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A New Synthesis and Some Reactions of Rhenium Nitrene Complexes

G. LA MONICA and S. CENINI
Istituto di Chimica Generale, Via Venezian 21, Milano, Italy

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Rhenium nitrene complexes, $Re(PPh_3)_2(NAr)Cl_3$ (I) (Ar = C_6H_5 (Ia), p-*MeC_6H_4 (Ib),* p-*$MeOC_6H_4$ (Ic)), have been obtained from the reactions of $Re(PPh_3)_2(O)Cl_3$ and the corresponding sulphynilamines, ArNSO, with the concomitant formation of sulphur dioxide. A carbonyl derivative, $Re(PPh_3)(CO)(NAr)Cl_3$ (II) (Ar =* p-*$MeOC_6H_4$), has been isolated from the reaction of (Ic) with carbon monoxide. The CO group is weakly bound in this complex and can be easily substituted by PPh_3 giving back (Ic) and by $R'NH_2$ (R' =* p-*MeC_6H_4) leading to $Re(PPh_3)(R'NH_2)(NAr)Cl_3$ (III). On the other hand the nitrene residue is involved in the reactions of (I) with $NaBH_4$ in the presence of CO or PPh_3, $ReH(CO)_3(PPh_3)_2$ and $ReH_x(PPh_3)_3$ (IV) (x probably five) being formed respectively, while the NAr groups are recovered as the corresponding amines. Similarly, the reactions of (I) with granular zinc in ethanol in the presence of CO give* trans-*$Re(PPh_3)_2(CO)_3Cl$ and $Zn(ArNH_2)_2Cl_2$. Finally, a remarkable reaction has been observed when (I) and dioxygen reacted in boiling toluene, $Re(OPPh_3)(ArNO)Cl_3$ (V) being isolated.*

Introduction

Our investigations on the reactions of organic molecules such as ArN_3 and ArNCO [1, 2] with transition metal complexes in low oxidation states have previously shown that because of the action of the metal, these reagents act as precursors of the nitrene residue NAr in mild conditions. However, in the cases so far studied by us nitrene complexes have never been isolated but they only could be postulated as intermediates in these reactions, and we have already discussed the factors affecting the stabilisation of the metal–nitrene bond [1]. Stable nitrene complexes have been prepared when the metals are in a relatively high oxidation state [3, 4], according to eq. 1:

$$Re(PR_3)_2(O)Cl_3 + ArNH_2 \text{ (or ArNCO)} \longrightarrow Re(PR_3)_2(NAr)Cl_3 + H_2O \text{ (or } CO_2) \quad (1)$$

Our recent investigations on the reactions of transition metal complexes toward other unsaturated nitrogen containing molecules, such as sulphynilamines [5], ArNSO, prompted us to extend reaction (1) to these organic species. We report here this new method of synthesis and some reactions of the obtained rhenium–nitrene complexes, $Re(PPh_3)_2(NAr)Cl_3$.

Results and Discussion

By reaction of $Re(PPh_3)_2(O)Cl_3$ with ArNSO in boiling benzene or in a benzene–n-hexane mixture, the rhenium–nitrene complexes, $Re(PPh_3)_2(NAr)Cl_3$ (I), have been isolated in good yields, (eq. 2):

$$Re(PPh_3)_2(O)Cl_3 + ArNSO \longrightarrow Re(PPh_3)_2(NAr)Cl_3 + SO_2 \quad (2)$$

(Ar = C_6H_5 (Ia), *p*-MeC_6H_4 (Ib), *p*-$MeOC_6H_4$ (Ic))

Compound (Ia) has already been prepared according to eq. 1 [4]. However, in our hands, among the three nitrene precursors $PhNH_2$, PhNCO and PhNSO, the last gave better yields and the isolation of the product required simpler handling, the aromatic sulphynilamines being much less sensitive to moisture when compared with the corresponding isocyanates [6]. It thus appears that only by using PhCONHNHPh as the nitrene precursor in the reaction with $Re(PPh_3)_2(O)Cl_3$ [7], a clean alternative method for the synthesis of (Ia) has to be considered.

In some preparations of (Ia) the formation of small amounts of a by-product containing coordinated aniline has been observed. The amine formation is presumably due to the presence of traces of water in the reaction medium. By treating the mixture of (Ia) and of this by-product with excess triphenylphosphine (see Experimental), the aniline containing by-product was completely transformed into (Ia). Our main interest in this work was to further investigate the reactivity of the coordinated nitrene in these complexes, although they are known to be rather inert [8] We found that (Ia) and (Ib) give uncharacterisable carbonyl derivatives when reacted with CO at 100 °C and 50 atm; however, the same reaction on (Ic) allowed the isolation of the carbonyl complex (II), (eq. 3):

$$\begin{tikzcd} Re(PPh_3)_2(NAr)Cl_3 \arrow[r, "pCO = 50\ atm", "100\ ^{\circ}C,\ toluene"'] & Re(PPh_3)(CO)(NAr)Cl_3 + PPh_3 \arrow[l, bend left, "PPh_3,\ 50\ ^{\circ}C/EtOH"] \end{tikzcd} \quad (Ar = p\text{-}MeOC_6H_4, (II)) \qquad (3)$$

Compound (II) shows in its i.r. spectrum a band at 2045 cm^{-1} which we assign to the carbonyl stretching mode. Derivative (II) thus represents an unusual carbonyl complex of rhenium with the metal in a high oxidation state. An alternative formulation, *i.e.* as an isocyanate complex, $Re(PPh_3)(ArNCO)Cl_3$, can be excluded since this compound does not react with acids such as HBF_4; this reaction should lead to a carbamoyl complex [1], while it is known that the nitrene residue in this type of complexes is inert to protonation reaction [1, 3]. Moreover compound (II) easily reacts with triphenylphosphine giving back the starting material (eq. 3). This reaction was also observed when (II) was left in ethanol at 50 °C; in this case rhenium by-products of unknown composition were also formed. A rhenium isocyanate complex, $Re(MeNCO)(DPE)_2Cl$, has been recently reported [9]; it shows νCO of the coordinated isocyanate group at 1835 cm^{-1} and reacts reversibly with acids giving a carbamoyl derivative [9]. The carbonyl group in (II) is also displaced by p-$MeC_6H_4NH_2$ with formation of $Re(PPh_3)(p\text{-}MeC_6H_4NH_2)(NAr)Cl_3$ (III). The reaction with carbon monoxide reported above confirms the inertness of the ArN species in these complexes, wherein it is bound by a formal triple bond to the metal [1, 3].

We thus studied some reactions under reducing conditions with the aim of enhancing the reactivity of the imido ligand by lowering the oxidation state of the metal [1].

By reaction with $NaBH_4$ the nitrene residue is displaced as the corresponding amine, while rhenium gives different products depending on the reaction conditions (eq. 4):

$$\begin{tikzcd} & ReH(CO)_3(PPh_3)_2 + ArNH_2 \\ \underset{(Ia, Ib, Ic)}{Re(PPh_3)_2(NAr)Cl_3} \arrow[ur, "NaBH_4/CO", "EtOH/75\ ^{\circ}C"'] \arrow[dr, "NaBH_4/PPh_3", "EtOH/75\ ^{\circ}C"'] & \\ & \underset{(IV)}{ReH_x(PPh_3)_3} + ArNH_2 \end{tikzcd} \qquad (4)$$

In the presence of carbon monoxide, the well known hydridocarbonyl complex, $ReH(CO)_3(PPh_3)_2$, is formed [10]. When this reaction was carried out in the presence of PPh_3, a light brown compound analysing as $ReH_x(PPh_3)_3$ (IV) was obtained. This derivative, which shows ν Re–H at 1910, 1935 and 1960 cm^{-1}, is converted into the yellow, already known $ReH_5(PPh_3)_3$ [11] (νRe–H at 1900 and 1970 cm^{-1}) when stirred in benzene under nitrogen. On the other hand, the ^1H n.m.r. spectrum of (IV) in deuterobenzene was identical to that of $ReH_5(PPh_3)_3$ [11]. No clathrated ethanol was detected for (IV), thereby excluding that it may be simply a solvate of the pentahydride. The ^1H n.mr.r. spectrum of (IV) at variable temperatures (down to –110 °C or from –60 °C up to room temperature) in solvents such as CS_2 or deuterated toluene, did not indicate any remarkable variation in the resonances of the hydridic hydrogens. These facts seem to indicate that (IV) is an isomer of the known $ReH_5(PPh_3)_3$, in which it converts rapidly when in solution, but there is no definite proof. However, it should be noted that no other rhenium hydrides with three phosphorus ligands are known [11b].

A reaction which supported the view that the nitrene residue becomes reactive in mild conditions when bound to rhenium in a lower oxidation state, was the reduction of (Ia, Ib, Ic) with zinc in ethanol in the presence of carbon monoxide, (eq. 5):

$$Re(PPh_3)_2(NAr)Cl_3 \xrightarrow[EtOH]{Zn/CO} trans\text{-}Re(CO)_3(PPh_3)_2Cl + Zn(ArNH_2)_2Cl_2 \qquad (5)$$

From this reaction the known rhenium(I) complex, *trans*-$Re(CO)_3(PPh_3)_2Cl$ [12], was isolated, while the amine derived from the nitrene was recovered as the zinc complex, $Zn(ArNH_2)_2Cl_2$. The latter is identical with an authentic sample prepared from $ZnCl_2$ and the amine in ethanol. We finally report on the only reaction in which the nitrene species is involved in a non-reducing medium, leading to a molecule that remains bound to the metal center (eq. 6):

$$Re(PPh_3)_2(NAr)Cl_3 \xrightarrow[toluene]{O_2/110\ ^{\circ}C} \underset{(V)}{Re(OPPh_3)(ArNO)Cl_3} + OPPh_3 \qquad (6)$$

Compounds (I) all react with dioxygen in boiling toluene giving (V) as the main products. These are insoluble in the reaction medium, while $OPPh_3$ and rhenium by-products still under investigation were detected in the mother liquor. Compound (Vb) (Ar = p-MeC_6H_4) was shown to be diamagnetic in the solid state. Solution measurements were precluded owing to the insolubility of these complexes in the common organic solvents. Their formulation is therefore based on elemental analyses (including chlorine and oxygen) and on their i.r. spectra. These clearly showed the presence of coordinated $OPPh_3$ (bands at *ca.* 1120, 1070 and 720 cm^{-1} in nujol mull [13]); an absorption band at *ca.* 1350 cm^{-1} was also present. We assign the latter to νNO of the N-bonded nitroso ligand on the basis of literature data (νNO in $Rh(PCy_3)_2(PhNO)Cl$ at 1357 cm^{-1} [14] and in $Re(PPh_3)_2(NO)(H{-}N{=}O)Cl_2$ at 1370 cm^{-1} [15]). Moreover a related pentacoordinated rhenium(III) derivative, $Re(OPPh_3)_2Cl_3$, is known and it has been reported to be diamagnetic [13b].

Reaction (6) was also carried out on compound (II), (Vc) being again obtained, but in milder conditions (at 50 °C in toluene).

Further studies are in progress in order to verify the enhanced reactivity of the nitrene group when bound to metals in a relatively low oxidation state and to extend the oxidation reaction by using other oxidant species and other nitrene complexes.

Experimental

$Re(PPh_3)_2(O)Cl_3$ [16] and N-sulphynilamines ArNSO [6] were prepared as reported in the literature. Solvents were dry and purified. IR spectra were obtained by using a Beckmann IR-33 and a Perkin-Elmer 457 instruments. ^1H NMR spectra were recorded on a Varian 60 spectrometer with Me_4Si as internal standard. Elemental analyses were carried out in the Analytical Laboratory of Milan University, except for oxygen analyses which were carried out by Pascher's Analytical Laboratories, Bonn.

$Re(PPh_3)_2(NC_6H_5)Cl_3$ (Ia)

To a suspension of $Re(PPh_3)_2(O)Cl_3$ (1 g) in benzene (25 ml), C_6H_5NSO (10 drops) was added. The mixture was heated at 60 °C for 12 h with stirring. (Ia) was recovered by filtration, washed with little benzene and dried *in vacuo*. The concomitant evolution of SO_2 was proved by using the usual analytical tests.

In some preparations (Ia) was obtained contaminated with a by-product containing coordinated aniline. This mixture was refluxed for 8 h in toluene in the presence of excess triphenylphosphine. By this procedure analytically pure (Ia) was recovered. The pale green product (Ia), already known, was identified by its elemental analyses and melting point. M.p. 215 °C. Found: C, 55.4; H, 4.18; N, 1.42; mol. wt. in chloroform, 1075. $C_{42}H_{35}Cl_3NP_2Re$ calcd.: C, 55.5; H, 3.9; N, 1.54%; mol. wt. 906.

$Re(PPh_3)_2(NC_6H_4Me\text{-}p)Cl_3$ (Ib)

The green compound was prepared as described for (Ia) but with a 8 h reaction time. M.p. 214 °C. Found: C, 55.93; H, 3.95; N, 1.49; mol. wt. in chloroform, 889. $C_{43}H_{37}Cl_3NP_2Re$ calcd.: C, 56.2; H, 4.0; N, 1.52%; mol. wt. 921. τ Me, 7.9 ($CDCl_3$).

$Re(PPh_3)_2(NC_6H_4OMe\text{-}p)Cl_3$ (Ic)

The pale green compound was obtained as above described, except for reaction medium which was a benzene–n-hexane mixture (1:1). M.p. 192 °C. Found: C, 54.8; H, 4.0; N, 1.55; O, 1.95; mol. wt. in chloroform, 878. $C_{43}H_{37}Cl_3NOP_2Re$ calcd.: C, 55.2; H, 3.9; N, 1.5; O, 1.7%; mol. wt. 937. τOMe, 6.3 ($CDCl_3$).

$Re(PPh_3)(CO)(NC_6H_4OMe\text{-}p)Cl_3\cdot(C_7H_8)$ (II)

(Ic) (0.15 g) and toluene (15 ml) were placed in a glass liner constructed to fit the autoclave. This was washed twice with CO at 30 atm and then charged to fifty atmospheres of carbon monoxide. Magnetic stirring was applied and the autoclave was heated to 100 °C. After 6 h it was left to cool to room temperature and vented. The brown product (II) was filtered off, washed with little toluene and dried *in vacuo*. It was shown to clathrate toluene. M.p. 145 °C (dec.). Found: C, 49.5; H, 3.65; N, 1.76; mol. wt. in chloroform, 670. $C_{33}H_{30}Cl_3NO_2PRe$ calcd.: C, 49.8; H, 3.78; N, 1.76%; mol. wt. 795. νCO, 2045 (vs) cm^{-1} (nujol mull). τOMe, 6.15; τMe, 7.67 ($CDCl_3$). These two signals were in a 1:1 ratio.

$Re(PPh_3)(NH_2C_6H_4Me\text{-}p)(NC_6H_4OMe\text{-}p)Cl_3$ (III)

To a suspension of (II) (0.08 g) in benzene (20 ml) *para*-toluidine (0.011 g) was added. The mixture was stirred overnight and the resulting solution evaporated to dryness. The residue was treated with ethyl ether and (III) recovered by filtration as a pale green product. M.p. 195 °C. Found: C, 50.3; H, 4.0; N, 3.8. $C_{32}H_{31}Cl_3N_2OPRe$ calcd.: C, 49.1; H, 3.9; N, 3.5%. νNH, 3280, 3200 and 3120 cm^{-1} (nujol mull).

Reduction Reactions of Nitrene Complexes

With $NaBH_4$ in the presence of PPh_3

This reaction has been carried out by using (Ia) or (Ib) or (Ic) as the starting material.

To a suspension of the nitrene complexes in ethanol, $NaBH_4$ and triphenylphosphine were added. The mixture was refluxed for 2 h. The obtained precipitate was filtered off and suspended in water for 1 h with stirring. The light brown product,

($ReH_x(PPh_3)_3$) (IV) (x probably five, see text), was filtered off, washed with little ethanol and dried *in vacuo.* M.p. 151 °C. Found: C, 66.1; H, 4.84; mol. wt. in benzene, 892. $C_{54}H_{50}P_3Re$ calcd.: C, 66.3; H, 5.12; mol wt. 977. νRe–H, 1960, 1935 and 1910 cm^{-1} (nujol mull). Compound (IV) shows in its ^1H NMR spectrum a quarted centered at τ = 14.8 (C_6D_6 or C_7D_8) and at τ = 15.45 (CS_2), J(P–H) 19 c.p.s. (see text). A benzene solution of (IV) was heated for 2 h under a nitrogen atmosphere and then evaporated to dryness. The residue was treated with ethanol and the pale yellow insoluble material filtered off. It was shown to be the pentahydride, $ReH_5(PPh_3)_3$, already described [11], by its elemental analyses, IR and ^1H NMR spectrum. A pure sample of $ReH_5(PPh_3)_3$ was prepared for useful comparison by the method reported in the literature [11a].

The same transformation from (IV) to $ReH_5(PPh_3)_3$ takes place even at room temperature, except that longer time is necessary (8 h). When the reaction with $NaBH_4$ and PPh_3 was carried out in a benzene–ethanol mixture (3:20), $ReH_5(PPh_3)_3$ was directly obtained.

The mother liquor of the reaction carried out in pure ethanol was shown to contain the amine corresponding to the nitrene residue present in the used imido complex.

With $NaBH_4$ in the presence of CO

For this reaction (Ia) (Ib) or (Ic) have been indifferently used. To 30 ml of an ethanol saturated solution of $NaBH_4$, the nitrene complex was added. The suspension was refluxed for 3 h, with bubbling carbon monoxide. The pale yellow insoluble product was filtered off and crystallized from benzene–ethanol, leaving a white material which was shown to be $ReH(CO)_3(PPh_3)_2$, already known [10], by its IR and ^1H NMR spectrum, melting point and elemental analyses. The filtered ethanol was evaporated to dryness and the residue was shown to contain the amine corresponding to the nitrene residue.

With granular zinc in the presence of CO

To a suspension of (Ib) in ethanol, little granular zinc was added and the mixture refluxed for 4 h with bubbling CO. The unreacted zinc was separated and the formed pale yellow product recovered by filtration. It was recognised as the already reported *trans*-$Re(PPh_3)_2(CO)_3Cl$ [12] by its melting point, IR spectrum and elemental analyses.

The filtered ethanol was evaporated to dryness and the residue treated with ethyl ether. The white insoluble product was shown to be $Zn(p\text{-}MeC_6H_4NH_2)_2Cl_2$ by its IR spectrum which was identical to that of an authentic sample prepared by reacting $ZnCl_2$ and *para*-toluidine (molar ratio 1:6) in refluxing ethanol. On cooling, the white compound precipitated; it was washed with ethanol and dried *in vacuo.* M.p. >220 °C. Found: C, 48.46; H, 5.1; N, 8.13. $C_{14}H_{18}Cl_2N_2Zn$ calcd.: C, 48.0; H, 5.1; N, 8.0%.

(Ia) and (Ib) behave analogously giving always *trans*-$Re(PPh_3)_2(CO)_3Cl$ and the zinc–amine complexes, $Zn(ArNH_2)_2Cl_2$.

$Re(OPPh_3)(C_6H_5NO)Cl_3$ (Va)

(Ia) (0.25 g) was suspended in toluene (50 ml) and oxygen was bubbled through. The suspension was heated at 110 °C for 2 h. The violet compound (Va) was filtered off, washed with little ethanol and dried *in vacuo*. M.p. 206 °C. Found: C, 42.8; H, 3.03; N, 2.04; O, 4.97. $C_{24}H_{20}Cl_3NO_2PRe$ calcd.: C, 42.5; H, 3.0; N, 2.1; O, 4.72. The IR spectrum of (Va) shows absorptions at 1130, 1080 and 720 cm^{-1} (nujol mull) arising from $OPPh_3$ and at 1350 cm^{-1} (HCBD mull) assigned to νN=O.

The mother liquor was evaporated to dryness and treated with ethanol. A brown insoluble material was obtained; its formulation is still under investigation. In the filtered ethanol the presence of $OPPh_3$ was recognised.

$Re(OPPh_3)(p\text{-}MeC_6H_4NO)Cl_3$ (Vb)

This violet compound was obtained as described for (Va). M.p. 233 °C. Found: C, 43.5; H, 3.27; N, 1.88; Cl, 14.95; O, 4.21. $C_{25}H_{22}Cl_3NO_2PRe$ calcd.: C, 43.4; H, 3.18; N, 2.0; Cl, 15.38; O, 4.63. The diamagnetic product (Vb) showed in its IR spectrum three bands at 1120, 1070 and 720 cm^{-1} (nujol mull) which were relevant for coordinated $OPPh_3$; νNO at 1360 cm^{-1} (HCBD mull).

$Re(OPPh_3)(p\text{-}MeOC_6H_4NO)Cl_3$ (Vc)

This violet compound was obtained similarly. M.p. 208 °C. Found; C, 42.73; H, 3.1; N, 1.83; O, 6.92. $C_{25}H_{22}Cl_3NO_3PRe$ caldc.: C, 42.4; H, 3.1; N, 1.98; O, 6.78. Its IR spectrum showed the same bands as (Vb), derived from coordinated $OPPh_3$ and *para*-methoxynitrosobenzene.

Reaction of (II) with PPh_3

To a suspension of (II) (0.05 g) in ethanol (20 ml) excess triphenylphosphine was added and the mixture stirred for 2 h at 60 °C. (Ic) in quantitative yields was obtained. When PPh_3 was absent, (Ic) was analogously recovered but in low yields, while in the mother liquor the presence of an unidentified rhenium by-product was noted.

Reaction of (II) with oxygen

Oxygen was bubbled through a toluene suspension of (II) while the temperature was maintained at 50 °C. After 1 h a violet insoluble product was filtered off, washed with ethanol and dried *in vacuo*. Its IR spectrum was identical to that of (Vc) described above.

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