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NOVEL ELECTRON IMPACT-INDUCED HYDROGEN REARRANGEMENTS IN THE MASS SPECTRA OF ORGANORHENIUM HYDRIDES AND ALKYLS

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ABSTRACT

The electron impact-induced hydrogen rearrangement of an organorhenium hydride is described, in which the remote hydrogen is identified to be the hydride hydrogen by deuterium-labelling experiments. Rearrangement accompanies intra-ligand cleavage of the triphenylphosphine ligand, an unusual event in itself, resulting in neutral loss of benzene from the molecular ion. Closer examination of the electron impact mass spectra of a series of organorhenium alkyl compounds indicates that another rearrangement of a beta hydrogen from the alkyl ligand onto the metal center produces the rhenium hydride, which then undergoes rearrangement and neutral loss. These two rearrangements serve to explain the heretofore anomalous fragment peaks in the spectra of the organorhenium alkyl compounds.

INTRODUCTION

Several series of $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(X)$ and $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(L)]^+$ organorhenium compounds, in which the fourth ligand is a hydride, halogen, alkyl, olefin, or acyl ligand, have been prepared and characterized by mass spectrometry using several ionization methods, electron impact, methane chemical ionization, and fast atom bombardment [1]. The unifying rule of fragmentation in most of these compounds has been that the bonds in the molecule which break in the mass spectrometer are those between the metal center and the various ligands. Fragmentation resulting in loss of a portion of a complex ligand, such as a phenyl moiety from the triphenylphosphine ligand, does not occur in the first structurally significant fragmentations.

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This behavior is consistent over a range of several transition metals which we have studied (Rh, Ir, Pt, Re) and several series of ligand systems and bonding patterns. Notable exceptions we have seen are in an unusual platinum ethylene pi complex [2], in a new series of cationic Pt(II) vinyl sigma-bonded compounds which we have very recently studied [3], and in a series of Pt(II) triethylphosphine complexes reported by Cottee et al. [4].

The organorhenium hydride $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(H)$ and, upon closer examination of the spectra, a series of organorhenium alkyl compounds are the first in our large collection of these compounds which show significant rearrangements and intra-ligand fragmentations.

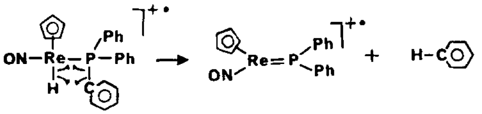
EXPERIMENTAL

Syntheses of the organorhenium hydride and organorhenium alkyl compounds are described in detail elsewhere [5–8].

Mass spectral measurements were made on a VG Analytical 7070-E mass spectrometer [9] under 70 eV electron impact ionization conditions. Samples were introduced on the direct insertion probe and heated to the vicinity of the melting point of the compounds in order to induce volatilization.

RESULTS AND DISCUSSION

An apparent anomaly in the large number of organorhenium compounds we have examined is that of $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(H)$ under electron impact ionization. This compound shows not only a fragmentation resulting in loss of a phenyl moiety from the triphenylphosphine ligand, but also rearrangement of a remote hydrogen, producing neutral loss of benzene (78 daltons) from the molecular ion, as proposed in Eq. (1). Figure 1 contains partial mass spectra of the compounds studied. Identifying the origin of the remote hydrogen involved in neutral loss of benzene was performed by studying the appropriately deuterium-labeled compounds [6,7].



(1)

Figure 1(a) contains the partial mass spectrum of the subject rhenium hydride showing the loss of 78 daltons from the *m/z* 545 molecular ion cluster to give the *m/z* 467 cluster. Figure 1(b) shows the mass spectrum of the rhenium deuteride, with a 79 dalton fragmentation resulting from loss of the deuteride along with a phenyl moiety from the triphenylphosphine ligand. Figure 1(c) and (d) are spectra of $[^2H_5]$cyclopentadienyl rhenium

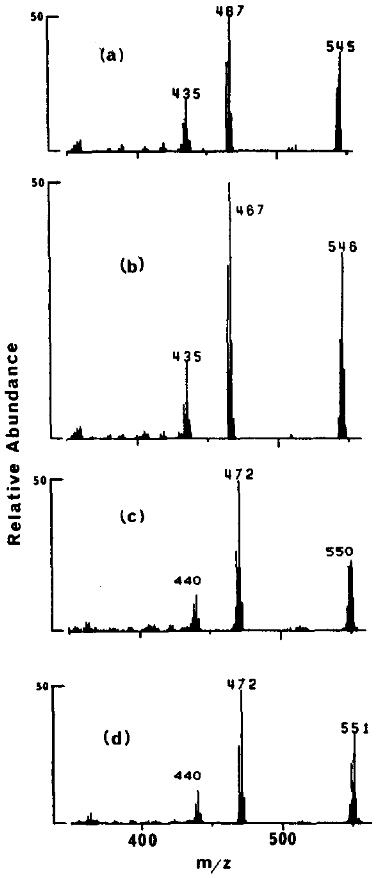


Fig. 1. Partial mass spectra, recorded at 70 eV electron impact ionization energy, of organorhenium hydrides. (a) Rhenium hydride; (b) rhenium deuteride; (c) [$^2H_5$]cyclopentadienyl rhenium hydride; (d) [$^2H_5$]cyclopentadienyl rhenium deuteride.

hydride and rhenium deuteride, respectively. Although the spectrum in Fig. 1(c) is of an incompletely deuterated compound, the mass loss from molecular ion to first fragment is 78 daltons, indicating that the cyclopentadienyl ligand is not contributing a hydrogen to the rearrangement. Upon replacing the hydride with deuteride, a 79 dalton fragment is lost [Fig. 1(d)].

Substitution of a pentamethylcyclopentadienyl ligand [8] for the cyclopentadienyl ligand makes benzene neutral loss from the molecular ion a slightly less favorable event, in that the relative abundances of the $[M]^{+\cdot}$ and $[M - C_6H_6]^{+\cdot}$ ions in the spectrum of this compound are nearly equal. $[M - C_6H_6]^{+\cdot}$ is base peak and the molecular ion is approximately 90%. Benzene neutral loss from $M^{+\cdot}$, however, is still the main feature in the spectrum.

TABLE 1

16 eV mass spectral data of rhenium alkyl compounds $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(R)$ [a]

Compound [b]	Molecular weight [c]	Ion intensities (for ^{187}Re) [d]		
		$M^{+\cdot}$	$[ReH]^{+\cdot}$	$[Re{=}PPh_2]^{+\cdot}$
2 $R = CH_2CH_3$	573	100	24	11
3 $R = CH_2CH_2CH_3$	587	100	54	20
4 $R = (CH_2)_4CH_3$	615	90	54	19
5 $R = CH_2CH(CH_3)_2$	601	100	76	57
6 $R = CH_2C(CH_3)_3$	615	35	0	0
8 $R = CH(CH_3)_2$	587	42	100	48
9 $R = CH_2CH_2C_6H_6$	649	45	47	32

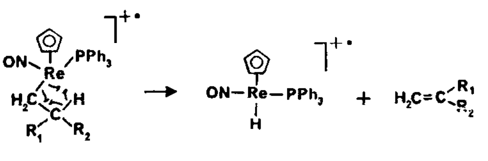
[a] Adapted from Table 2 of Kiel et al. [5].

[b] Compound numbers assigned in Kiel et al. [5] are retained here for consistency.

[c] Calculated using the most abundant ^{187}Re isotope.

[d] Intensity of ^{187}Re-containing peak in the isotope cluster, normalized to the largest peak above m/z 262, inclusive.

Another apparent hydrogen rearrangement is evident in the data presented by Kiel et al. [5] on the low energy electron impact mass spectra of seven alkyl complexes of the formula $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(R)$. Their data, partially reproduced here in Table 1, indicate significant intensities for $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(H)]^{+\cdot}$ and $[(\eta^5\text{-}C_5H_5)Re(NO)({=}PPh_2)]^{+\cdot}$ in addition to details consistent with the indicated rhenium alkyl structures. Chemical criteria exist demonstrating that the rhenium alkyl compounds were not contaminated with rhenium hydride. One possibility is that, during heating of the samples in the mass spectrometer to induce volatilization, thermal decomposition of the alkyl compound produced the hydride. We propose, rather, that these rhenium alkyl compounds undergo an electron impact-induced hydrogen rearrangement, shown in Eq. (2), to produce the rhenium hydride molecular cation at m/z 545, and that subsequent rearrangement of the hydride cation [Eq. (1)] produces the m/z 467 $[(\eta^5\text{-}C_5H_5)Re(NO)({=}PPh_2)]^{+\cdot}$ cation. The most convincing evidence substantiating this proposal is that the rearrangement of Eq. (2) requires the presence of a hydrogen on the alkyl ligand beta to the metal. Compound **6**, $R = CH_2C(CH_3)_3$, is the only compound in the series which does not have beta hydrogens and the only one which shows no mass spectral intensities at either m/z 545 or m/z 467.



(2)

The neutral counterpart of the radical cation $[(\eta^5\text{-}C_5H_5)Re(NO)(=PPh_2)]^{+\cdot}$, $(\eta^5\text{-}C_5H_5)Re(NO)(=PPh_2)$, is an 18-electron complex that contains a 3-electron-donor phosphide ligand. Although such phosphide ligands are common, they have not been previously generated, to our knowledge, by a thermal 1,2-elimination reaction. Malisch and co-workers [10], however, have reported that base effects the 1,2-elimination of HCl from phosphine complex $(\eta^5\text{-}C_5H_5)W(CO)_2(Cl)(PR_2H)$ to give phosphide complex $(\eta^5\text{-}C_5H_5)W(CO)_2(=PR_2)$. A similar 1,2-elimination has recently been used to generate a transient phosphinidine complex. $L_nM = PR$ [11].

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