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Substitution of a Nitrile by P-Donor Ligands in $[Re_3(\mu\text{-}H)_3(CO)_{11}(NCMe)]$ and Axial–Equatorial Isomerization of the Entering Ligands: A Kinetic Study

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The substitution of the axially coordinated nitrile by P-donor ligands [PPh_3, PPh_2Me, $PPhMe_2$, PMe_3, $P(n\text{-}Bu)_3$, $P(OMe)_3$] in the triangular cluster complex $[Re_3(\mu\text{-}H)_3(CO)_{11}(NCMe)]$ (**1**) gives axial derivatives **2**, which then transform reversibly into the equatorial isomers **3**. The kinetics of both substitution and isomerization reactions have been studied, by using the hydridic region of ^1H NMR spectra to evaluate the concentrations of the three complexes. The data for the substitution have been accounted for by a reversible dissociative mechanism, with rate $r = (k_1k_2[\mathbf{1}][PR_3])/(k_{-1}[MeCN] + k_2[PR_3])$. The constant k_1, which is independent of the nature of the entering ligand, was evaluated under pseudo-first-order conditions, at five temperatures, allowing the estimation of the activation parameters ($E_a = 118.3 \pm 1.8$ kJ mol^{-1}, $\Delta H^* = 115.9 \pm 1.7$ kJ mol^{-1}, $\Delta S^* = 70.3 \pm 5.6$ J K^{-1} mol^{-1}). The values of the *competition ratios* k_2/k_{-1} for the six ligands have been determined at 300 K (range 0.12–0.91). For the three smaller ligands, ln k_2 increases linearly with the σ-donicity (measured by the pK_a of HPR_3^+) and the *steric profile* of the reaction shows that k_2 decreases for ligands with cone angles higher than about 125–130° (steric threshold) The kinetic constants k_3 for the axial–equatorial isomerization (obtained by computer optimization) have values between 8.3×10^{-6} and 4.7×10^{-5} s^{-1} (300 K) and depend on both steric and electronic parameters, increasing with the σ-basicity and the steric hindrance of the ligands. The activation parameters have been estimated for PPh_2Me and for PPh_3. The equilibrium constants $K_e = k_3/k_{-3}$ (evaluated from the equilibrium ratios [**3**]/[**2**], range 1.9–8.7) do not vary significantly with the temperature (292–314 K) and are affected mainly by electronic factors, increasing with the σ-basicity of the ligands.

Kinetic studies of substitution reactions in metal carbonyl clusters have been published,[1] but none of them concern rhenium compounds. We report here the kinetic investigation of the substitution of acetonitrile by P-donor ligands in the triangular hydrido–carbonyl cluster complex $[Re_3(\mu\text{-}H)_3(CO)_{11}(NCMe)]$ (**1**). This compound is the first member of the recently synthesized[2] series of clusters of formula $[Re_3(\mu\text{-}H)_3(CO)_{12-n}(NCMe)_n]$ (n varying from 1 to 3), which are useful intermediates for the synthesis of substitution derivatives of $[Re_3(\mu\text{-}H)_3(CO)_{12}]$. It was therefore of interest to ascertain the mechanism of substitution, to quantify the lability of the nitrile ligand, and to compare the behavior of the rhenium complex **1** with that of the related osmium cluster $[Os_3(CO)_{11}(NCMe)]$, recently kinetically investigated.[3]

The nitrile in **1** occupies an axial position (no equatorial isomer has been observed, either in solid or in solution, for any one of the three nitrile complexes of rhenium mentioned above), and therefore the axial isomer of $[Re_3(\mu\text{-}H)_3(CO)_{11}(PR_3)]$ [R = PPh_3, PPh_2Me, $PPhMe_2$, PMe_3, $P(n\text{-}Bu)_3$, $P(OMe)_3$] (**2**) is the kinetic product of the substitution. This species then slowly converts, reversibly, into the equatorial isomer **3**, which is always dominant at the equilibrium.

As the rates of the two processes (substitution and isomerization) are comparable, most of the kinetic experiments give data concerning also the isomerization, allowing us to estimate kinetic and thermodynamic constants for this second process. The axial–equatorial isomerization in some $[Re_3(\mu\text{-}H)_3(CO)_{11}(PR_3)]$ derivatives has been previously investigated,[4] but unfortunately very few data are available[5,6] to compare with our results.

Experimental Section

The complex $[Re_3(\mu\text{-}H)_3(CO)_{11}(NCMe)]$ was prepared as already described[2] and was carefully purified by flash chromatography followed by crystallization. Triphenylphosphine (Merck), diphenylmethylphosphine (Strem), dimethylphenylphosphine (Strem), trimethylphosphine (Strem), tri-n-butylphosphine (Strem), and trimethyl phosphite (Aldrich) were used as received. All manipulations were performed under nitrogen. The purity of the air-sensitive phosphines was checked by ^{31}P NMR spectroscopy, and these ligands were stored in vials sealed under nitrogen immediately after their use. Deuterated chloroform (Merck) was simply deoxygenated before use.

The solutions for kinetic studies were obtained by adding the proper amount of P-donor ligand (measured by weight or by a microsyringe) to a prethermostated solution of **1** (10 mg, 0.01 mmol, dissolved in 0.5 cm^3 of $CDCl_3$ containing the proper volume of acetonitrile, in a 5-mm NMR tube). The run with $P(OMe)_3$ was performed in $CDCl_3$ dried by distillation under N_2 over P_2O_5. Immediately after mixing, the tubes were placed in the probe of a Bruker 80 WP NMR spectrometer and kept there throughout the run, to avoid temperature fluctuations on changing the thermostated medium. The samples were placed outside the probe, in a thermostat, only for the determination of the equilibrium ratio between the two isomers, which required several days of reaction. The temperature was controlled by the B-VT1000 equipment of the spectrometer and was calibrated before each run by using a MeOH–MeOD solution.[7] A microprogram was used for the automatic acquisition of 100 transients for each spectrum, using a 90° pulse (8 μs) and a relaxation delay set to ensure the complete recovery of the magnetization of the hydrides, leading to an overall sampling time of 250 s.

The concentrations of compounds **1**–**3** were obtained, by normalization, from the integrated intensities I_i of the hydridic resonances. Significant errors can affect the molar fractions x_i so obtained ($x_i = I_i/\sum I_i$), which were estimated by assuming that the uncertainties in the evaluation of I_i [$\sigma(I)$] were proportional to $I^{1/2}$ [i.e., $\sigma^2(I) = c^2I$], the assumptions of constant absolute or relative uncertainties seeming inappropriate. The proportionality constant c^2 was set equal to $3 \times 10^{-3}\sum I_i$, in order to obtain reasonable values of $\sigma(I)$. The usual formula of propagation of errors led to the equation $\sigma^2(x_i) = [x_i(1 - x_i)]c^2/\sum I_i$, while the errors affecting the equilibrium constants K_e, obtained from the ratios I_{eq}/I_{ax}, were provided by the relationship $\sigma^2(K_e) = (K_e/x_{ax}^2)(c^2/\sum I_i)$.

Besides the uncertainties in the evaluation of the concentrations, other experimental limits were imposed by the use of NMR spectroscopy to monitor the reaction progress. First of all, the availability of the spectrometer restricted the number of experiments and imposed the lower limit for the measurable reaction rates. The low sensitivity of NMR spectroscopy caused the use of rather concentrated solutions (ca. 0.015 M, near the solubility limit) and made it impossible to vary significantly the concentration of **1**. The acquisition of each spectrum took ca. 5 min (in order to obtain a satisfactory signal-to-noise ratio), setting an upper limit for the measurable reaction rates. The precision and the accuracy of the temperature control equipment were only of about ±1 K. For this reason, the least-squares fits of the Arrhenius plots were performed by a home-written program that takes into account also the uncertainties in the independent variable.[8] Finally, both dynamic range problems and the inability to follow reactions too fast or too slow hampered the use of great excess of phosphines or acetonitrile, which would have been useful

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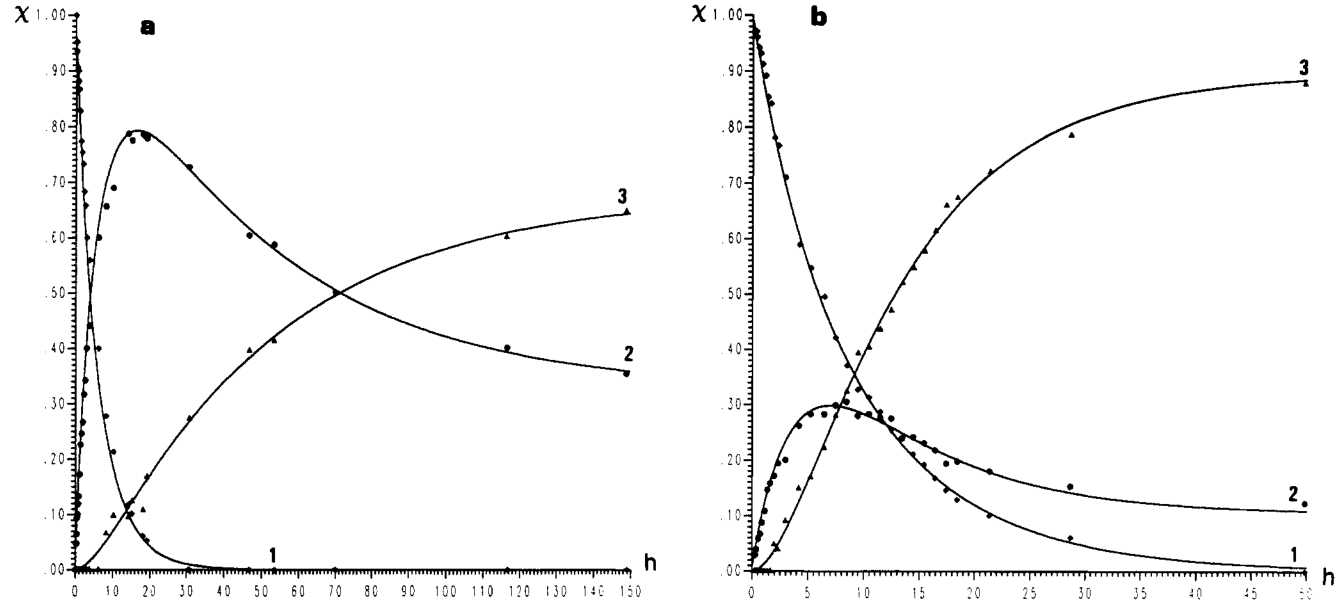

Figure 1. Plots vs time of experimental and calculated values of the molar fractions of compounds **1**–**3** for $P(OMe)_3$ (a) and for $P(n\text{-}Bu)_3$ (b).

to set the limiting conditions to simplify the kinetic equation of the substitution reaction.

Weighted linear least-squares fits were used to calculate pseudo-first-order or second-order constants for the substitution, by plots vs time of ln [**1**] or $\{1/([P]_0 - [\mathbf{1}]_0)\} \ln ([\mathbf{1}]_0[P]/[\mathbf{1}][P]_0)$, respectively, where [P] indicates the concentration of the phosphines. Weights $w_i = 1/\sigma_i^2$ were used, where σ_i indicates the errors affecting the ordinates of the plots, estimated from the above $\sigma^2(x_i)$ by the standard formula of propagation of errors. Analogously computed were least-squares fits of $\ln \{([x_2]_0(1 + K_e) - 1)/([x_2](1 + K_e) - 1)\}$ vs time, which was used to estimate the kinetic constant for the isomerization in some experiments.

Most values of k_3 and k_{-1}/k_2 were obtained by optimization, using computer programs, written in FORTRAN and running on an IBM 3090 computer, assembled by the authors using standard routines: the subroutine RK4,[9] which resolves systems of differential equations through the fourth-order Runge–Kutta method, and either the subroutine VA04A or the program MINUIT (from the CERN Computer Center), either of which finds the set of parameters that minimize a function, using respectively the method of Powell[9] (VA04A) or both a simplex[10a] and a variable-metric[10b] method (MINUIT). Both the programs minimize a χ^2 function $\sum[(y_{is} - y_{ic})^2/\sigma_i^2]$, where y_{is} and y_{ic} are respectively the experimental and calculated values of the concentrations of compounds **1**–**3** and σ_i^2 are the $\sigma^2(x_i)$, defined above, multiplied by the square of the molarity of the starting compound. The values of the kinetic constants provided by the two programs were in very good agreement. In Table II we have reported the values obtained from MINUIT, because it computes also the standard deviations of the estimated parameters. The goodness-of-fit was assessed by the values of χ^2 (always close to the number of degrees of freedom) and by the conventional agreement index $R = \sum \mathrm{ABS}(y_{is} - y_{ic})/y_{ic}$.

The program MINUIT was used also to fit the values of k_3 and K_e at 300 K to eq 10. The actual minimization was performed on the reduced model $(\ln k)' = bpK_a' + c\theta'$, where the primes indicate the reduced variables, obtained by subtracting the mean values from each variable. The bias coefficient a was computed from $(\ln k)_{av} - b(pK_a)_{av} - c\theta_{av}$.

Results

The reactions studied in this work are the following:

$$[Re_3(\mu\text{-}H)_3(CO)_{11}(NCMe)] \xrightarrow[-MeCN]{PR_3} [Re_3(\mu\text{-}H)_3(CO)_{11}(PR_3)]_{ax} \rightleftharpoons [Re_3(\mu\text{-}H)_3(CO)_{11}(PR_3)]_{eq}$$

(**1**, **2**, **3** respectively)

The products were characterized by ^1H NMR spectroscopy (Table I): in agreement with their idealized symmetry, the axial isomers always show two hydridic resonances (a singlet and doublet, intensity 1:2), while the equatorial isomers give three signals, only one of them always showing significant H–P couplings. The identification of the isomers of the PPh_3 derivative was confirmed by comparison with literature data.[6]

Table I. Hydridic Resonances in the ^1H NMR Spectra[a] of the Complexes $[Re_3(\mu\text{-}H)_3(CO)_{11}(PR_3)]$

ligand	isomer	δ, ppm
MeCN		−14.52 (2), −17.21 (1)
PPh_3	ax	−15.93 (2, 13), −17.63 (1)
	eq	−15.88 (1, 17), −17.08 (1),[b] −17.16 (1)
$PMePh_2$	ax	−16.08 (2, 14), −17.76 (1)
	eq	−16.07 (1, 20), −16.69 (1),[b] −17.25 (1)
PMe_2Ph	ax	−16.20 (2, 13), −17.86 (1)
	eq	−16.27 (1, 15), −16.45 (1, 6), −17.34 (1)
PMe_3	ax	−16.39 (2, 16), −17.81 (1)
	eq	−16.31 (1, 8), −16.48 (1, 18), −17.35 (1)
$P(OMe)_3$	ax	−16.95 (2, 18.6), −17.63 (1)
	eq	−16.81 (1, 18.7), −17.03 (1), −17.33 (1)
$P(n\text{-}Bu)_3$	ax	−16.48 (2, 14), −17.79 (1)
	eq	−16.58 (1, 13), −16.6 (1, nd), −17.3 (1)

[a] $CDCl_3$, 300 K. In parentheses are given relative intensities and J_{H-P} in Hz (all doublets). [b] Signal broadened by unresolved couplings with the lowest field hydride and phosphorus.

For all ligands, at least one of the hydridic resonances of the three species is well separated from all the others, and therefore the progress of the reactions, performed directly in NMR tubes, in $CDCl_3$, could be followed by monitoring the hydridic region of the spectra. The limits of NMR as an analytical tool were considered in the treatment of data, as extensively discussed in the Experimental Section. In Figure 1 are reported two examples of plots vs time of the concentrations of the three components, as determined from the integrated intensities of the hydridic resonances. The pattern is characteristic of two consecutive reactions, the second step being reversible. The axial isomer **2** is the intermediate species.

Surprisingly enough, the substitution reaction showed some reversibility: the addition of a large excess of acetonitrile (50 equiv) to an equilibrium mixture of **2** and **3** (PR_3 = PPh_3 and PMe_3), caused the formation of a little amount of **1** (about 5%). In both cases, however, for the reaction **1** ⇌ **2**, equilibrium constants K_{12} higher than 10^3 were estimated. We can confidently consider this high value of K_{12} valid for the whole series of ligands used in the work, since the two phosphines are at the two opposite ends of the range of steric and electronic properties. Moreover, in all kinetic runs we observed the "complete" consumption of **1**. The reverse reaction is therefore significant only in the presence of very low concentrations of **1** or very high nitrile to phosphine

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Table II. Rate Constants for the Substitution and Isomerization Reactions

		conditions of the run				kinetic constants[a]					
						linear least-squares			optimization		
run no.	ligand	T, (K)	[1] × 10^2	equiv of PR_3	equiv of MeCN	k^{I}_{obs}[b] × 10^5	k^{II}_{obs}[c] × 10^4	k_{-1}/k_2	k_{-1}/k_2	k_3[b] × 10^5	R × 10^2
1	PPh_3	300	1.94	11.3	13.5	1.71 (4)[d]		8.74 (26)	8.35 (14)	1.41 (5)[f]	3.53
2		300	1.40	10.2	26.2	0.89 (3)[d]		8.21 (28)	8.16 (15)	1.57 (7)[f]	3.54
3		300	1.41	20.6	10.8	3.68 (6)[d]		8.31 (24)	8.17 (12)	1.59 (5)[f]	3.45
4		300	1.21	11.9	21.9	1.22 (3)[d]		8.27 (25)	8.68 (10)	n.d.[g]	
5		307	1.56	9.8	5.0		7.06 (15)	7.88 (29)	8.01 (9)	3.28 (5)[f]	2.82
6		313	1.45	9.6	5.3		17.0 (9)	8.88 (55)	8.14 (12)	6.44 (12)[f]	3.59
7	PPh_2Me	285	1.18	25.5	0	1.58 (3)[e]				n.d.[g]	
8		292	1.33	22.7	0	4.83 (8)[e]				0.63 (1)[h]	3.10
9		300	1.36	18.7	0	20.1 (8)[e]				1.75 (3)[h]	3.85
10		300	1.01	20.4	10.3	8.43 (25)[d]	4.20 (12)	2.56 (15)	2.65 (5)	1.67 (3)[h]	3.50
11		307	1.41	21.4	0	54.1 (12)[e]				3.83 (7)[h,i]	2.94
12		313	1.60	20.0	0	139. (1)[e]				7.42 (11)[h]	3.02
13	$PPhMe_2$	300	1.24	9.5	0	19.4 (8)[e]				n.d.[g]	
14		300	1.38	10.9	5.9		6.85 (19)	1.69 (11)	1.61 (3)	0.83 (1)	2.34
15	PMe_3	300	1.78	9.2	4.2		7.85 (16)	1.17 (9)	1.10 (5)	2.37 (4)[i]	3.95
16	$P(n\text{-}Bu)_3$	300	1.24	5.4	5.3		5.04 (12)	4.93 (17)	4.78 (6)	4.94 (9)	2.98
17		300	2.17	10.8	5.2		2.27 (5)	5.61 (21)	5.25 (6)	4.25 (6)	3.47
18		300	1.32	27.6	0	19.4 (8)[e]				n.d.[g]	
19	$P(OMe)_3$	300	1.32	5.3	5.0		6.27 (14)	3.70 (13)	2.84 (5)	0.38 (1)	3.30

[a] In parentheses are reported the standard deviations, referred to the last digits. [b] In s^{-1}. [c] In L mol^{-1} s^{-1}. [d] From plots under pseudo-first-order conditions, with k_{obs} obeying eq 4. Least-squares fit of $1/k^{I}_{obs}$ vs [N]/[P] for runs 1–4 (eq 4, Figure 2) gave the values $k_1 = 2.0\ (4) \times 10^4$ and $k_{-1}/k_2 = 8.6\ (1.9)$. [e] From plots under pseudo-first-order conditions, with $k_{obs} = k_1$. [f] Activation parameters for PPh_3: $E_a = 86\ (4)$ kJ mol^{-1}, $\Delta H^{\ddagger} = 84\ (3)$ kJ mol^{-1}, and $\Delta S^{\ddagger} = -58\ (11)$ J mol^{-1} K^{-1}. [g] Not determined, since the reaction was not followed for a long enough time. [h] Activation parameters for PPh_2Me: $E_a = 89\ (1)$ kJ mol^{-1}, $\Delta H^{\ddagger} = 87\ (1)$ kJ mol^{-1}, and $\Delta S^{\ddagger} = -46\ (4)$ J mol^{-1} K^{-1}. [i] From least-squares fits according to eq 7; k_3 equal to $4.0\ (5) \times 10^{-5}$ and $2.3\ (4) \times 10^{-5}$ s^{-1} were estimated for runs 11 and 15, respectively.

ratios: similar conditions not being used to estimate the kinetic constants for the substitution, the reverse reaction was not taken into account. The implications of the reversibility in the isomerization step will be discussed in the following part.

Preliminary runs, performed by using mainly PPh_3, showed that both the reactions are clean, apart from the formation of a minor amount of a bisubstituted derivative in some experiments, as discussed below.

Pseudo-first-order constants k^{I}_{obs} were obtained by least-squares fits of ln [1] vs time, in four experiments with PPh_3, at 300 K (runs 1–4 of Table II) in which [MeCN] and [PPh_3] values that were high enough to be considered constant during the reactions were used. The reciprocals of these k^{I}_{obs} value varied linearly against the ratio $[MeCN]_0/[PPh_3]_0$, as shown in Figure 2.

The rate increased significantly when PPh_3 was replaced by PPh_2Me (run 10 of Table II, to be compared with run 3). Experiments were then performed, at the same temperature, in the absence of added acetonitrile, by using three different phosphines (PPh_2Me, $PPhMe_2$, and $P(n\text{-}Bu)_3$; runs 9, 13, and 18 of Table II). Plots of ln ([1]/$[1]_0$) vs time were linear, with the data for the three phosphines lying all on the same line, with a slope of $(1.97 \pm 0.03) \times 10^{-4}$ s^{-1} (separated least-squares fits for each phosphine gave the values of k^{I}_{obs} reported in Table II).

These results are in line with the reversible dissociative mechanism (eqs 1 and 2) often found in substitution reactions, even in the case of labile ligands.[3,11-13]

$$[Re_3(\mu\text{-}H)_3(CO)_{11}(NCMe)] \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} [Re_3(\mu\text{-}H)_3(CO)_{11}] + MeCN \quad (1)$$

$$[Re_3(\mu\text{-}H)_3(CO)_{11}] + PR_3 \xrightarrow{k_2} [Re_3(\mu\text{-}H)_3(CO)_{11}(PR_3)]_{ax} \quad (2)$$

Assuming a steady-state concentration of the coordinatively unsaturated intermediate, rate law 3 is derived, where [N] and [P] indicate the concentrations of the leaving and the entering ligands, respectively.[14]

$$-d[1]/dt = k_1[P][1]/\{(k_{-1}/k_2)[N] + [P]\} \quad (3)$$

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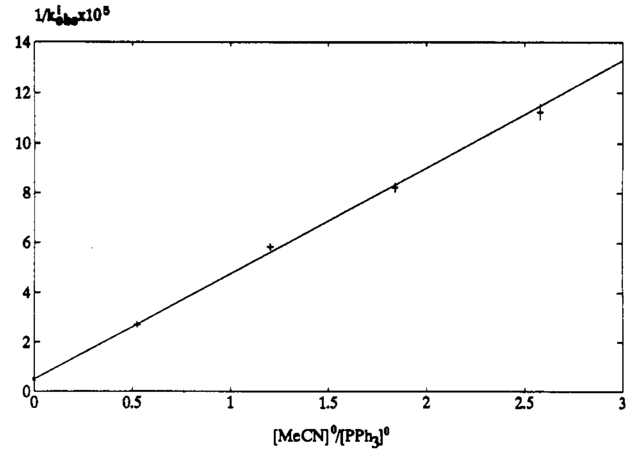

Figure 2. Plots of the reciprocal of the values of k^{I}_{obs} determined in runs 1–4 (PPh_3, 300 K) against the ratio $[MeCN]_0/[PR_3]_0$. The vertical lines are proportional to the estimated standard deviations of each experimental value. The point on the vertical axis represents the reciprocal of k^{I}_{obs} obtained in the experiments without added nitrile, using PPh_2Me, PMe_3, and $P(n\text{-}Bu)_3$, in which k^{I}_{obs} coincides with k_1.

According to eq 3, for high concentrations of both MeCN and PPh_3 (as in runs 1–4), k^{I}_{obs} must obey eq 4 and a plot of the reciprocals of the k^{I}_{obs} determined in different experiments vs $[N]_0/[P]_0$ must be linear. The values of the intercept and the slope of the straight line of Figure 2 give therefore the kinetic constants k_1 and k_{-1}/k_2 (Table II), affected by high errors for the uncertainty in the estimation of the intercept.

$$(1/k_{obs}) = (1/k_1)\{1 + (k_{-1}/k_2)[N]_0/[P]_0\} \quad (4)$$

In experiments with an excess of phosphine and in the absence of added nitrile, it results $[P] \gg (k_{-1}/k_2)[N]$. In these limit conditions, from eq 3 it is expected that k^{I}_{obs} coincides with k_1 and the substitution rate becomes independent not only of the concentration of the entering ligand but also of its nature. This

(14) If the reversibility of reaction 2 had been considered, the term $-(k_{-1}/k_2)k_{-2}[N][2]$ should have been added to the numerator of eq 3. This term can be safely left out of the equation, due to the high values of the overall equilibrium constants reported above ($K_{12} > 10^3$; $(k_{-1}/k_2)k_{-2} = k_1/K_{12}$).

has been verified in the three runs with PPh_2Me, $PPhMe_2$, and $P(n\text{-}Bu)_3$ reported above: the slope of the plot of ln ([1]/[1]$_0$) vs time [$(1.97 \pm 0.03) \times 10^{-4}$ s^{-1}] provides therefore a measure of k_1, which is in excellent agreement with that estimated for PPh_3 [$(2.0 \pm 0.4) \times 10^{-4}$ s^{-1}], as shown also in Figure 2. These results provide a further confirmation of rate law 3, because any significant associative contribution would imply a dependence of k^{I}_{obs} both on the nature of the phosphine and on the concentration of the phosphine.

Through the last method, using PPh_2Me only, the values of k_1 were determined at four other temperatures, in the range 285–313 K (runs 7, 8, 11, and 12 of Table II), allowing an estimation of the activation parameters concerning the dissociative step of the substitution process: $E_a = 118.3 \pm 1.8$ kJ mol^{-1}, $\Delta H^* = 115.9 \pm 1.7$ kJ mol^{-1}, and $\Delta S^* = 70.3 \pm 5.6$ J K^{-1} mol^{-1}.

The values of k_{-1}/k_2 for phosphines different from PPh_3, at 300 K (runs 10, 14, 15, 16, 17, and 19 of Table II), and for PPh_3, at temperatures different from 300 K (runs 5 and 6), were estimated from only one experiment, assuming pseudo-second-order limiting conditions, which are more easily met than first-order ones. Least-squares fits of standard second-order plots provided the values of k^{II}_{obs}, from which the values of k_{-1}/k_2 were calculated according to eq 5, by using the values of k_1 determined in the experiments with $k^{I}_{obs} = k_1$.

$$k^{II}_{obs} = k_1/\{(k_{-1}/k_2)[N]_0 + [P]_0\} \qquad (5)$$

As to the axial–equatorial isomerization, either a direct pathway (likely intramolecular) or a dissociative mechanism (due to the reversibility of reaction 2) can be supposed.[15]

$$[Re_3(\mu\text{-}H)_3(CO)_{11}(PR_3)]_{ax} \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} [Re_3(\mu\text{-}H)_3(CO)_{11}(PR_3)]_{eq} \qquad (6)$$

$$[Re_3(\mu\text{-}H)_3(CO)_{11}(PR_3)]_{ax} \underset{k_2,\, PR_3}{\overset{k_{-2}}{\rightleftharpoons}} [Re_3(\mu\text{-}H)_3(CO)_{11}] \underset{k_{-4}}{\overset{k_4,\, PR_3}{\rightleftharpoons}} [Re_3(\mu\text{-}H)_3(CO)_{11}(PR_3)]_{eq}$$

The experimental data indicate that the direct pathway is the dominant one. In fact, the following points may be made:

(i) The profile of [3] vs time (Figure 1) clearly shows that **3** originates mainly from **2**, while the mechanism via the coordinatively unsaturated intermediate would imply a direct pathway from **1** to **3** (through reaction 1).

(ii) The *maxima* values of k_{-2} estimated from the values of the overall equilibrium constants K_{12} for PPh_3 and PMe_3 [$K_{12} > 10^3$; $k_{-2} = (k_1/K_{12})/(k_{-1}/k_2)$] are about 1 order of magnitude lower than the isomerization constants determined below.

(iii) When the equilibrium mixture of **2** and **3** from run 14 ($PR_3 = PPhMe_2$) was kept at 300 K in the presence of 10 equiv of PPh_3, no formation of the PPh_3 derivatives was detected for a time as long as 5 days, which is the time computed to attain the equilibrium, starting from pure **2** or **3** (PR_3=$PPhMe_2$).[16]

We have therefore used only the constants k_3 and k_{-3} to describe the isomerization reaction.

The ratios k_3/k_{-3} (i.e., the equilibrium constants K_e = [3]/[2]) were determined by allowing the reactions to proceed until constant ratios of the two isomers were observed.

Equation 7, which describes the first-order evolution toward the equilibrium, could have been used to determine the constants ($k_3 + k_{-3}$), if compounds **2** and **3** were the only components of the reaction mixture since the early stages of isomerization. This occurred only in two of the available experiments (runs 11 and 15). In most cases, in fact, the complete consumption of **1** occurred when the isomerization had already proceeded too far. In other cases, the system was complicated by the formation of bisubstituted species (see below).

A reasonable evaluation of the constants k_3 was however obtained by optimization, using a computer program which finds

$$\ln \{([2]_0 - [2]_e)/([2] - [2]_e)\} = \ln \{([x_2]_0(1 + K_e) - 1)/([x_2](1 + K_e) - 1)\} = (k_3 + k_{-3})t \qquad (7)$$

the set of kinetic constants that allows the best fit of the experimental data, solving repeatedly the system of differential equations eqs 3, 8 and 9 (see Experimental Section).

$$d[2]/dt = -d[1]/dt - k_3[2] + (k_3/K_e)[3] \qquad (8)$$

$$d[3]/dt = k_3[2] - (k_3/K_e)[3] \qquad (9)$$

The optimization was also used to obtain alternative estimates of the ratios k_{-1}/k_2. The constants k_1 and K_e, on the contrary, were fixed to the values obtained as previously described, to overcome the correlation between k_1 and k_{-1}/k_2 (and, in minor measure, between k_3 and K_e). Figure 1 shows examples of the fit between the experimental data and the values calculated. Apart from such visual inspection, the goodness of the fits was assessed by the conventional agreement indices *R*, reported in Table II. Table II shows also the close agreement between the values obtained by least-squares fits and those provided by the optimization.[17]

The activation parameters for k_3, determined only for the PPh_2Me and PPh_3 derivatives, are reported in Table II. Values of K_e at different temperatures have been determined for PPh_3, PPh_2Me, and PMe_3: the variations were within the experimental errors, and therefore no attempt could be made to estimate the thermodynamic parameters of this equilibrium.

In some experiments (mainly at temperatures higher than 300 K) at longer reaction times, it was observed the formation of a low amount (typically 5–10%) of a byproduct, identified as the trans–diaxial bisubstituted derivative $[Re_3(\mu\text{-}H)_3(CO)_{10}(PR_3)_2]$ (**4**), by comparison with the hydridic resonances of an authentic sample, obtained by reaction of *trans-diaxial*-$[Re_3(\mu\text{-}H)_3(CO)_{10}(NCMe)_2]$ with PPh_3.[18] In the optimization of these experiments (runs 5, 6, 10, 12, and 14), it was therefore necessary to consider also the formation of compound **4**, in order to respect the balance of material. Fortunately, the values of k_3 and k_{-1}/k_2 provided by the optimizations resulted in little sensitivity to the model[19] used to fit the concentration of **4**, the variations being lower than 5%.

Discussion

The results concerning the substitution step agree well with those obtained by Poë et al.[3] for the closely related triangular cluster $[Os_3(CO)_{11}(NCMe)]$. In both cases, the experimental data could be accounted for by a reversible dissociative mechanism, without significant associative contribution, as expected for the lability of nitrile ligand. The activation parameters concerning the dissociative step (k_1) are quite similar: E_a 115 (Os) vs 118.3 ± 1.8 (Re) kJ mol^{-1}; ΔH^* 112.4 ± 1.8 (Os) vs 115.9 ± 1.7 (Re) kJ mol^{-1}; ΔS^* 92.6 ± 6.4 (Os) vs 70.3 ± 5.6 (Re) J K^{-1} mol^{-1}. The higher value of k_1 for Os (ca. 50 times, at 300 K, as computed from the activation data) arises therefore mainly from the entropic term. Following Poë et al.,[3] this could be the result of a stronger Re–NCMe bond, with respect to the Os–NCMe one, the extent of bond breaking in the transition state being then larger for Os than for Re. Alternatively, the difference in the solvent used in the experiments ($CDCl_3$ vs toluene) should be taken into account, because of the possibility of some degree of interaction with the solvent in the transition state in the case of Re (recently complexes with coordinated CH_2Cl_2 have been postulated and even isolated[20]).

(15) An associative mechanism is ruled out because the rate of isomerization is insensitive to the PR_3 concentration, as shown not only in runs 1–3, 16, and 17, but also from preliminary experiments using approximately equimolar ratios of PR_3 and **1**.

(16) This experiment was suggested by a reviewer.

(17) The only significant difference is observed in the case of k_{-1}/k_2 for $P(OMe)_3$, where the pseudo-second-order approximation is not strictly valid: the optimization value is therefore more reliable, being obtained through the complete form of eq 3.

(18) δ −15.9 (t, 1, J_{H-P} = 8 Hz) and δ −15.1 (d, 2, J_{H-P} = 15.5 Hz): Ciani, G.; Sironi, A.; D'Alfonso, G.; Romiti, P.; Freni, M. *J. Organomet. Chem.* **1983**, *254*, C37.

(19) Several semiempirical models were tried, assuming as parent compound the axial isomer only or both the isomers and postulating either an associative mechanism or a reversible dissociative process. In Table II, we have reported the values obtained using the dissociative mechanism starting from compound **2** that gave generally the best results (obviously we cannot give any mechanicistical meaning to this).

Table III. Kinetic and Thermodynamic Data[a] for the Six Ligands at 300 K

ligand	k_{-1}/k_2	k_2/k_{-1}	K_e	$k_3 \times 10^5$, s^{-1}	$k_{-3} \times 10^6$,[b] s^{-1}	θ[c]	pK_a[d]
PPh_3	8.34 (6)[e]	0.120 (4)	2.4 (3)	1.52 (3)[e]	6.3 (9)	145	2.73
PPh_2Me	2.65 (5)	0.377 (7)	2.4 (3)	1.71 (3)[e]	7.1 (9)	136	4.59
$PPhMe_2$	1.61 (3)	0.621 (12)	2.9 (4)	0.83 (1)	2.9 (4)	122	6.49
PMe_3	1.10 (5)	0.909 (41)	7.3 (10)	2.37 (4)	3.2 (4)	118	8.65
$P(n\text{-}Bu)_3$	5.03 (8)	0.199 (3)	8.7 (12)	4.69 (5)[e]	5.3 (9)	132	8.43
$P(OMe)_3$	2.84 (5)	0.352 (6)	1.9 (2)	0.38 (1)	2.0 (2)	107	2.60

[a] The values of k_{-1}/k_2 and k_3 are those from optimization. In parentheses are given the standard deviations, referred to the last digits. [b] Computed from k_3/K_e. [c] Values (deg) of the cone angle of Tolman.[23] For $P(n\text{-}Bu)_3$ and $P(OMe)_3$, the values revised according to ref 25 are 137 and 128°, respectively. [d] From ref 20a. [e] Weighted averages of the values reported in Table II at 300 K (in parentheses are given the standard deviations, as computed by the propagation of errors).

Also the constant k_{-1}/k_2 has a value quite comparable with that found in the osmium cluster (ca. 10, at 30 °C, for PPh_3, which is the only ligand common to both studies), indicating that the similarity between Os and Re systems concerns also the relative reactivities of the unsaturated intermediates toward MeCN and PPh_3.

The values of k_{-1}/k_2 for most P-donor ligands have been estimated from only one experiment. However, the good reproducibility of the different determinations of k_{-1}/k_2 for PPh_3 at 300 K (Table II) makes these numbers substantially trustworthy. The constant k_2/k_{-1} measures the "competition ratio"[11,12] between the entering and leaving ligand: ordering the ligands according to the increase of the ratio k_2/k_{-1} (at 300 K, Table III), the following scale of increasing nucleophilicity can be stated:

$$PPH_3 < P(n\text{-}Bu)_3 < P(OMe)_3 < PPh_2Me < PPhMe_2 < PMe_3 < MeCN$$

The range of values of k_2/k_{-1} is modest, in agreement with the relatively high reactivity (small selectivity) of a coordinatively unsaturated intermediate.[11,12,21]

Methods of factorizing thermodynamic and kinetic data for associative reactions of metal carbonyls with P-donor ligands into electronic and steric effects have been reported.[22-24] Linear free-energy relationships have been observed[23] between ln k (or ln K_e) and electronic parameters (such as pK_a of HPR_3^+),[22a] and "steric profiles" have been obtained by plots of ln $k - \alpha pK_a$ against the cone angle of the phosphine, θ.[25] This analysis can be applied also to the competition ratios k_2/k_{-1}, ln k_{-1} being a constant term. Figure 3 shows that for the three smaller ligands PMe_3, PMe_2Ph, and $P(OMe)_3$ ln (k_2/k_{-1}) varies linearly against pK_a of HPR_3^+ (R^2 = 0.998), suggesting that steric effects became significant only for bulkier ligands. The slope of the line (0.150 ± 0.007), comparable for instance with that found for $Ru_3(CO)_{12}$,[23b] shows that the unsaturated intermediate $Re_3H_3(CO)_{11}$ is somewhat discriminating electronically.

The plot against θ of the values of ln (k_2/k_{-1}) corrected for electronic effects (Figure 4) provides the steric profile of the reaction,[26] setting the steric threshold at about 125–130°. Above this value, the rate drops quickly with increasing cone angle, and no reaction was observed with $P(t\text{-}Bu)_3$ (θ = 182°) and $P(i\text{-}Pr)_3$ (θ = 160°).

The position of $P(n\text{-}Bu)_3$ is anomalous, as observed also in other cases: $P(n\text{-}Bu)_3$ resulted in a nucleophile even worse than PPh_3 in the competition toward the coordinatively unsaturated intermediates $Mo(CO)_4(PPh_3)$[11] and $[Co_2(C_2Ph_2)(CO)_5]$.[21b] This prompted the authors to speculate on the possibility of mechanisms

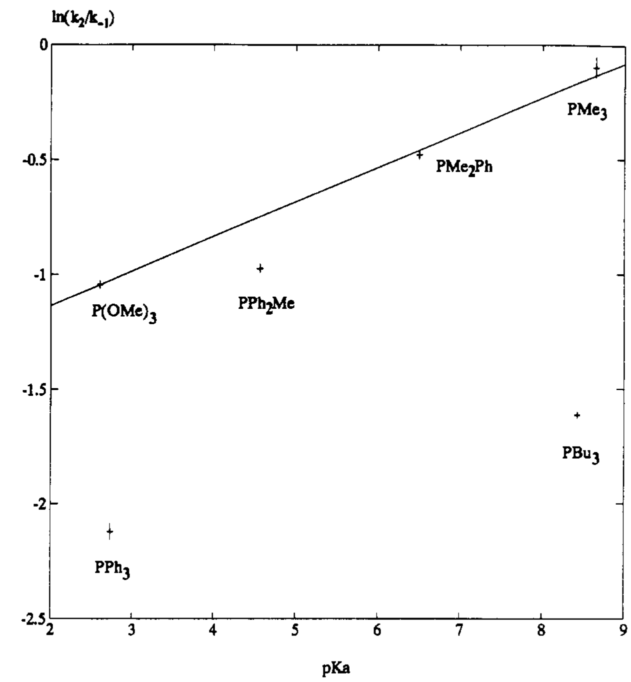

Figure 3. Plot of ln (k_2/k_{-1}) vs pK_a for the six ligands, showing the linear relationship for the three smaller ones. The vertical lines are proportional to the estimated standard deviations of each experimental value.

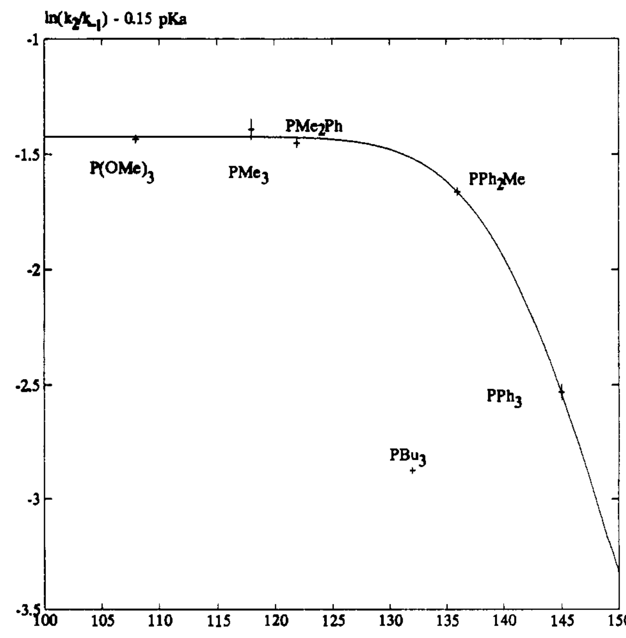

Figure 4. Plot against θ of ln $(k_2/k_{-1}) - 0.15\ pK_a$, showing the steric profile of the reaction of the coordinatively unsaturated intermediate $Re_3(\mu\text{-}H)_3(CO)_{11}$ with PR_3.

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(26) If the revised value[27] of 128° was used as measure of θ for $P(OMe)_3$, a slightly higher steric threshold would be obtained.

different from a simply dissociative one, leading to the same rate law. We cannot rule out this hypothesis, but it is also possible that the Tolman cone angle significantly underestimates the steric hindrance of $P(n\text{-}Bu)_3$, due to the assumption that all the alkyl chains are folded back. In fact, as recently pointed out[27] for $P(OMe)_3$ and PEt_3, two of the three groups bound to P are prevented from pointing back by repulsive $CH_3 \cdots CH_3$ interactions. In spite of the high conformational flexibility of the n-butyl chains, a cone angle not lower than that of PEt_3 (revised[27] as 137°) should be assumed. Still higher values (141–150°) have been evaluated from X-ray data,[28] but lattice effects could influence these values.

Values of k_{-1}/k_2 at different temperatures have been determined only for PPh_3: no significant variation was observed, indicating a little difference of E_a for the two competitive reactions of the intermediate $Re_3H_3(CO)_{11}$. The better nucleophilicity of MeCN with respect to the phosphines derives likely from entropic factors: the permanence of MeCN in the solvent cage would be in line with this.

In the case of the reaction of $[Os_3(CO)_{11}(NCMe)]$ with phosphines, the product contains the ligand in equatorial position, while the leaving MeCN was axially coordinated. For all the phosphine-substituted triangular clusters of the iron triad, axial isomers had never been observed,[29] due to steric hindrance. The k_2 constant accounts therefore also for this stereochemical rearrangement. In $[Re_3(\mu\text{-}H)_3(CO)_{11}(NCMe)]$, on the contrary, the substitution gives the axial isomer **2**, and at equilibrium significant concentrations of this species are still present. As already observed,[2,5] this difference can be attributed to the bridging hydrides, which cause two relevant structural modifications: (i) longer metal-metal distances, which release the steric hindrance between the axial carbonyls and the groups bound to an axially co-ordinated P atom; (ii) smaller L_{eq}–M–L_{eq} angles, which increase the interligand repulsive interactions for an equatorially coordinated bulky ligand. In the rhenium case, therefore, it is not possible to predict qualitatively the preference of a bulky ligand for an axial or an equatorial location.

The values of K_e measured in this work show that the equatorial isomers are the preferred ones also in the rhenium case,[30] but the major preference for these isomers is displayed by the more basic phosphines PMe_3 and $P(n\text{-}Bu)_3$, rather than by the bulkier ones (Table III). Also the values of the coefficients of linear correlation (r) of ln K_e with pK_a (0.918) and θ (−0.237, using for $P(n\text{-}Bu)_3$ and $P(OMe)_3$ the revised values[27]) show that K_e is mainly affected by electronic factors. Taking into account both parameters, through eq 10, r increases only slightly (0.950). Regression analysis provided the values of the coefficients of the equation (Figure 5a): the increase of K_e with θ is quite modest and overwhelmed by the increase with the basicity of the ligand.

$$\ln K_e = a + b\mathrm{p}K_a + c\theta \qquad (10)$$

This is quite surprising, because electronic factors are usually assumed to favor isomers with minimum mutually trans CO ligands.[31] In triangular clusters containing ligands less sterically demanding than phosphines, such as nitriles and isonitriles, the axial substitution is always favored, even for metals of group VIII.[32]

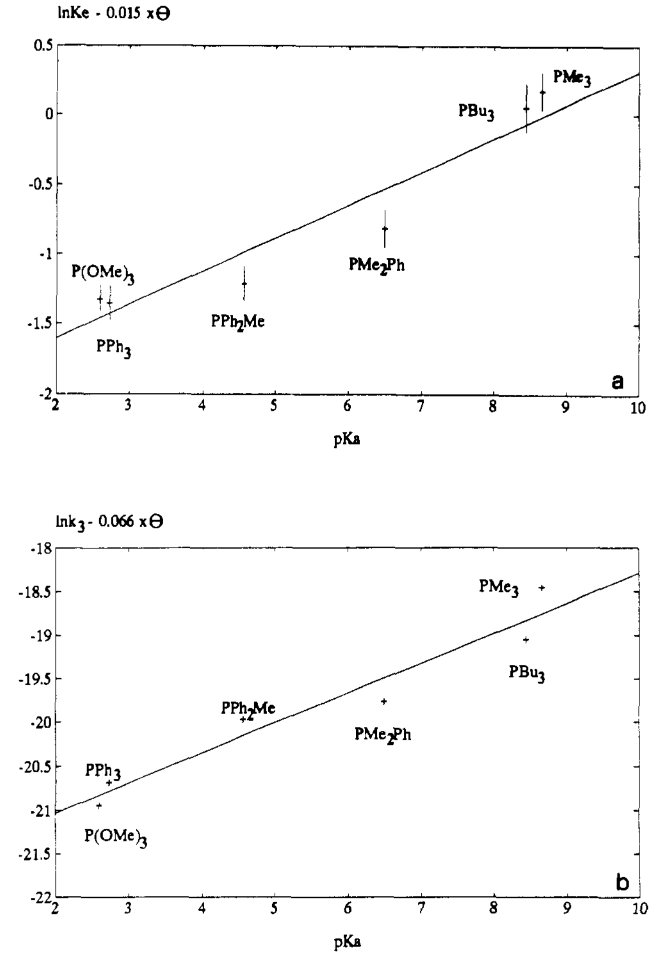

Figure 5. Plots against pK_a of experimental and calculated values of ln K_e (a) and ln k_3 (b) corrected by steric effects, according to eq 10, using the values of the coefficients provided by regression [a = −2.1 (1.5), b = 0.24 (4), and c = 0.015 (11) for K_e; a = −22 (1), b = 0.34 (4), and c = 0.066 (10) for k_3, the conventional agreement indices R being 0.16 and 0.20, respectively]. The vertical lines are proportional to the estimated standard deviations of each experimental value. The corresponding plots vs θ are similarly scattered.

As to the kinetic data, also the values of k_3 can be roughly fitted by an equation of the form of eq 10, with an overall correlation coefficient of 0.965 (the individual r being 0.688 and 0.254 for pK_a and θ, respectively). The equation, whose numerical parameters were provided by regression (Figure 5b), requires that k_3 about doubles for a 2-fold increase of the order of magnitude of K_a and for an increase of θ of 10°.[33]

Intramolecular rearrangements[35] in octahedral complexes are usually assumed to occur via a trigonal-twist mechanism,[36] and

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(30) An equilibrium mixture consisting of 71% of the equatorial form (corresponding to K_e = 2.45) is quoted in ref 6. Values of E_a slightly higher than ours (Table II) for the interconversion *axial* to *equatorial* are reported in ref 5 for PPh_3, PEt_3, and $P(OMe)_3$: 25 ± 1 kcal mol^{-1}.
(31) See, for instance: (a) Darensbourg, D. J.; Gray, R. L. *Inorg. Chem.* **1984**, *23*, 2993. (b) Harris, G. W.; Boeyens, J. C. A.; Coville, N. J. *J. Chem. Soc., Dalton Trans.* **1985**, 2277. (c) Zuffa, J. L.; Kivi, S. J.; Gladfelter, W. L. *Inorg. Chem.* **1989**, *28*, 1888 and references therein.
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(33) A much better fit of the data to eq 10 is obtained when only the four phosphines of the series PPh_3, PPh_2Me, $PPhMe_2$, and PMe_3 are considered: in this case a = −35.5 (1), b = 0.77 (4), and c = 0.154 (9) (r = 0.998, R = 0.018) for k_3 and a = −12 (1), b = 0.55 (4), and c = 0.077 (8) (r = 0.963, R = 0.086) for K_e. The data for $P(OMe)_3$ and $P(n\text{-}Bu)_3$ are however definitely out of the straight lines defined by the other four ligands and in opposite directions. This is reminiscent of the plot of $E°$ against pK_a for the complexes $MeCp(CO)_2MnL$, where the opposite deviations from the linearity were used as quantitative measures of the opposite π-properties of the ligands [acid $P(OMe)_3$, basic $P(n\text{-}Bu)_3$][22a] It is doubtful if this observation is mechanicistically meaningful, also due to the significant correlation (r = 0.975) between the values of pK_a and θ for the four phosphines. The use of Bartik's χ values,[34] instead of pK_a values, led to an even worst fit for $P(OMe)_3$ and $P(n\text{-}Bu)_3$.
(34) Bartik, T.; Himmler, T.; Schulte, H. G.; Seevogel, K. *J. Organomet. Chem.* **1984**, *272*, 29.
(35) A significant contribution of a mechanism based on PR_3 dissociation has been already ruled out; moreover it would not be consistent with the activation parameters (Table II).
(36) Hansen, L. M.; Marynick, D. S. *Inorg. Chem.* **1990**, *29*, 2482.

the relative rates have been shown to be affected both by steric and electronic effects.[37] In cluster chemistry, however, intramolecular mechanisms are possible involving intermediates with one metal coordinatively unsaturated: the break of a Re(μ-H)Re interaction, for instance, would make a rhenium atom pentacoordinate and therefore stereochemically nonrigid. The isomerization rate would therefore be related to the cis-labilizing power of the phosphine, which is expected to increase not only with the size of the ligand but also with its donor ability.

No definite mechanistic conclusion, however, can be drawn from the data concerning the isomerization. A theoretical approach, based on MO and molecular mechanic computations, is on schedule, in order to better understand electronic and steric properties of the two ground states and their possible interconversion paths.

Acknowledgment. We are indebted to Prof. Angelo Sironi for many helpful discussions and suggestions.

(37) See, for instance: Dixon, D. T.; Kola, J. C.; Howell, J. A. S. *J. Chem. Soc., Dalton Trans.* **1984**, 1307.

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Ecole Polytechnique Fédérale, CH-1015 Lausanne, Switzerland

Base Hydrolysis of Acidato Pentakis(methylamine) Complexes of Cobalt(III): Evidence for the Pentacoordinated Intermediate $Co(NH_2CH_3)_4(NHCH_3)^{2+}$ Exhibiting a Lifetime of ≈1 ns

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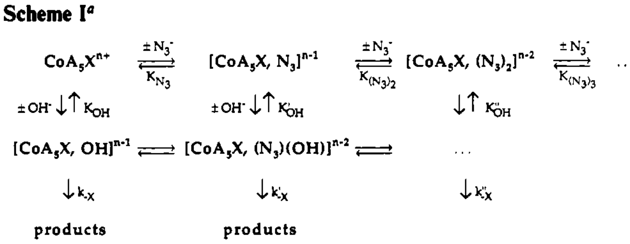
The kinetics and products of the base hydrolysis of two $Co(NH_2CH_3)_5X^{n+}$ complexes (X = Cl^-, DMF) have been studied at 25 °C in 0.02–1.0 M azide and ≈(0.2–8) × 10^{-3} M hydroxide (at variable ionic strength). The products, $Co(NH_2CH_3)_5OH^{2+}$ and $Co(NH_2CH_3)_5N_3^{2+}$, are formed via the genuine pentacoordinated intermediate $Co(NH_2CH_3)_4(NHCH_3)^{2+}$ and its ion-aggregates with azide, viz. $[Co(NH_2CH_3)_4(NHCH_3),N_3]^+$ and $[Co(NH_2CH_3)_4(NHCH_3),(N_3)_2]$. The free intermediate $Co(NH_2CH_3)_4(NHCH_3)^{2+}$ collapses with water, whereas both the ion aggregates collapse exclusively with azide to form $Co(NH_2CH_3)_5N_3^{2+}$. The intermediates are not at equilibrium with azide from the bulk solution because of their fast collapse rates. The lifetime of the pentacoordinated intermediate is ≈1 ns. Base hydrolysis of $Co(NH_2CH_3)_5Cl^{2+}$ has also been studied at 25 °C and I = 1 M in the presence of competitors other than azide, and competition ratios have been obtained via a new method. Interestingly, fluoride competes efficiently for the pentacoordinated intermediate, but not for the hexacoordinated ones.

Introduction

Base hydrolysis[1] of acidato pentaammine complexes of cobalt(III), $Co(NH_3)_5X^{n+}$, has been shown[2,3] to proceed via hexacoordinated intermediates. The reactions presented in Scheme I (A_5 is equal to $(NH_3)_5$ in this case) did not allow us to rationalize both kinetic[2] and competition[3] data obtained at variable ionic strength. Scheme I—being consistent with the kinetics[2]—turns out incomplete, since the kinetically predicted competition ratios (R) are much larger than the measured ones. This apparent discrepancy has been suggested[2,3] to be due to the existence of intermediates arising *after* the activation of the Co–X bond (i.e. the rate-determining step). They escape kinetic detection and exhibit[3] a sufficiently long lifetime to establish ion-aggregation equilibria with anions from the bulk solution. These intermediates are hexacoordinated, because the ionic strength dependence of the competition ratios showed unambigously[3] that the leaving group is present in the first coordination sphere during the product formation step. The facts presented above[2,3] as well as a quantum mechanical study[4] support the existence of hexacoordinated intermediates in the base hydrolysis of the $Co(NH_3)_5X^{n+}$ complexes. The latter are the least strained and constrained (acidato)pentaaminecobalt(III) compounds.

The more strained $Co(NH_2CH_3)_5X^{n+}$ complexes are well-known[1,5] for their enhanced sensitivity to base hydrolysis. This effect is known[5] as steric acceleration. It was expected that strain in the ligand sphere would destabilize the weak[4] Co–X bond of hypothetical hexacoordinated intermediates and favor the formation of pentacoordinated ones. This study reports on the kinetics and reaction products of the base hydrolysis of two $Co(NH_2CH_3)_5X^{n+}$ complexes (X = Cl^-, DMF). Various models for product formation involving either intermediates or just transition states are discussed in detail.

Scheme I[a]



[a] A_5 = pentaamine ligand, i.e. $(NH_3)_5$ or $(NH_2CH_3)_5$.

Experimental Section

Physical Measurements. The equipment and the general procedures have been described previously.[2,3]

Synthesis. $[Co(NH_2CH_3)_5Cl]Cl_2$ and $[Co(NH_2CH_3)_5DMF](CF_3SO_3)_3$ were prepared as described in the literature.[6–8] $[Co(NH_2CH_3)_5N_3](NO_3)_2\cdot{}^1/_2H_2O$ was prepared by adding 200 mg of $[Co(NH_2CH_3)_5Cl]Cl_2$ dissolved in 10 mL of 2 mM $HClO_4$ to a solution containing 10 mL of 5 M NaN_3 and 2 mL of 0.4 M KOH. After about 5 s, 15 mL of 4 M $HClO_4$ was added and the solution diluted 10 times and adsorbed on an ion-exchange column (Dowex 50W-X2 200–400 mesh, H^+ form) under exclusion light. The desired product was eluted with 1 M NH_4Cl at pH = 2 (HCl), the eluent evaporated, and the NH_4Cl removed by washing with ethanol. The crude chloride was dissolved in water and precipitated with $NaNO_3$. Finally, the crude nitrate was redissolved in water, the solution filtered to remove solid impurities, and the product precipitated by adding a saturated $NaNO_3$ solution. The crystals were filtered off, washed with ethanol, and air-dried. Anal.

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