPh_3, ν(NH) = 3 100, δ(NH) = 1 551, ν(R_3P^+) = 1 118, and ν(PN) = 970 cm^{-1}.

Iminotriphenylphosphorane.—Aminotriphenylphosphonium chloride (1.3522 g, 4.3 mmol) and sodium amide (0.159 g, 4.3 mmol) were refluxed together in benzene (50 cm^3) for 4 h, and then stirred until all the sodium amide had reacted and no phosphonium chloride remained (*ca.* 18 h). This reaction mixture was filtered to remove sodium chloride, the filtrate evaporated to dryness, and the resulting white solid recrystallised from hot cyclohexane to give white needles of the *product* (0.9 g, 75%), m.p. 131.5 °C (lit.,[21] 128 °C). $^{31}P-\{^1H\}$ N.m.r. spectrum (benzene), δ 25.2 p.p.m. (s). ^1H N.m.r. ($CDCl_3$), δ 7.5 (m, 15 H), 1.55 p.p.m. (s, 1 H). Mass spectrum, *m/e* 277 (Ph_3PNH^+), 262 (Ph_3P), 200 (Ph_2PNH), 185 (Ph_2P^+), 77 (Ph^+).

Reaction of Triphenylphosphine with Trithiazyl Trichloride.—Triphenylphosphine (50 mg, 0.19 mmol) in CH_2Cl_2 or thf (5 cm^3) and trithiazyl trichloride (0.1555 g, 1.9 mmol) in thf (4 cm^3), were stirred together. On mixing the solution became very briefly orange, it then turned bright green and over 10 min lightened to yellow. After stirring for 2 h the resulting orange-brown solution was pumped down to give an orange-brown *oil*. The oil was extracted into thf or CH_2Cl_2 and a $^{31}P-\{^1H\}$ n.m.r. spectrum recorded (see Results and Discussion section). The insoluble solid remaining from these reactions was shown by i.r. to be S_4N_3Cl with a small amount of S_4N_4 also present.

Reaction of Metal Phosphine Complexes with Trithiazyl Trichloride.—In a typical reaction the metal phosphine complex (0.1 mmol) was dissolved in thf or CH_2Cl_2 (5 cm^3), and to this was added 'monomeric' NSCl·thf adduct (0.1 or 1.0 mmol) as a solution in thf (*ca.* 5 cm^3). The resulting mixture was stirred

Table 4. Fractional atomic co-ordinates ($\times 10^4$) for $[Ph_3PNH_2]Cl{\cdot}CH_2Cl_2$

Atom	*x*	*y*	*z*
P(1)	6 844(1)	2 574(1)	2 602(1)
N(1)	6 269(5)	1 657(4)	4 079(4)
C(11)	8 731(4)	2 828(4)	2 306(4)
C(12)	9 262(5)	1 848(5)	2 487(5)
C(13)	10 719(6)	2 052(5)	2 274(6)
C(14)	11 606(6)	3 200(5)	1 879(6)
C(15)	11 079(5)	4 169(5)	1 714(7)
C(16)	9 629(5)	3 987(4)	1 925(6)
C(21)	6 558(4)	3 999(4)	2 911(5)
C(22)	6 857(5)	4 472(4)	4 261(5)
C(23)	6 747(6)	5 624(5)	4 475(6)
C(24)	6 331(5)	6 280(4)	3 366(6)
C(25)	6 030(7)	5 808(5)	2 030(7)
C(26)	6 141(6)	4 674(4)	1 794(6)
C(31)	5 989(4)	2 047(3)	956(4)
C(32)	4 529(5)	1 488(4)	1 062(5)
C(33)	3 831(5)	1 088(5)	−180(6)
C(34)	4 580(6)	1 235(5)	−1 516(6)
C(35)	6 019(7)	1 782(5)	−1 639(6)
C(36)	6 744(5)	2 195(4)	−402(5)
C(1)	9 922(7)	1 683(6)	6 566(7)
Cl(1)	9 586(2)	3 087(2)	6 276(2)
Cl(2)	10 159(2)	1 354(2)	8 436(2)
Cl(3)	7 134(1)	−758(1)	5 122(1)
H(1)	6 617(50)	1 045(44)	4 264(52)
H(2)	5 489(48)	1 542(40)	4 314(47)
H(3)	9 114(72)	1 081(62)	6 206(73)
H(4)	10 750(59)	1 809(49)	6 070(58)

for *ca.* 1 h. In the case of reactions involving $[RuCl_2(PPh_3)_3]$, as the metal phosphine complex, treatment of the reaction mixtures with methanol precipitated shiny brown crystals of cis-*trichloro*(*thionitrosyl*)*bis*(*triphenylphosphine*)*ruthenium.* ^{31}P N.m.r. δ 13.3 p.p.m. ν(NS) = 1 316, ν(RuCl) = 334, 304 cm^{-1}.

In the reactions involving rhodium starting materials the reaction mixture was evaporated to dryness and then extracted into benzene. $^{31}P\text{-}\{^1H\}$ N.m.r. spectra were then recorded for samples of these benzene solutions.

The sample of $[Ph_3PNH_2]Cl{\cdot}CH_2Cl_2$ for crystallography was obtained by treatment of $[RuCl_2(PPh_3)_3]$ (1.9 g, 2 mmol) in CH_2Cl_2 (50 cm^3) with a solution of $(NSCl)_3$ (1.5 g, 6 mmol) in thf (25 cm^3). After stirring overnight the solution was reduced to dryness and the solid residue washed with diethyl ether (50 cm^3) and extracted into ethanol (50 cm^3). The ethanol was removed *in vacuo* and the solid recrystallised from CH_2Cl_2–light petroleum to give $[Ph_3PNH_2]Cl{\cdot}CH_2Cl_2$ (0.28 g) (Found: C, 56.9; H, 4.80; N, 3.75. Calc. for $C_{19}H_{19}Cl_3NP$: C, 57.2; H, 4.75; N, 3.50%).

Crystal Data.—$[C_{18}H_{17}NP]^+Cl^-{\cdot}CH_2Cl_2$, $M = 398.5$, triclinic, $a = 9.884(4)$, $b = 11.526(2)$, $c = 9.061(1)$ Å, $\alpha = 86.04(1)$, $\beta = 87.63(3)$, $\gamma = 107.72(3)°$, $U = 978.8$ Å^3, space group $P1$, $Z = 2$, $D_c = 1.35$ g cm^{-3}, $F(000) = 412$, $\lambda = 0.710\,69$ Å, $\mu(\text{Mo-}K_\alpha) = 5.03$ cm^{-1}.

Data Collection.—Unit-cell parameters were determined and intensity data collected at room temperature on an Enraf-Nonius CAD4 diffractometer using graphite-monochromated Mo-K_α radiation and an ω–2θ scan procedure.[22] 3 575 Data ($1.5 \leqslant \theta \leqslant 25°$) were measured of which 3 437 were unique and 2 195 considered observed [$I \geqslant 1.5\sigma(I)$]. Three intensity controls measured every hour during data collection each showed a non-uniform reduction in diffracted intensity which reached 25% by the end of collection. A biphasic linear fade correction was applied to the observed data. In addition to Lorentz and polarisation corrections a semi-empirical absorption correction using normalised and averaged ψ-scan measurements[23] from three reflections was applied to the data; the maximum and minimum transmission factors were 99.9 and 90.9%, respectively.

Structure Solution and Refinement.—The structure was solved using direct methods (SHELXS 84 Program for Crystal Structure Solution). Following refinement of all non-hydrogen atoms with anisotropic thermal parameters, difference-Fourier maps revealed the location of all hydrogen atoms, including those on the dichloromethane solvent present in the crystal lattice. These were refined with individual isotropic thermal parameters and without any geometric constraints. Scattering factors for neutral atoms were used for all atoms except the chloride anion Cl(3).[24] The final full-matrix least-squares refinement, using a unit weighting scheme, gave $R = \Sigma|\Delta F|/\Sigma|F_o| = 0.042$ and $R' = (\Sigma|\Delta F|^2/\Sigma|F_o|^2)^{\frac{1}{2}} = 0.045$.

All computations were made using SHELX 76[25] on a DEC VAX-11/750 computer. Selected final bond lengths and angles are given in Table 3 and fractional atomic co-ordinates, except phenyl hydrogens, in Table 4.

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References

1 B. W. S. Kolthammer and P. Legzdins, *J. Am. Chem. Soc.*, 1978, **100**, 2247.

2 K. K. Pandey and U. C. Agarwala, *Z. Anorg. Allg. Chem.*, 1980, **461**, 231.

3 K. K. Pandey, S. Datta, and U. C. Agarwala, *Z. Anorg. Allg. Chem.*, 1980, **468**, 228.

4 K. K. Pandey and U. C. Agarwala, *Inorg. Chem.*, 1981, **20**, 1309.

5 K. K. Pandey, U. C. Agarwala, and K. C. Jain, *Inorg. Chim. Acta*, 1981, **48**, 23.

6 H. W. Roesky and K. K. Pandey, *Adv. Inorg. Chem. Radiochem.*, 1983, **26**, 337.

7 H. W. Roesky, K. K. Pandey, W. Clegg, M. Noltemeyer, and G. M. Sheldrick, *J. Chem. Soc., Dalton Trans.*, 1984, 719.

8 M. W. Bishop, J. Chatt, and J. R. Dilworth, *J. Chem. Soc., Dalton Trans.*, 1979, 1.

9 R. Appel, R. Kleinstuck, K. D. Ziehn, and F. Knoll, *Chem. Ber.*, 1970, **103**, 3631.

10 L. C. Thomas, 'Interpretation of the Infrared Spectra of Organophosphorous Compounds,' Heyden, London, 1974.

11 L. Vallarino, *J. Inorg. Nucl. Chem.*, 1958, **8**, 288.

12 T. J. Greenough, B. W. S. Kolthammer, P. Legzdins, and J. Trotter, *Inorg. Chem.*, 1979, **18**, 3548.

13 T. Behling and G. Wilkinson, personal communication.

14 W. R. Roper (University of Auckland), personal communication.

15 K. N. Udupa, K. C. Jain, M. I. Khan, and U. C. Agarwala, *Inorg. Chim. Acta*, 1983, **74**, 191.

16 W. L. Jolly and K. D. Maguire, *Inorg. Synth.*, 1967, **9**, 107.

17 T. A. Stephenson and G. Wilkinson, *J. Inorg. Nucl. Chem.*, 1966, **28**, 945.

18 J. A. Osborn, F. H. Jardine, J. F. Young, and G. Wilkinson, *J. Chem. Soc. A*, 1966, 1711.
19 N. Ahmad, J. J. Levison, S. D. Robinson, and M. F. Uttley, *Inorg. Synth.*, 1974, **15**, 61.
20 D. Evans, J. Osborn, and G. Wilkinson, *Inorg. Synth.*, 1968, **11**, 99.
21 R. Appel and A. Hans, *Chem. Ber.*, 1960, **93**, 405.
22 M. B. Hursthouse, R. A. Jones, K. M. A. Malik, and G. Wilkinson, *J. Am. Chem. Soc.*, 1979, **101**, 4128.
23 A. C. T. North, D. C. Phillips, and F. S. Mathews, *Acta Crystallogr., Sect. A*, 1968, **24**, 351.
24 'International Tables for *X*-Ray Crystallography,' Kynoch Press, Birmingham, 1976, vol. 4, pp. 99—101.
25 G. M. Sheldrick, SHELX 76 Program for Crystal Structure Determination, University of Cambridge, 1976.

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