The reaction of azide ions, N_3^-, with metal carbonyl compounds; an electrospray mass spectrometry study[1]

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Abstract

Mono- and poly-nuclear metal carbonyls, and substituted analogues, have been analysed in the presence of N_3^- ions by negative-ion electrospray mass spectrometry. Most complexes yield the appropriate isocyanate-containing anions by conversion of a CO ligand to an NCO^- one with elimination of N_2. In some cases $[M + N_3]^-$ ions are observed; for species such as $H_2Os_3(CO)_{10}$ or $Ru_5C(CO)_{15}$ these arise from addition at a metal–metal bond, but in other cases they may represent the first-formed adduct from attack of N_3^- at a CO ligand. For hydride-containing clusters such as $H_4Ru_4(CO)_{12}$, the azide ion can act as a base, abstracting H^+ and forming $[M-H]^-$ ions in competition with nucleophilic attack. © 1999 Elsevier Science S.A. All rights reserved.

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1. Introduction

We have recently reported [1] a derivatisation method for preparing neutral metal carbonyls for analysis by electrospray mass spectrometry (ESMS), namely by nucleophilic addition of alkoxide ion to CO ligands to give a detectable ion Eq. (1).

$$L_nM-C\equiv O + OMe^- \rightarrow L_nM-C(O)OMe]^- \qquad (1)$$
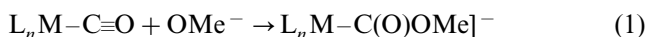
This process had been well-established on a macroscopic scale for a wide range of mono-nuclear and cluster metal carbonyls [2]. It attracts special interest as a model for part of the water–gas shift reaction (WGSR) [3].

As an extension we are now examining the reactions of other nucleophiles towards metal carbonyl substrates, monitored by electrospray mass spectrometry to detect intermediates and to characterise products on a micro-scale. In this paper we discuss reactions of the azide ion, N_3^-, with a range of metal carbonyls. It has long been known [4,5] for mononuclear metal carbonyls that this reagent can convert –CO ligands to –NCO^- ones with concomitant loss of N_2 (Eq. (2))

$$W(CO)_6 + N_3^- \rightarrow [W(CO)_5(NCO)]^- + N_2 \qquad (2)$$
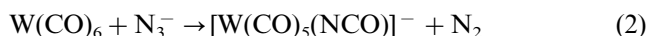
More recently the same transformation has been studied preparatively [6] and mechanistically [7] for $Ru_3(CO)_{12}$. It is generally assumed that the first step in the reaction is attack at the CO by N_3^-, analogous to the process shown in Eq. (1), but the subsequent rearrangement to NCO^- with elimination of N_2 is so rapid that the first-formed adduct has never been detected, even as an transitory intermediate. The ability of ESMS to sample directly from solution makes it an ideal technique for screening reactions and searching for short-lived intermediates [8].

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[1] Dedicated to Professor Brian Johnson, in recognition of his many contributions to metal carbonyl chemistry.

2. Experimental details

2.1. General

Electrospray mass spectra were obtained with a VG Platform II mass spectrometer with the mobile phase (usually MeCN) driven at 0.02 ml min^{-1} using a Thermo Separation Products SpectraSystem P1000 LC pump. Samples were injected via a Rheodyne valve fitted with a 10 μl sample loop. The nebuliser tip was at 3500 V and 60°C, with nitrogen used both as a drying and a nebulising gas. The skimmer cone voltage was usually 15 V or lower when clean parent ions were required, and was varied up to 140 V to investigate fragmentation processes.

Samples were prepared by dissolving the metal carbonyl compound (10–100 μg) in a drop of CH_2Cl_2. To this was added ca. 0.5 ml of saturated solution of NaN_3 in MeCN immediately before injecting the sample into the mass spectrometer. The metal carbonyl substrates used were generally available in our laboratories, or were kindly donated (see footnote to Table 1).

Peaks were assigned from the m/z values and from the isotope distribution patterns which were simulated using the *Isotope* program [9]. The m/z values given are for the most intense peak in the envelope in each case.

Results obtained in the ESMS experiments are summarised in Table 1.

3. Results and discussion

The negative-ion electrospray mass spectrum from a solution of $W(CO)_6 + N_3^-$ in MeCN is shown in Fig. 1. The main envelope is readily assigned to the expected product ion $[W(CO)_5(NCO)]^-$, while the small peak arises from loss of a CO. This small scale experiment parallels the results from macroscopic studies [4]. It should be noted that there is a potential ambiguity in the assignment for these reactions in that both CO and N_2 have a mass of 28 units so the peak at m/z 366 could also be attributed to $[W(CO)_5(N_3)]^-$. However, the earlier studies [4] show unambiguously that this azido species is only formed from photo-chemically activated $W(CO)_6$ (in THF) so we are confident that it is the isocyanate complex that is being observed in the mass spectrometer for this example.

The corresponding reaction with $Mo(CO)_6$ gave similar results, although more fragmentation of the $[Mo(CO)_5(NCO)]^-$ ion occurred in the mass spectrometer under the same conditions, reflecting the lower M–C bond energies. There were also other unassigned peaks in the spectrum which parallels the early preparative studies where it was noted that the molybdenum reaction was less specific than that of tungsten car-

bonyl. With $Cr(CO)_6$ on the other hand, no sensible peaks were observed, even though $[Cr(CO)_5(NCO)]^-$ is a known product of the reaction of $Cr(CO)_6$ with N_3^-, albeit formed more slowly than the heavier congeners [4].

The dimeric metal carbonyl $Re_2(CO)_{10}$ gave a clean mass spectrum consisting of a single peak at m/z 666 assigned to $[Re_2(CO)_9(NCO)]^-$. We are not aware of preparative-scale investigation of this reaction, but our

Table 1

Observed peaks and assignments in the negative-ion electrospray mass spectra of metal carbonyls treated with azide ions in MeCN

Compound	Species present (m/z)*, relative intensity
$W(CO)_6$	$[W(CO)_5(NCO)]^-$ (366) 100%; $[W(CO)_4(NCO)]^-$ (338) 20%
$Mo(CO)_6$	$[Mo(CO)_5(NCO)]^-$ (280) 40%; $[Mo(CO)_4(NCO)]^-$ (252) 80%; (242)** 50%; (214)** 100%
$Mn_2(CO)_{10}$	$[Mn_2(CO)_9(NCO)]^-$ (404) 100%; $[Mn_2(CO)_8(NCO)]^-$ (376) 35%; $[Mn_2(CO)_7(NCO)]^-$ (348) 10%
$Re_2(CO)_{10}$	$[Re_2(CO)_9(NCO)]^-$ (666)
$Co_2(CO)_8$	(365)** 10%; $[Co(CO)_4]^-$ (171) 100%
$Ru_3(CO)_{12}$	$[Ru_3(CO)_{11}(NCO)]^-$ (655) 30%; $[Ru_3(CN)(CO)_{11}]^-$ (639) 25%; $[Ru_3(CO)_{10}(NCO)]^-$ (627) 100%; $[Ru_3(CO)_9(NCO)]^-$ (599) 20%
$Os_3(CO)_{12}$	$[Os_3(CO)_{11}(NCO)]^-$ (922)
$Ir_4(CO)_{12}$	$[Ir_4(CO)_{11}(NCO)]^-$ (1120) 100%
$H_4Ru_4(CO)_{12}$	$[H_4Ru_4(CO)_{11}(NCO)]^-$ (760) 60%; $[H_4Ru_4(CO)_{10}(NCO)]^-$ (732) 80%; $[H_3Ru_4(CO)_{12}]^-$ (745) 100%; $[H_3Ru_4(CO)_{11}]^-$ (717) 70%
$H_3NiRu_3(CO)_9Cp^a$	$[H_3NiRu_3(CO)_8(NCO)Cp]^-$ (697) 15%; $[H_2NiRu_3(CO)_9Cp]^-$ (682) 100%; $[H_2NiRu_3(CO)_8Cp]^-$ (654) 100%
$H_2Os_3(CO)_{10}$	$[H_2Os_3(CO)_{10}+N_3]^-$ (896) 100%; $[H_2Os_3(CO)_9+N_3]^-$ (868) 10%
$Ru_5C(CO)_{15}$	$[Ru_5C(CO)_{15}+N_3]^-$ (980) 30%; $[Ru_5C(CO)_{14}+N_3]^-$ (952) 100%
$HRu_3(C_2Bu^t)(CO)_9^b$	$[HRu_3(C_2Bu^t)(CO)_9+N_3]^-$ (681) 10%; $[Ru_3(C_2Bu^t)(CO)_9]^-$ (638) 100%
$HRu_3(C_2Bu^t)(CO)_7(dppm)^c$	$[HRu_3(C_2Bu^t)(CO)_7(dppm)+N_3]^-$ (1009) 65%; $[Ru_3(C_2Bu^t)(CO)_7(dppm)]^-$ (966) 100%
$HRu_3(C_2Ph)(CO)_7(dppm)$	$[HRu_3(C_2Ph)(CO)_7(dppm)+N_3]^-$ (1029) 100%; $[Ru_3(C_2Ph)(CO)_7(dppm)]^-$ (986) 75%
$Ru_4(CO)_{10}(PhC_2H_2Ph)^d$	$[Ru_4(CO)_{10}(PhC_2H_2Ph)+N_3]^-$ (908)
$H_2Os_4(CO)_{10}(C_6H_6)^e$	$[H_2Os_4(CO)_{10}(C_6H_6)+N_3]^-$ (1164) 10%; $[HOs_4(CO)_{10}(C_6H_6)]^-$ (1121) 100%; (1099)** 10%

[a] Lavigne et al. [17]; [b] Sappa et al. [18]; [c] Predieri et al. [19]; [d] Dyson [20]; [e] Chen et al. [21].

* The m/z value quoted is for the most intense peak in the isotope pattern.
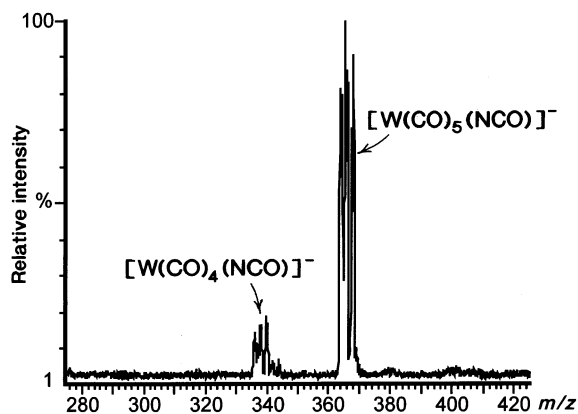
** Unassigned.

Fig. 1. The negative-ion mass spectrum from $W(CO)_6$ with N_3^-.

results indicate it should be readily isolated. With $Mn_2(CO)_{10}$ the analogous isocyanate complex gave a peak at m/z 404, although CO-loss peaks at m/z 376 and 348, assigned to $[Mn_2(CO)_n(NCO)]^-$ ($n = 8$, 7, respectively) appeared even under mild conditions, suggesting labile CO groups. There was no sign of ions arising from Mn–Mn bond cleavage in the mass spectrometer which was a significant breakdown process for the ion corresponding to the analogous alkoxide adduct $[Mn_2(CO)_9(COOMe)]^-$ [1].

With $Co_2(CO)_8$, azide ion induced a different reaction; the main signal was at m/z 171 and clearly arises from a disproportionation reaction giving $[Co(CO)_4]^-$; Werner et al. [4] reported the same species, identified by IR spectroscopy.

The reaction of $Ru_3(CO)_{12}$ with azide ions is one that has been studied in detail, both preparatively and kinetically [6,7]. These earlier studies showed that a sequence of reactions took place rapidly. It was assumed that N_3^- initially attacked at a CO ligand to give a $[Ru_3(CO)_{11}\{C(N_3)O\}]^-$ species (not detected) which underwent a rapid loss of N_2 to generate $[Ru_3(CO)_{11}(NCO)]^-$ in the established manner. This complex then underwent facile CO loss to give $[Ru_3(CO)_{10}(NCO)]^-$ with a bridging isocyanate ligand,

and a subsequent very slow rearrangement ultimately yielded $[Ru_4(CO)_{13}(NCO)]^-$ [7]. The rather complicated ESMS results shown in Fig. 2 can be readily interpreted by comparison. The envelope at m/z 655 is the first-formed isocyanate species $[Ru_3(CO)_{11}(NCO)]^-$, but this is unusually weak with the dominant ion at m/z 627 being the bridged species $[Ru_3(CO)_{10}(NCO)]^-$. There is also a small peak arising from loss of a further CO ligand. The Ru_4 species was just discernible at m/z 813 but was of low intensity, as expected in a short-duration reaction. More interesting is a peak at m/z 639 which corresponds to $[Ru_3(CO)_{11}(CN)]^-$. This species has been tentatively identified in the reaction of $Ru_3(CO)_{12}$ with CN^-, although attempts to isolate it gave a doubly-CN^- bridged dimer [10]. The in situ conversion of a CO ligand to a CN^- is known with $N(SiMe_3)_2^-$ as a nucleophile [11], but as far as we are aware it has not been previously suggested with azide ions.

In contrast, the equivalent reaction of azide ion with $Os_3(CO)_{12}$ was straightforward, giving a strong $[Os_3(CO)_{11}(NCO)]^-$ peak at m/z 922. Only at higher cone voltages were significant CO losses induced, which once again parallels macroscopic studies where $[Os_3(CO)_{11}(NCO)]^-$ was isolated in high yield [12].

The only binary tetra-metal species examined was $Ir_4(CO)_{12}$ which gave a single peak at m/z 1120. This is clearly the $[Ir_4(CO)_{11}(NCO)]^-$ ion which does not appear to have been reported previously. The ESMS results suggest it would be a readily isolated compound.

With $H_4Ru_4(CO)_{12}$ the N_3^- ion generated two series of peaks; one was the expected $[H_4Ru_4(CO)_n(NCO)]^-$ with $n = 11$, 10, while the other was $[H_3Ru_4(CO)_n]^-$, $n = 12$, 11. The former were generated by processes paralleling those discussed above while the latter are a result of H^+ abstraction, presumably by N_3^- acting as a base. In situ anion formation by abstraction of protons from hydrido clusters was also found as a process which competed with addition at CO in our earlier studies with alkoxide ions [1]. The mixed-metal cluster
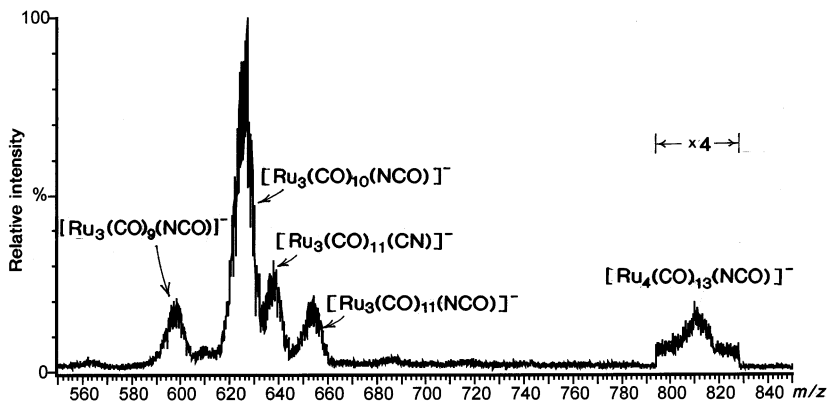

Fig. 2. The negative-ion electrospray mass spectrum from $Ru_3(CO)_{12}$ with N_3^- in MeCN.

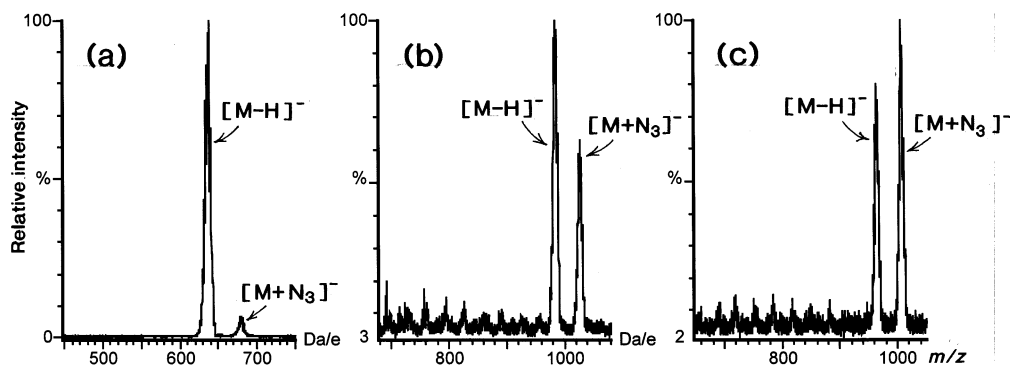Fig. 3. The negative-ion mass spectra in MeCN with added N_3^- for: (a) $HRu_3(C_2Bu^t)(CO)_9$; (b) $HRu_3(C_2Bu^t)(CO)_7(dppm)$; and (c) $HRu_3(C_2Ph)(CO)_7(dppm)$ showing signals from N_3^- addition and H^+ abstraction.

$H_3NiRu_3(CO)_9Cp$ behaved similarly, giving a weak peak at m/z 697 which is the isocyanate product $[H_3NiRu_3(CO)_8(NCO)Cp]^-$, together with stronger peaks at 682 and 654 assigned to $[H_2NiRu_3(CO)_nCp]^-$, ($n = 9,\ 8$) arising from abstraction of H^+.

For all of the reactions so far discussed, no sign of the initial azide adduct was seen. However when a solution of $H_2Os_3(CO)_{10}$ was treated with N_3^- a strong peak at m/z 896 could be assigned to $[H_2Os_3(CO)_{10} + N_3]^-$. This is unlikely to be the result of addition of the azide ion to a CO ligand since it is known that this unsaturated Os_3 cluster very readily adds halide ions and organic azides at the Os=Os bond [13–15], and so N_3^- is undoubtedly acting in a similar fashion as a pseudo-halide. Following on from this, the small peak at m/z 867 (28 mass units below the initial one) is assigned as a CO-loss species $[H_2Os_3(CO)_9(N_3)]^-$ rather than a N_2-loss isocyanate complex $[H_2Os_3(CO)_9(NCO)]^-$. The electrospray mass spectra cannot distinguish these possibilities so a small scale reaction was monitored by IR spectra. Addition of N_3^- ion to a purple solution of $H_2Os_3(CO)_{10}$ in MeCN gave a yellow solution with main broad ν(CO) bands at 2054 and 2005 cm^{-1}, similar to those of $[H_2Os_3(CO)_{10}Cl]^-$ [14]. No peaks attributable to a NCO^- ligand were present.

A similar observation arose from $Ru_5C(CO)_{15}$ where the highest mass peak at m/z 980 could be assigned to a $[M + N_3]^-$ adduct, although whether this species has arisen from addition at a CO ligand or by reaction at a Ru–Ru bond (known to be facile with this cluster [16]) cannot be judged from the ESMS result alone. Once again a small-scale IR study indicated the latter possibility was most likely, with a mixture of $Ru_5C(CO)_{15}$ and N_3^- in MeCN giving ν(CO) peaks at 2096(w), 2058(m), 2043(m) and 2006(vs) cm^{-1}, closely matching those [16] of the Cl^--addition species $[Ru_5C(CO)_{15}Cl]^-$. The higher mass peak in the ESMS spectrum is therefore assigned as $[Ru_5C(CO)_{15}(N_3)]^-$ and the most intense peak at m/z 952 is assigned as $[Ru_5C(CO)_{14}(N_3)]^-$, formed by facile CO loss and reformation of the Ru–Ru bond.

Similar observations were made with the three ruthenium μ_3-acetylide clusters $HRu_3(C_2Bu^t)(CO)_9$ and $HRu_3(C_2R)(CO)_7(dppm)$ ($R = Bu^t$ or Ph). The ESMS spectra obtained when these were treated with N_3^- ions are shown in Fig. 3. In each case the higher mass peak corresponds to a $[M + N_3]^-$ ion, while the lower mass one arises from abstraction of H^+ to give $[M-H]^-$. The dppm-substituted precursors gave the most stable higher-mass ion. There are no obvious alternative positions of reactivity for these clusters so assignment of the higher mass peak as the elusive azido-carbonyl adduct is possible, though addition of N_3^- at the acetylide ligand cannot be ruled out in the absence of larger scale reactions.

The arene-substituted complexes $Ru_4(CO)_{10}$ (PhC_2H_2Ph) and $H_2Os_4(CO)_{10}(C_6H_6)$ also gave very clean $[M + N_3^-]$ ions with azide (the latter in competition with $[M-H]^-$ species) but again the site of attack cannot be deduced from the mass spectra; these too would be interesting clusters to examine in more detail.

4. Conclusion

The results obtained show that addition of azide ions to metal carbonyl compounds provides an alternative method of derivatisation for analysis by electrospray mass spectrometry. The method does not appear to be quite as general as the previously reported alkoxide derivatisation procedure, though excellent quality spectra result in cases where addition does occur. Interpretation is made more difficult because the species detected is usually a rearrangement product, after loss of N_2, rather than the first formed adduct. Hence the technique is not likely to be especially useful as a simple characterisation procedure.

Where ESMS studies of this type may find application is in the guidance of preparative studies. The experiments are rapid and involve small quantities of

chemicals so provide a useful screen to select systems which are likely to produce isolable derivatives. In this context the observation of $[M + N_3]^-$ ions in some cases is especially interesting since these have not been detected by any other spectroscopic means in cases where attack is at the CO ligand, so more detailed work on these systems is likely to be rewarding.

Acknowledgements

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