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Arylimido-hydrido complexes of Rhenium, $Re(PPh_3)_2(NAr)(H)Cl_2$ and $Re(PPh_3)_2(NAr)(OR)(H)Cl$

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By reaction of $Re(PPh_3)_2(NAr)Cl_3$ ($Ar = C_6H_4Me$-p, A) with sodium isopropanolate in isopropanol, the arylimido-hydrido complex, $Re(PPh_3)_2(NAr)(H)Cl_2$ (1a) has been obtained. Compound (1a) as well as the corresponding (1b) ($Ar = C_6H_4OMe$-p) was also obtained by using zinc oxide instead of sodium isopropanolate. When compound (A) was reacted with zinc oxide or with triethylamine in ethanol, the arylimido-ethoxohydrido derivative, $Re(PPh_3)_2(NC_6H_4Me$-p$)(OEt)(H)Cl$ (2) was isolated, compound (1a) being the intermediate. When the latter reaction was carried out in C_2D_5OD, the corresponding deuterated complex, $Re(PPh_3)_2(NC_6H_4Me$-p$)(OC_2D_5)(D)Cl$, was obtained. When CH_3OH or CD_3OD were used as the reaction media, the complexes $Re(PPh_3)_2(NAr)(OCH_3)Cl_2$ (3) and $Re(PPh_3)_2(NAr)(OCD_3)Cl_2$ (4) ($Ar = C_6H_4Me$-p) were respectively formed. The hydrido-methoxo complex, $Re(PPh_3)_2(NC_6H_4Me$-p$)(H)(OCH_3)Cl$ (5), was indirectly obtained by reacting (1a) with zinc oxide in methanol.

Compound (2) reacts with KCl or HCl leading to (1a). When in solution, compound (2) undergoes a reductive elimination reaction, ethanol being released, while the fate of the rhenium moiety has not been yet clarified. By reaction of (1a) with chlorine, the starting arylimido complex (A) was obtained.

Introduction

The chemistry of transition-metal complexes having an imido group RN as ligand, an important organic intermediate [1], has received increasing attention in the last few years [2]. We have recently reported on a new method for the synthesis of rhenium arylimido complexes [3] and their reactivity has been extensively investigated [3, 4]. As a continuation of these studies, we report here on the reactions of rhenium(V) arylimido complexes, $Re(PPh_3)_2(NAr)Cl_3$ ($Ar = C_6H_4Me$-*p*, A; $Ar = C_6H_4OMe$-*p*, B) with sodium isopropanolate in isopropanol and with zinc oxide or triethylamine in alcoholic media, which allowed the isolation of the first examples of complexes having arylimido and hydrido as ligands.

Results and Discussion

Synthesis of the Arylimido-hydrido Complexes

By reaction of $Re(PPh_3)_2(NC_6H_4Me$-*p*$)Cl_3$ (A) with sodium isopropanolate in refluxing isopropanol under a nitrogen atmosphere, the arylimido hydrido complex $Re(PPh_3)_2(NC_6H_4Me$-*p*$)(H)Cl_2$ (1a) (Table I), has been obtained as the only product, (eq. 1):

$$\underset{(A)}{Re(PPh_3)_2(NAr)Cl_3} \xrightarrow[Pr^iOH]{NaOPr^i} \underset{(1a)}{Re(PPh_3)_2(NAr)(H)Cl_2} \qquad (1)$$

($Ar = C_6H_4Me$-*p*)

An alkoxo complex is probably intermediately formed, which, by hydrogen abstraction, leads to the hydridic derivative [5]. As a matter of fact, no reaction was observed between (A) and Bu^tOK in Bu^tOH at 100 °C. At the beginning of this research, the formation of (1a) was also observed when (A) was reacted with technical granular zinc in isopropanol, although longer reaction times were necessary. However it was later verified that granular zinc, when washed with dilute HCl and water before use, was unreactive. Thus zinc oxide was the most likely candidate as the reactive species and in fact compounds (1a) and $Re(PPh_3)_2(NC_6H_4OMe$-*p*$)(H)Cl_2$ (1b), have been readily obtained when the corresponding arylimido-trichloro complexes were treated with zinc oxide in refluxing isopropanol.

When compound (A) was treated with technical granular zinc (see above) in ethanol, compound (1a) was obtained but in mixture with another product, which was characterized as $Re(PPh_3)_2(NAr)(H)(OEt)Cl$ (2), the only isolable product when the reaction was carried out using zinc oxide, (eqn. 2):

$$\underset{(A)}{Re(PPh_3)_2(NAr)Cl_3} \xrightarrow[EtOH]{ZnO} \underset{(1a)}{Re(PPh_3)_2(NAr)(H)Cl_2}$$

$$\xrightarrow[EtOH]{ZnO} \underset{(2)}{Re(PPh_3)_2(NAr)(H)(OEt)Cl} \qquad (2)$$

($Ar = C_6H_4Me$-*p*)

TABLE I. Analytical Data.

Compound[a]	Colour	M.p. (°C)	Analyses (%)[b]		
			C	H	N
(1a) $Re(PPh_3)_2(NAr)(H)Cl_2$[c]	grey-green	205	57.8 (58.2)	4.3 (4.3)	1.6 (1.6)
(1b) $Re(PPh_3)_2(NAr')(H)Cl_2$	green	203	56.9 (57.1)	4.2 (4.2)	1.5 (1.5)
(2) $Re(PPh_3)_2(NAr)(H)(OC_2H_5)Cl$[d,e]	pale-green	174	59.7 (60.2)	4.7 (4.8)	1.5 (1.6)
(3) $Re(PPh_3)_2(NAr)(OCH_3)Cl_2$	pale-green	180	58.0 (57.6)	4.1 (4.4)	1.5 (1.5)
(4) $Re(PPh_3)_2(NAr)(OCD_3)Cl_2$[f]	pale-green	178	57.8 (57.4)	4.2 (4.3)	1.6 (1.5)
(5) $Re(PPh_3)_2(NAr)(H)(OCH_3)Cl$[g]	pale-green	205	59.5 (59.8)	4.5 (4.6)	1.5 (1.6)

[a] Ar = C_6H_4Me-*p*; Ar' = C_6H_4OMe-*p*. [b] Calculated values are given in parentheses. [c] Cl, 7.8 (8.0). [d] O, 1.8 (1.8). [e] Cl, 4.0 (3.9). [f] Calculated and found values for hydrogen are referred on considering D as H. [g] Cl, 4.1 (4.0).

Since compound (2) is unstable when in solution (see later), it was purified from inorganic materials ($ZnCl_2$ and excess ZnO) by repeated washing with water and dilute acetic acid.

The role of (1a) as the intermediate leading to (2), has been confirmed by further reacting (1a), obtained according to eqn. 1, with zinc oxide in ethanol.

In order to ascertain the role of zinc oxide as an alkoxide promoter in these reactions, we have carried out reaction (2) using triethylamine instead of ZnO in a stoichiometric amount: compound (2) was again formed. Further support arises from the observation that the formation of the oxo-ethoxo complex, $Re(PPh_3)_2(O)(OEt)Cl_2$, from $Re(PPh_3)_2(O)Cl_3$ in boiling ethanol [6] can be greatly accelerated by addition of zinc oxide.

When the arylimido complex (A) was reacted with zinc oxide but in methanol, we did not observe the formation of any hydridic derivative, the methoxo-complex (3) being the only product, (eqn. 3):

$$\underset{(A)}{Re(PPh_3)_2(NAr)Cl_3} \xrightarrow[CH_3OH]{ZnO} \underset{(3)}{Re(PPh_3)_2(NAr)(OCH_3)Cl_2} \qquad (3)$$

(Ar = C_6H_4Me-*p*)

The isolation of compound (3) suggests again that in the previous reactions an alkoxo species is the intermediate which, by hydrogen abstraction, gives the hydridic derivative, although it is not clear why in this case no subsequent hydrogen abstraction occurs leading to the hydrido-derivative, a reaction already observed [7].

The hydrido-methoxo complex, $Re(PPh_3)_2(NAr)(H)(OCH_3)Cl$ (5) (Ar = C_6H_4Me-*p*), was indirectly obtained by reacting (1a) with zinc oxide in methanol, (eqn. 4):

$$\underset{(1a)}{Re(PPh_3)_2(NAr)(H)Cl_2} \xrightarrow[CH_3OH]{ZnO} \underset{(5)}{Re(PPh_3)_2(NAr)(H)(OCH_3)Cl} \qquad (4)$$

Spectroscopic Properties and Reactivity of the Arylimido-hydrido Complexes

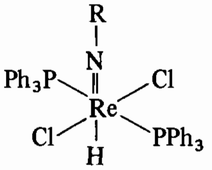
Compounds (1a) and (1b) show in their IR spectra a medium sharp band around 2000 cm^{-1} (Table II) attributable to ν(Re–H). The hypothesis of a vibration associated with a terminal carbonyl ligand was excluded, oxygen in complex (1a) being absent. In their ^1H NMR spectra compounds (1a) and (1b) showed the expected resonances due to the *para* methyl and methoxo substituents of the arylimido ligands (Table II), while the corresponding aromatic protons appeared as a sharp singlet at τ3.55 in (1a) or as an A_2B_2 system centered at τ3.7 (J(AB) = 9 Hz) in (1b). Moreover a careful examination of the ^1H NMR spectra in CD_2Cl_2 and $CDCl_3$ of (1a) and (1b) showed a triplet centered at around τ6.5 while the region at high field with respect to TMS was clear. The origin of this multiplet from a coupling with two equivalent phosphorous atoms (J(PH) = 15 Hz), was confirmed by recording the spectra at 60 and 100 MHz. All these facts support the formulation of (1) as hydrido derivatives, although no isotopic exchange was observed between (1a) and D_2O in benzene.

TABLE II. Spectroscopic Data.

Complex	IR data Significant absorptions[a]	^{1}H NMR data
(1a)	2000 [ν(Re–H)]	$\tau(C_6H_4)$ 3.55(s); τ(Re–H) 6.62(t) [J(PH) = 15 Hz]; τ(*p*Me) 8.0[b]
(1b)	2020 [ν(Re–H)]	$\tau(C_6H_4)$ 3.7(q) [J(AB) = 9 Hz]; τ(*p*OMe) 6.35; τ(Re–H) 6.48(t) [J(PH) = 15 Hz][b]
(2)	1975 [ν(Re–H)]; 1050 [ν(C–O)]; 895 [δ (OCH$_2$)][c]	$\tau(CH_2)$ 6.14(q); τ(*p*Me) 8.26 $\tau(CH_3)$ 9.43(t)[d,e]
(3)	f	$\tau(CH_3)$ 7.14; τ(*p*Me) 7.9[b]
(4)	2040 [ν(C–D)]; 1055 [ν(C–O)]	τ(*p*Me) 8.3[d]
(5)	2010 [ν(Re–H)]; 1055 [ν(C–O)]	g

[a] Measured in cm^{-1} (Nujol). [b] ^{1}H NMR spectrum in CDCl$_3$. [c] The corresponding deuterated compound, Re(PPh$_3$)$_2$(NC$_6$H$_4$Me-*p*)(D)(OC$_2$D$_5$)Cl, shows ν(C–O) at 1045 and δ (OCD$_2$) at 895 cm^{-1}. [d] ^{1}H NMR spectrum in C$_6$D$_6$. [e] New signals, whose intensity increases with time, were observed at $\tau(CH_2)$ 6.55(q), τ(*p*Me) 8.35, $\tau(CH_3)$ 8.94(t). [f] The strong absorption at 1100 cm^{-1} due to the triphenylphosphine ligand showed a shoulder at 1070 cm^{-1}, possibly arising from ν(C–O). [g] A complex number of signals was observed in the 6–9τ region..

The positions of the signals arising from the hydridic hydrogens of compounds (1) in their ^{1}H NMR spectra, are rather unusual, and only a few other hydridic derivatives have been reported to exhibit the same peculiarity [8a, 8b]. For the related complex, Re(PPh$_3$)$_2$(O)Cl$_3$, it has been pointed out that the oxo ligand has a labilising effect on the chlorine atom in the *trans* position [9]. In fact the ethoxo-oxo derivative, Re(PPh$_3$)$_2$(O)(OC$_2$H$_5$)Cl$_2$, obtained from the parent trichloro-oxo compound in refluxing ethanol, has a structure with the OC$_2$H$_5$ group *trans* to the oxo ligand [9]. Since the oxo and the arylimido groups are isoelectronic and comparable ligands [2b, 10], it is reasonable to suppose that even for the rhenium-arylimido complexes, Re(PPh$_3$)$_2$(NAr)Cl$_3$, the chlorine atom *trans* to the arylimido group [11] is the most labile. Thus the following geometry can be assigned to compounds (1) as the most plausible:



Compound (2) showed in its IR spectrum a weak broad absorption at 1975 cm^{-1} [ν(Re–H)] and significant bands at 1050 [ν(C–O)] and 895 cm^{-1} [δ(OCH$_2$)] [12]. For this derivative, which has a complex number of signals in its ^{1}H NMR spectrum in the 6–7 τ region (see later), the presence of the hydridic ligand was confirmed by carrying out reaction (2) in d_6-ethanol. The product, Re(PPh$_3$)$_2$(NC$_6$H$_4$Me-*p*)(D)(OC$_2$D$_5$)Cl, which was not purified from the inorganic materials as described above for (2) in order to avoid any isotopic exchange, did not show any absorption in its IR spectrum in the 1800–2000 cm^{-1} region, while the ν(Re–D) stretching could not be detected, probably lying under the absorptions of the triphenylphosphine ligands in the 1400 cm^{-1} region.

The IR spectrum of compound (3), Re(PPh$_3$)$_2$(NC$_6$H$_4$Me-*p*)(OCH$_3$)Cl$_2$, did not show any characteristic band besides those due to phosphines and the arylimido ligand, while its ^{1}H NMR spectrum showed the expected resonances due to the OMe and *para*-Me groups (Table II), in 1:1 ratio. In order to obtain further evidence about the nature of (3), we have also carried out reaction (3) in d$_4$-methanol, obtaining Re(PPh$_3$)$_2$(NC$_6$H$_4$Me-*p*)(OCD$_3$)Cl$_2$ (4). Complex (4), which shows the expected signal due to the *para*-Me group in its ^{1}H NMR spectrum, has an IR band at 1055 cm^{-1} attributable to ν(C–O). However a comparison of the IR spectra of (3) and (4) did not display any other shift which could be associated with the presence of a hydridic ligand. On the other hand the hydrido–methoxo complex, Re(PPh$_3$)$_2$(NC$_6$H$_4$Me-*p*)(H)(OCH$_3$)Cl (5), obtained according to eqn. 4, showed the expected ν(Re–H) at 2010 cm^{-1} in its IR spectrum. However, although the 6–7τ region is in this case clear (a region where for the ethoxo complex (2) the resonances due to the –CH$_2$ groups free and complexed are observed, see later), it was not possible to clearly detect the triplet associated with the hydridic hydrogen, possibly owing to some transformations occurring also for this alkoxo complex when in solution.

When reaction (4) was carried out in CD_3OD, the corresponding deuterated complex, $Re(PPh_3)_2(NC_6H_4Me\text{-}p)(H)(OCD_3)Cl$ (ν(Re–H) = 2000 cm^{-1}; ν(C–O) = 1035 cm^{-1}), was isolated.

Compound (2), when in solution, undergoes a reductive elimination, losing ethanol. This reaction has been qualitatively followed by ^1H NMR spectroscopy in C_6D_6: together with the signals of the starting complex (Table II), new signals, whose intensity increased with time, were noted at τ6.55 and τ8.94, the last two being close to those arising from free ethanol in deuterated benzene. The formation of free ethanol from complex (2) in benzene, has been confirmed by gas-chromatography. From these benzene solutions a brown rhenium-containing material was obtained. This material did not show any ν(NH) in its IR spectrum, while its elemental analyses indicated that the organic ligand was still present. The nature of this rhenium complex is still under investigation. By reacting compound (2) with gaseous HCl in diethyl ether at room temperature, the dichloro-hydrido derivative (1a) was readily obtained, (eqn. 5):

$$\underset{(2)}{Re(PPh_3)_2(NAr)(H)(OC_2H_5)Cl} \xrightarrow[\text{R.T.}]{HCl/Et_2O} \underset{(1a)}{Re(PPh_3)_2(NAr)(H)Cl_2} + C_2H_5OH \quad (5)$$

(Ar = C_6H_4Me-p)

The same compound (1a) was recovered by using KCl in aqueous ethanol at 50 °C. The inertness of the hydridic ligand in (1a) and (1b) with respect to HCl, together with their very low τ values in their ^1H NMR spectra, suggest a peculiar nature of the metal–hydrogen interaction in these compounds. The same inertness was observed for tungsten-hydrido complexes, $W(PMe_2Ph)_3(NNH_2)(H)X_3$, which showed a low field resonance of the hydridic hydrogen [8b]. As a matter of fact, (1a) reacts with chlorine, giving the starting arylimido complex, $Re(PPh_3)_2(NC_6H_4Me\text{-}p)Cl_3$ (A), (eqn. 6):

$$\underset{(1a)}{Re(PPh_3)_2(NAr)(H)Cl_2} \xrightarrow[\text{R.T.}]{Cl_2/Et_2O} \underset{(A)}{Re(PPh_3)_2(NAr)Cl_3} \quad (6)$$

(Ar = C_6H_4Me-p)

The reductive elimination reaction of ethanol occurring for compound (2), should give rise to a coordinatively unsaturated species having the arylimido ligand bound to a metal in a low oxidation state. This situation should induce a marked reactivity of the nitrene ligand [2, 10], and we are currently investigating the behaviour of (2) towards unsaturated reagents such as carbon monoxide and alkenes.

Experimental

Arylimido complexes, $Re(PPh_3)_2(NAr)Cl_3$ (Ar = C_6H_4Me-p (A), C_6H_4OMe-p (B)) were prepared as reported [3]. Alcohols were purified by distillation. Infrared spectra were obtained by using Beckmann IR-33 and IR-4210 instruments. ^1H NMR spectra were recorded on Varian 60 and XL-100 spectrometers. Gas-chromatographic analyses were carried out by using a DANI 3600 instrument equipped with a 5 m stainless steel column filled with 20% weight of 550 Silicone on 60/80 Chromosorb W. 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).

$Re(PPh_3)_2(NAr)(H)Cl_2$ (Ar = C_6H_4Me-p) (1a)

To an isopropanol suspension (15 ml) of $Re(PPh_3)_2(NAr)Cl_3$ (A) (0.275 g), zinc oxide (0.037 g) was added and the mixture refluxed for 5 h with stirring. After cooling, the insoluble compound (1a) was filtered off, washed with ethanol and stirred for 1 h with dilute HCl. (1a) was recovered by filtration; it was washed several times with water, ethanol and dried *in vacuo*.

(1a) can be analogously prepared by using sodium isopropanolate instead of zinc oxide (ratio (A): Pr^iONa = 1:3).

$Re(PPh_3)_2(NAr)(H)Cl_2$ (Ar = C_6H_4OMe-p) (1b)

This complex was obtained as described for (1a) by using the arylimido complex (B) and zinc oxide (ratio (B): ZnO = 1:0.5).

$Re(PPh_3)_2(NAr)(H)(OC_2H_5)Cl$ (Ar = C_6H_4Me-p) (2)

To an ethanol suspension (15 ml) of (A) (0.228 g), zinc oxide (0.031 g) was added and the mixture refluxed for 3 h with stirring. The insoluble compound (2) was filtered off, washed with ethanol and stirred for 1.5 h with dilute acetic acid. (2) was recovered by filtration; it was washed several times with water, ethanol, petroleum ether and dried *in vacuo*. Compound (2) was alternatively obtained, in a cleaner manner, by reacting (A) (0.197 g) with triethylamine (0.042 g) in ethanol for 2 h at 55 °C. The insoluble product was filtered off, washed with ethanol, water, ethanol, petroleum ether and dried *in vacuo*.

Compound (2) can be prepared by reacting (1a) with zinc oxide in refluxing ethanol (ratio (1a):ZnO = 1:0.5).

$Re(PPh_3)_2(NAr)(OCH_3)Cl_2$ ($Ar = C_6H_4Me$-p) (3)

The reaction leading to (3) was carried out as described for (1a) by using zinc oxide in methanol. Complex (3) was recovered as an insoluble pale-green compound. It was washed with methanol, water, dilute acetic acid, methanol, petroleum ether and dried *in vacuo.*

$Re(PPh_3)_2(NAr)(OCD_3)Cl_2$ ($Ar = C_6H_4Me$-p) (4)

It was obtained as described for compound (3) but using zinc oxide in d_4-methanol.

$Re(PPh_3)_2(NAr)(H)(OCH_3)Cl$ ($Ar = C_6H_4Me$-p) (5)

To a methanol suspension (10 ml) of (1a) (0.165 g), zinc oxide (0.025 g) was added and the mixture refluxed for 4 h. The insoluble pale-green compound (5) was filtered off and washed with methanol. It was purified from inorganic materials as described for (2).

Reaction of (2) with KCl or HCl (g)

a) Compound (2) was suspended in diethyl ether containing gaseous HCl and the mixture stirred for 3 h. The insoluble product was filtered off, washed several times with diethyl ether and dried *in vacuo.* It was shown to be $Re(PPh_3)_2(NC_6H_4Me\text{-}p)(H)Cl_2$ (1a) by its IR spectrum and elemental analysis.

b) Compound (2) was suspended in aqueous ethanol containing KCl and the mixture maintained at 50 °C for 2 h. The insoluble product was again shown to be (1a).

Reaction of (1a) with Cl_2

Compound (1a) was added to diethyl ether saturated with chlorine. An instantaneous reaction was observed. After 2 h stirring, the insoluble green product was filtered off, washed with diethyl ether and dried *in vacuo.* It was shown to be the starting arylimido complex, $Re(PPh_3)_2(NC_6H_4Me\text{-}p)Cl_3$ (A), by its IR spectrum and elemental analyses.

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