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A mass spectral investigation of site selective CO loss from isotopically labelled $[MnRe(CO)_{10}]^+$

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Abstract

A mass spectral investigation of $[Mn(CO)_5Re(^{13}CO)_5]$ (91% ^{13}C label) has been carried out, and an analysis of the ions $[MnRe(CO)_x]^+$ ($x = 1–5$) has revealed that the CO is lost preferentially from Mn. This represents the first conclusive evidence for site-selective ligand loss from a heterobimetallic complex. The results were confirmed by a mass spectral analysis of a related complex $[Mn(CO)_5Re(^{13}CO)_4(CNBu\text{-}t)]$, which also showed selective CO loss from Mn in the bimetallic ion in the mass spectrometer.

Introduction

During the past decade the study of heterometallic transition metal dimer and cluster complexes has become a focus of considerable attention [1,2]. This in part relates to the potential cooperative effects that can be envisaged when two (or more) metal atoms are in close proximity to each other and can be manifested by a change in the physical and chemical properties of the respective metal atoms. For instance, these changes could be revealed by a change in the chemical and/or catalytic [3,4] reactivity of a metal atom when in contact with other metal atoms.

$[MnRe(CO)_{10}]$ provides one of the simplest low oxidation state heterobimetallic complexes available for investigation of cooperative metal effects in mixed metal complexes. X-ray crystallographic studies have confirmed the presence of an unsupported Mn–Re bond [5], and numerous studies have been performed on this complex to delineate its chemical and physical properties [6]. The unusual CO substitution behaviour of $[MnRe(CO)_{10}]$ has also been described [7,8].

In this publication we report on a mass spectral investigation of the ^{13}CO labelled complex $[Mn(CO)_5Re(^{13}CO)_5]$ and one of its derivatives. This study was undertaken to establish whether site selective loss of CO from $[Mn(CO)_5Re(^{13}CO)_5]^+$, generated in the mass spectrometer, could be identified.

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Experimental

Mass spectra were recorded on a Finnegan MAT 8200 spectrometer operating at 70 eV. The ^{13}CO (Prochem Limited) was analysed by Mr.D.Hazelby (Kratos Instruments, U.K.) as containing 98% ^{13}C, 6% ^{17}O and 1% ^{18}O. $[Re_2(^{13}CO)_{10}]$ (91% ^{13}CO label) was synthesized as described previously [9]. The IR spectrum ($\nu(CO)$ region) and the parent ion of the dimer observed in the mass spectrum are shown in Fig. 1. $[Re(^{13}CO)_5Br]$ was synthesized by cleavage of $[Re_2(^{13}CO)_{10}]$ with Br_2, and the IR spectrum as well as the experimental and simulated mass spectral parent ion are shown in Fig. 2. These data confirm that $[Re(^{13}CO)_5Br]$ also contains 91% ^{13}CO. Conversion of $[Re(^{13}CO)_5Br]$ to $[Re(^{13}CO)_5OSO_2CF_3]$ (IR, CH_2Cl_2, $\nu(CO)$: 2064vw, 2018s, 1956m) was achieved by published procedures [10]. $[Mn(CO)_5Re(^{13}CO)_5]$ was prepared from $Na[Mn(CO)_5]$ and $[Re(^{13}CO)_5OSO_2CF_3]$ as described previously [9,10]. All reactions were carried out under argon with degassed and distilled solvents.

Preparation of $[Re(^{13}CO)_4(CNBu\text{-}t)Br]$. $[Re(^{13}CO)_5Br]$ (0.2 mmol) t-BuNC (1.1 equivalents) and PdO (10 mg) were added to benzene (10 ml) and the mixture was stirred at room temperature. The reaction was monitored by TLC (silica; eluent 50/50 hexane/benzene) and IR spectroscopy. On completion of the reaction (20 min) the solution was concentrated and subjected to preparative scale TLC (silica; eluent 50/50 hexane/benzene). The $[Re(^{13}CO)_4CNBu\text{-}t)Br]$ containing fraction was isolated, the complex extracted with CH_2Cl_2, and the extract pumped to dryness to yield the pure material, which was characterized by mass spectrometry. *m/z* (int. %): 465(24), 436(10), 411(38), 380(47), 351(59), 324(28), 295(21), 266(23), 187(15),

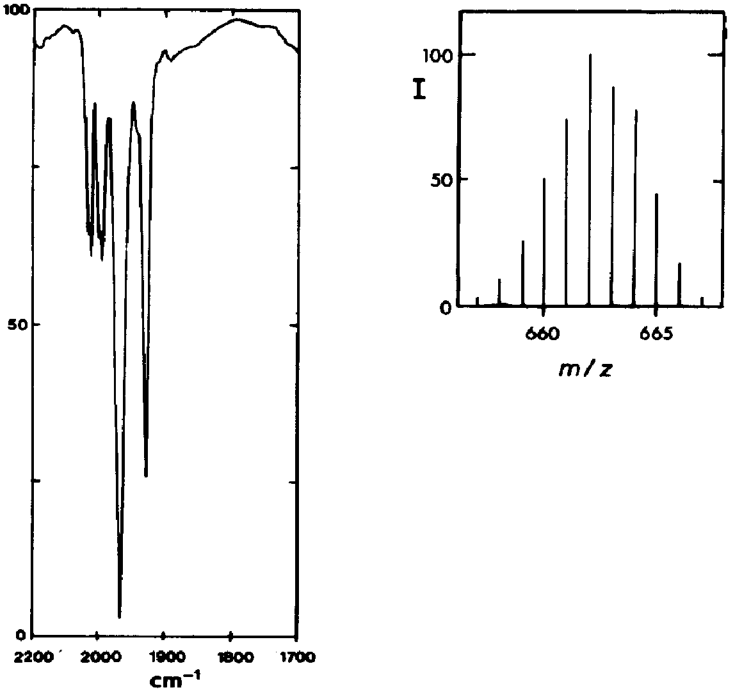

Fig. 1. IR and mass spectral data (parent ion) for $[Re_2(^{13}CO)_{10}]$.

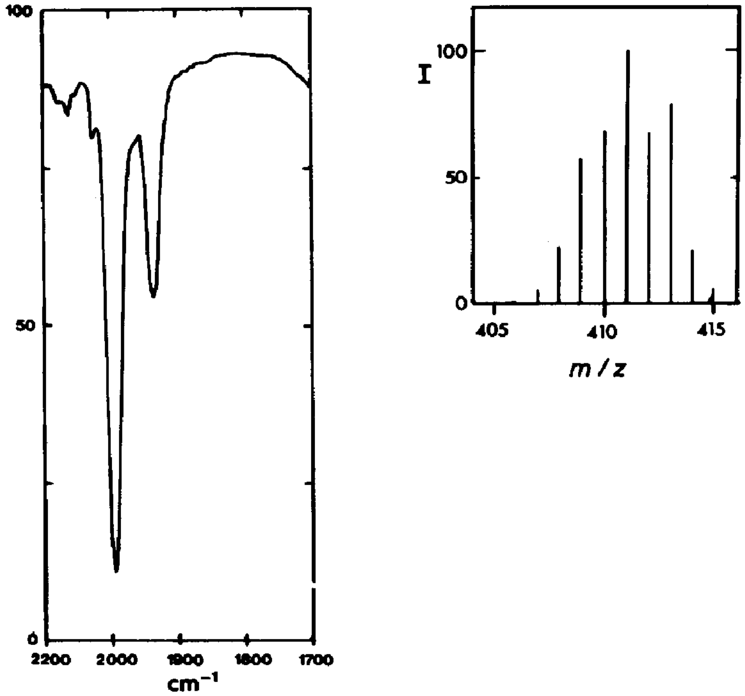

Fig. 2. IR and mass spectral data (parent ion) for [Re(^{13}CO)$_5$Br].

97(13), 83(15), 78(23), 71(18), 57(100), (only the most abundant isotope peak in each band and > 10% of largest peak at $m/z = 57$ are recorded).

Preparation of [Mn(CO)$_5$Re(^{13}CO)$_4$(CNBu-t)]. [Re(^{13}CO)$_4$(CNBu-t)Br] (0.08 mmol) was converted into the triflate by use of Ag[OSO$_2$CF$_3$] (1.05 equivalents) in CH_2Cl_2 (10 ml). Upon completion of the reaction, as revealed by IR spectroscopy, the solution was centrifuged, the supernatant liquid decanted and the solvent removed in vacuo. The white crystalline residue was taken up in THF (5 ml) and the solution added to a freshly prepared solution of Na[Mn(CO)$_5$] (1.0 equivalents) in THF (5 ml). The mixture was stirred for 5 min and the solvent then removed. The desired complex was then extracted from the residue with 3 × 5 ml hexane/benzene (50/50), and the extract filtered and pumped to dryness. The residue was purified by TLC (silica, eluent; 90/10 hexane/benzene) and identified from its mass spectrum. m/z (int. %): 581(39), 440(14), 412(15), 383(100), 356(39), 327(35), 288(51), 271(15), 242(14). The mass spectrum of [MnRe(CO)$_9$(CNBu-t)], which was synthesized from [MnRe(CO)$_{10}$] and t-BuNC [9], showed peaks at m/z (int. %): 577(15), 437(57), 410(20), 381(100), 353(47), 325(34), 297(21), 268(12), 242(5). In both of the above mass spectra only fragments containing the MnRe residue are reported.

Results and Discussion

^{13}CO-labelled [MnRe(CO)$_{10}$] was previously synthesized by Schmidt et al. [10], and a similar synthetic procedure was used in this study. The procedure is fast, and gave the 91% labelled material, [MnCO)$_5$Re(^{13}CO)$_5$], in which < 5% scrambling of the ^{13}CO label had occurred during the synthesis and work up [9]. The kinetic

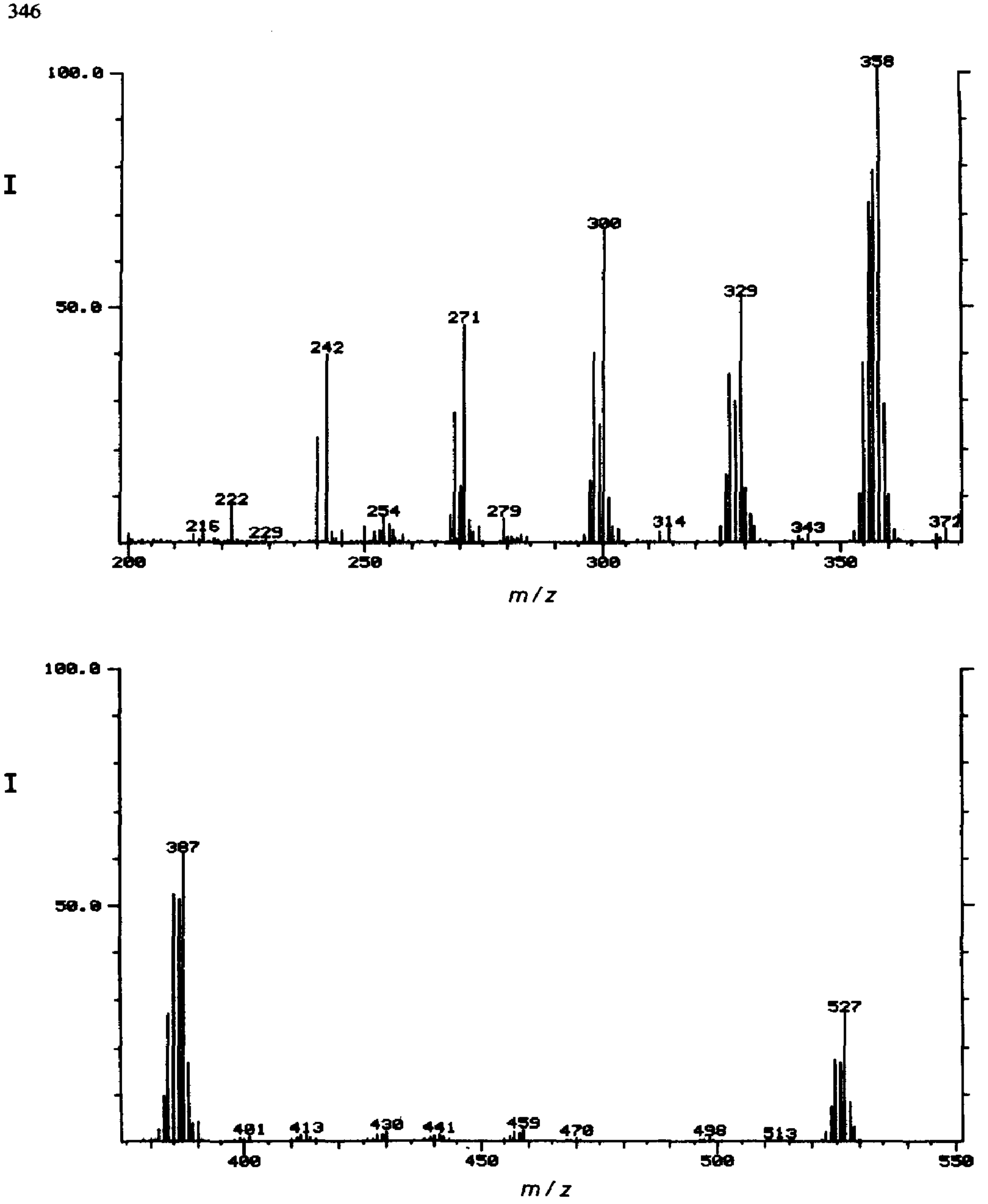

Fig. 3. Mass spectrum of [MnRe(CO)$_{10}$] (91% ^{13}CO label on Re); only fragments with $m/z > 200$ are shown.

investigation by Schmidt et al. [10] of the ^{13}CO exchange process between Mn and Re in the dimer revealed that earlier studies on site selective labelling in the dimer had provided a product with random labelling between Mn and Re [11].

The mass spectrum of [Mn(CO)$_5$Re(^{13}CO)$_5$], purified by HPLC [9], is shown in Fig. 3. The mass spectrum of [MnRe(CO)$_{10}$] has been previously reported [12–16] and is very similar. A comparison of the two spectra is given in Table 1.

Of significance is the analysis of the CO loss fragments [MnRe(CO)$_x$]$^+$ ($x = 1$–5) which suggest preferential loss of ^{12}CO from the dimer. This was further confirmed

Table 1

Comparison of the mass spectrum of labelled and unlabelled $[MnRe(CO)_{10}]$ [a,b]

Ion	Relative intensity (%)		
	1 [c]	2 [d]	3 [e]
$[MnRe(CO)_{10}]^+$	25	34.9	26.9
$[MnRe(CO)_9]^+$	1	–	1
$[MnRe(CO)_8]^+$	0	–	1
$[MnRe(CO)_7]^+$	2	–	2
$[MnRe(CO)_6]^+$	2	–	2
$[MnRe(CO)_5]^+$	75	87.1	60.6
$[MnRe(CO)_4]^+$	100	100.0	100.0
$[MnRe(CO)_3]^+$	50	51.9	51.8
$[MnRe(CO)_2]^+$	87.5	56.7	66.3
$[MnRe(CO)]^+$	45.0	41.7	46.1
$[MnReC]^+$	8.5	6.7	5.0
$[MnRe]^+$	32.5	43.2	39.7

[a] Only dimer peaks are shown and only the largest CO loss ion has been used to generate the intensity data for the dimer fragments. [b] All spectra were recorded at 70 eV electron impact. [c] Ref. 12, unlabelled $[MnRe(CO)_{10}]$. [d] Ref. 15. unlabelled $[MnRe(CO)_{10}]$. [e] This work, labelled $[MnRe(CO)_{10}]$.

by simulation of the spectrum, which revealed > 80% ^{13}CO remaining on the MnRe fragments (Fig. 4, and Table 2). As can be seen, an excellent fit of the simulated and observed fragments was achieved. The experimental and simulated intensity data for the ions are available from the authors.

These results provide a ready explanation of the low intensity of the $[MnRe(CO)_x]^+$ ($x = 6$–9) fragments, which are evidently formed by rapid loss of CO groups from the Mn atom, rather than the Re atom. The first major ion observed thus corresponds to the ion with 5 CO groups attached to the Re atom, $[MnRe(^{13}CO)_5]^+$. Our data thus confirm the observations made by Johnson et al. [12] some 20 years ago in which the high intensities of the unlabelled $[MnRe(CO)_x]^+$ ($x = 1$–5) ions were observed (Table 1).

To the best of our knowledge, these results, provide the first conclusive evidence of site selective loss of ligands from heterometallic ions in the mass spectrometer.

Further evidence in favour of this conclusion is provided by the mass spectral data for the related complex $[Mn(CO)_5Re(^{13}CO)_4(CNBu\text{-}t)]$, which was synthesized by two methods. The first, indirect, method started from labelled $[Re(^{13}CO)_5Br]$.

Table 2

Composition of CO used to simulate the spectra in Fig. 4

Ion	%			
	^{13}C	^{16}O	^{17}O	^{18}O
$[MnRe(CO)_{10}]^+$	91	94	5.4	0.6
$[MnRe(CO)_5]^+$	86	92	6.5	1.5
$[MnRe(CO)_4]^+$	85	92	6.6	1.6
$[MnRe(CO)_3]^+$	85	92	6.6	1.6
$[MnRe(CO)_2]^+$	84	92	6.6	1.6
$[MnRe(CO)]^+$	82	92	6.6	1.5

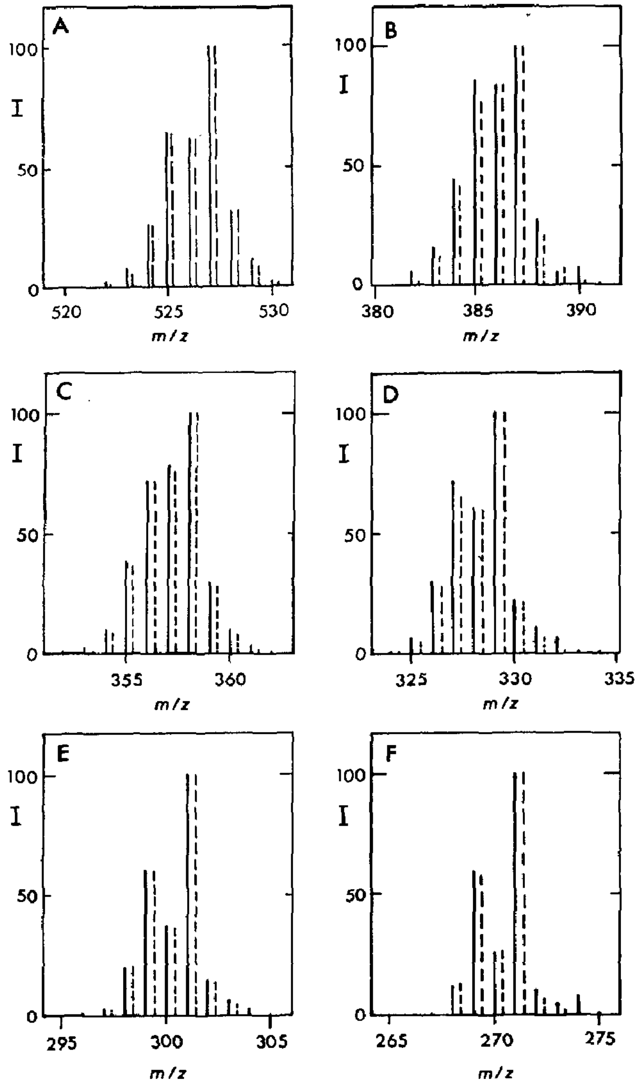

Fig. 4. Experimental and simulated mass spectral data for the ions $[MnRe(CO)_x]^+$ ($x=1$–5, 10); (a) $[MnRe(CO)_{10}]^+$; (b) $[MnRe(CO)_5]^+$; (c) $[MnRe(CO)_4]^+$,; (d) $[MnRe(CO)_3]^+$; (e) $[MnRe(CO)_2]^+$; (f) $MnRe(CO)]^+$.

The PdO-catalysed reaction between $[Re(^{13}CO)_5Br]$ and t-BuNC readily gave $[Re(^{13}CO)_4(CNBu\text{-}t)Br]$, whose structure was confirmed by mass spectrometry. Figure 5 shows the experimental and simulated mass spectral parent ion peak $[Re(^{13}CO)_4(CNBu\text{-}t)Br]$ (91% ^{13}CO label). Subsequent conversion of $[Re(^{13}CO)_4(CNBu\text{-}t)Br]$ into the triflate and reaction with $Na[Mn(CO)_5]$ gave the required complex [9].

In the second method direct reaction between $[Mn(CO)_5Re(^{13}CO)_5]$ and t-BuNC in the presence of PdO gave the required product [9].

The products $[Mn(CO)_5Re(^{13}CO)_4(CNBu\text{-}t)]$ from the two routes gave identical mass spectra. Although the mass spectrum of the above product is more complex than that of $[Mn(CO)_5Re(^{13}CO)_5]$ owing to the presence of fragments containing

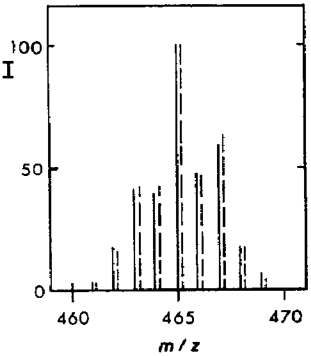

Fig. 5. Experimental and simulated mass spectral data for the parent ion from [Re(^{13}CO)$_4$(CNBu-t)Br].

the t-BuNC ligand or breakdown fragments of the ligand, two key features are readily detected:

(i) Large intensity ions for [MnRe(CO)$_x$(CNBut)]$^+$ $x < 4$, suggesting that five CO ligands are readily lost from the dimer.

(ii) Preferential loss of ^{12}CO. This can readily be seen by comparing the mass spectra of [Mn(CO)$_5$Re(^{13}CO)$_4$(CNBu-t)] and [Mn(CO)$_5$Re(^{12}CO)$_4$(CNBu-t)] (see Experimental section for m/z listing). The ion [MnRe(CO)]$^+$ indicates an intensity ratio of 4/1 for the peaks at $m/z = 271$ and 270, respectively, corresponding to an 80/20 mixture of ^{13}CO and ^{12}CO in the ion. A shift of from one to four m/z units upwards can be seen for other ions by comparison of the spectra of the labelled with unlabelled dimer, although quantification was more difficult because of the presence of the t-BuNC ligand.

The above spectra further support the proposal that there is site-selective loss of CO from Mn in the MnRe substituted dimer ion. Presumably this is a general phenomenon applying to a wide range of transition metal dimers and clusters, and further studies to determine the generality of our findings are in progress.

Our results thus reveal a very simple route for CO loss from the [MnRe(CO)$_{10}$] dimer. The overall findings for CO loss or substitution from [MnRe(CO)$_{10}$] can now be summarized as follows:

(i) [MnRe(CO)$_{10}$] $\xrightarrow{h\nu}$ [Mn(CO)$_4$(μ-CO)Re(CO)$_4$] with CO loss from Mn [18].

(ii) [MnRe(CO)$_{10}$] $\xrightarrow{\text{PdO,L}}$ [Mn(CO)$_5$Re(CO)$_4$L] with CO loss from Re [9].

(iii) [MnRe(CO)$_{10}$] $\xrightarrow{e^-}$ [MnRe(CO)$_{10}$]$^+$ $\rightarrow$ [Mn(CO)$_4$Re(CO)$_5$]$^+$ with CO loss from Mn (this work).

(iv) [MnRe(CO)$_{10}$] $\xrightarrow{\Delta,\,L}$ [MnRe(CO)$_9$L] with unproven mechanism.

As yet there is still no evidence for thermal CO loss from Mn, followed by formation of a bridging CO group *and* generation of [Mn(CO)$_5$Re(CO)$_4$L] [7]. Similarly there is no proof of direct CO loss from Re in the uncatalysed thermal reaction.

It is apparent that a rich chemistry arises from the presence of a metal–metal bond in transition metal carbonyl dimer complexes, and further complexities can be expected for the chemical reactions of the metal carbonyl cluster complexes.

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