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GAS PHASE ION MOLECULE REACTIONS OF ORGANOMETALLIC COMPOUNDS; PROTONATION OF SELECTED η^6-ARENETRICARBONYLCHROMIUM COMPLEXES AND η^6-CYCLOHEPTATRIENE COMPLEXES OF THE GROUP VI METALS WITH VARIOUS BRØNSTED ACID REAGENT IONS

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Summary

η^6-Arenetricarbonylchromium(0) complexes, (with the η^6-arene = benzene, toluene, methylbenzoate and acetophenone) and η^6-cycloheptatrienetricarbonyl complexes of chromium(0), molybdenum(0) and tungsten(0) undergo reactions in the gas phase with the Brønsted acid reagent ions H_3^+, CH_5^+, t-$C_4H_9^+$, $(NH_3)_nH^+$ which depend on the Brønsted acid strengths of these ions and also on the basicity of the metal complexes. Processes which involve either metal or ligand proton attachment, as well as charge exchange, electrophilic addition and rearrangement reactions have been identified. Some comparisons are drawn between these gas phase observations and the solution phase behaviour of these compounds.

Introduction

Recently, we have embarked on a systematic examination of gas phase ion/molecule reactions which involve proton transfer from various Brønsted acid reagent ions to selected organometallic compounds [1]. These studies are complementary to our investigations of electron attachment to metal-organic compounds in the gas phase [2—6]. In the solution phase, it is already well established that transition metal carbonyls as well as their derivatives may function as bases, and under such conditions the concept of metal basicity has often been invoked to rationalize and systematize many reactions which involve protonation of organometallic complexes [7—11]. Particularly useful, in this context, is the establishment of orders of basicity for transition metal organometallic compounds relative to specific Lewis or Brønsted acids, although these acid—

base processes are influenced greatly by the particular solvent media used [12—14]. In the gas phase, protonation reactions are uninfluenced by solvents or by the coordinating ability of the anion of the protonating acid. However, investigations of gas phase proton transfer processes of this nature, of necessity, require the use of a variety of Brønsted acid reagent ions of differing acid strengths, so that as complete an assessment as possible can be obtained relating to the occurrence of protonation, charge exchange, electrophilic addition, as well as rearrangement reactions.

We now report details of proton transfer and associated ion/molecule reactions with two series of organometallic complexes, respectively, a series of η^6-arenetricarbonylchromium(0) complexes, as well as a η^6-cycloheptatrienetricarbonylmetal(0) series with the Group VI metals, chromium, molybdenum and tungsten. The Brønsted acid reagent ions which have been interacted with these compounds are H_3^+, CH_5^+ (as well as $C_2H_5^+$ and $C_3H_5^+$), t-$C_4H_9^+$, and $(NH_3)_nH^+$ (with n = 1—3). These ions have been generated according to present standard practices which are now routinely adopted for protonation of a wide variety of organic molecules in order to obtain structural and ion decomposition/fragmentation data [15—17]. There is, however, a dearth of information available concerning the gas phase reactions of Brønsted acid reagent ions of widely differing acid strengths with organometallic compounds. Two earlier papers have provided some details of proton transfer to selected organometallic compounds by the use only of the reagent ions derived from methane [18,19]. However, in a previous report [1], we have indicated the desirability of working with Brønsted reagent ions of differing acid strengths to effect protonation to various η^4-dienetricarbonyliron(0) and η^4-polyenetricarbonyliron(0) complexes, and this has prompted an extension of that earlier study now to encompass these selected η^6-arene and η^6-cycloheptatriene derivatives of selected Group VI metal carbonyls.

Experimental

The three η^6-arenetricarbonylchromium(0) complexes together with η^6-cycloheptatrienetricarbonyl-chromium(0) and -molybdenum(0) were obtained from Strem Chemicals Inc., Newburyport, Mass., U.S.A., and were purified by vacuum sublimation prior to their insertion into the mass spectrometer. They were also characterized from their E.I. positive ion mass spectra. η^6-Acetophenonetricarbonylchromium(0) and η^6-cycloheptatrienetricarbonyltungsten(0) were prepared by standard methods [20,21] and similarly purified and characterized. Reagent gases which were used for the generation of the Brønsted acid reagent ions were Matheson UHP hydrogen (99.995%), C.P. methane (99.0%), instrument grade isobutane (99.5%) and anhydrous ammonia (99.99%).

Proton transfer reactions and mass spectra were carried out with an AEI MS-902 mass spectrometer fitted with a SRI CIS II high pressure ion source, under experimental conditions which have been described previously [1,15—17]. As it is well known that thermolysis of organometallic compounds can occur in mass spectrometer ion sources [22], checks were made on the effect of temperature on the compounds and their spectra, so that all proton transfer mass spectra were obtained at the minimum practicable ion source temperatures of 100—110° C.

Results and discussion

Table 1 presents the results of proton transfer mass spectra obtained for the series of η^6-arenetricarbonylchromium(0) compounds, I—IV, where the η^6-arene ligands were respectively, η^6-benzene, -toluene, -methylbenzoate and -acetophenone. All ions in the various mass spectra have been identified, and the results are given in terms of the percentages of the total ion currents carried by each ion. In addition, Scheme 1 illustrates the sequence of CO eliminations from protonated ions, and is representative of compounds I—IV, at least when hydrogen was used as the reagent gas:

SCHEME 1

$$\begin{tikzcd} {[M + H]^{+}} \arrow[r] \arrow[rr, bend right] & {[M + H - CO]^{+}} \arrow[r] & {[M + H - 2CO]^{+}} \arrow[r] & {[M + H - 3CO]^{+}} \end{tikzcd}$$

High abundances of $[M + H]^+$ ions were obtained for I—IV when H_2, CH_4 and i-C_4H_{10} were used as reagent gases. For III and IV in particular there is an obvious trend towards higher $[M + H]^+$ ion yields which parallels the decreasing Brønsted acid strengths of the principal ions effecting protonation, viz. H_3^+, CH_5^+ and t-$C_4H_9^+$. This also parallels the well recognized decrease in the exothermicity of protonation reactions of many organic compounds effected by these respective reagent ions [15].

Relatively high yields of $M^{+\cdot}$ ions are also given by I—IV, particularly when CH_4 is used as the reagent gas. A similar situation has been recognized when protonation of metallocenes has been effected by the reagent ions derived from CH_4 [18]. In that investigation the formation of $M^{+\cdot}$ ions has been attributed to a charge exchange reaction between the metallocene and the ethyl cation [18]. It is reasonable that such a reaction should be favoured on energetic grounds, since the ionization energies of metallocenes (6.2—7.8 eV) [18,23,24], are known to be lower than that of the ethyl radical (8.4 eV) [25]. A similar explanation may be offered for the observation of the $M^{+\cdot}$ ions in relatively high abundance for I—IV, especially when CH_4 functioned as the reagent gas, as ionization energy measurements for I—IV have been determined, as a result of independent studies, to lie in the range 7.19—7.44 eV [26] or 6.69—7.02 eV [27], while yet another report gives an ionization energy of 7.39 ± 0.1 eV for I [24]. It is now possible to account for the differences in these measurements by recourse to a detailed review of appearance potential measurements [28], which is outside the scope of this paper. However, the necessary agreement is forthcoming from these data to indicate that the ionization energies of I—IV are lower, by at least 1 eV, than that of the ethyl cation. Hence it may be envisaged that a charge transfer mechanism, viz.,

$$\eta^6\text{-AreneCr(CO)}_3 + C_2H_5^+ \rightarrow \eta^6\text{-AreneCr(CO)}_3^{+\cdot} + C_2H_5^{\cdot}$$

which is of the type suggested for the analogous metallocene reaction [18], is

TABLE 1

PERCENT OF THE TOTAL IRON CURRENT CARRIED BY THE SIGNIFICANT IONS IN THE PROTON TRANSFER MASS SPECTRA OF η^6-ARENETRICARBONYLCHROMIUM COMPLEXES [a, b]

Ions	Arene: Benzene (I)				Toluene (II)			
Reagent Gas:	H_2	CH_4	i-C_4H_{10}	NH_3	H_2	CH_4	i-C_4H_{10}	NH_3
$[M + N_2H_7]^+$ (%ΣI)	—	—	—	11	—	—	—	52
$[M + NH_4]^+$	—	—	—	22	—	—	—	37
$[M + C_2H_5]^+$	—	0	—	—	—	0	—	—
$[M + H]^+$	76	70	68	28	86	77	74	8
$[M]^{+\cdot}$	10	20	4	35	13	18	3	4
$[M - H]^+$	0	0.3	<0.1	0	<0.1	<0.1	<0.1	0
$[M + H - CO]^+$	9	1	<0.1	0.3	0.6	1	0.1	0
$[M - CO]^{+\cdot}$	0.1	0.2	0	0.5	<0.1	<0.1	<0.1	0
$[M - H - CO]^+$	<0.1	<0.1	0	0	<0.1	0	0	0
$[M + H - CH_3OH]^+$	—	—	—	—	—	—	—	—
$[M + H - 2\ CO]^+$	0.4	1	8	0.4	<0.1	1	10	0
$[M - 2\ CO]^{+\cdot}$	0.6	2	10	1	0.1	2	2	0
$[M - H - 2\ CO]^+$	<0.1	<0.1	<0.1	0	0	0	0	0
$[M + H - 3\ CO]^+$	0.1	0.5	8	0	<0.1	0.4	9	0
$[M - 3\ CO]^{+\cdot}$	2	1	1	0	0.2	1	2	0
$[M - H - 3\ CO]^+$	<0.1	0.1	<0.1	0	0	0	0	0
$[\text{Arene} + H]^+$	1	1	2	0	0.1	1	0	0
$[\text{Arene}]^{+\cdot}$	0.4	0	0	0	0.1	0	0	0.2
$[\text{Arene} - H]^+$	0	0	0	0	0.1	0	0	0.3

[a] All isotopes of all atoms in the various clusters are considered. [b] Mass spectra were obtained with minimum practically attainable ionization source temperatures in the range 100—110° C.

operative for the formation of $M^{+\cdot}$ species for I—IV. Additional evidence, which supports the view that $M^{+\cdot}$ species owe their origins to charge exchange rather than electron ionization processes, comes from an examination of the E.I. spectra of these and similar compounds [24,29,30], in which $[M - 3\ CO]^{+\cdot}$ and Cr^+ species are the most abundant. From the data contained in Table 1, it can be seen that the intensities of $[M - 3\ CO]^{+\cdot}$ species are low, and Cr^+ ions were not observed.

Other reactions of note which involve hydrocarbon reagent ions are the electrophilic attachment reactions of the $C_2H_5^+$ ion to III and IV. Similar reactions have been observed with the metallocenes [18], as well as in an earlier gas phase protonation study with I and III using only CH_4 as a reagent gas. In these reactions $C_2H_5^+$ functions both as an electrophile and as an electron abstracting reagents [16].

Only low abundances of $[M - H]^+$ species were obtained for I—IV with all reagent gases, and thus hydride abstraction from the ligands may be considered to be an insignificant reaction in all cases. It is noteworthy, too, that low yields of $[\text{AreneH}]^+$ ions were observed with all compounds, and this provides at least some evidence to indicate that the preferred protonation site was the metal, rather than the η^6-arene ligand for I—IV. A similar conclusion has been reached for I and II [19].

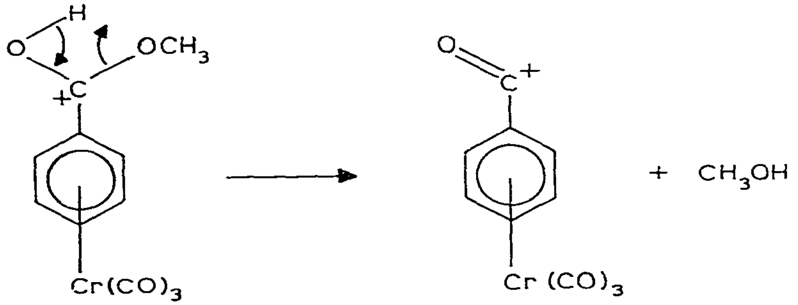
Evidence is also forthcoming from solution phase protonation studies to indicate that the preferred protonation site for I and II, together with other η^6-arenetricarbonylchromium(0) compounds, in $BF_3 \cdot H_2O/CF_3COOH$ is the

TABLE 1 (continued)

Methyl benzoate (III)				Acetophenone (IV)			
H_2	CH_4	$i\text{-}C_4H_{10}$	NH_3	H_2	CH_4	$i\text{-}C_4H_{10}$	NH_3
—	—	—	8	—	—	—	7
—	—	—	90	—	—	—	79
—	2	—	—	—	<0.1	—	—
52	52	90	0.7	47	74	81	14
10	22	2	2	10	6	2	2
<0.1	<0.1	0	0	<0.1	0.3	0.3	0
0.8	1	1	0	6	1	0.3	0
<0.1	0	0	0	0.5	<0.1	<0.1	0
<0.1	0	0	0	<0.1	<0.1	<0.1	0
10	9	<1	0	—	—	—	—
8	7	0.4	0	24	7	7	0
0.9	2	0.3	0	1	1	0.3	0
0.7	0	0	0	0	<0.1	<0.1	0
7	2	0	0	3	5	5	0
4	0.6	0	0	3	2	1	0
2	0.2	0	0	0.2	0.3	0.1	0
5	2	6	0	4	5	0	0
0	0.2	0	0	0.2	0	0	0
0	0	0	0	0	0	0	0

chromium atom [8,13]. However, in the solution phase, reversible keto-protonation has been reported in cases where the aromatic ligand contains a carbonyl group [31].

No clear evidence for ligand keto-protonation has been obtained from our studies with η^6-acetophenonetricarbonylchromium(0), IV, as significantly different fragment ions were not observed when this compound was protonated, compared with I or II. However, there is some evidence which comes from an ion rearrangement reaction which indicates that III was protonated at the ester functional group, because of the observation of an $[M + H - CH_3OH]^+$ ion in the spectrum and also the assignment of a metastable peak for the reaction $[M + H]^+ \rightarrow [M + H - CH_3OH]^+$. The abundances of this rearrangement ion were seen to decrease in parallel with the decreases in the Brønsted acid strengths of the reagent ions derived from H_2, CH_4 and $i\text{-}C_4H_{10}$ respectively. As the oxygen atom of a carbonyl group is known to be a preferred site for gas phase proton attachment [17,31], the elimination of CH_3OH from $[M + H]^+$ for III may be illustrated schematically as follows:



More compelling evidence for protonation of the ester group rather than the metal comes from the observation of the $[M + C_2H_5]^+$ ion in small, but significant, abundance for III. This is the most abundant $[M + C_2H_5]^+$ ion observed for I—IV, and as such ions are commonly observed in the CH_4 proton transfer mass spectra of organic esters [16], this is additional evidence to support the view that the ester group provides the site for proton attachment to III.

Proton transfer mass spectra that were obtained for I—IV by the use of ammonia as the reagent gas were of considerable interest. All compounds formed $[M + (NH_3)_nH]^+$ with $n = 1, 2$; and $[M + H]^+$ ions under these conditions. It is known that $(NH_3)_nH^+$ ions may function either as electrophiles or weak Brønsted acids towards organic molecules, as it has been reported that amines, amides and α,β-unsaturated ketones are the only common compounds which arc sufficiently basic to accept a proton from the ammonium ion [32]. On the other hand, ketones and esters undergo electrophilic attachment by NH_4^+, but are not protonated in the gas phase, whereas alkanes, aromatics and many other organic molecules fail to react with NH_4^+ in the gas phase under the usual mass spectrometer high pressure ion source conditions [32]. Proton transfer and electrophilic attachment may thus be seen to be competing processes with compounds I—IV. Comparison of the proportions of the total ion currents carried by the $[M + (NH_3)_nH]^+$ and $[M + H]^+$ ions for I—IV when NH_3 was used as the reagent gas provides information which allows for a qualitative assessment of the relative gas phase basicities of I—IV to be inferred (Table 2). It may be assumed that proton transfer to the organometallic complex will only occur if the proton affinity of the sample exceeds that of ammonia, and if this condition is not met the competing electrophilic attachment reactions of $(NH_3)_nH^+$ ions may become predominant. From the data in Table 2 it can be seen that I was the complex most readily protonated, thereby exhibiting the highest degree of basicity in the series, since $[M + H]^+$ ions carried 28% of the total ion current. On the other hand, the very low proportion of the total ion current carried by $[M + H]^+$ for III, together with the high proportion of the total ion current carried by $[M + NH_4]^+$ indicates that it was the least basic of these complexes. The data for II and IV indicate that their gas phase basicities were similar. In qualitative terms at least, the descending order of the gas phase basicities for these complexes is: $1 > II \sim IV > III$.

Results of the proton transfer mass spectra which were obtained with η^6-cycloheptatrienetricarbonyl complexes of chromium(0), molybdenum(0) and tungsten(0) compounds V—VII, are given in Table 3. Protonation of V—VII was effected by the reagent ions derived from H_2, CH_4 and i-C_4H_{10}, with increasing $[M + H]^+$ ion abundances paralleling the decreasing Brønsted acid strengths of the protonating ions, as was the case for III and IV. The pro-

TABLE 2

RELATIVE INTENSITIES OF ELECTROPHILIC ATTACHMENT AND PROTONATED IONS OF I—IV

Compound	I	II	III	IV
$[M + (NH_3)_nH]^+$ (%Σ)	33	89	98	86
$[M + H]^+$	28	8	0.7	14

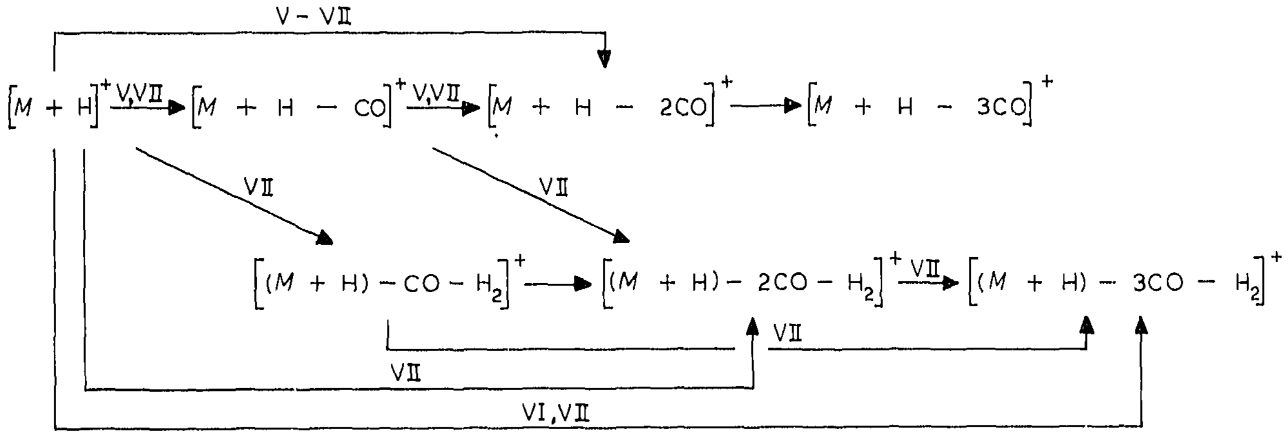
TABLE 3

PERCENT OF THE TOTAL ION CURRENT CARRIED BY THE SIGNIFICANT IONS IN THE PROTON TRANSFER MASS SPECTRA OF η^6-CYCLOHEPTATRIENETRICARBONYLCHROMIUM, -MOLYBDENUM AND -TUNGSTEN COMPLEXES [a,b]

Ion	Metal: Chromium (V)				Molybdenum (VI)				Tungsten (VII)			
Reagent Gas:	H_2	CH_4	i-C_4H_{10}	NH_3	H_2	CH_4	i-C_4H_{10}	NH_3	H_2	CH_4	i-C_4H_{10}	NH_3
$[M + N_2H_7]^+$ (%ΣI)	—	—	—	66	—	—	—	5	—	—	—	9
$[M + NH_4]^+$	—	—	—	16	—	—	—	57	—	—	—	80
$[M + N_2H_7 - CO]^+$	—	—	—	0	—	—	—	12	—	—	—	0
$[M + H]^+$	36	63	85	0	50	67	72	12	51	73	77	5
$[M]^{+\cdot}$	23	29	13	9	15	8	2	0	14	11	7	0.4
$[M - H]^+$	0.3	1	1	0	0	0	00	0	7	5	0	0
$[M + NH_4 - CO]^+$	—	—	—	9	—	—	—	14	—	—	—	4
$[M + H - CO]^+$	12	4	0.8	0	8	0.9	0.1	0	12	2	1	0
$[M - CO]^{+\cdot}$	3	2	0.3	0	3	2	0.3	0	2	2	<0.1	0.6
$[M - H - CO]^+$	0.9	2	0.3	0	3	2	8	0	2	3	7	1
$[M + H - 2\,CO]^+$	14	0	0	0	12	5	0.2	0	1	2	0	0
$[M - 2\,CO]^{+\cdot}$	1	0	0	0	1	0.7	0.1	0	0.8	0.5	0.3	0
$[M - H - 2\,CO]^+$	<0.1	0	0	0	0	1	6	0	0.1	0.4	3	0
$[M + H - 3\,CO]^+$	0.8	0	0	0	0.8	0.1	0.1	0	0.5	0	0	0
$[M - 3\,CO]^{+\cdot}$	3	0	0	0	2	0.6	<0.1	0	0.9	0	0.5	0
$[(M + H) - 3\,CO - H_2]^+$ and $[M - H - 3\,CO]^+$	0.2	0	0	0	0	0.8	5	0	0	0	1	0
$[C_7H_8 + H]^+$	0.8	0	0	0	3	11	3	0	5	4	2	0
$[C_7H_8]^{+\cdot}$	0.8	0	0	0	0	0	0	0	0	0	0	0
$[C_7H_8 - H]^+$	4	0	0	0	4	0	5	0	4	0	0	0

[a] All isotopes of all atoms in the various clusters are considered. [b] Mass spectra were obtained with ionization source temperatures in the range 100—110°C.

SCHEME 2
ION DECOMPOSITION PATHWAYS FOR THE η^6-CYCLOHEPTATRIENETRICARBONYLMETAL(0) COMPLEXES, V-VII, WHERE H_3^+ WAS USED AS THE PROTONATING REAGENT ION.



ton transfer mass spectra of the isomeric conpounds II and V are very similar, except for the reactions of these compounds with $(NH_3)_nH^+$ ions. In addition, the proton transfer mass spectra obtained for V—VII differ in very significant respects from the positive ion E.I. spectra reported for these compounds, in which high abundances of Cr^+, $C_7H_8^{+\cdot}$, $C_7H_8 \cdot \text{metal}^{+\cdot}$ and $M^{+\cdot}$ ions were observed [30,33]. Furthermore, as the ionization energy of at least one member of this series, V, has been reported as 7.10 eV, the occurrence of $M^{+\cdot}$ ions for V—VII may be attributed to charge transfer processes for reasons similar to those given previously for I—IV. E.I. contributions to the proton transfer mass spectra of V—VII given in Table 3, are thus considered to be minimal.

Significantly different ion decomposition pathways were followed by V—VII, and these are illustrated in Scheme 2, which has been elucidated as a result of the assignment of metastable peaks. Whereas the protonated chromium complex ion of V decomposed by both simultaneous and consecutive elimination of CO ligands, the protonated molybdenum and tungsten complex ions derived from VI and VII, usually eliminated H_2 in conjuction with the loss of 1—3 CO ligands.

In addition, for VI and VII, there were observed small but significant abundances of $[C_7H_9]^+$ ions in their spectra. Moreover, for VII, $[M - H]^+$ ions which were formed as a result of hydride abstraction were present to the extent of 7% and 5% when H_2 and CH_4 were the reagent gases. This provides at least some evidence to suggest that protonation of the hydrocarbon ligand was a significant process for both VI and VII. It can be envisaged that elimination of H_2 together with at least one CO molecule could result in a rearrangement to give a coordinated tropylium type ($C_7H_7^+$) ligand:

$$C_7H_8 \cdot \text{Metal(CO)}_3 \xrightarrow{H^+} C_7^+H_9 \cdot \text{Metal(CO)}_3 \xrightarrow[-H_2,\ -CO]{\text{rearrangement}} C_7^+H_7 \cdot \text{Metal(CO)}_2$$

Results of solution phase protonation reactions of VI also provide evidence of ring protonation, as isolatable products containing the $[\eta^5\text{-}C_7H_9 \cdot Mo(CO)_3]^+$ ion have been obtained from HBF_4 and HCl protonation of VI [34].

The inability of $(NH_3)_nH^+$ ions to protonate V indicates that this chromium complex has a lower proton affinity than that of ammonia. On the other hand, the molybdenum and tungsten complexes, VI and VII, were protonated under similar conditions to V and this, taken with the data from Table 3, indicates a qualitative basicity order for this series of: VII ~ VI > V. This order is in agreement with that derived from solution phase protonation studies where it is now generally accepted that the basicity of these types of organometallic complexes increases as Group VI is descended [8,9]. It should also be emphasised that electrophilic attachment reactions involving the NH_4^+ and $N_2H_7^+$ ions and VI—VII were also significant and competitive with the protonation reactions of these complexes.

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References

1 M.R. Blake, J.L. Garnett, I.K. Gregor and D. Nelson, J. Organometal. Chem., 188 (1980) 203.
2 M.R. Blake, I.W. Fraser, J.L. Garnett, I.K. Gregor and R. Levot, J. Chem. Soc., Chem. Commun., (1974) 1004.
3 M.R. Blake, J.L. Garnett, I.K. Gregor and S.B. Wild, Org. Mass Spectrom., 13 (1978) 20.
4 M.R. Blake, J.L. Garnett, I.K. Gregor and S.B. Wild, J. Chem. Soc., Chem. Commun., (1979) 496.
5 M.R. Blake, J.L. Garnett, I.K. Gregor and S.B. Wild, J. Organometal. Chem., 178 (1979) C37.
6 M.R. Blake, J.L. Garnett, I.K. Gregor and S.B. Wild, Org. Mass Spectrom., in press.
7 W. Hieber, Adv. Organometal. Chem., 8 (1970) 1.
8 J.C. Kotz and D.G. Pedrotty, Organometal. Chem. Rev. A, 4 (1969) 479.
9 D.F. Shriver, Accs. Chem. Res., 3 (1970) 321, and references therein.
10 M.A. Haas, Organometal. Chem. Rev. A, 4 (1969) 307, and references therein.
11 D.F. Shriver, J. Organometal. Chem., 94 (1975) 259.
12 J.E. Ellis, J. Organometal. Chem., 86 (1975) 1.
13 A. Davidson, W. McFarlane, L. Pratt and G. Wilkinson, J. Chem. Soc., (1962) 3653.
14 M. Brookhart, T.H. Whitesides and J.M. Crockett, Inorg. Chem., 15 (1976) 1550.
15 B. Munson, Anal. Chem., 43 (1971) 28A; 49 (1977) 772A, and references therein.
16 W.J. Richter and H. Schwarz, Angew. Chem. Int. Ed. Engl., 17 (1978) 424, and references therein.
17 F.H. Field, in A. Maccoll (Ed.), MTP International Review of Science, Series 1, Vol. 5, Butterworths, London, 1972, Ch. 5.
18 D.F. Hunt, J.W. Russell and R.L. Torian, J. Organometal. Chem., 43 (1972) 175.
19 W.P. Anderson, N. Hsu, C.W. Stanger and B. Munson, J. Organometal. Chem., 69 (1974) 249.
20 B. Nicholls and M.C. Whiting, J. Chem. Soc., (1959) 551.
21 G. Klopman and F. Calderazzo, Inorg. Chem., 6 (1967) 977.
22 S. Pignataro and F.P. Lossing, J. Organometal. Chem., 11 (1968) 571.
23 M. Cais and M.S. Lupin, Adv. Organometal. Chem., 8 (1970) 211.
24 S. Pignataro and F.P. Lossing, J. Organometal. Chem., 10 (1967) 531.
25 F.P. Lossing and G.P. Semeluk, Can. J. Chem., 48 (1970) 955.
26 J. Müller, J. Organometal. Chem., 18 (1969) 321.
27 J.R. Gilbert, W.P. Leach and J.R. Miller, J. Organometal. Chem., 49 (1973) 219.
28 J.H. Beynon, R.G. Cooks, K.R. Jennings and A.J. Ferrer-Correia, Int. J. Mass Spectrom. Ion Phys., 18 (1975) 87.
29 J. Müller and P. Gösser, Chem. Ber., 102 (1969) 3314.
30 J. Müller and K. Fenderl, Chem. Ber., 103 (1970) 3128.
31 D.K. Wells and W.S. Trahanovsky, J. Amer. Chem. Soc., 91 (1969) 5871.
32 D.F. Hunt, Adv. Mass Spectrometry, 7 (1974) 517.
33 R.B. King, Appl. Spectry., 23 (1969) 536.
34 A. Salzer and H. Werner, J. Organometal. Chem., 87 (1975) 101.