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Protonation reactions of the triangular cluster anion $[Re_3(\mu\text{-}H)_3(\mu\text{-}NC_5H_4)(CO)_{10}]^-$ containing an orthometalated pyridine molecule

Tiziana Beringhelli, Giuseppe D'Alfonso *, Monica Panigati

Dipartimento di Chimica Inorganica, Metallorganica e Analitica e Centro CNR, Via Venezian 21, 20133 Milano, Italy

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Abstract

The $[Re_3(\mu\text{-}H)_3(\mu\text{-}NC_5H_4)(CO)_{10}]^-$ triangular cluster anion **2** containing a bridging orthometalated pyridine moiety reacts with strong acids, in the presence of acetonitrile, to give the *cisoid* and *transoid* diaxial isomers of $[Re_3(\mu\text{-}H)_3(CO)_{10}(NCMe)(Py)]$ (**4a** and **4b**) containing a terminally bound pyridine. The major isomer **4a**, identified as the *transoid* species, is thermodynamically favoured in solvents of low polarity (**4a**/**4b** equilibrium ratio, at 295 K, 1.9 in MeCN, 2.5 in Me_2CO, 4.9 in CH_2Cl_2). The rate of interconversion of the isomers varies with the solvent, ruling out an intramolecular process. Experiments with deuterated isotopomers of **2** have shown that the added proton is distributed among two of the three hydridic sites and the *ortho*-position of the terminally bound pyridine. The protonation has also been performed in the absence of added ligands, with acids with weakly coordinating anions (CF_3SO_3H or HBF_4/Et_2O): the NMR data suggest the formation of derivatives analogous to the isomers **4**, in which the nitrile ligand is replaced by very poor donors, such as $CF_3SO_3^-$, BF_4^- or Et_2O. Successive substitution reactions indicate the following thermodynamic scale of nucleophilicity towards the vacant site of the $Re_3(\mu\text{-}H)_3(CO)_{10}(Py)$ fragment: BF_4^-, Et_2O, $H_2O < CF_3SO_3^- < Me_2CO \ll MeCN < Cl^-$, Py. Under CO atmosphere, both the isomers **4** give the novel neutral complex $[Re_3(\mu\text{-}H)_3(CO)_{11}(Py)]$ ($k^1_{obs} = 4.21(2) \times 10^{-5}\ s^{-1}$, at 300 K, in CO saturated acetone solution), which has been also obtained by protonation of the previously known $[Re_3(\mu\text{-}H)_2(CO)_{11}(Py)]^-$ anion. The reaction of **4** with pyridine is much faster than with CO, and in a few minutes both the isomers give the previously known *trans*-diaxial $[Re_3(\mu\text{-}H)_3(CO)_{10}(Py)_2]$ (**7a**) complex. The same complex is obtained by reacting *trans*-diaxial $[Re_3(\mu\text{-}H)_3(CO)_{10}(NCMe)_2]$ with pyridine, the monosubstitution derivatives **4** being present only as intermediates, with a low steady state concentration. A kinetic *cis*/*trans* ratio higher than the thermodynamic one has been found both for **4** and **7**, in all the reactions studied.

Keywords: Rhenium; Clusters; Hydrides; Pyridine; Orthometalation; Weak ligands

1. Introduction

It has recently been reported [1] that the reaction of the electronically unsaturated anion $[Re_3(\mu\text{-}H)_4(CO)_{10}]^-$ (**1**, 46 valence electrons) with pyridine gives the $[Re_3(\mu\text{-}H)_3(\mu\text{-}NC_5H_4)(CO)_{10}]^-$ anion (**2**, Scheme 1) containing an orthometalated pyridine molecule bridging a cluster edge. The reversibility of the C–H oxidative addition has subsequently been proved by several pieces of evidence [2]: (i) under high H_2 pressure the orthometalated derivative **2** transforms back into the parent unsaturated anion **1**; (ii) H/D exchanges between the hydrides and the α-position of the orthometalated pyridine have been observed in partially deuterated isotopomers of **2**; (iii) in the presence of CO both **1** and **2** give the $[Re_3(\mu\text{-}H)_2(CO)_{11}(Py)]^-$ anion (**3**), which can be viewed as an addition derivative to the intermediate **I2** of Scheme 1.

We have now investigated the reactivity of the anion **2** with strong acids, and found that in this case also the C_α–H bond of pyridine is restored, resulting in the formation of triangular clusters containing a terminally bound pyridine. Experiments with deuterated isotopomers of **2** have also shown that the reaction path does not involve the simple protonation of the metalated C atom.

* Corresponding author. Tel.: +39 2 26680622; Fax: +39 2 2362748; E-mail dalf@mail.csmtbo.mi.cnr.it.

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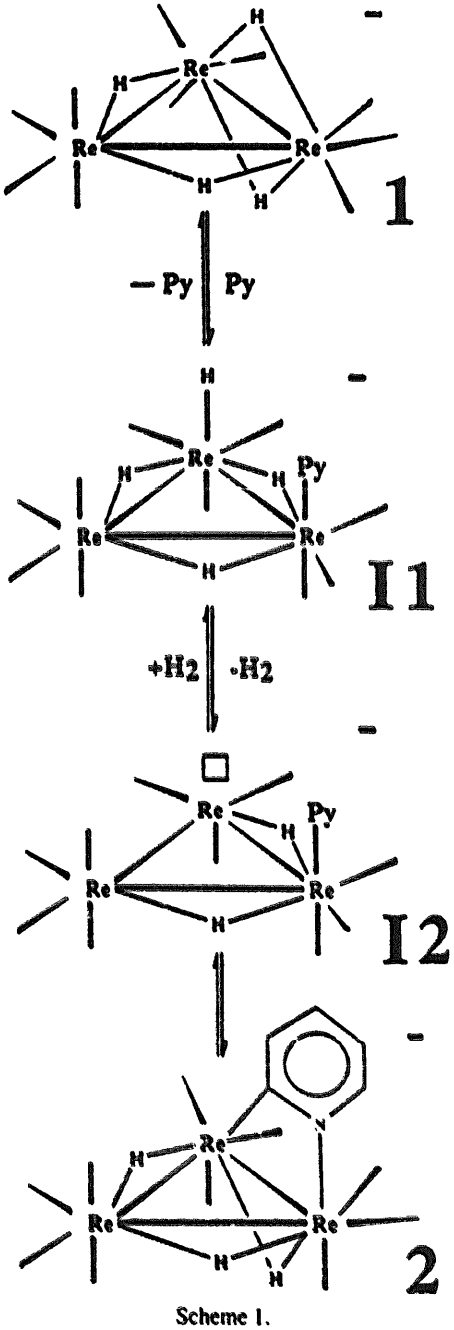
2. Results and discussion

2.1. Protonation of 2 in the presence of acetonitrile

The addition of 1 equiv. of HBF_4 (in diethylether) to an acetonitrile solution of **2**, at room temperature, caused the instantaneous disappearance of the pale yellow colour of **2** and the formation of two novel species **4a** and **4b**, in a ratio of about 2:1, each responsible for three hydridic resonances (1:1:1) in the ^1H NMR spectrum (see Table 1). The ratio between the two products **4a** and **4b** varied with the reaction temperature and with the solvent, **4a** usually being dominant. The two species



Scheme 1.

Table 1
^1H NMR data (CD_2Cl_2, 193K) for the $[Re_3(\mu\text{-}H)_3(CO)_{10}L(Py)]$ complexes obtained in this work, the labels of the hydrido ligands refer to Scheme 2

Compound	L	H_a	H_b	H_c	H_o	H_p	H_m
4a	MeCN [a]	−10.84	−13.19	−14.44	8.73	7.72	7.26
4b	MeCN [b]	−10.69	−13.36	−14.75	[c]	[c]	[c]
5a	$CF_3SO_3^-$	−8.58	−13.20	−12.38	8.61	7.62	7.14
5b	$CF_3SO_3^-$	−8.55	−13.04	−12.07	8.75	7.66	7.24
6a	n.i. [d]	−8.34	−12.96	−12.18	8.74	7.73	7.26
6b	n.i. [d]	−8.67	−13.09	−12.09	[e]	[e]	[e]
6c	n.i. [d]	−8.57	−13.25	−12.46	[e]	[e]	[e]
7a	Me_2CO [f]	−8.87	−13.04	−12.06	8.75	7.73	7.27
7b	Me_2CO [g]	−8.58	−13.19	−12.59	8.55	[h]	[h]
8a	Cl^- [i]	−9.54	−13.24	−13.49	8.71 [j]	7.57	7.08
8b	Cl^- [i]	−9.61	−13.04	−13.09	8.68 [j]	7.61	7.16
10a	Py	−9.17	−12.92	−12.92	9.07	8.00	7.58
10b	Py	−9.17	−13.30	−13.30	[c]	[c]	[c]
11	CO [k]	−13.14	−13.14	−17.04	9.06	8.03	7.65

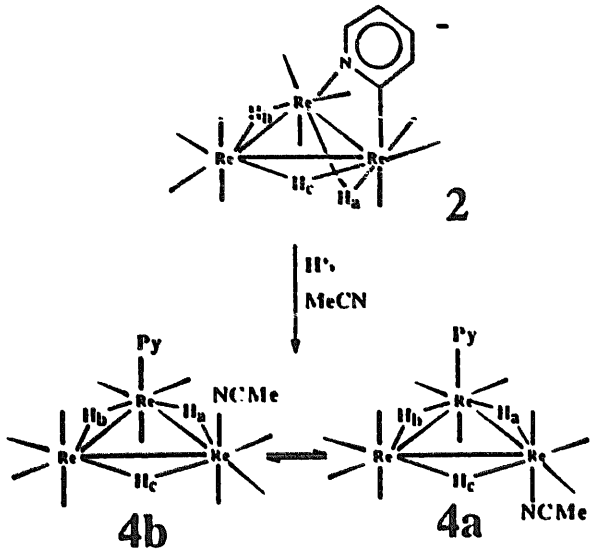
[a] δ Coordinated CH_3CN 2.30 ppm.
[b] δ Coordinated CH_3CN 1.72 ppm.
[c] Signals overlapping with those of the major isomer; the pyridinic resonances of **4b** were separated from those of **4a** only at higher temperatures or in a different solvent (see Section 3).
[d] The L ligand bound to this species has not been identified, Et_2O, BF_4^- or H_2O being the most likely candidates.
[e] Signals overlapping with those of **6a**.
[f] δ Coordinated $(CH_3)_2CO$ 2.35 ppm
[g] δ Coordinated $(CH_3)_2CO$ 1.95 ppm.
[h] Signals overlapping with those of **7a**.
[i] In this case the attribution of the resonances to H_b and H_c is arbitrary.
[j] δ For the pyridinic resonances at 280K.
[k] Data in acetone-d_6 solution.

4a and **4b** have been separated in almost pure form (ca. 90%) owing to their different solubility in diethylether, as detailed in Section 3. On the basis of the spectroscopic and chemical evidence discussed below, we formulate compounds **4a** and **4b** as the *transoid* and *cisoid* diaxial isomers of the triangular cluster complex $[Re_3(\mu\text{-}H)_3(CO)_{10}(NCMe)(Py)]$ (see Scheme 2), formed according to reaction (1).

$$[Re_3(\mu\text{-}H)_3(\mu\text{-}NC_5H_4)(CO)_{10}]^- + H^+ + MeCN \rightarrow [Re_3(\mu\text{-}H)_3(CO)_{10}(NCMe)(Py)] \quad (1)$$

A first evidence that **4a** and **4b** are two isomers was provided (Fig. 1) by the clean transformation of **4b** into an equilibrium mixture of **4a** and **4b**, observed in the absence of free pyridine or acetonitrile and in different solvents (acetone or methylenedichloride).

Furthermore, resonances attributable to pyridine and acetonitrile coordinated in both the species, with intensities varying with the isomer ratio, have been identified (see Section 3). The δ value for the nitrile coordinated in **4b** is ca. 0.5 ppm lower than in **4a**, and in CD_2Cl_2 it is at higher field even with respect to free acetonitrile. This is quite unusual, the resonances of MeCN bound in rhenium clusters usually being shifted in the opposite



Scheme 2.

sense [3,4], and can be attributed to the shielding effect of the pyridine π-electrons. On these grounds **4b** can be identified as the *cis* isomer, in agreement with the solvent effect on the equilibrium ratio **4a/4b**, as discussed below.

Finally, the chemical shift values of the hydridic resonances are in close agreement with the empirical 'additivity rules' [3,4] followed by $[Re_3(\mu\text{-}H)_3(CO)_{12-n}L_n]$ complexes (L = MeCN or pyridine): in particular, it has been observed that every axial MeCN or pyridine ligand causes a downfield shift (with respect to the δ value of ca. −17 ppm typical of $(CO)_4Re(\mu\text{-}H)Re(CO)_4$ systems) of ca. 2.5 or 4 ppm respectively for the bridging hydrides bound to Re vertices bearing the L ligand (see Table 2). In agreement with this, **4a** shows a resonance at about −14.5 ppm attributable to H_c (bound to an $Re(CO)_3(NCMe)$ vertex), another one at about −13.2 ppm attributable to H_b (bound to an $Re(CO)_3(Py)$ vertex), and a third one at about −10.8 ppm attributable to H_a (bound to both $Re(CO)_3(Py)$ and $Re(CO)_3(NCMe)$ groups). The resonances of **4b** have been attributed in the same way (Table 1).

Table 2
Hydridic resonances of $[Re_3(\mu\text{-}H)_3(CO)_{12-n}L_n]$ triangular clusters (L = MeCN or py) containing the L ligands in axial position; for n = 2 the values reported here refer to the *transoid* isomer

L	n	δ (relative intensity)		Ref.
MeCN	1	−14.37(2)	−17.00(1)	[3]
	2	−11.90(1)	−14.38(2)	[3]
	3	−11.58(1)	−11.94(2)	[3]
Py	1	−13.13(2)	−17.04(1)	this work
	2	−13.00(1)	−9.24(2)	[9]
	3	−8.77(1)	−9.13(2)	[10]

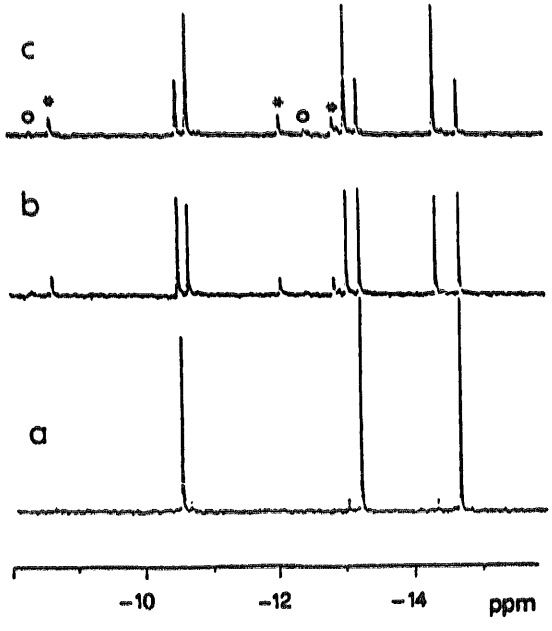


Fig. 1. ^1H NMR monitoring of the transformation of **4b** into the equilibrium mixture **4a/4b**, in acetone-d_6, at 295 K: (a) starting mixture, (b) after 30 min, (c) after 90 min. The resonances marked with * and o are attributable to the solvent o species **7a** and **7b** respectively (Table 1).

2.2. The interconversion of the isomers 4

When the protonation reaction was performed in acetonitrile-d_3 solution at low temperature (243 K), NMR monitoring showed that the two isomers had been formed in almost equimolar ratio (**4a/4b** 0.95). This was a kinetic ratio, the rate of isomer interconversion being very low at this temperature. On raising the temperature the isomerization reaction became faster and the relative amount of **4a** slowly increased. The equilibrium ratio **4a/4b** could be evaluated at different temperatures in the range between 283 and 313 K. The changes with temperature were quite small, almost within the uncertainties in the estimate: 1.82(5) at 283 K, 1.91(2) at 293 K, 2.00(4) at 313 K (standard deviation from repeated measurements in parentheses). These values allowed us to estimate $\Delta H^\circ = 2.0(5)$ kJ mol^{-1} for the **4b** → **4a** reaction and a thermodynamic **4a/4b** ratio of ca. 1.5 at 243 K.

The equilibrium constant is quite sensitive to the solvent, ranging, at room temperature, from ca. 1.9 in acetonitrile to 2.5 in acetone to 4.9 in methylenedichloride. The relative amount of the minor isomer **4b** therefore increases on increasing the polarity of the solvent, in agreement with the higher dipole moment expected for a *cis* isomer. Also the kinetic ratio **4a/4b** measured at 193 K in CD_2Cl_2 containing ca. 15% in volume of MeCN was much higher than in acetonitrile (ca. 3.7 vs. 1).

On using samples of isolated **4a** or **4b**, the rate of attainment of the equilibrium has been measured in different solvents. The kinetic constants have been obtained by fitting the decrease in intensity of the resonances of the starting isomer as a reversible first-order process, using the equilibrium ratios previously reported. The rate of isomerization varied with the solvent: for the **4b** → **4a** transformation, at 280 K, $k = 1.4(2) \times 10^{-4}\ s^{-1}$ in acetonitrile-d_3, $k = 3.8(3) \times 10^{-5}\ s^{-1}$ in acetone-d_6, $k = 2.1(1) \times 10^{-4}\ s^{-1}$ in CD_2Cl_2. At room temperature, the rate in CD_2Cl_2 or acetonitrile-d_3 was too fast to allow kinetic measurement by NMR, while in acetone-d_6 at 293 K it was found that $k = 5.1(1) \times 10^{-4}\ s^{-1}$ (Fig. 1). The dependence of the rate on the solvent suggests that the isomerization could not be an intramolecular process.

2.3. The site of the protonation

The anion **2** is stable in acetonitrile solution, also at room temperature, and therefore reaction (1) cannot proceed by nucleophilic attack of the nitrile on **2**. Moreover, the high rate of the reaction allows us to rule out any mechanism involving attack of the acid on the unbridged Re–Re bond of the intermediate **I2** of Scheme 1, formed by C–H reductive elimination. Previous studies [2] have in fact shown that such reductive elimination occurs with a rate (k ca. $5 \times 10^{-6}\ s^{-1}$, in acetone at room temperature) much slower than that of the protonation, which is almost instantaneous even at low temperature. The formation of NC_5H_5, therefore, cannot occur before the attack of the acid on **2**.

In order to identify the site of this attack, the protonation reaction has been investigated using a deuterated isotopomer of **2**. The reaction of **1** with pyridine-d_5 [1] gives the isotopomer $[Re_3(\mu\text{-}H)_2(\mu\text{-}D)(\mu\text{-}NC_5D_4)(CO)_{10}]^-$, which contains a deuteride ligand equally distributed on the two lateral sites H_b and H_c of the triangle due to a fluxional process that interconverts these two sites. In py-d_5, slow deuteration of all the hydridic sites occurs, through several reversible cycles of pyridine reductive elimination [2]. A fully deuterated sample of **2** was then prepared in this way and treated with HBF_4, in CD_2Cl_2/CD_3CN (6:1), at 203 K. The NMR spectrum (Fig. 2) showed in both the isomers a homogeneous ^1H population of the pyridinic H_α and of two out of the three hydridic sites (H_b and H_c). The fraction of protium located in H_a was significantly lower. This can be accounted for by a mechanism involving protonation on the Re–C bond to give an intermediate in which the agostic hydrogen is in fast exchange with the hydridic site H_b (and therefore with H_c). Similar examples of formation of agostic species upon protonation of M–C interactions have previously been observed, as well as examples of H interchange between M–H–C and M–H–M sites, see for instance Ref. [5].

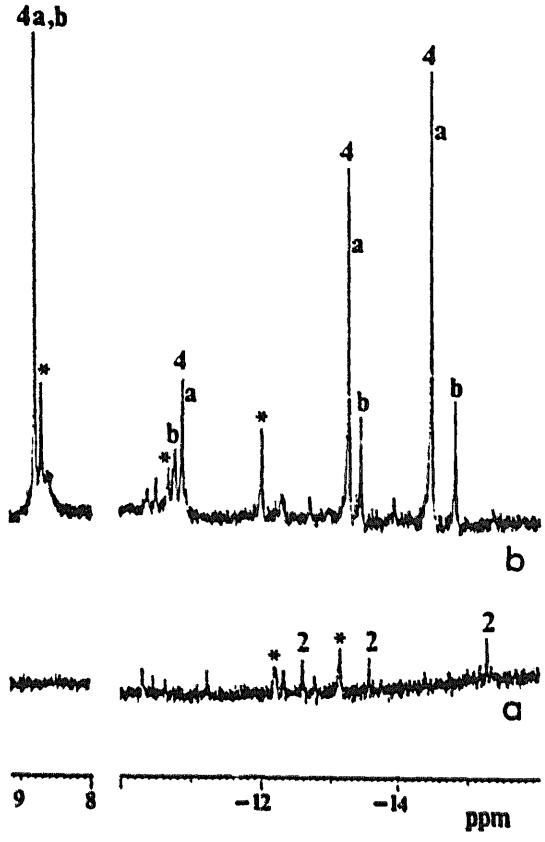


Fig. 2. Hydridic and pyridinic regions of the ^1H NMR spectra of a 'fully' deuterated sample of **2** (a) before and (b) after the addition of 1 equiv. HBF_4, in CD_2Cl_2/CD_3CN, at 193 K. The asterisks mark the main unattributed signals.

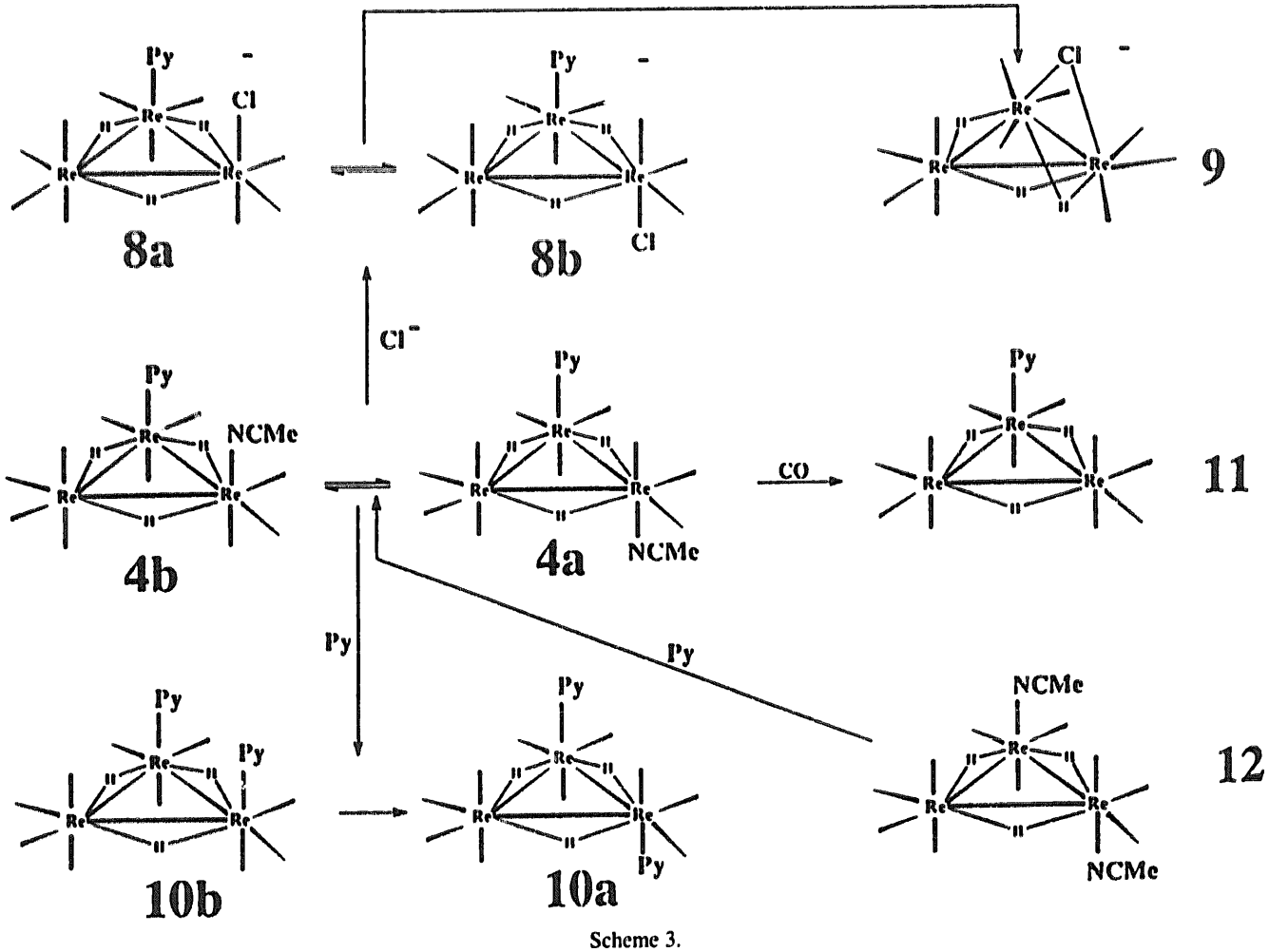
2.4. The protonation 'in the absence' of ligands

To get evidence of the postulated agostic intermediate, the protonation of **2** was performed at low temperature, directly into NMR tubes, in a non-coordinating solvent (CD_2Cl_2), using acids with 'non-coordinating' (or, better, weakly coordinating [6]) anions, such as HBF_4 or CF_3SO_3H. The NMR spectra (acquired at 193 K immediately after the addition of the acid) showed that, whatever the acid used, the four resonances of the orthometalated pyridine had been substituted by three resonances, in the ratio 2:1:2, typical of the *ortho*, *para* and *meta* hydrogens of pyridine. The agostic derivative, therefore, if formed, had rapidly reacted further. As to the nature of the reaction products, the pattern of hydridic resonances was clearly indicative of the formation of a series of $[Re_3(\mu\text{-}H)_3(CO)_{10}L(Py)]$ derivatives, differing in the labile L ligand. On using triflic acid as protonating agent, the clean formation of two species **5a** and **5b** was observed, in the ratio ca. 2:1, which can be formulated as the *transoid* and the *cisoid* isomers of the

$[Re_3(\mu\text{-}H)_3(CO)_{10}(CF_3SO_3)(Py)]^-$ anion. On the contrary, when etherated HBF_4 was used, three species (**6a**, **6b** and **6c** of Table 1) were formed, whose relative ratio varied rather erratically in different experiments, even if **6a** was usually dominant. Diethylether, the BF_4^- anion or H_2O (always present at trace levels) are the most likely candidates as L ligands, but this point has not been further investigated. The addition of $(NEt_4)CF_3SO_3$ to these mixtures resulted in the formation of the above mentioned **5a** and **5b** species, indicating that the triflate anion has a higher coordinating capability than diethylether, BF_4^- or H_2O (whatever the ligands bound to **6**, these species were all present in solution).

On raising the temperature, the relative amount of **5b** increased (at 263 K, **5a**:**5b** 1.7) and a significant broadening of the hydridic resonances was observed up to coalescence, at 298 K (the pyridinic signals, on the contrary, showed an almost negligible broadening). This behaviour is likely attributable to the lability of the triflate ligand, allowing fast interconversion of the isomers. Still more dramatic changes occurred for the mixture of species labelled **6**. Decomposition of the samples at higher temperatures prevented a more detailed analysis of the dynamic processes.

In order to establish a relative scale of increasing nucleophilicity, the reaction mixture obtained by protonating the anion **2** with HBF_4/OEt_2 in CD_2Cl_2 has been treated with different weak ligands in succession. All the reactions were performed at 203 K and 2 equiv. were added for each ligand. At first the triflate anion displaced the ligands coordinated in **6**, giving the two isomers **5**. The successive addition of acetone gave a mixture containing, besides some unreacted **5**, two novel species which can be formulated as the two isomers of an $[Re_3(\mu\text{-}H)_3(CO)_{10}(OCMe_2)(Py)]$ complex (**7a** and **7b**, the first one being largely dominant, **7a**/**7b**>10). The amount of unreacted **5** did not change after keeping the sample at room temperature, showing that this was a thermodynamic and not a kinetic effect. [In a separate experiment it was shown that the complete displacement of the triflate anion requires an excess of acetone (7 equiv.). In the same experiment it was also observed



Scheme 3.

that the hydridic resonances of **7** (different from those of **5** and **6**) are only moderately broadened at 280 K, where the equilibrium ratio **7a/7b** is close to 15.]

Acetonitrile was then added to the previous mixture, causing the quantitative conversion of the above species **5** and **7** into **4a** and **4b**. This mixture was then treated with NEt_4Cl, but no reaction occurred at low temperature. On keeping the sample at room temperature, however, the slow formation of two novel species **8a** and **8b** was observed. Their spectroscopic data (Table 1) suggest that they are the two isomers of the cluster anion $[Re_3(\mu\text{-}H)_3Cl(CO)_{10}(Py)]^-$, containing a terminally bound Cl^- ligand. The formation of **8** was much faster when NEt_4Cl was added (at 280 K) to a solution containing **7**, in line with the higher lability of acetone with respect to acetonitrile. The equilibrium ratio between the two isomers **8** at room temperature is likely close to unity, but an accurate measurement was hampered by the fast transformation of **8** into the previously known [7] $[Re_3(\mu\text{-}H)_3(\mu\text{-}Cl)(CO)_{10}]^-$ anion (**9**). The concentration of **9** increased so rapidly that it became the main species before complete transformation of **4** into **8**. The chloride anion is therefore able not only to substitute MeCN, but also to displace pyridine, likely owing to its intramolecular bridging coordination.

The displacement reactions described above allow us to establish the following thermodynamic scale of nucleophilicity towards an *ax*-"$Re_3(\mu\text{-}H)_3(CO)_{10}(Py)$" fragment:

$$BF_4^- , Et_2O, H_2O < CF_3SO_3^- < Me_2CO \ll MeCN < Cl^- , Py$$

2.5. Substitution of MeCN by CO in 4: the novel complex $[Re_3(\mu\text{-}H)_3(CO)_{11}(Py)]$ (11)

Upon treatment with CO, at room temperature, both **4a** and **4b** slowly gave the same product, namely *ax*-$[Re_3(\mu\text{-}H)_3(CO)_{11}(Py)]$ (**11**, reaction (2), Scheme 3), thus confirming that they differ only by the relative orientation of MeCN and pyridine.

$$[Re_3(\mu\text{-}H)_3(CO)_{10}(NCMe)(Py)] + CO \rightarrow [Re_3(\mu\text{-}H)_3(CO)_{11}(Py)] + MeCN \quad (2)$$

The progress of the reaction was monitored by NMR in a tube saturated with CO, in deuteroacetone, at 300 K, and it was found that the overall amount of the two isomers decreased according to pseudo-first-order kinetics, with $k_{obs} = 4.21(2) \times 10^{-5}\ s^{-1}$, corresponding to $t_{1/2} = 4.6$ h. The ratio between the isomers remained constant during the reaction, the rate of **4a/4b** interconversion being about one order of magnitude higher (see above).

The novel compound **11** has also been obtained by protonation of the previously known [2] $[Re_3(\mu\text{-}H)_2(CO)_{11}(Py)]^-$ anion (**3**) with CF_3SO_3H. This provides further support to the formulation of **11**, because the structure of **3** is known from X-ray analysis [2].

$$[Re_3(\mu\text{-}H)_2(CO)_{11}(Py)]^- + H^+ \rightarrow [Re_3(\mu\text{-}H)_3(CO)_{11}(Py)] \quad (3)$$

The reaction of **4** with CO also gave some $[Re_3(\mu\text{-}H)_3(CO)_{11}(NCMe)]$ [3], but only a very low amount (ca. 5%), confirming that the ligand MeCN is significantly more labile than pyridine.

2.6. Substitution of acetonitrile by pyridine in $[Re_3(\mu\text{-}H)_3(CO)_{10}(NCMe)_2]$ and in 4

The bis-nitrile derivative $[Re_3(\mu\text{-}H)_3(CO)_{10}(NCMe)_2]$ (**12**), containing two labile nitrile molecules *trans*-diaxially coordinated [3,8] (Scheme 3), could provide a convenient starting material, alternative to the anion **2**, for the synthesis of **4**. The reaction of **12** with pyridine, however, gave as main product the previously structurally characterized [9] *trans*-diaxial derivative $[Re_3(\mu\text{-}H)_3(CO)_{10}(Py)_2]$ (**10a**), even on using only 1 equiv. of pyridine.

NMR monitoring of the reaction (acetone-d_6, 300 K, 2 equiv. pyridine) revealed several interesting features.

(i) The two isomers **4** were observed as minor intermediates, with an overall steady state concentration of ca. 10–15%, and at the end (about 3 h) they disappeared.

(ii) The ratio **4a/4b** was close to unity at the beginning of the reaction, then slowly increased up to the usual equilibrium ratio.

(iii) The *trans*-diaxial isomer **10a** was the only product present at the end of the reaction, but NMR monitoring revealed the intermediate formation of a species whose NMR data (Table 1) suggest a formulation as the previously unknown kinetic isomer **10b** with *cis*-diaxial stereochemistry. The **10b/10a** ratio at the beginning was about 1, then progressively decreased down to zero.

The small steady state concentration of **4** in the above reaction indicates that nitrile substitution in **12** is slower than in **4**, that is, a pyridine ligand has a labilizing effect towards a vicinal nitrile. In line with this, the reaction of **4** with pyridine under the same conditions as above (acetone-d_6, 300 K, 2 equiv. pyridine) was very fast, one half of **4** being transformed into **10a** and **10b** in ca. 2–3 min. This rate is higher than the rate of isomer interconversion ($t_{1/2} = 23$ min under the same conditions, see above), but the isomer ratio **4a/4b** did not change significantly during the reaction, indicating that both the isomers **4a** and **4b** are affected by the labilizing effect of pyridine.

2.7. Conclusions

Strong acids are able to cleave the Re–C bond of an orthometalated NC_5H_4 ligand, μ-η^2-coordinated on a

cluster edge, giving a derivative with a pyridine molecule terminally bound on the cluster. The added proton, however, has been found not only in the α-position of the pyridine but also in two of the three hydridic sites. This could result from a fluxional behaviour of a kinetic Re–H–C_α agostic intermediate, even if such intramolecular stabilization has been found thermodynamically (enthalpically) disfavoured with respect to the coordination of even very poor donor species, such as diethylether or acetone or the triflate and tetrafluoborate anions.

The reaction led to $[Re_3(\mu\text{-}H)_3(CO)_{10}L(Py)]$ derivatives, to which a diaxial geometry (*cisoid* and *transoid*) has been attributed. The axial substitution, electronically favoured with respect to the equatorial one, is indeed more common in triangular Re carbonyl clusters than in the analogous compounds of the Fe triads, because the long hydrogen-bridged Re–Re distances reduce the steric interactions among axial ligands. Even the trisubstituted derivatives $[Re_3(\mu\text{-}H)_3(CO)_9L_3]$ (L = MeCN [3] or py [10]) have been found with a triaxial geometry, with two *transoid* and one *cisoid* configurations of the vicinal L ligands. The L ligands usually being bulkier than carbonyls, the *transoid* configuration is expected to be much more stable than the *cisoid* one. Only the *trans* isomers were indeed observed for the known disubstituted $[Re_3(\mu\text{-}H)_3(CO)_{10}L_2]$ derivatives, with L = MeCN, **12** [3,8] or py, **10a** [9]. On these grounds the small difference in stability between the *cis* and *trans* isomers of the mixed MeCN-pyridine derivatives **4a** and **4b** is at first surprising and likely indicates that the repulsive interactions between the flat pyridine molecule and the adjacent axial ligands can be better minimized in the mixed derivatives.

The labilizing effect of the pyridine ligand towards a vicinal nitrile can be related to the higher σ-donor capability of pyridine, with respect to a nitrile, allowing a better stabilization of the unsaturated transition state. The increase of the rate of dissociative reactions on increasing the electron donor capability of co-ligands is a well known feature (see the classical S_N1 of organic chemistry) and therefore provides a further indication of a dissociative mechanism for nitrile substitution in these clusters [11]. In line with this, the rate of nitrile substitution by CO was much higher in $[Re_3(\mu\text{-}H)_3(CO)_{10}(NCMe)_2]$ than in $[Re_3(\mu\text{-}H)_3(CO)_{11}(NCMe)]$ [3], MeCN being a better σ-donor than CO.

Finally, the kinetic *cis/trans* ratio, always higher than the equilibrium ratio, is noteworthy. Particularly remarkable is the formation of *cisoid* intermediates (**4b**, **10b**) in the transformation of the *trans*-bis-nitrile reagent **12** in the *trans*-bis-pyridine product **10a**. Several mechanisms could account for this and detailed kinetic studies are scheduled in order to determine the relative rates of the successive steps in the substitution and isomerization reactions here described.

3. Experimental section

The reactions were performed under N_2, and solvents were dried and deoxygenated by standard methods. Pyridine (Fluka) was distilled over KOH and then over molecular sieves, MeCN was distilled over P_4O_{10}, just before reaction. HBF_4 (about 54% in diethyl ether, Merck-Schuchardt) and CF_3SO_3H (Fluka) were used as received. Published methods were used for the syntheses of $[NEt_4][Re_3(\mu\text{-}H)_4(CO)_{10}]$ [12], $[NEt_4][Re_3(\mu\text{-}H)_3(\mu\text{-}NC_5H_4)(CO)_{10}]$ [1], $[NEt_4][Re_3(\mu\text{-}H)_2(CO)_{11}(Py)]$ [2] and $[Re_3(\mu\text{-}H)_3(CO)_{10}(NCMe)_2]$ [3]. The NMR spectra were acquired on Bruker WP80 or AC200 and on Varian Gemini 200 spectrometers. Infrared spectra were obtained on a Perkin–Elmer 781 grating spectrophotometer.

3.1. Synthesis of $[Re_3(\mu\text{-}H)_3(CO)_{10}(NCMe)(Py)]$ (4a and 4b)

A sample of $[NEt_4][Re_3(\mu\text{-}H)_3(\mu\text{-}NC_5H_4)(CO)_{10}]$, $[NEt_4]$**2**, (30.6 mg, 0.029 mmol) was dissolved, at room temperature, in freshly distilled MeCN (2 ml). Addition of HBF_4 (54% in diethyl ether, 5 μl, 0.036 mmol) made the solution colourless. IR (MeCN): ν(CO) 2103 w, 2039 m, 2023 vs, 1998 s, 1962 m, 1933 s cm^{-1}. Addition of H_2O gave a white precipitate that was dried under vacuum and then further purified by precipitation from CH_2Cl_2/n-hexane (18.4 mg, 0.017 mmol, isolated yield 58.3%). NMR analysis (CD_2Cl_2, 0.5 ml) showed the precipitate to be a **4a**/**4b** mixture in the ratio ca. 5:1. The mixture of isomers was stirred for 2 h in MeCN (in order to increase the relative amount of **4b**), then evaporated to dryness. The residue was treated with ca. 1 ml of diethylether at 233 K, giving a solution and a precipitate that were separated by decantation. NMR analysis (acetone-d_6, 0.5 ml, 233 K) showed the residue to be mainly **4b** (containing ca. 10% **4a**), while the solution contained mainly **4a** (with ca. 10% **4b**). NMR data (acetone-d_6, 0.5 ml, 203 K): **4a** δ 9.06 (m, 2, py-*ortho*), 8.02 (m, 1, py-*para*), 7.58 (m, 2, py-*meta*), 2.61 (s, 3, MeCN), −10.69 (s, 1, H_a), −13.07 (s, 1, H_b), −14.44 (s, 1, H_c); **4b** δ 9.06 (m, 2, py-*ortho*), 8.07 (m, 1, py-*para*), 7.64 (m, 2, py-*meta*), 2.14 (s, 3, MeCN), −10.60 (s, 1, H_a), −13.24 (s, 1, H_b), −14.75 (s, 1, H_c).

3.2. Low temperature NMR monitoring of the protonation of $[NEt_4]$2

3.2.1. Reaction in CD_3CN at 243 K

A sample of $[NEt_4]$**2** (8 mg, 0.0076 mmol) was dissolved in CD_3CN (0.5 ml) in an NMR tube which was carefully cooled at 238 K. After addition of HBF_4 at the same temperature (9 μl of a 0.73 M solution of etherated HBF_4 in CD_3CN), the NMR spectrum (243 K)

showed the formation of **4a** and **4b** in the ratio ca. 0.95:1. The temperature was then raised to 283 K and the isomerization reaction was monitored up to an equilibrium ratio of 1.82(5). The temperature was further increased to 293 K and then to 313 K, allowing the estimate of equilibrium ratios of 1.91(2) and 2.00(4) respectively.

3.2.2. Reactions in CD_2Cl_2/CD_3CN at 193 K with deuterated isotopomers of 2

(a) A sample of $[NEt_4][Re_3(\mu\text{-}H)_2(\mu\text{-}D)(\mu\text{-}NC_5D_4)(CO)_{10}]$ (11.2 mg, 0.0105 mmol) dissolved in an NMR tube in 0.5 ml of CD_2Cl_2 and 80 μl of CD_3CN was treated at 193 K with HBF_4 (54% in diethyl ether, 1.4 μl, 0.0105 mmol). The NMR spectrum (193 K) showed the formation of **4a** and **4b** (ratio ca. 4:1). The temperature was then raised to 283 K, causing the ratio **4a/4b** to increase to ca. 5.

(b) The reaction was repeated as above, using a sample of **2b** maintained in py-d_5 for 15 days and therefore transformed into the almost pure fully deuterated isotopomer $[Re_3(\mu\text{-}D)_3(\mu\text{-}NC_5D_4)(CO)_{10}]^-$ [2]. The spectrum acquired at 193 K after the addition of the acid is shown in Fig. 2.

3.3. Interconversion of the isomers 4a and 4b

The process has been investigated by monitoring via NMR the transformation of **4b** into the equilibrium mixture of the two isomers, in different solvents, at 280 and 295 K. Typically, samples of almost pure **4b** (ca. 90%), obtained as described above, were dissolved in the proper solvent (0.5 ml) in an NMR tube, at low temperature, then transferred into the probe at the reaction temperature. Spectra were acquired at different times, until equilibrium. The concentrations of the two isomers were estimated from the intensities of the hydridic resonances. Least-squares fittings of the integrated equation for first-order reversible processes [13] provided the values of the first-order constants for the **4b** → **4a** transformation.

3.4. Protonation of $[NEt_4]$ 2 in the absence of coordinating ligands

In a typical reaction a sample of $[NEt_4]$**2** (10 mg, 0.01 mmol) was dissolved, in an NMR tube in CD_2Cl_2 (0.5 ml) at low temperature (203 K). After addition of a strong acid (CF_3SO_3H or HBF_4 54% in diethyl ether), the tube was briefly shaken, causing a sudden change of the colour of the solution from pale yellow to orange. The NMR spectra at low temperature showed the instantaneous formation of the species labelled **5** or **6** (see Table 1).

3.5. The scale of nucleophilicity of the labile ligands

A sample of $[NEt_4]$**2** (16.1 mg, 0.0154 mmol) in CD_2Cl_2 (0.5 ml) was protonated with HBF_4 (54% in diethyl ether, 2 μl, 0.0154 mmol) at 193 K. The NMR spectrum, acquired at the same temperature, showed the formation of **6a**, **6b** and **6c**, with **6a** largely dominant. Addition of NEt_4BF_4 (3.3 mg, 0.0154 mmol) produced the increase in intensities of the signals of **6b** and **6c** (**6b** from 4.5% to 8.0%, **6c** from 9.0% to 15.0%), thus suggesting that **6a** contains Et_2O or H_2O. When $(NEt_4)(CF_3SO_3)$ (8.4 mg, 0.0308 mmol) was added, at 193 K, the NMR spectrum showed the formation of **5a** and **5b** (ratio ca. 2:1) and the presence of a small amount of unreacted **6** (ca. 7%). The spectrum did not change after 5 min at room temperature. The addition of acetone (2.2 μl, 0.0308 mmol) caused the transformation of unreacted **6** and most of **5** into **7a** and **7b**. No changes were observed after 5 min at room temperature. The addition of acetonitrile (1.6 μl, 0.0308 mmol) caused the transformation of all the above species into **4a** and **4b**. The mixture was then treated with anhydrous NEt_4Cl (5.1 mg, 0.0308 mmol), obtained from commercial reagent (Fluka) by crystallization from acetone/ethanol/tetrahydrofuran. No reaction was observed at 193 K. The sample was then maintained at room temperature for increasing times and the NMR spectra showed the progressive formation of **8a** and **8b** (50% and 8% respectively after ca. 30 min).

The spectrum showed also the two hydridic resonances at $\delta = -10.83$ (1) and -14.35 (2) of the anion **9** $[Re_3(\mu\text{-}H)_3(\mu\text{-}Cl)(CO)_{10}]^-$ (10% after 30 min). At longer times the concentration of **9** increased and it became the main product (77%) after 3 h, when the disappearance of **4a** and **4b** was complete. In the meantime, the concentration of **8a** and **8b**, as well as the ratio **8a/8b**, decreased (ca. 10% of each isomer after 3 h).

3.6. Reaction of $[Re_3(\mu\text{-}H)_3(CO)_{10}(NCMe)(Py)]$ (4) with CO

A sample containing **4a** and **4b** in the ratio 2:1 (10 mg, 0.009 mmol) was dissolved in acetone-d_6 (0.5 ml) in a screw cap NMR tube. The solution was saturated with CO at 193 K and the progress of the reaction was monitored via ^1H NMR for 12 h at 295 K. The signals of **4a** and **4b** progressively decreased (their ratio remaining constant) and were replaced mainly by those of $[Re_3(\mu\text{-}H)_3(CO)_{11}(Py)]$ (**11**) (Table 1). The only other hydridic product was $[Re_3(\mu\text{-}H)_3(CO)_{11}(NCMe)]$, whose highest concentration, at the end of the reaction, was 5.8%. A first-order plot of the overall concentration of **4** was linear up to a high conversion, allowing the estimate of the kinetic constant $k = 4.21(2) \times 10^{-5}\ s^{-1}$.

3.7. Reaction of $[NEt_4][Re_3(\mu\text{-}H)_2(CO)_{11}(Py)]$ with CF_3SO_3H

A sample of $[NEt_4][Re_3(\mu\text{-}H)_2(CO)_{11}(Py)]$, $[NEt_4]$**3**, (17 mg, 0.015 mmol) was dissolved in acetone-d_6 (0.5 ml) at room temperature and treated with CF_3SO_3H (1.40 μl, 0.0159 mmol). The NMR spectrum showed only the resonances of $[Re_3(\mu\text{-}H)_3(CO)_{11}(Py)]$ (**11**).

3.8. Reaction of $[Re_3(\mu\text{-}H)_3(CO)_{10}(NCMe)_2]$ (12) with pyridine at 300 K

A sample of $[Re_3(\mu\text{-}H)_3(CO)_{10}(NCMe)_2]$ (**12**) (8 mg, 0.0086 mmol) dissolved in acetone-d_6 (0.5 ml) in an NMR tube was treated with 2 equiv. of pyridine (1.4 μl, 0.017 mmol) at 243 K. NMR spectra, acquired at 300 K, showed the formation of the previously known *trans-ax,ax*-$[Re_3(\mu\text{-}H)_3(CO)_{10}(Py)_2]$ (**10a**, ca. 24% after 25 min when ca. 50% of **12** had reacted) and of a novel species with hydridic resonances quite similar to those of **10a** (δ −9.17 and −13.30, ratio 1:2), and therefore formulated as a *cis* isomer **10b** (ca. 12% at the same time). The overall amount of the monosubstitution derivatives **4** always remained very low (about 10%) during the reaction, while the ratio **4a/4b** increased from 1 at early reaction stages to about 2.5 at the end. The ratio **10b/10a** was approximately 1 at the beginning of the reaction, then decreased progressively to zero; **10b** attained its highest concentration (ca. 18%, ratio **10a/10b** 3) after ca. 1 h, when about 3/4 of **12** had reacted.

3.9. Reaction of 4a and 4b with pyridine at 300 K

The reaction was performed as described above, in acetone-d_6 (0.5 ml), using an equilibrium mixture of **4a** and **4b** (0.01 mmol) and ca. 2 equiv. of pyridine (1.3 μl). The NMR spectra, at 300 K, showed the fast decrease of **4** (about 50% in the first spectrum after 3 min without significant modification of the **4a/4b** ratio) to give the two species **10a** (33%) and **10b** (16%). The disappearance of **4** was complete after about 30 min. **10b** then more slowly transformed into **10a** (70% **10a** after 50 min), which was the only product after one night.

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