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A MASS SPECTRAL STUDY OF SELECTED POLYMER SUPPORTS AND TRANSITION METAL-SUPPORTED REAGENTS

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Summary

A series of functionalized polymers which are commonly used to support transition metal catalysts have been analysed by mass spectrometry. Both qualitative and quantitative analyses of brominated, phosphinated and CH_2Cl functionalized polystyrene (cross-linked with 2% divinylbenzene) have been achieved. Preliminary data on the mass spectra of transition metals supported on the functionalized polymers (e.g. $RuCl_2(PPh_3)_3$, η^5-$C_5H_5Fe(CO)_2H$ and $[\eta^5$-$C_5H_5Fe(CO)_2]_2$) have as yet revealed no fragments which can be associated with the transition metal.

Introduction

A major problem associated with the field of homogeneous catalysis is the difficulty experienced in separating catalyst from product (or reactant) at the end of a reaction. Attachment of a catalyst, usually a transition metal, to a solvent insoluble polymer is one method used to overcome this problem [1]. This is achieved by functionalizing the polymer and reacting a transition metal with the functionalized polymer. Unfortunately both quantitative and qualitative analysis of the functionalized polymer and the polymer supported catalyst is a non-trivial problem [1—4]. In general, the method of choice involves the use of elemental analyses and, if possible, this is supported by changes in the IR spectrum of the polymer on functionalization.

We have commenced an investigation of some catalytic reactions of rhodium [5], ruthenium and iron [6] complexes supported on polystyrene, cross-linked with 2% divinylbenzene (**1**). As a preliminary to this investigation it was necessary to prepare and analyse functionalized polystyrene supports containing bromine (**2**), PPh_2 (**3**), and $CH_2C_5H_5$ (**5**) (Fig. 1). In our search for physical methods for the quantitative and qualitative analyses of the polymers we have found mass spectrometry to be a useful tool. The use of mass spectrometry in

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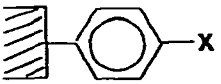


X		X	
H	(1)[a]	CH_2Cl	(4)
Br	(2)	$CH_2C_5H_5$	(5)
PPh_2	(3)	$ML_n^{\cdot}$	(6)

[a] Representation of polystyrene cross linked with 2% divinylbenzene

Fig. 1. Polystyrene derivatives.

polymer chemistry is well documented [7] and provided the polymer can degrade under the conditions of temperature and pressure used in the mass spectrometer, polymers of unknown structure can be characterized from an identification of the fragments observed. We have used this principle to determine (a) the chemical nature of the functionalized polymer and (b) the degree of substitution that has taken place.

Experimental

Polystyrene cross-linked with 2% divinylbenzene (200—400 mesh, Dow Chemicals); was purified by the method of Relles and Schluenz [8]. The polymers containing varying amounts of functionalized groups were prepared by the literature methods (Br [8], PPh_2 [9,10], CH_2Cl [11], $CH_2C_5H_5$ [12]). Mass spectra were recorded on a Varian CH5 spectrometer (70 eV) in the temperature range 300—450°C unless otherwise stated. IR spectra were recorded as KBr pellets on a PE 521 spectrometer. Elemental analyses were determined by the Microanalytical Laboratories, CSIR, Pretoria (C, H, Br, Cl) or by Robertson Laboratories, New Jersey (C, H, P).

Results and discussion

Bromination and phosphination of 1

A well established route for the preparation of transition metal catalysts, ML_n (M = metal, L = ligand), supported on polystyrene, **6**, is via phosphine attachment [1].

$$\mathbf{1} \xrightarrow{Br_2/BF_3} \mathbf{2} \xrightarrow{PPh_2Li} \mathbf{3} \xrightarrow{ML_n} \mathbf{6}$$

By varying the quantities of reactants we have prepared polymers of types **2** and **3** with different amounts of bromine and phosphine (Tables 1 and 2). Mass spectra were recorded on all the brominated polymers **2** and the spectrum of the most highly substituted derivative (sample No. 1) is shown in Fig. 2a.

Since bromine has two isotopes, ^{79}Br and ^{81}Br of 50.54 and 49.46% natural abundance [13], fragments containing bromine can readily be observed. We have identified monomeric to tetrameric fragments in the mass spectrum of the brominated polymers and the fragments (Fig. 3), their assignments and intensi-

TABLE 1

ANALYTICAL AND MASS SPECTRAL DATA FOR THE BROMINATED POLYMERS 2

Sample No.	Analysis (%)			Ring substitution (%)[a]	Mass spectral (MS) data[b]	
	C	H	Br		I_{368}/I_{288}	I_{182}/I_{312}
1	53.12	4.10	42.09	95.5	1.31	
2	56.27	4.22	39.66	86	0.91	
3	55.35	4.19	38.95	83.5	0.86	
4	66.19	5.25	29.21	55	0.29	
5	66.18	5.29	28.32	53	0.25	
6	69.24	5.62	25.68	46	0.18	23.81
7	79.36	6.43	14.13	22		5.34
8	80.64	6.68	11.69	17.5		2.52
9	81.79	6.89	10.66	16		2.43
10	83.56	6.80	9.54	14		1.66
11	86.11	7.26	7.37	10.5		1.44
12	86.46	7.38	6.42	9		0.92
13	87.05	7.47	4.68	6.5		0.55
14[c]	76.39	6.20	18.02	29.5[d]		11.7
15[c]	82.80	6.89	10.23	15[e]		2.2
16[c]	86.33	7.15	5.98	8.5[f]		0.8

[a] Refers to % brominated polystyrene rings. [b] Ratio of intensities of fragment peaks (see Fig. 3). [c] Recorded on 60—80 mesh brominated beads. [d] 28.0% from MS data. [e] 15.5% from MS data. [f] 8.0% from MS data.

ties, have been recorded in Table 3. Even when the degree of ring substitution is low (<7%), brominated fragments can readily be detected. Fragments observed in the mass spectrum of the unfunctionalized polymer support, together with their assignments are listed in Table 4 for comparison.

We have also attempted to obtain quantitative data on the degree of ring substitution using mass spectrometry. By using high molecular mass fragments ($m/z > 150$), and in particular fragments containing bromine, we have been able to quantify the % ring substitution (i.e. bromine content of a polymer) directly from mass spectral analysis. After a trial-and-error search for fragments that would give a quantitative analysis for bromine we have found the following: (a) Internal standards are necessary to make the analysis feasible and easy to use; consequently we have used the intensity ratios of fragments as a measure of the polymer content. (b) Peaks of low m/z value cannot be used as these fragments can originate from a number of fragmentation pathways.

To obtain a satisfactory degree of accuracy over the whole substitution range (0—100% ring substitution) we have found it necessary to make use of two sets of intensity ratio data. Thus, for the 40—100% substitution range, the ratio of the intensities of the fragments **16** and **13**, i.e. I_{368}/I_{288}, was employed (Fig. 4). At low substitution (<50%), $I_{368} \rightarrow 0$ and the ratio $\rightarrow 0$. Thus an alternative set of data was used. This lower range can be covered by the ratio of the intensity of fragments **9** and **14**, i.e. I_{182}/I_{312} (Fig. 5).

An error of ~3% ring bromination can be expected from our technique. The error arises from two major sources: (a) measurement of low intensity peaks in the mass spectrum, and (b) repeat mass spectra on identical samples give an error of ±2% in the intensity ratio. (Determination of bromine by elemental

TABLE 2

ANALYTICAL AND MASS SPECTRAL DATA FOR THE PHOSPHINATED POLYMERS 3

Sample No.	Original % Br	Analysis (%)				Mass spectral data			Ring substitution (%)			
		C	H	P	Br	I_{288}	I_{182}	I_{182}/I_{312}	Analysis [a]		MS [b,c]	
									PPh_2	Br	PPh_2	Br
17	95.5	81.76	6.27	6.98	3.74	43.5	4.5		83.5	12.0	86.5	9.0
18	95.5	79.46	6.04	5.45	5.75	35.0	9.0		78.0	17.5	76.0	19.5
19	83.5	84.72	6.77	4.91	3.63	23.5	2.5		72.5	11.0	75.5	8.0
20	83.5	87.83	5.94	6.18	7.71	47.5	22.0		61.0	22.5	57.0	26.5
21	46.0	87.17	7.21	3.53	1.50			0.31	42.5	3.5	42.5	3.5
22	22.0	84.69	7.76	1.29	1.15			0.11	20.5	1.5	20.0	2.0
23	16.0	89.21	7.63	3.13	1.26			0.33	14.0	2.0	11.5	4.5
24	14.0	90.28	7.53	1.04	1.47			0.25	11.5	2.5	10.5	3.5
25	10.5	89.65	7.47	2.45	0.90			0.10	9.0	1.5	8.5	2.0

[a] See text for explanation. [b] For original % Br > 50%, ring substitution obtained from the intensities of m/z = 288 and 182 fragments. [c] For original % Br < 50%, % Br obtained from Fig. 5.

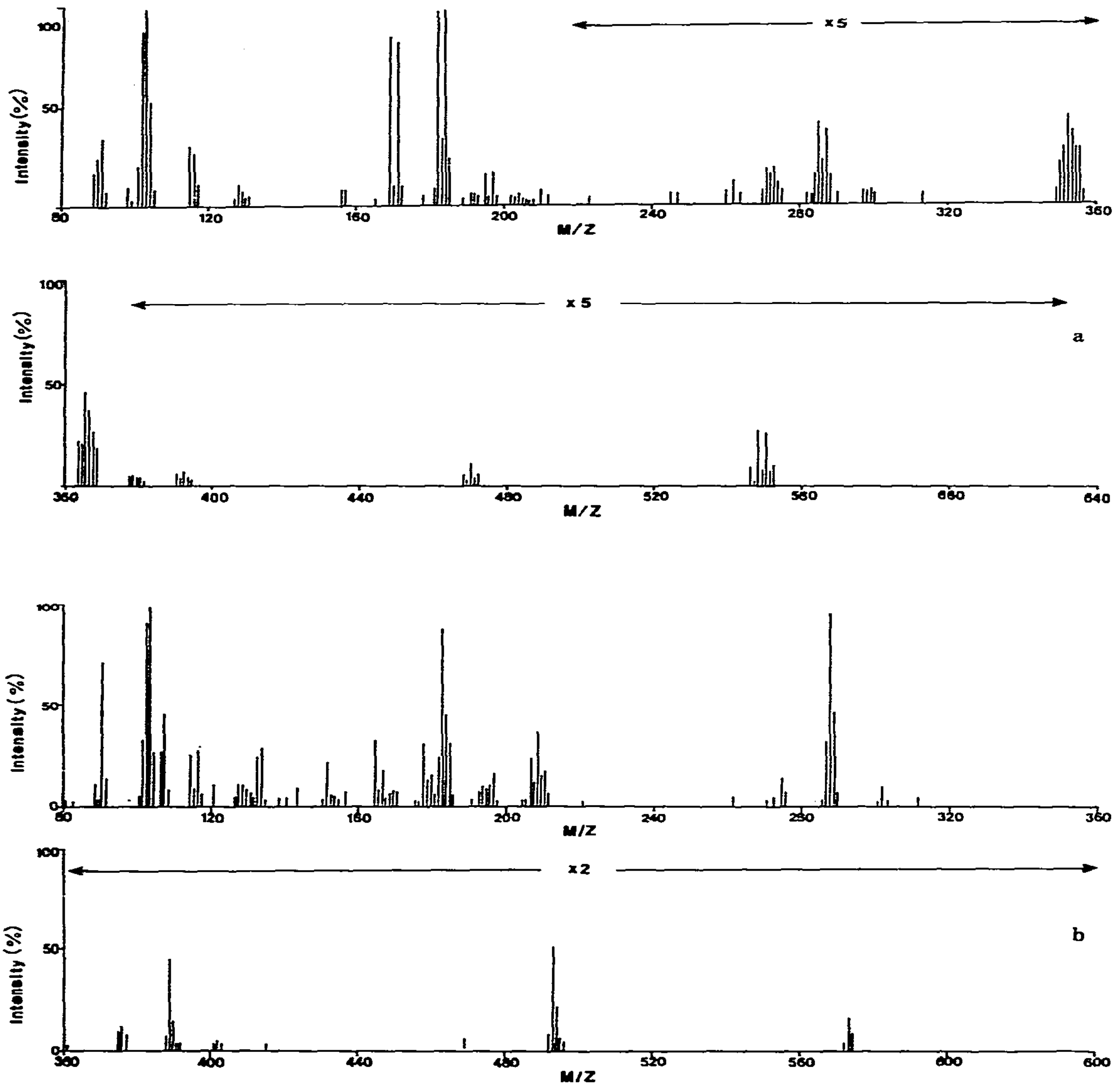
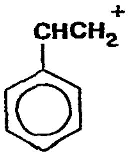


Fig. 2. (a) Mass spectrum of **2** (Sample No. 1); (b) Mass spectrum of **3** (Sample No. 18).

analysis gives an error of ±2% (ring bromination).)

Our results were found to be independent of bead size. This was determined from a mass spectral analysis of 20—60 mesh beads (Strem Chemicals) which had been brominated. The analytical results obtained were as predicted from the intensity of the required fragments using Figs. 4 and 5 (Table 1, samples 14—16).

At the high temperatures (±370°C) at which the spectra were recorded inaccuracy in the measurement of the temperature could give rise to errors in the intensity ratio data. We have thus recorded the intensity ratios of our required fragments at different temperatures, 235—450°C (Table 5), and found that the



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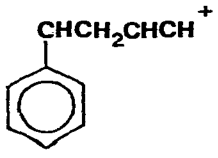

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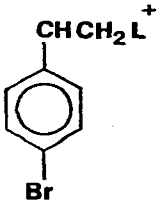
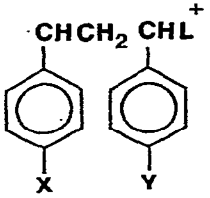


L	M/Z[a]	
–	184	(9)
CH	197	(10)



L	X	Y	M/Z[a]	
CH_2	H	H	208	(11)
–	H	Br	274	(12)
CH_2	H	Br	288	(13)
$C_3H_5C_6H_5$[b]	H	H	312	(14)
–	Br	Br	354	(15)
CH_2	Br	Br	368	(16)

[a] ^{81}Br isotope [b] Trimeric unsubstituted fragment.

Fig. 3. Fragments observed in the mass spectrum of **2**.

ratio is almost invariant with temperature and that the effect on the % ring substitution is within our accuracy level.

Figures 4 and 5 can be used to determine the % ring substitution directly by

TABLE 3

MASS SPECTRUM OF 2[a,b]

m/z	Rel. int. (%)	Assignment	*m/z*	Rel. int. (%)	Assignment
90	25	$C_6H_5CH^+$	264	2	?
91	35	$C_6H_5CH_2^+$	272, 274	4	12^+
92	8	$C_6H_5CH_3^+$	285, 287	11	$[13-H]^+$
101	21	$[7-3H]^+$	286, 288	5	13^+
102	89	$[7-2H]^+$	312	~1	14^+
103	100	$[7-H]^+$	354[c]	9	15^+
104	52	7^+	355[c]	8	$[15^+H]^+$
105	8	$[7+H]^+$	367[c]	8	$[16-H]^+$
115	32	$[8-CH_3]^+$	368[c]	6	16^+
116	28	$[8-CH_2]^+$	380[c]	2	$[16+C]^+$
117	12	$[8-CH]^+$	392	2	$[14+Br-H]^+$
128	11	$[8-2H]^+$	472[c]	2	$[16+(C_6H_5)C_2H_3]^+$
169, 171	84	$[9-CH]^+$	552[d]	3	$[16+(C_6H_4Br)C_2H_3]^+$
182, 184	100	9^+	596[c]	<1	$[11+16]^+$
195, 197	16	10^+	624	<1	$[14+14]^+$
208	5	11^+	656[d]	<1	$[16+13]^+$
247	2	$[11+C_3H_3]^+$			

[a] Sample No. 1, Table 1; recorded at 370°C. [b] Only major and significant fragments in the range *m/z* 90—700 listed. [c] For fragments containing 3 Br atoms a 1 : 2 : 1 ratio of peaks is expected. The intensity and *m/z* value for the ^{81}Br fragment is recorded. [d] A 1 : 2 : 2 : 1 ratio of peaks is observed corresponding to the presence of 3 Br atoms in the fragment.

TABLE 4

MASS SPECTRUM OF 1 [a]

m/z	Rel. int. (%)	Assignment	m/z	Rel. int. (%)	Assignment
77	34	$C_6H_5^+$	115	8	$[8-CH_3]^+$
78	56	$C_6H_6^+$	117	24	$[8-CH]^+$
91	85	$C_6H_5CH_2^+$	129	4	$[8-H]^+$
92	11	$C_6H_5CH_3^+$	130	4	8^+
102	10	$[7-2\,H]^+$	193	4	$[11-CH_3]^+$
103	53	$[7-H]^+$	194	6	$[11-CH_2]^+$
104	100	7	207	7	$[11-H]^+$
105	15	$[7+H]^+$	208	4	11^+

[a] Recorded at 370°C. Only fragments in the range m/z 70—300 are listed.

mass spectrometry, even on impure samples. This has the advantage that the polymer can be analysed during a reaction without purification. The long and tedious washing procedures required to purify a functionalized polymer can thus be avoided and rapid, quantitative data become readily available.

The phosphinated polymer, **3**, prepared by reaction of **2** with PPh_2Li [9,10], was also subjected to a mass spectral study in the 300—450°C range. In no instance did we prepare a polymer with complete substitution of all the bromine by PPh_2 groups (Table 2), and typical samples revealed that 3—30% of the rings contained residual bromine. Thus all phosphinated polymers contained varying amounts of x, y and z (Fig. 6).

Assignment and intensities of the major fragments (Fig. 7) of one of the most

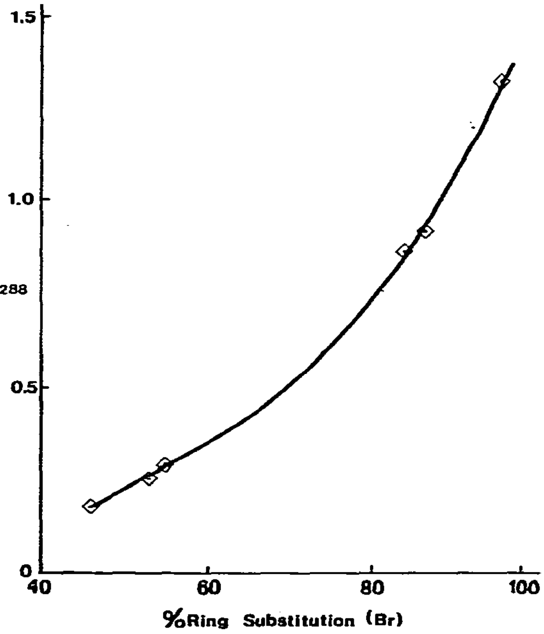


Fig. 4. Plot of the mass spectral intensity data (I_{368}/I_{288}) versus % ring substitution for polymer **2**.

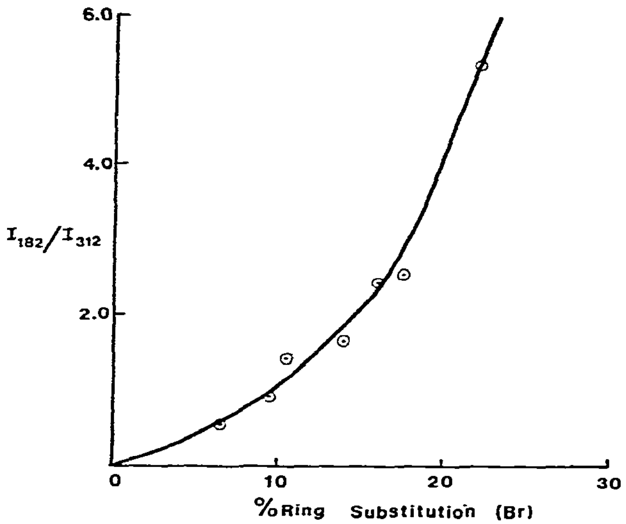


Fig. 5. Plot of the mass spectral intensity data (I_{182}/I_{312}) versus % ring substitution for polymer **2**.

highly phosphinated polymers (sample No. 18, Table 2) is given in Table 6. Monomeric, dimeric and trimeric fragments can readily be detected in the spectrum (Fig. 2b).

Unfortunately, we have not been able to obtain a quantitative measure of the % ring substitution by PPh_2 groups directly from their mass spectra. Fragments containing the PPh_2 group **3**, give intensities which are either too strong relative to, or overlap with, bromine-containing fragments and consequently poor analytical data are obtained by direct methods. A further important problem relates to the accuracy of ring substitution data that can be obtained from phosphorus elemental analyses. Calculation of the maximum amount of phosphorus that can be obtained on 100% ring phosphination is equal to 10% by mass. This implies that 1% P (elemental analysis) corresponds to 10% ring substitution. Thus small errors in the elemental analysis lead to significant errors in the % ring substitution. For this reason we have determined the % phosphination via indirect methods involving the residual % Br. Two methods have been used depending on the initial % ring bromination.

TABLE 5

EFFECT OF TEMPERATURE ON THE FRAGMENT INTENSITY RATIOS

Sample No.	T (°C)	I_{182}/I_{312}	I_{368}/I_{288}	Ring subs. (%)
1	235		1.25	94
	300		1.15	92
	375		1.31	95.5
13	300	0.50		5.5
	350	0.50		5.5
	360	0.53		6
	370	0.56		6.5
	450	0.52		6

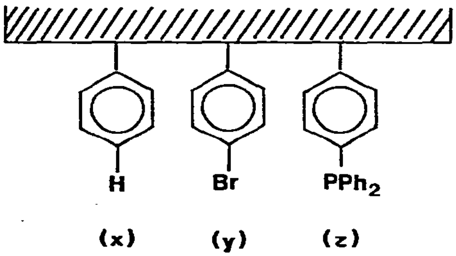
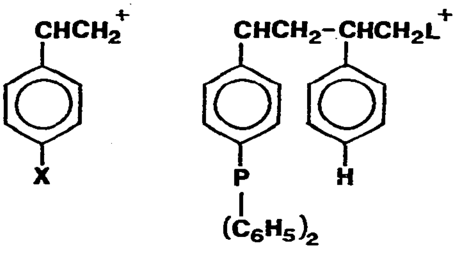


Fig. 6. Phosphinated polymer containing residual bromine.

For polymers initially containing <50% brominated rings, Fig. 5 can be used to calculate the residual % brominated rings after phosphination. The fragment $m/z = 312$ (**14**) remains invariant during the phosphination reaction and the ratio I_{182}/I_{312} then gives a measure of the residual bromine. The degree of ring phosphination can then be calculated by difference, i.e. it is equal to the (initial % — residual %) ring bromination.

When the original % ring bromination is >50% an alternate procedure is required. Neither of the curves (Figs. 4 and 5) can be used as either I_{312} is too small to measure accurately or the $m/z = 288$ fragment is found to arise almost exclusively from fragment **19**, a phosphinated fragment. Instead, we have used the intensities I_{182} and I_{288}, corresponding to a brominated fragment **9** and a phosphinated fragment **19**, as a measure of the reaction. The method used is based on the assumption that the two intensities (I_{182} and I_{288}) are directly proportional to the relative amounts (% substitution) of Br and PPh_2, respectively. Thus, the residual % ring bromination is obtained from $[I_{182}/(I_{182}+I_{288})] \times$ original % ring bromination, and the % ring phosphination is again calculated by difference. These results are listed in Table 2. A comparison of the above results with the % ring bromination obtained from elemental analyses (bromine)



X	M/Z	
P	134	(17)
$P(C_6H_5)$	210	(18)
$P(C_6H_5)_2$	288	(19)

L	M/Z	
–	392	(20)
$CHCH_2C_6H_5$	496	(21)

Fig. 7. Fragments observed in the mass spectrum of **3**.

TABLE 6

MASS SPECTRUM OF 3 [a]

m/z	Rel. int. (%)	Assignment	m/z	Rel. int. (%)	Assignment
91	90	$C_6H_5CH_2^+$	209	39	$[11 + H]^+$
92	14	$C_6H_5CH_3^+$	210	18	$[18 - H]^+$
102	34	$[7 - 2\ H]^+$	211	20	18^+
103	92	$[7 - H]^+$	275	15	$[19 - CH]^+$
104	100	7^+	287	33	$[19 - H]^+$
105	28	$[7 + H]^+$	288	97	19^+
107	29	$[PC_6H_5 - H]^+$	289	48	$[19 + H]^+$
108	47	$PC_6H_5^+$	302	12	$[19 + CH_2]^+$
115	27	$[8 - CH_3]^+$	312	4	14^+
117	32	$[8 - CH]^+$	376	6	$[20 - CH_4]^+$
133	25	$[17 - H]^+$	389	23	$[20 - 3\ H]^+$
134	31	17^+	390	8	$[20 - 2\ H]^+$
152	23	—	402	3	$[4 + 7 - CH_2]^+$
165	34	—	416	2	$[14 + 7]^+$
167	20	—	468	3	$[19 + 10 - CH]^+$
169, 171	7	$[9 - CH]^+$	481	1	$[19 + 10]^+$
182	26	9^+	493	26	$[21 - 3\ H]^+$
183	90	$[P(C_6H_5)_2 - 2\ H]^+$	494	11	$[2 - 4\ H]^+$
184	46	$[P(C_6H_5)_2 - H]^+$ or 9	521	2	$[14 + H + H]^+$
185	33	$P(C_6H_5)_2^+$	561	1	$[19 + 19 - CH_3]^+$
195	10	10^+	576	8	$[19 + 19]^+$
197	18	10 or $[18 - CH_2]^+$	~603	3	$[19 + 19 + C_2H_3]^+$
207	26	$[11 - H]^+$	~688	8	$[19 + 20]^+$
208	13	11^+	~760	1	
			~874	2	$[19 + 19 + 19]^+$

[a] Sample No. 18; recorded at 370°C.

shows a good correlation (Table 2). (Note: The % ring bromination obtained from elemental analysis is determined as follows. From a knowledge of the initial % ring bromination theoretical curves showing % Br vs. % ring bromination, as Br is replaced by PPh_2, can be generated. Since the Br elemental analysis can be obtained a value for the residual % ring bromination can readily be determined from the above curves. The % ring phosphination is then obtained by difference).

We have also detected fragments due to phosphine oxide (m/z = 304) in some of our phosphinated samples. The intensity of this fragment is generally low, even in highly functionalized polymers. However, the fragment intensity does become significant on polymer metallation (vide infra).

Chloromethylation and subsequent reaction with cyclopentadiene

Another general route to the synthesis of polymer-supported catalysts is via a cyclopentadiene functionalized polymer:

$$1 \xrightarrow{ClCH_2OCH_3} 4 \xrightarrow{C_5H_5Na} 5 \xrightarrow{ML_n} 6$$

The chloromethylation reaction can be catalysed by either $SnCl_4$ [11] or BF_3 [8], and we have prepared polymers with varying amounts of CH_2Cl and

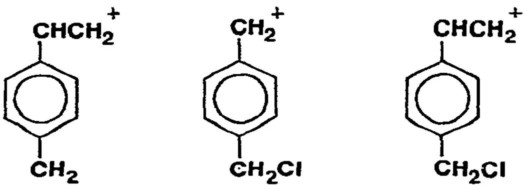
$CH_2C_5H_5$ groups by these routes. As Cl has two isotopes [13], ^{35}Cl (75.53%) and ^{37}Cl (24.47%) fragments containing Cl can readily be detected in the mass spectrometer [14]. For instance, fragments **23** and **24** (Fig. 8) can readily be observed in the mass spectrum of **4**, even when the degree of ring substitution <5%. It has further been observed that the ratio of the fragments corresponding to **7** and **22**, i.e. I_{117}/I_{104}, gives an accurate measure of the degree of CH_2Cl ring-functionalization. These data, together with a comparison of ring-substitution data obtained from IR spectroscopy will be reported in a forthcoming publication.

Reaction of **4** with C_5H_5Na to give **5** [12] was carried out under nitrogen. Subsequent washings, to remove excess reactants, were also carried out in an inert atmosphere with dry, degassed solvents. Mass spectra (300—450°C) recorded on **5** showed no fragments containing the $CH_2C_5H_5$ group, but variation in the intensity of fragment ratios relative to the mass spectrum of polystyrene could readily be detected. At lower temperatures (~60°C) fragments corresponding to $C_5H_5^+$, $C_5H_6^+$, $C_5H_7^+$ could be observed. No quantitative measure of the ring substitution has as yet been obtained using these data.

Metallation reactions

(a) Reaction of **3** *with* $RuCl_2(PPh_3)_3$. Attachment of $RuCl_2(PPh_3)_3$ to **3** to give **25** and subsequently **26** (Fig. 9) has been achieved and the use of **26** as a catalyst for olefin hydrogenation reactions will be reported in due course [6]. As a result of low volatility, $RuCl_2(PPh_3)_3$ does not generate a mass spectrum which is useful for product characterization. However, it was hoped that the mass spectrum of **25** or **26** would generate polymer fragments which would be different from those obtained from the non-metallated reagent **3**. It was found that in general, only minor differences in peak intensities were observed. Of significance, however, was the appearance of a fragment at $m/z = 304$ corresponding to a phosphine oxide fragment. The intensity of this fragment was found to be variable and, in a number of samples, of considerable size. Subsequent IR spectra of the metallated polymers also indicated the presence of phosphine oxide ($\nu(P{=}O) \sim 1180$ cm^{-1}) in these polymers. This phenomenon of phosphine oxide formation (possibly catalysed by transition metals) from phosphine attached to polymer supports has been commented on previously [15].

(b) Reaction of **5** *with* $Fe(CO)_5$ *and* $Fe_2(CO)_9$. Attachment of η^5-C_5H_5Fe-



(22) (23) (24)

Fig. 8. Fragments observed in the mass spectrum of **4**.

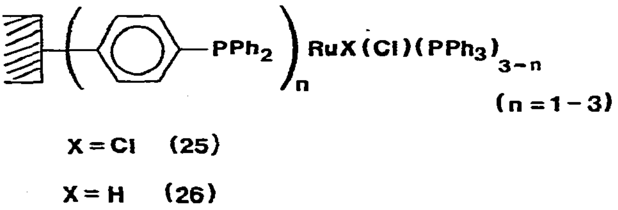


Fig. 9. Polymer-supported ruthenium complexes.

$(CO)_2H$ [16] and $[\eta^5\text{-}C_5H_5Fe(CO)_2]_2$ to the polymer support has been achieved using 5 and $Fe(CO)_5$ or $Fe_2(CO)_9$ [6]. We chose to investigate these polymer supported transition metals by mass spectrometry as (a) $[\eta^5\text{-}C_5H_5Fe(CO)_2]_2$ has been shown to be a catalyst for the synthesis of organometallic complexes [17] and (b) fragments containing iron should be observed in the mass spectrum [18]. The mass spectrum of the polymer-supported iron carbonyls was recorded over the range 50—370°C. No iron-containing fragments were observed.

We believe that in principle this technique should be applicable to a study of transition metal-supported reagents. However, a judicious choice of organometallic complex and polymer support will be required if low mass fragments containing transition metals are to be observed in the mass spectrum.

Conclusion

The use of mass spectrometry as an analytical tool in the area of polymer support chemistry has been indicated. The technique reveals that a quantitative measure of ring functionalization can be obtained, even for polymers which have been minimally functionalized. The method has the advantage that unwashed samples can be analysed and consequently the course of the reaction can be followed by mass spectral analysis.

Attempts to extend this technique to a study of polymer-supported transition metals have so far met with little success. However, the importance of the problem, the accurate determination of the composition of polymer-supported catalysts, suggests that an investigation of alternate supports which would be amenable to a mass spectral investigation is necessary.

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