# Further Investigations on the Reactivity of Rhenium Arylimido-complexes and the Deoxygenation Reaction of RNO in [$ReCl_3$(RNO)($OPPh_3$)] †

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By treating [$ReCl_3(NR)(PPh_3)_2$] (R = $C_6H_4Me$-*p*) (1) with elemental sulphur, [$\{ReCl_3(NR)(PPh_3)\}_n$] (2) (*n* probably two) is formed, one phosphine being removed as S=$PPh_3$. By the action of $PPh_3$, complex (2) can easily be converted into (1). Compound (2) proved to be more reactive than (1). The reaction with dioxygen, leading to [$ReCl_3(RNO)(OPPh_3)$] (3), requires milder conditions when (2) is used instead of (1) and was shown to occur even with such a mild oxidant as $MeC_6H_4NO_2$-*p*. As a by-product of the reaction with dioxygen, the paramagnetic [$ReCl_4(NR)(OPPh_3)$] (4) was formed; compound (4) is the main product when the reaction of (2) with $O_2$ is carried out in $CCl_4$. The reactions of (2) with neutral ligands such as CO, $CNC_6H_{11}$, $OCNC_6H_{11}$, and $NH_2(C_6H_{11})$ have been studied, the complexes [$ReCl_3(NR)(PPh_3)(CO)$] (5), [$ReCl_3(NR)(PPh_3)(CNC_6H_{11})$] (6), [$ReCl_3(NR)(PPh_3)\{NH_2(C_6H_{11})\}$] (7), and [$\{ReCl_2(NR)[NH_2(C_6H_{11})][NH(C_6H_{11})]\}_2$] (8) being obtained respectively. The arylnitroso-ligand of complex (3) can be deoxygenated by reaction with tertiary phosphines $PR'_2Ph$ (R' = Ph or Et) leading to [$ReCl_3(NR)(PR'_2Ph)_2$] with concomitant displacement of $OPPh_3$ and $OPR'_2Ph$, or with $CNC_6H_{11}$ leading to [$ReCl_3(NR)(CNC_6H_{11})_2$] (9) and [$\{ReCl_3(NR)(CNC_6H_{11})\}_2O$] (10), the fate of $CNC_6H_{11}$ being unclear.

ALTHOUGH rhenium imido-complexes have been known for a long time,[1] few studies have been devoted to the reactivity of these and other transition-metal imido-derivatives.[2,3] We have recently reported on a new method for the synthesis of the known compounds [$ReCl_3(NR)(PPh_3)_2$] *via* the reaction of sulphinyl amines, RNSO, with [$ReCl_3(O)(PPh_3)_2$] and on some reactions of these derivatives,[4] particularly the reaction with molecular oxygen which allowed the isolation of the arylnitroso-complexes [$ReCl_3(RNO)(OPPh_3)$]. As a continuation of these studies, we report here the reaction of [$ReCl_3(NR)(PPh_3)_2$] (R = $C_6H_4Me$-*p*) (1) with elemental sulphur, which gives rise to [$\{ReCl_3(NR)(PPh_3)\}_n$] (2). The reactivity of (2) has been extensively investigated and compared with that of (1). We also report here the ready reaction of oxygen transfer from the arylnitroso-ligand in [$ReCl_3(RNO)(OPPh_3)$] to tertiary phosphines and cyclohexyl isocyanide, producing arylimido-rhenium complexes.

## RESULTS AND DISCUSSION

*Synthesis of* [$\{ReCl_3(NR)(PPh_3)\}_n$] (2).—By treating [$ReCl_3(NR)(PPh_3)_2$] (R = $C_6H_4Me$-*p*) (1)[4] with elemental sulphur at 80 °C a mustard-yellow diamagnetic complex analysing as [$\{ReCl_3(NR)(PPh_3)\}_n$] (2), insoluble in the reaction medium, was obtained (Table) [equation (i)]. Strangely enough, the same reaction

$$n[\mathrm{ReCl_3(NR)(PPh_3)_2}] \underset{\mathrm{PPh_3}\ (ii)}{\overset{\text{Sulphur } (i)}{\rightleftharpoons}} [\{\mathrm{ReCl_3(NR)(PPh_3)}\}_n] + n\ \mathrm{S{=}PPh_3} \qquad \text{(i)}$$

(*i*) toluene, cyclohexane, or carbon tetrachloride at 80 °C; (*ii*) benzene at 50 °C

conducted on the arylimido-complexes having R = $C_6H_5$ or $C_6H_4OMe$-*p* did not allow the isolation of any characterizable product.

The presence of triphenylphosphine sulphide was detected in the mother-liquor of reaction (1). When the same reaction was carried out in refluxing benzene, the same complex but with one mole of benzene per mole of rhenium was obtained. Compound (2) was shown to react readily with $PPh_3$, regenerating (1), no other species being formed in this reaction. The new imido-complex (2), which did not contain sulphur or oxygen, was too insoluble in solvents such as chloroform or benzene for a molecular weight determination. However, compound (2) was soluble in dimethyl sulphoxide but the molecular weight (32) found was meaningless.

In its i.r. spectrum compound (2) shows medium-strong bands at 1 340 and 1 160 cm$^{-1}$; the same bands are also present in the parent compound (1) but they are very weak (Table). Moreover, the i.r. spectra of (1) and (2) at low frequencies (200—600 cm$^{-1}$) are very similar. On the basis of these data, the hypothesis of bridging arylimido-ligands instead of chlorines in complex (2) cannot be excluded.

*Reactivity of* (2).—Compound (2) proved to be more reactive than (1). It reacts with dioxygen in benzene

$$\left.\begin{array}{l} [\mathrm{ReCl_3(NR)(PPh_3)_2}] \xrightarrow[\text{Reflux}]{\mathrm{O_2},\ \text{toluene}} \\ \qquad (1) \\[1em] [\{\mathrm{ReCl_3(NR)(PPh_3)}\}_n] \xrightarrow[\text{Reflux}]{\mathrm{O_2},\ \text{benzene or } \mathrm{CCl_4}} \\ \qquad (2) \end{array}\right| \longrightarrow$$

$$\begin{array}{c} [\mathrm{ReCl_3(RNO)(OPPh_3)}] + \\ (3) \\ [\mathrm{ReCl_4(NR)(OPPh_3)}] + \\ (4) \\ \mathrm{OPPh_3} + \text{by-products} \quad \text{(ii)} \end{array}$$

at 80 °C leading to the already reported [$ReCl_3(RNO)(OPPh_3)$] as the main product, while a higher temperature is required when (1) is used as the starting material[4] [equation (ii)]. In both cases another rhenium complex

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† First presented at the 19th International Conference on Co-ordination Chemistry, Prague, 1978.

Analytical and i.r. data

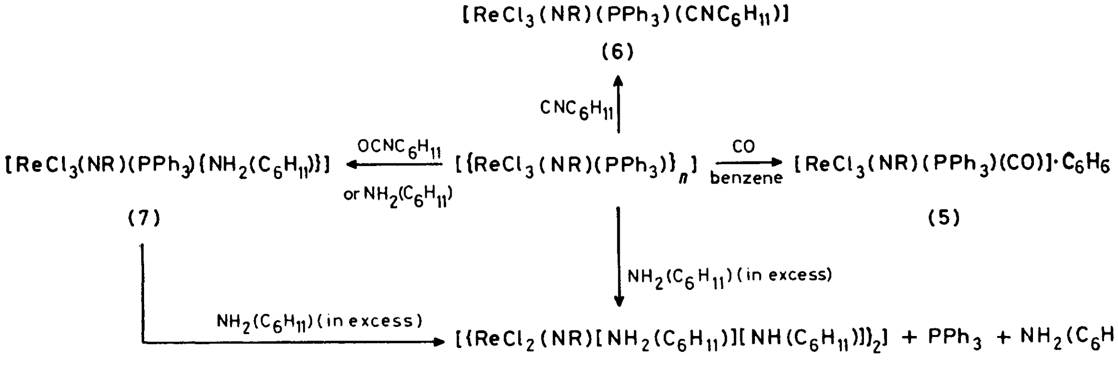
| | Compound [a] | Colour | M.p. ($\theta_c$/°C) | Analyses (%) [b] C | H | N | O | Cl | Significant absorptions [c] |
|---|---|---|---|---|---|---|---|---|---|
| (2) | $[\{ReCl_3(NR)(PPh_3)\}_n]$ [d] | Mustard-yellow | 170 | 45.7<br>(45.4) | 3.4<br>(3.3) | 2.1<br>(2.1) | | | 1 340, 1 160 |
| (4) | $[ReCl_4(NR)(OPPh_3)]$ | Brownish | 225 | 42.4<br>(42.2) | 3.2<br>(3.1) | 1.9<br>(2.0) | 2.4<br>(2.2) | 19.7<br>(19.9) | 1 120, 1 070, 720 ($OPPh_3$) |
| (5) | $[ReCl_3(NR)(PPh_3)(CO)]\cdot C_6H_6$ | Green | 176 | 49.8<br>(50.1) | 3.8<br>(3.7) | 1.8<br>(1.8) | 2.0<br>(2.0) | | $\nu(CO) = 2\,040$ |
| (6) | $[ReCl_3(NR)(PPh_3)(CNC_6H_{11})]$ | Light green | 205 | 49.6<br>(49.9) | 4.3<br>(4.3) | 3.6<br>(3.6) | | | $\nu(NC) = 2\,200$ |
| (7) | $[ReCl_3(NR)(PPh_3)\{NH_2(C_6H_{11})\}]$ | Light green | 197 | 49.2<br>(49.0) | 4.7<br>(4.6) | 3.8<br>(3.7) | | | $\nu(NH_2) = 3\,290, 3\,230$ |
| (8) | $[\{ReCl_2(NR)[NH_2(C_6H_{11})][NH(C_6H_{11})]\}_2]$ [e] | Green | 224 | 41.2<br>(40.8) | 5.9<br>(5.7) | 7.4<br>(7.5) | | 13.2<br>(12.7) | $\nu(NH_2) = 3\,220, 3\,180$;<br>$\nu(NH) = 3\,110$ |
| (8a) | $[\{ReCl_2(NPh)[NH_2(C_6H_{11})]-[NH(C_6H_{11})]\}_2]$ [f] | Green | 206 | 40.4<br>(39.6) | 5.4<br>(5.5) | 7.6<br>(7.7) | | | $\nu(NH_2) = 3\,230, 3\,200$;<br>$\nu(NH) = 3\,120$ |
| (9) | $[ReCl_3(NR)(CNC_6H_{11})_2]$ | Green | 238 | 40.0<br>(40.9) | 4.7<br>(4.7) | 6.7<br>(6.8) | | | $\nu(NC) = 2\,220, 2\,200$ |
| (10) | $[\{ReCl_3(NR)(CNC_6H_{11})\}_2O]$ | Deep violet | 194 | 33.2<br>(32.7) | 3.4<br>(3.3) | 5.4<br>(5.4) | 1.6<br>(1.6) | 19.8<br>(20.7) | $\nu(NC) = 2\,245$ |
| (11) | $[ReCl_3(NR')(PEtPh_2)_2]$ [g] | Green | 195 | 50.0<br>(49.9) | 4.5<br>(4.4) | 1.6<br>(1.7) | | | |

[a] R = $C_6H_4Me$-*p*. [b] Calculated values are given in parentheses. [c] Measured in $cm^{-1}$ (Nujol). [d] When obtained in refluxing benzene, $[\{ReCl_3(NR)(PPh_3)\cdot C_6H_6\}_n]$ is formed: C, 49.8 (50.4); H, 3.7 (3.8); Cl, 14.8 (14.4); N, 1.9 (1.9%). [e] *M* ($CHCl_3$), 1 088 (1 118). [f] *M* ($CHCl_3$), 1 061 (1 090). [g] R' = $C_6H_4OMe$-*p*.

is formed; this has been characterized as $[ReCl_4(NR)(OPPh_3)]$ (4) (Table). Complex (3) can also be obtained in a one-step synthesis from $[ReCl_3(O)(PPh_3)(SMe_2O)]$,[5] according to equation (iii).

$$[ReCl_3(O)(PPh_3)(SMe_2O)] + RNSO \xrightarrow[\text{benzene}/O_2]{\text{Reflux}} \underset{(3)}{[ReCl_3(RNO)(OPPh_3)]} + SO_2 + SMe_2O \qquad \text{(iii)}$$

The oxidation of (2) to (3) can also be carried out at 80—90 °C by using $MeC_6H_4NO_2$-*p* as the oxidant; in this case (3) is the only rhenium-containing characterizable product, while the nitrotoluene is converted into *para*-toluidine. It is noteworthy that the oxidation reaction with the nitrotoluene does not proceed when (1) is used. Moreover, both (1) and (2) do not react at all with dioxygen when an excess of free triphenylphosphine is present in the reaction medium. Compound (4) was shown to be the main product when the reaction between (2) and dioxygen is carried out in refluxing $CCl_4$. Furthermore, (4) is also slowly formed when a chloroform suspension of (2) is left in the presence of dioxygen at room temperature for a long time (5 d). This derivative, which is a non-electrolyte in nitrobenzene, showed a magnetic moment of 1.61 B.M.* (determined by the Evans method), a value in agreement with its formulation as a rhenium(VI) arylimido-complex. It is noteworthy that complexes of formula $[ReCl_4(O)L]$ (L = $H_2O$, $CH_3CN$, or $PCl_3O$) are known, and their magnetic moments are close to that found for (4).[6] Compound (2) reacts with neutral ligands in refluxing benzene, according to Scheme 1. The reaction with carbon monoxide leading to (5) [$\nu(CO) = 2\,040\ cm^{-1}$] proceeds at atmospheric pressure; this carbonyl derivative is analogous to the complex obtained from $[ReCl_3(NR')(PPh_3)_2]$ (R' = $C_6H_4OMe$-*p*) operating with a CO pressure of 50 atm and at a temperature of 100 °C.[4] Compound (5) is always recovered with one mole of solvent of crystallisation (benzene or toluene). In the latter case



(8)

SCHEME 1

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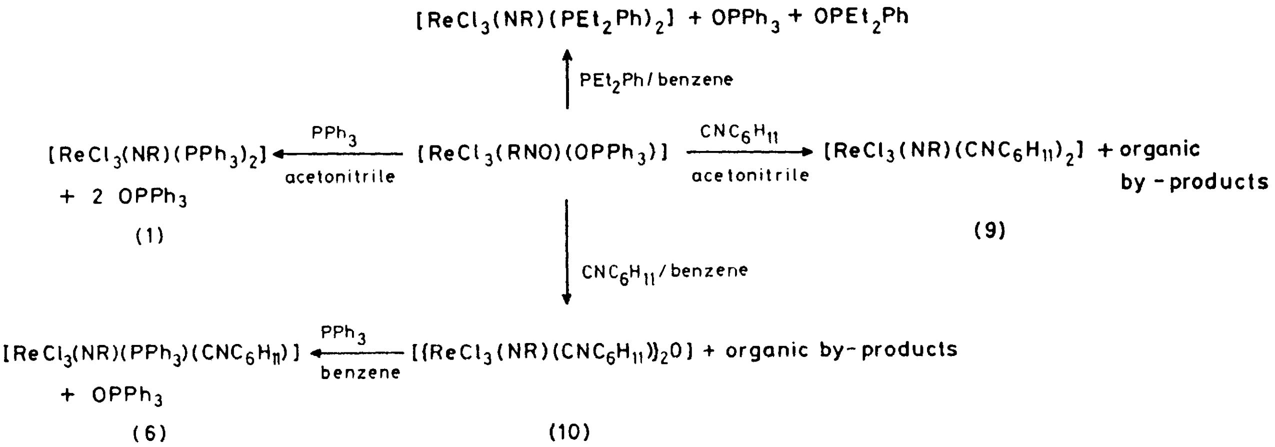
* Throughout this paper: 1 B.M. = $9.274 \times 10^{-24}$ A $m^2$; 1 atm = 101 325 Pa.

the $^1$H n.m.r. spectrum of (5) showed two signals at τ 7.7 and 7.8 in a 1 : 1 ratio, due to the methyl groups of the arylimido-ligand and of the toluene. For this type of product, we have already excluded the alternative formulation as an isocyanate complex, $[ReCl_3(OCNR)(PPh_3)]$.[4] Similarly, (2) reacts with $CNC_6H_{11}$ giving (6), $[ReCl_3(NR)(PPh_3)(CNC_6H_{11})]$ [$\nu(NC) = 2\,200$ cm$^{-1}$]. This compound, together with other isocyanide complexes which will be described later, are among the few examples of isocyanide complexes of rhenium(v) and the observed ν(NC) supports the high oxidation state of the metal.[7]

When (2) was treated with a stoicheiometric amount of $NH_2(C_6H_{11})$, a 1 : 1 adduct with this ligand, (7), was obtained [$\nu(NH_2) = 3\,290, 3\,230$ cm$^{-1}$]; however, by this route compound (7) was always recovered contaminated by another complex. The other complex was shown to be $[\{ReCl_2(NR)[NH_2(C_6H_{11})][NH(C_6H_{11})]\}_2]$ (8), which is the only product together with $NH_2(C_6H_{11})\cdot HCl$ and $PPh_3$ formed when (2) was treated with cyclohexylamine in a ratio Re : $NH_2(C_6H_{11})$ of 1 : 3. The impure (7) was entirely transformed into (8) by reaction with 2 mol $NH_2(C_6H_{11})$. Similarly, $[\{ReCl_2(NPh)[NH_2(C_6H_{11})][NH(C_6H_{11})]\}_2]$ (8a) was obtained by treating $[ReCl_3(NPh)(NH_2Ph)(PPh_3)]$ [4] with 3 mol $NH_2(C_6H_{11})$. When a large excess of $NH_2(C_6H_{11})$ was used in these reactions, no characterizable rhenium compounds were isolated. For both (8) and (8a), the proposed dimeric formulations are supported by molecular weight determinations in chloroform solution (Table). Compound (7) can be obtained pure by treating (2) with $OCNC_6H_{11}$. Since cyclohexyl isocyanate alone was shown to be insensitive to moisture under the reaction conditions, the formation of (7) from $OCNC_6H_{11}$ is probably assisted by initial co-ordination of the isocyanate to the metal. Compound (7) was also obtained by reaction of $[ReCl_3(NR)(PPh_3)_2]$ (1) with $OCNC_6H_{11}$. In the latter case the mother-liquor was shown to contain the biuret $[OCNH(C_6H_{11})]_2NC_6H_{11}$. The formation of this organic product is ascribed to the presence of free triphenylphosphine, displaced from complex (1). The action of triphenylphosphine in order to obtain biuret has been confirmed by reacting $OCNC_6H_{11}$ in wet benzene with a catalytic amount of $PPh_3$; the catalytic activity of phosphines on various reactions involving organic isocyanates is well documented in the literature.[8] Compounds (8) and (8a) represent remarkable examples of complexes containing three different types of ligands having nitrogen as the donor atom: the amine, the amido-, and the arylimido-ligands.



Scheme 2

*Reactivity of* $[ReCl_3(RNO)(OPPh_3)]$ (R = $C_6H_4Me$-*p*) (3).—The arylnitroso-ligand, RNO, of compound (3) can easily be deoxygenated by transferring the oxygen to a reducing agent such as tertiary phosphine, $PR_3$, or cyclohexyl isocyanide (Scheme 2). When $PPh_3$ is used, the starting arylimido-complex (1) is obtained, while $PEt_2Ph$ gives the known compound $[ReCl_3(NR)(PEt_2Ph)_2]$.[9] The reaction with triphenylphosphine requires acetonitrile as solvent, while with the more basic $PEt_2Ph$ the deoxygenation reaction takes place even in benzene. This reaction has been extended to the arylnitroso-complex $[ReCl_3(MeOC_6H_4NO$-*p*$)(OPPh_3)]$ [4] which gave $[ReCl_3(NC_6H_4OMe$-*p*$)(PEtPh_2)_2]$ on treatment with $PEtPh_2$.

Strangely enough the arylimido-complexes having mixed alkyl and aryl phosphines as ligands do not react with dioxygen even in refluxing toluene and they are recovered unchanged.

Acetonitrile also plays an important role in the reaction of (3) with cyclohexyl isocyanide; in fact when $CH_3CN$ is used as the reaction medium, $[ReCl_3(NR)(CNC_6H_{11})_2]$ (9) [$\nu(NC) = 2\,220, 2\,200$ cm$^{-1}$] is formed. While carrying out this reaction in benzene, a deep violet insoluble complex was obtained. Repeated elemental analyses, including oxygen, indicate the stoicheiometry $[ReCl_3(NR)(CNC_6H_{11})O_{0.5}]$. Thus a formulation of this complex as a μ-oxo-rhenium(vi) derivative, $[\{ReCl_3(NR)(CNC_6H_{11})\}_2O]$ (10), seems reasonable. Compound (10), which shows ν(NC) at 2 245 cm$^{-1}$, is diamagnetic in the solid state, as has already been observed in μ-oxo $[(ReOCl_4)_2O]^{2-}$.[10] Several bands are present in the 600—800 cm$^{-1}$ region, of which that at

650m cm$^{-1}$ could be associated with the Re–O–Re vibration.

In the reactions with $CNC_6H_{11}$ an organic product was always obtained, which showed in its i.r. spectrum two significant absorptions at 1 650 and 3 210 cm$^{-1}$, probably associated with the presence of C=O and NH groups. The nature of this organic compound has not been fully determined.

Finally, the oxo-bridged complex (10) can be converted into $[ReCl_3(NR)(PPh_3)(CNC_6H_{11})]$ (6) by reaction with triphenylphosphine, the latter being recovered as the corresponding oxide $OPPh_3$.

*Conclusions.*—The reaction of $[ReCl_3(NR)(PPh_3)_2]$ with elemental sulphur did not occur with attack of the arylimido-ligand leading to arylthionitroso-species, RNS, unstable in the free state. Sulphur caused only the removal of one phosphine as the corresponding sulphide $SPPh_3$. Similarly, as has been recently reported,[11] $[ReCl_2N(PR_3)_3]$ derivatives failed to react with elemental sulphur to give the thionitrosyl complexes $[ReCl_2(NS)(PR_3)_3]$, $S_2Cl_2$ being required in this case.

On the other hand, the deoxygenation of the RNO ligand by tertiary phosphines studied here parallels the sulphur abstraction reaction of the thionitrosyl ligand by the action of the same agents to give nitrido-complexes.[11]

An easy N–O bond cleavage of the co-ordinated PhNO in $[Ni(PhNO)(CNBu^t)_2]$ by $CNBu^t$ and $PPh_3$ has been observed.[12] In this case the phenylimido–nickel complex formed was not isolated, the PhN residue being involved in subsequent reactions. This may be related to the different types of bonding of the arylimido-ligand when attached to metals in high and low oxidation states. In the former case a formal triple bond is present,[1] while in the latter a bent doubly bonded arylimido-species is more likely.[13] Although in complex (3) the RNO ligand is bound to the rhenium *via* the nitrogen atom,[4] and not in a side-on $\eta^2$ fashion as in $[Ni(PhNO)(CNBu^t)_2]$,[12] the oxygen atom is nevertheless easily removed by some reducing agents. This is probably due to the marked stability of the rhenium arylimido-complexes generated by the deoxygenation reaction.

We are currently investigating the deoxygenation of the arylnitroso-ligand in various complexes of transition metals in a relatively high oxidation state, in order to verify if this reaction could represent a general route leading to arylimido-derivatives.

## EXPERIMENTAL

Arylimido-complexes, $[ReCl_3(NR)(PPh_3)_2]$ [R = $C_6H_4$-Me-*p* (1) or $C_6H_4OMe$-*p*], were prepared as reported.[4] Infrared spectra were obtained by using Beckmann IR-33 and IR-4210 instruments. Hydrogen-1 n.m.r. spectra were recorded on a Varian 60 spectrometer. Elemental analyses were carried out in the Analytical Laboratory of Milan University, except for oxygen analyses which were performed by Pascher's Analytical Laboratories (Bonn).

$[\{ReCl_3(NR)(PPh_3)\}_n]$ (R = $C_6H_4Me$-*p*) (2).—To a toluene suspension (20 cm$^3$) of $[ReCl_3(NR)(PPh_3)_2]$ (1) (0.1 g), elemental sulphur (0.022 g) was added and the mixture maintained at 80 °C for 3 h. After cooling, the insoluble mustard-yellow compound (2) was filtered off, washed several times with nitrogen-degassed toluene, and dried *in vacuo*. The mother-liquor, evaporated to dryness, gave a residue which was shown to contain $SPPh_3$, by comparison of its i.r. spectrum with that of an authentic sample. When the same reaction was carried out in benzene, complex (2) was recovered as $[\{ReCl_3(NR)(PPh_3)\cdot C_6H_6\}_n]$, m.p. 185 °C [Found: C, 49.8; H, 3.70; Cl, 14.75; N, 1.90. Calc. for $C_{31}H_{28}Cl_3NPRe$: C, 50.4; H, 3.8; Cl, 14.45; N, 1.9%).

Complex (2), free of solvent, was also obtained by carrying out the reaction in solvents such as cyclohexane and $CCl_4$.

1. *Reactivity of* (2).—(*a*) *With* $PPh_3$. To a benzene suspension (70 cm$^3$) of (2) (0.075 g) an excess of triphenylphosphine (0.082 g) was added and the mixture refluxed for 2 h. After cooling, the insoluble green arylimido-complex $[ReCl_3(NR)(PPh_3)_2]$ (1) was quantitatively recovered by filtration.

(*b*) *With* CO. Through a benzene suspension of (2), carbon monoxide was bubbled, while the temperature was maintained at 80 °C for 2 h. The insoluble green derivative, $[ReCl_3(NR)(PPh_3)(CO)]\cdot C_6H_6$ (5), was filtered off, washed with benzene, and dried *in vacuo*. From the mother-liquor a further quantity of (5) was recovered; no other by-products were detected.

When this reaction was carried out in toluene, $[ReCl_3(NR)(PPh_3)(CO)]\cdot C_7H_8$ was obtained, elemental analyses being consistent with its formulation. The $^1H$ n.m.r. spectrum confirmed the presence of toluene of crystallisation (see text).

(*c*) *With* $CNC_6H_{11}$. To a benzene suspension (15 cm$^3$) of (2) (0.160 g), cyclohexyl isocyanide (0.079 g) was added and the mixture refluxed for 1.5 h. The green solution was evaporated to dryness and the residue treated with diethyl ether. The light green compound, $[ReCl_3(NR)(PPh_3)(CNC_6H_{11})]$ (6), was filtered off, washed several times with diethyl ether, and dried *in vacuo*.

The compound $[ReCl_3(NR)(PPh_3)(CNC_6H_{11})]$ (6) can be also obtained by reacting $[ReCl_3(NR)(PPh_3)_2]$ (1) with an excess of $CNC_6H_{11}$ in refluxing benzene for 3 h.

(*d*) *With* $OCNC_6H_{11}$. To a benzene suspension (30 cm$^3$) of (2) (0.130 g), freshly distilled $OCNC_6H_{11}$ (0.17 g) was added and the mixture refluxed for 5 h. The light green solution was evaporated to dryness and the residue treated with diethyl ether. The insoluble pale green complex, $[ReCl_3(NR)(PPh_3)\{NH_2(C_6H_{11})\}]$ (7), was filtered off, washed with ethanol, and dried *in vacuo*.

Compound (7) can be also obtained by treating (2) with an equimolar amount of $NH_2(C_6H_{11})$ in refluxing benzene for 2 h. But in this case compound (7) was always recovered contaminated by another rhenium-containing complex [see compound (8)].

(*e*) *With* $NH_2(C_6H_{11})$. To a benzene suspension (30 cm$^3$) of (2) (0.31 g), cyclohexylamine [0.058 g, ratio (2) : $NH_2(C_6H_{11})$ = 1 : 3.5] was added and the mixture refluxed for 3 h. After cooling, a white insoluble material, identified as $NH_2(C_6H_{11})\cdot HCl$, was filtered off and the green solution was evaporated to dryness. The residue, washed with ethanol, gave the product $[\{ReCl_2(NR)[NH_2(C_6H_{11})][NH(C_6H_{11})]\}_2]$ (8). In the ethanol washing free triphenylphosphine was shown to be present. When the mixture of (7) and (8) obtained as described above was treated with more $NH_2(C_6H_{11})$, compound (8) in an analytically pure form was obtained, while $NH_2(C_6H_{11})\cdot HCl$ and $PPh_3$ were again shown to be the only other reaction products.

(*f*) *With* $O_2$. Through a benzene suspension of (2), maintained at 80 °C, dioxygen was bubbled for 1.5 h. After cooling, the violet arylnitroso-complex, $[ReCl_3(RNO)(OPPh_3)]$ (3),[4] was obtained as the insoluble product. The mother-liquor was evaporated to dryness and the residue treated with ethanol, the insoluble light brown complex $[ReCl_4(NR)(OPPh_3)]$ (4) being recovered. This was shown to be paramagnetic in $CHCl_3$ solution ($\mu_{eff.} = 1.61$ B.M., determined by the Evans method). In the ethanol filtrate, $OPPh_3$ was present together with unidentified rhenium-containing by-products.

When the reaction with dioxygen was carried out in refluxing $CCl_4$ for 6 h, (4) was the only characterizable complex. It is also the by-product when the reaction with dioxygen is carried out using $[ReCl_3(NR)(PPh_3)_2]$ (1).[4]

(*g*) *With* $MeC_6H_4NO_2$-*p*. To a toluene suspension (75 cm$^3$) of (2) (0.120 g), an excess of *para*-nitrotoluene was added and the mixture maintained at 90 °C for 5 h. On cooling, a violet insoluble compound precipitated. It was filtered off, washed with ethanol, and dried *in vacuo*. Its i.r. spectrum was identical to that of $[ReCl_3(RNO)(OPPh_3)]$ (3).[4] In the mother-liquor the presence of $OPPh_3$, $MeC_6H_4$-$NH_2$-*p*, and the excess of $MeC_6H_4NO_2$-*p* was confirmed by i.r. spectroscopy and thin-layer chromatography.

2. *Reactivity of* $[ReCl_3(RNO)(OPPh_3)]$ ($R = C_6H_4Me$-*p*) (3).—(*a*) *With* $PPh_3$. To an acetonitrile suspension (30 cm$^3$) of (3) (0.25 g), triphenylphosphine [0.29 g, molar ratio $PPh_3$ : (3) = 3 : 1] was added and the mixture refluxed for 5 h. On cooling, a green product precipitated which was filtered off, washed with benzene, and dried *in vacuo*. This was shown to be $[ReCl_3(NR)(PPh_3)_2]$ (1) by elemental analyses and by its i.r. spectrum. In the mother-liquor the presence of $OPPh_3$ was confirmed.

(*b*) *With* $PEt_2Ph$. This reaction has been carried out in refluxing benzene. The already reported $[ReCl_3(NR)(PEt_2Ph)_2]$ [9] was obtained, together with $OPPh_3$ and $OPEt_2Ph$.

(*c*) *With* $CNC_6H_{11}$. To a benzene suspension (20 cm$^3$) of (3) (0.06 g), an excess of $CNC_6H_{11}$ (0.08 g) was added and the mixture refluxed for 3 h. The deep violet insoluble product $[\{ReCl_3(NR)(CNC_6H_{11})\}_2O]$ (10) was filtered off, washed with benzene and $CH_2Cl_2$, and dried *in vacuo*. The mother-liquor was evaporated to dryness and the resulting mixture was separated by column chromatography (20-cm column of silica gel). By using benzene as eluant, the excess cyclohexyl isocyanide was recovered; subsequent elution with $OEt_2$ gave an organic product not yet fully identified (see text). By eluting with $CH_2Cl_2$ a green solution was obtained. This was evaporated to dryness and the residue treated with ethanol; compound (9), $[ReCl_3(NR)(CNC_6H_{11})_2]$, being recovered in small amounts as a green insoluble product.

When the reaction of (3) with $CNC_6H_{11}$ was carried out using $CH_3CN$ as solvent at 80 °C for 2.5 h, complex (9) was the only characterizable rhenium-containing product. The reaction mixture was separated by column chromatography as described above.

3. *Reaction of* $[\{ReCl_3(NR)(CNC_6H_{11})\}_2O]$ (10) *with* $PPh_3$.—To a benzene suspension (15 cm$^3$) of (10) (0.03 g) an excess of $PPh_3$ was added and the mixture refluxed for 2 h. The resulting green solution was evaporated to dryness and the residue treated with diethyl ether and with ethanol. The light green complex $[ReCl_3(NR)(PPh_3)(CNC_6H_{11})]$ (6) was thus obtained. The mother-liquor was shown to contain $OPPh_3$.

4. *Reaction of* $[ReCl_3(NR)(PPh_3)_2]$ (1) *with* $OCNC_6H_{11}$.—To a benzene suspension (20 cm$^3$) of (1) (0.120 g), freshly distilled $OCNC_6H_{11}$ (0.21 g) was added and the mixture refluxed for 2 h. After cooling, a white compound precipitated from the green solution. It was collected by filtration, washed with benzene, and dried *in vacuo*. This material was recognised as the biuret $[OCNH(C_6H_{11})]_2$-$NC_6H_{11}$ by elemental analysis and by comparison of its i.r. spectrum with that of an authentic sample obtained by two routes: (*a*) by reacting $OCNC_6H_{11}$ with cyclohexylurea, $C_6H_{11}NHCONHC_6H_{11}$, in refluxing benzene for 1 h and (*b*) by refluxing a mixture of $OCNC_6H_{11}$ and $PPh_3$ in wet benzene. The green solution obtained above was evaporated to dryness and the residue treated with diethyl ether giving a green product whose i.r. spectrum was identical to that of $[ReCl_3(NR)(PPh_3)\{NH_2(C_6H_{11})\}]$ (7), obtained from (2) with $OCNC_6H_{11}$ [see 1(*d*)].

$[\{ReCl_2(NPh)[NH_2(C_6H_{11})][NH(C_6H_{11})]\}_2]$ (8a).—This complex was obtained by treating a benzene solution (30 cm$^3$) of $[ReCl_3(NPh)(NH_2Ph)(PPh_3)]$ [4] (0.065 g) with cyclohexylamine [mol ratio $Re : NH_2(C_6H_{11}) = 1 : 3.2$]. The work-up of the reaction was identical to that described in 1(*e*).

$[ReCl_3(NC_6H_4OMe$-*p*$)(PEtPh_2)_2]$ (11).—This arylimido-complex has been obtained by the deoxygenation reaction of $[ReCl_3(MeOC_6H_4NO$-*p*$)(OPPh_3)]$ [4] with $PEtPh_2$ as described in 2(*b*).

We thank Dr. P. Giannoccaro (University of Bari) for magnetic susceptibility measurements in the solid state.

[9/1094 *Received, 13th July,* 1979]

REFERENCES

[1] J. Chatt and G. A. Rowe, *J. Chem. Soc.*, 1962, 4019.

[2] J. Chatt, R. J. Dosser, F. King, and G. J. Leigh, *J.C.S. Dalton*, 1976, 2435.

[3] A. O. Chong, K. Oshima, and K. B. Sharpless, *J. Amer. Chem. Soc.*, 1977, **99**, 3420.

[4] G. La Monica and S. Cenini, *Inorg. Chim. Acta*, 1978, **29**, 183.

[5] D. E. Grove and G. Wilkinson, *J. Chem. Soc.* (*A*), 1966, 1224.

[6] A. Guest and C. J. L. Lock, *Canad. J. Chem.*, 1971, **49**, 603; D. A. Edwards and R. T. Ward, *J.C.S. Dalton*, 1972, 89.

[7] L. Malatesta and F. Bonati, 'Isonitrile Complexes of Metals,' Wiley, New York, 1969.

[8] R. G. Arnold, J. A. Nelson, and J. J. Verbanc, *Chem. Rev.*, 1957, **57**, 47.

[9] J. Chatt, J. D. Garforth, N. P. Johnson, and G. A. Rowe, *J. Chem. Soc.*, 1964, 1012.

[10] B. J. Brisdon and D. A. Edwards, *Inorg. Chem.*, 1968, **7**, 1898.

[11] M. W. Bishop, J. Chatt, and J. R. Dilworth, *J.C.S. Dalton*, 1979, 1.

[12] S. Otsuka, Y. Aotani, Y. Tatsuno, and T. Yoshida, *Inorg. Chem.*, 1976, **15**, 656.

[13] S. Cenini and G. La Monica, *Inorg. Chim. Acta Rev.*, 1976, **18**, 279.