Ligand Effects on the Fragmentation of Ion–Molecule Complexes of Transition-metal Ions with Amines†

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The dissociations of a series of metastable RNH_2–$CoCl^+$ complex ions (R = alkyl) have been studied using *B*/*E* linked scan techniques. These reactions were compared with those of corresponding RNH_2–Co^+ ions. Ligand effects on the metal-ion reactivity and ligand–ligand coupling are presented.

Although the chemistry of naked metal ions in the gas phase has been extensively reported,[1] relatively little is known about ligated metal ions. In fact, studies of the latter species may provide deeper insight into the chemistry of metal ions in the condensed phase such as catalytic processes. Ligand effects are usually complicated and not well understood. The ligands may affect the reactivity of the metal ions by distorting the electronic structures of the metals or by ligand–ligand coupling. For instance, $CrCl^+$ has two bonding configurations, a covalent σ bond and a π bond, which permits it to act as a diradical species and to insert into a C–H bond of alkanes.[2,3] In contrast, Cr^+ is unreactive towards alkanes. More evidence has been found for ligand–ligand coupling.[4] For example, it occurs in the form of Diels–Alder reactions when alkene–M^+ reacts with alkenes.[5] It is very pronounced for Co^+, while limited for Fe^+ and basically non-existent for Ni^+.

We have recently found that alkene–CoL^+–NH_3 (L = RNH_2) complexes, formed from $Co(amine)_2{}^+$, fragment by losing NH_3 rather than the alkenes.[6] The fact that the alkene–Co^+ bond-dissociation energies are lower than that of NH_3–Co^+ ‡ is probably due to ligand–ligand repulsion between ammonia and the RNH_2 ligand, and increased π bonding between the alkenes and the cobalt ion.[8] In this paper, we report the reactions of amine–$CoCl^+$ and compare these with amine–Co^+.

Experimental

A Concept IS double-focusing mass spectrometer of *E*/*B* configuration (Kratos Analytical, Urmstrom, Manchester, UK) was used. It was controlled by a Kratos DS 90 Data General Eclipse based computer system. A Kratos Mach 3 data system running on a SUN SPARC station was used for further data work-up. The normal fast atom bombardment (FAB) source was modified with an extra hole in the side so that it could accept a reservoir probe as the source of gaseous molecules *via* the normal electron ionization/chemical ionization probe lock. The source was also modified to operate at higher pressure than the conventional FAB source. Detailed descriptions of the modified instrument and operating conditions are given elsewhere.[9] Briefly, the instrument was fitted with an Ion Tech saddle-field atom gun. Xenon was used as the fast-atom source. The fast atom-beam energy was 8 keV (*ca.* 1.28×10^{-15} J) with a density corresponding to an emission current of about 1 mA. The source was operated at 25 °C, a pressure of about 10^{-5} Torr (*ca.* 1.33×10^{-3} Pa) (measured in the source housing rather than in the reaction region) and an accelerating voltage of 6 kV. Normal mass spectra were recorded at a resolving power of ≈ 1000. Metastable ion (MI) fragmentations in the first field-free region were monitored by *B*/*E* linked scans. The FAB source however, produces metastable ions with lower internal energies than obtained in conventional EI sources. Naked metal ions were generated from $FeSO_4$·$7H_2O$, $CoCl_2$·$6H_2O$ and $NiCl_2$·$6H_2O$ which had been dissolved in water and deposited by evaporation onto the FAB probe tip. The amine (≈ 3 μl) was introduced into the source using the reservoir probe. Labelled $CD_3CH_2CH_2NH_2$ was synthesised by aminolysis of $CD_3CH_2CH_2Br$. Other samples were commercially available and used without further purification.

Results and Discussion

Under the FAB source conditions, $CoCl_2$·$6H_2O$ for the most part generates Co^+ and $CoCl^+$ after ionization. These ions react with an amine in the source to produce mono-adducts and metal-bound dimer ions, RNH_2–$Co^+(Cl)$ and $Co(RNH_2)_2{}^+(Cl)$. The MI spectral data for the RNH_2–$CoCl^+$ ions are given in Table 1. We will discuss these MI reactions and compare them with those of RNH_2–Co^+ ions (Table 2).

Except for *t*-$C_4H_9NH_2$–$CoCl^+$, all of the RNH_2–$CoCl^+$ ions eliminate H_2. Dehydrogenation is the most important fragmentation for the RNH_2–$CoCl^+$ ions which contain large amines such as those with R = C_5H_{11}, C_6H_{13} and *cyclo*-C_6H_{11}. In order to determine the origin of H_2, the spectra of labelled *i*-$C_3D_7NH_2$–$CoCl^+$ and $CD_3CH_2CH_2NH_2$–$CoCl^+$ ions have been investigated (Table 3). The MI spectrum of the *i*-$C_3D_7NH_2$–$CoCl^+$ ion shows both HD and D_2 losses with a relative intensity of HD : D_2 = 3 : 1, revealing that both the alkyl and the amino groups contribute to the dehydrogenation. For the $CD_3CH_2CH_2NH_2$–$CoCl^+$ ion only HD loss is observed. Obviously, the neutral HD species comprises a deuterium from the terminal CD_3 group and a hydrogen from either the alkyl chain or the amine group.

Although a series of RNH_2–Co^+ complexes have been studied in the past ten years,[1] no investigation on the analogous RNH_2–$CoCl^+$ ions appears in the literature. Radecki and Allison[10] reported that a HD elimination predominates when Co^+ reacts with $C_2H_5ND_2$. However, for other primary amines (larger than ethylamine) with Fe^+ and Co^+, Schwarz and co-workers[11,12] found that the hydrogen originates *via* an 1,2 elimination from the terminal ethyl group of the alkyl chains. The specific terminal 1,2 elimination was described in terms of 'remote functionalization'.[13] Furthermore, for analogous complexes of Ni^+, all of the hydrogens from both the alkyl chain and the amino group contribute to the dehydrogenation, due to extensive hydrogen-scrambling processes.[12] Our results show that *i*-$C_3D_7NH_2$–Co^+ eliminates D_2 exclusively from the alkyl chain (see Table 3). We thus propose that the remote-

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† *Non-SI unit employed:* cal = 4.184 J.

‡ Although RNH_2–Co^+ bond energies are not available, it is found, in general, that *D*(RNH_2–M^+) > *D*(alkene–M^+). For example, NH_3–Co^+ (58.8) > C_2H_4–Co^+ (37 kcal mol^{-1}).[7]

Table 1 Metastable ion spectral data (% relative intensities) for RNH_2–$CoCl^+$ complex ions

	R											
Neutral loss*	C_2H_5	*n*-C_3H_7	*i*-C_3H_7	*n*-C_4H_9	*i*-C_4H_9	*s*-C_4H_9	*t*-C_4H_9	*n*-C_5H_{11}	*n*-C_6H_{13}	*cyclo*-C_6H_{11}	$PhCH_2$	$PhCH_2CH_2$
H_2	14	41	54	75	59	77		100	100	100	30	21
HCl	19	21	5	50	37	19					2	100
HCl + H_2	3	6	13	38	11	18		58	55	23	24	5
CoCl(H)	100	100	100	100	100	100		47	45	29	7	62
C_4H_8							56					
$CoCl(NH_2)$							100			34	100	2
CH_2NH												47

* The actual structures of the neutral products cannot be identified in this work. The formulas given here are based on energy considerations.

Table 2 Metastable ion spectral data (% relative intensities) for RNH_2–Co^+ complex ions

	R											
Neutral loss*	C_2H_5	*n*-C_3H_7	*i*-C_3H_7	*n*-C_4H_9	*i*-C_4H_9	*s*-C_4H_9	*t*-C_4H_9	*n*-C_5H_{11}	*n*-C_6H_{13}	*cyclo*-C_6H_{11}[b]	$PhCH_2$	$PhCH_2CH_2$
H_2	65	12	100	100	32	100		25	17	100	100	100
CH_4			35		100	6	100					
NH_3							7					5
C_2H_4	13	100		39		39		100	16			8
C_3H_6				1	17	16		6	100	1		
C_4H_8							18					
CoH	100	8	8	3	3	1		2		5	3	
RNH_2												
$CoCH_3$			4				9					
$PhCH_3$												6

[a] See footnote * in Table 1. [b] The ion *cyclo*-$C_6H_{11}NH_2$–Co^+ produces additional fragments, $NH_2 + 2H_2$ (2) and $NH_3 + 2H_2$ (1%).

Table 3 Isotopic products formed from *i*-$C_3D_7NH_2$–$CoCl^+$, $CD_3CH_2CH_2NH_2$–$CoCl^+$ and *i*-$C_3D_7NH_2$–M^+ (M = Co, Ni or Fe) complex ions*

	R in RNH_2–$CoCl^+$			M in *i*-$C_3D_7NH_2$–M^+		
Neutral products	*i*-C_3D_7	$CD_3CH_2CH_2$	Neutral products	Co	Ni	Fe
			H_2		1	
HD	75	100	DH		22	< 1
D_2	25		D_2	100	77	> 99
DCl	100		CD_4	100	100	100
HCl		100				
DCl + D_2	10		NH_2D			100
DCl + DH	90					
HCl + DH		100	MD	100	100	100
CoCl(H)		100	MCD_3	100	100	
CoCl(D)	100					

* Intensities are given in % Σ fragments = 100% for each class of neutral product respectively.

functionalization mechanism accounts for the dehydrogenation from *i*-$C_3D_7NH_2$–Co^+, because it can explain the exclusive D_2 elimination. Compared with *i*-$C_3D_7NH_2$–Co^+, the major contribution of the NH_2 group to the formation of HD from the *i*-$C_3D_7NH_2$–$CoCl^+$ ion demonstrates the ligand effects of Cl which lead to extensive hydrogen-scrambling processes, *i.e.* fast D/H exchange between the NH_2 and the *i*-C_3D_7 groups prior to the dehydrogenation.

In addition to dehydrogenation, most of the RNH_2–$CoCl^+$ ions eliminate HCl and consecutive HCl + H_2. With the smaller amines the former process is favoured, while those with alkyl chains longer than C_4 exclusively undergo the latter reaction. A similar loss of HCl or HCl + H_2 has been reported for $TiCl_2^+$ and $TiCl_3^+$ upon reacting with small alkenes.[14] The data for labelled *i*-$C_3D_7NH_2$–$CoCl^+$ indicate that DCl arises by combination of a deuterium from the alkyl chain with chloride from the cobalt, before or after dehydrogenation (Table 3). The *i*-$C_3D_7NH_2$–$CoCl^+$ ion also produces neutral CoCl(D) species. It is thus likely that the DCl loss involves the same intermediate as in the elimination of CoCl(D) which corresponds to the most important reaction of the small alkylamines ($\leqslant C_4$). Furthermore, the loss of CoCl(H) seems similar to an analogous loss of CoH from the RNH_2–Co^+ ions where CoH arises *via* an α-hydride abstraction accompanied by the formation of an iminium ion.[10,11a,12] However, compared with the loss of CoCl(H) from the RNH_2–$CoCl^+$ ions, the loss of CoH from RNH_2–Co^+ is much less important and even absent for larger amines [see Table 2 and refs. 11(*b*) and 11(*c*)]. This suggests that neutral CoCl(H) is more stable than CoH, probably due to the stronger covalent Co–Cl bond [D° (298 K) = 93 kcal mol^{-1}][15] than the Co–H bond [D° (298 K) = 35.1 kcal mol^{-1} (1 value)].[16]

A different situation exists for the *t*-$C_4H_9NH_2$–$CoCl^+$ ion. None of the H_2, HCl, HCl + H_2 or CoCl(H) loss is observed; instead, it loses C_4H_8 and $CoCl(NH_2)$ to generate NH_3–$CoCl^+$ and *t*-$C_4H_9^+$ ions, respectively. These reactions can be described in terms of $CoCl^+$ inserting into the C–N bond followed by β-H transfer and reductive elimination of isobutene

Table 4 Metastable ion spectral data (% relative intensities) for RNH_2–Ni^+ complex ions

	R											
Neutral loss*	C_2H_5	n-C_3H_7	i-C_3H_7	n-C_4H_9	i-C_4H_9	s-C_4H_9	t-C_4H_9	n-C_5H_{11}	n-C_6H_{13}	$cyclo$-C_6H_{11}	$PhCH_2$	$PhCH_2CH_2$
H_2	13	7	84	19	18	4		39	43	100	100	76
CH_4			100		3	< 1	100					
NH_3							3			11		2
C_2H_3												22
C_2H_4	11	100		18		100		100	85	38		6
C_3H_6				100	100				100	33		
C_4H_8							7	17				
NiH	100	3	46	2	3	2				37	4	
RNH_2												
$NiCH_3$			42				52					100
$PhCH_3$												

* See footnote * in Table 1.

Table 5 Metastable ion spectral data (% relative intensities) for RNH_2–Fe^+ complex ions

	R											
Neutral loss*	C_2H_5	n-C_3H_7	i-C_3H_7	n-C_4H_9	i-C_4H_9	s-C_4H_9	t-C_4H_9	n-C_5H_{11}	n-C_6H_{13}	$cyclo$-C_6H_{11}	$PhCH_2$	$PhCH_2CH_2$
H_2	100	18	100	100	45	5		100	100	100	100	16
$2H_2$									20			
CH_4			6		100		50					
$CH_4 + H_2$							26					
NH_3		3	5			12	100				1	37
$NH_2 + 2H_2$										14		
$NH_3 + 2H_2$										2		
C_2H_4	8	100		9				63	4			100
C_2H_5				6				33	20			
C_2H_6									36			
C_3H_6		8			42	100			29			
C_4H_8							82					
FeH	19		7	3				15	2	9	1	
RNH_2	13						5			3		
$PhCH_3$												8
C_6H_{10}										2		

* See footnote * in Table 1.

or by direct C–Co bond cleavage to produce $CoCl(NH_2)$ and t-$C_4H_9{}^+$ ions. The driving force for the reactions is probably due to the energetically favourable intermediate, t- C_4H_9–$CoCl^+$–NH_2, and the high stability of the t-$C_4H_9{}^+$ ion ($\Delta H_f{}^0$ = 165.8 kcal mol^{-1}).[16] Similarly, $cyclo$-$C_6H_{11}NH_2$–$CoCl^+$ and $PhCH_2NH_2$–$CoCl^+$ produce highly stable $cyclo$-$C_6H_{11}{}^+$ and $PhCH_2{}^+$ ions, respectively, after eliminating the neutral $CoCl(NH_2)$ species. For $PhCH_2CH_2NH_2$, $CoCl^+$ can also insert into the β-C–C bond, forming a $PhCH_2$–$CoCl^+$–CH_2NH_2 intermediate from which CH_2NH is eventually eliminated after β-H(NH) transfer.

We have discussed, above, the fragmentation mechanism of the RNH_2–$CoCl^+$ ions. An overall comparison will now be made between the fragmentations of the RNH_2–$CoCl^+$ and the corresponding RNH_2–Co^+ ions. The reactions of naked transition-metal ions with most of the alkylamines listed in Table 2 have been studied using ion-beam,[17] Fourier-transform mass spectroscopy,[18] ion cyclotron resonance[10,19] and sector instruments.[11–13] Previous studies give similar results with some differences due to the different methods employed. Our results in Table 2 are approximately the same as those obtained by Schwarz and co-workers[11–13] using a multiple-sector spectrometer. Moreover, we observe a loss of NH_3 from t-$C_4H_9NH_2$– Co^+ and $PhCH_2CH_2NH_2$–Co^+ ions. The deamination of n-$C_3H_7NH_2$ by Fe^+, but not Co^+ and Ni^+, has been explained in terms of the promotion energy required to achieve a metal-ion configuration conductive to the formation of two σ bonds;[19a] Fe^+ has a lower promotion energy than those of Ni^+ and Co^+ and is thus able to insert into the C–N bond. This and previous work shows that all the RNH_2–Co^+ ions give C–H, C–C or C–N (for some amines) activation products. In contrast, the $CoCl^+$ ion activates only the C–H bonds of the alkylamines (except for i-$C_4H_9NH_2$ and $cyclo$-$C_6H_{11}NH_2$). This may be understood on the basis that chlorine ligating to Co^+ reduces the ion reactivity, compared to the naked Co^+ ion, while ligand–ligand coupling on the metal centre after the C–H activation becomes dominant. For the RNH_2–$CoCl^+$ ions (R = t-C_4H_9, $cyclo$-C_6H_{11}, $PhCH_2$ as well as $PhCH_2CH_2$), C–C and/or C–N bond activation are also observed. As discussed above, this could be due to the energetically favourable intermediates and the stable products.

In the course of this work, MI data for the RNH_2–Ni^+ and RNH_2–Fe^+ ions have also been collected (Tables 4 and 5). The data for RNH_2–M^+ (R = n-C_5H_{11}, n-C_6H_{13}, $PhCH_2$ or $PhCH_2CH_2$) are reported for the first time. Overall, Fe^+ shows a higher reactivity than do Co^+ and Ni^+, and is able to insert into various bonds. Its insertion into the C–N bonds of RNH_2 (R = n-C_3H_7, i-C_3H_7, s-C_4H_9, t-C_4H_9, n-C_6H_{13}, $PhCH_2$ or $PhCH_2CH_2$) induces loss of NH_3. The higher reactivity of Fe^+ is consistent with its lower promotion energy. Note, however, that Ni^+ but not Co^+ and even Fe^+ can activate the $cyclo$-C_6H_{11}–NH_2 bond, representing an exceptional case.[6]

In conclusion, the $CoCl^+$ ion is differentiated from the naked Co^+ ion upon reacting with amines after complexation.

The chloride ligand reduces the metal-ion reactivity while the ligand–ligand coupling becomes important. Further studies including theoretical treatments are necessary.

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