Inorg. Chem. **1998,** *37,* 6288−6294

$[MP_y]^+$ and $[M_xP_y]^-$ Clusters Generated by Laser Ablation and Investigated by Fourier Transform Ion Cyclotron Resonance Mass Spectrometry

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Received June 19, 1998

Laser (1064 nm) ablation of pressed mixtures of red phosphorus with powders of the metals cobalt or nickel generates positive ions $[MP_y]^+$ ($y = 2,4,6,8$) and negative ions $[M_xP_y]^-$, monitored by Fourier transform ion cyclotron resonance (FTICR) mass spectrometry. At least 110 negative ions have been identified, more for Co than for Ni. The ions $[M_xP_y]^-$ are distributed through the range $2 \leq x \leq 16$, $4 \leq y \leq 17$, with $[Co_xP_8]^-$ ($x = 2$, 3, 4, 5), $[Co_xP_{10}]^-$ ($x = 5$, 6, 7), $[Ni_xP_6]^-$ ($x = 4$, 5, 7, 8), and $[Ni_xP_8]^-$ ($x = 2$, 3, 4, 6, 7) as more abundant ions. The best negative ion spectra are obtained with 10:1 M/P mixtures, and high laser powers. The preponderance of even numbers of P atoms suggests that P_2 units are bound to the metals, and this is supported by the collisional dissociation of $[MP_y]^+$ ions (M = Co and Ni, $y = 2$, 4, 6) where loss of P_2 is the major pathway. For both $[CoP_8]^+$ and $[NiP_8]^+$ initial loss of P_4 is important. The reactions of $[MP_2]^+$, $[MP_4]^+$ and $[MP_8]^+$ with σ-ligands ammonia and methanol, and π-ligands C_2H_2, C_2H_4 and C_6H_6, involve addition and substitution processes.

Introduction

Chemistry in the gas phase is fundamental and provides information about intrinsic structure and reactivity. In the more familiar solution phase, reactivity is moderated by substantial solvation energies. In crystals, from which most definitive structural data are obtained, the structures of inorganic compounds may be different (for example, ligand bridging can cause nonmolecular structure) or modified by the supramolecular energies of peripheral ligands.[1,2] Gas-phase data provide a reference point for supramolecular chemistry, and for the rational development of vapor deposition technologies. Accordingly, we have a program of research on gas-phase inorganic chemistry, encompassing binary metal chalcogenides M_xE_y,[3−17] metallofullerenes,[18−20] metal cyanides,[21,22] and metal thiolates.[23−26]

While there is a plethora of metal−phosphide, metal−polyphosphide, and metal−organophosphide chemistry in crystal and solution phases, very little research in the gas phase has been undertaken. Most investigations have involved elemental phosphorus[27−31] or metal phosphide clusters[32] such as the indium

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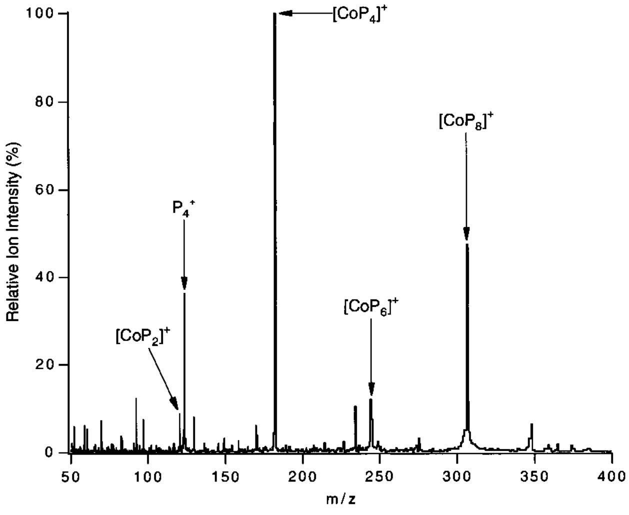

Figure 1. Positive ion spectrum of a 1:1 (w/w) mixture of cobalt metal and red phosphorus ablated with a laser power of 600 MWcm^{-2}.

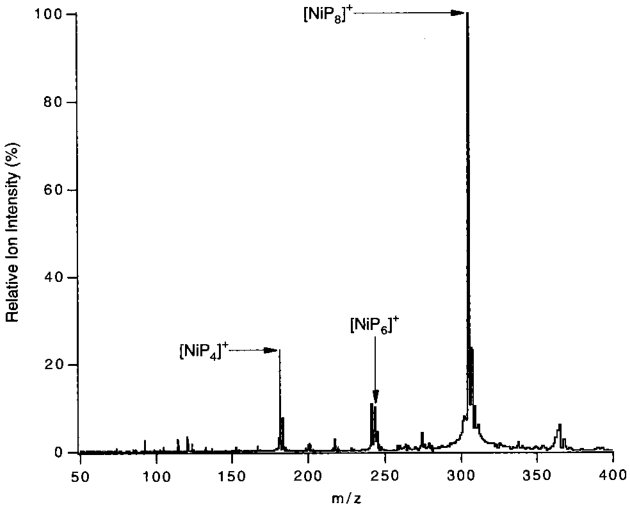

Figure 2. Mass spectrum of $[NiP_y]^+$ ions obtained after ablation of a 1:1 (w/w) mixture of Ni and red phosphorus with a laser power of 280 kWcm^{-2}.

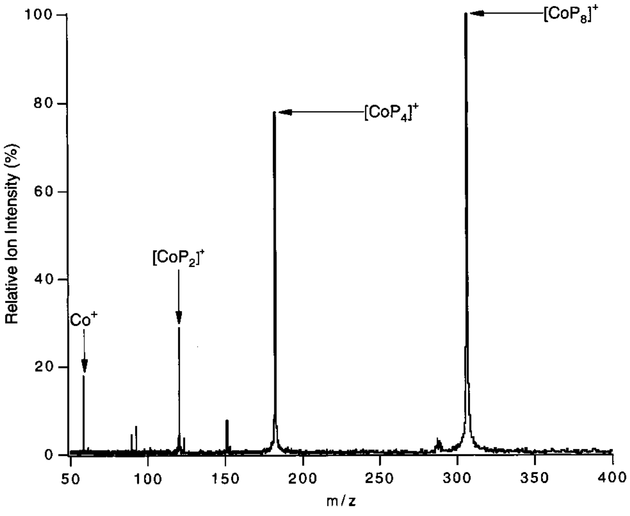

Figure 3. Collision-induced dissociation of $[CoP_8]^+$ (25 eV) showing $[CoP_4]^+$, $[CoP_2]^+$ and Co^+ as major product ions.

phosphides.[33,34] There have been three studies of metal ions reacting with organophosphines.[35−37]

In contrast, the range and diversity of inorganic metal-phosphorus and polyphosphide compounds is impressive.[38−40] P_2 units may bridge two metals.[41,42] A triangular P_3 unit has been observed coordinated to $Cp(CO)_2Cr$.[41] P_4 species have been observed with a distorted tetrahedral geometry coordinated by up to four metals,[43,44] or as a square coordinated by four or five metals.[45,46] P_5 systems are often cyclic and planar[41,47−49] but ring opening and ring distortion have been observed.[50] The P_6 ligand may be planar,[51] bicyclic,[52] distorted trigonal prismatic,[53] or part cubic.[54] P_7 normally forms a nortricyclane cage structure in alkali metal salts,[55] organometal complexes[53,56] and $(Ph_3M)_3P_7$ compounds where M = Si, Ge, Sn.[57] P_8 has been observed as a cuneane structure which is a subunit of Hittorf's monoclinic phosphorus allotrope, bonded to four, five, or six metals.[44,58] P_{10} as a ligand has been observed to be a cage structure with three homocyclic P_5 rings and one phosphorus atom appended to one of the rings.[59,60] P_{14} as a ligand is essentially two P_7 units linked with a norbornane-like structure.[53]

Alkali metal polyphosphides are numerous and ions such as P_{11}^{3-}, P_{16}^{2-}, P_{21}^{3-}, and P_{26}^{4-} have all been characterized. They have strands of phosphorus atoms similar to the proposed structure of red phosphorus.[61] There are also many polyphosphorus hydrides (polyphosphanes) and organic polyphosphides which have been reviewed by Baudler.[62,63]

Thus, stimulated by the marvellous condensed-phase chemistry, and cognizant of the limited scope of investigations of comparable gas-phase chemistry, we use various methods for

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Table 1. Products of Dissociation of $[CoP_y]^+$ and $[NiP_y]^+$ Induced by Collision with Argon

parent ion	major daughter ions	minor daughter ions
$[CoP_2]^+$	Co^+	$[CoP]^+$
$[CoP_4]^+$	$[CoP_2]^+$ Co^+	$[CoP]^+$ P_4^+
$[CoP_6]^+$	$[CoP_4]^+$ $[CoP_2]^+$ Co^+	$[CoP]^+$
$[CoP_8]^+$	$[CoP_4]^+$ $[CoP_2]^+$ Co^+	$[CoP_3]^+$ $[CoP]^+$ P_3^+
$[NiP_2]^+$	Ni^+	$[NiP]^+$ P_3^+
$[NiP_4]^+$	$[NiP_2]^+$ Ni^+	$[NiP_3]^+$ $[NiP]^+$ P_4^+ P_3^+
$[NiP_6]^+$	$[NiP_2]^+$ Ni^+ P_4^+	$[NiP_3]^+$ $[NiP]^+$
$[NiP_8]^+$	$[NiP_4]^+$ Ni^+	$[NiP_2]^+$

generation of metal−phosphorus compounds in the gas phase. The new species are trapped in a Fourier transform ion cyclotron resonance mass spectrometer, where their compositions, reactions, and dissociations can be readily investigated.[11] In this paper we report on our experimental research with cobalt and nickel phosphide ions produced by laser ablation of mixtures of the metals with red phosphorus. Supporting density functional calculations of the structures and reaction mechanisms for the new species are reported separately.[64] We have described the reactions of copper sulfide anions with gaseous P_4[16] and with phosphines.[13] Our recent studies of bare transition-metal ions with P_4 and PH_3 are soon to be reported.[64] The reaction of small carbon anions with P_4 has yielded addition products with one or two phosphorus atoms and even unprecedented carbon polyphosphide anions.[65,66]

Experimental Section

The Spectrospin CMS-47 Fourier transform mass spectrometer, with 4.7 T magnet and cylindrical cell used in this study has been described previously.[12,36] Samples were prepared by intimately mixing the powdered transition metal (Co, Ni) with powdered red phosphorus under anaerobic conditions, followed by compression in a (KBr) disk press. These disks were then powdered and pressed into the probe tip, which was introduced into the ICR cell and located flush with the trapping plate. The compositions of the samples ranged from 10:1 to 1:1 M/P. Mixtures more concentrated in phosphorus could not be investigated because the high vapor pressure of red phosphorus is not compatible with the low-pressure detection requirements of the FTICR mass spectrometer. The reactivity of the solid samples was revealed by the detection of $[P_xO_y]^-$ ions which were more abundant if the samples were not well-protected from the atmosphere during preparation. The purity of reactant gases was checked by electron impact mass spectrometry.

The 1064 nm fundamental of a Nd:YAG laser (Spectra Physics, DCR) was focused through the ICR cell to an area approximately 0.1 mm diameter on the sample surface. The laser was operated in long pulse and Q-switched modes, and the laser irradiances were varied (using netrual density filters) in the range of 20−280 kW cm^{-2} for a 230 μs long pulse, and the range 100−6000 MW cm^{-2} for an 8 ns Q-switch pulse. A single pulse of the laser was usually sufficient to generate enough ions for detection.

Pulse programs for the observation of ions, the collision-induced dissociation of ions and the reaction of ions have been previously given.[12]

For measurement of the reactions of the ions the (uncorrected) pressure of the reactant gases in the ICR cell chamber was typically 1×10^{-5} Pa. After the laser generation of ions and their equilibration through collisions in the presence of the reactant gas, all ions except the target ion to be investigated were removed from the cell with double resonance ejection pulses. The subsequent reactions were monitored after delays in the range from 1 ms to 60 s.

Table 2. Patterns of Four Reaction Types for $[MP_y]^+$ Clusters with Representative Reactants, Listed in the Order NH_3, CH_3Oh, C_2H_2, C_2H_4, C_6H_6: A Void Means No Reaction

ion	complete substitution (eq 2)	partial substitution (eq 3)	addition (eq 4)	collisional dissociation (eq 5)
$[CoP_2]^+$	NH_3		NH_3	
	C_2H_2			
	C_2H_4			
	C_6H_6			
$[NiP_2]^+$	NH_3			
			CH_3OH	
	C_2H_2			
	C_2H_4			
	C_6H_6			
$[CoP_4]^+$	NH_3	NH_3		
			CH_3OH	
	C_2H_2		C_2H_2	
			C_2H_4	
	C_6H_6			
$[NiP_4]^+$	NH_3	NH_3		
			CH_3OH	
				C_2H_2
			C_2H_4	
	C_6H_6			
$[CoP_8]^+$	NH_3	NH_3		
		CH_3OH		
				C_2H_2
		C_2H_4		
				C_6H_6
$[NiP_8]^+$	NH_3	NH_3		
		CH_3OH	CH_3OH	
				C_2H_2
				C_6H_6

Collisionally induced dissociation (CID) experiments were performed with the positive ions: the lower intensities and broader manifolds of the negative ions precluded CID (except for a few of the most abundant ions) and ion−molecule experiments. The CID was performed with argon at 1×10^{-5} Pa. as the collision gas. Ions of interest were selected and unwanted ions ejected using a chirp pulse (this process was carried out twice) followed by an acceleration pulse and variable delays ranging from 0.01 to 0.05 s to allow one or two collisions. The energies of the ions have been calculated and some values reported as center-of-mass energies.[67]

Results and Discussion

Laser Ablation and Gas-Phase Synthetic Processes. Mixtures of metal powders (M = Co, Ni) and red phosphorus provide convenient sources of high-energy atoms, molecules and ions (of M and P) in the plasma generated by laser ablation. There are no metal phosphorus-bonded species in the initially ablated sample, and so an associative synthesis occurs in the gas phase. A secondary observation is the generation of very different distributions of positive and negative ions, this also demonstrates that the products are formed by associative rather than desorptive processes.

There were some variations in the abundances of the ions generated, because the laser pulse generates very high temperatures (thousands of degrees) at the surface of the sample and etches a hole in the samples. In the spectra monitoring negative ions, and moreso for Ni, the ion yields decreased with the number of laser shots and depth of the hole etched in the sample. This effect, observed by others,[68] is most likely due to

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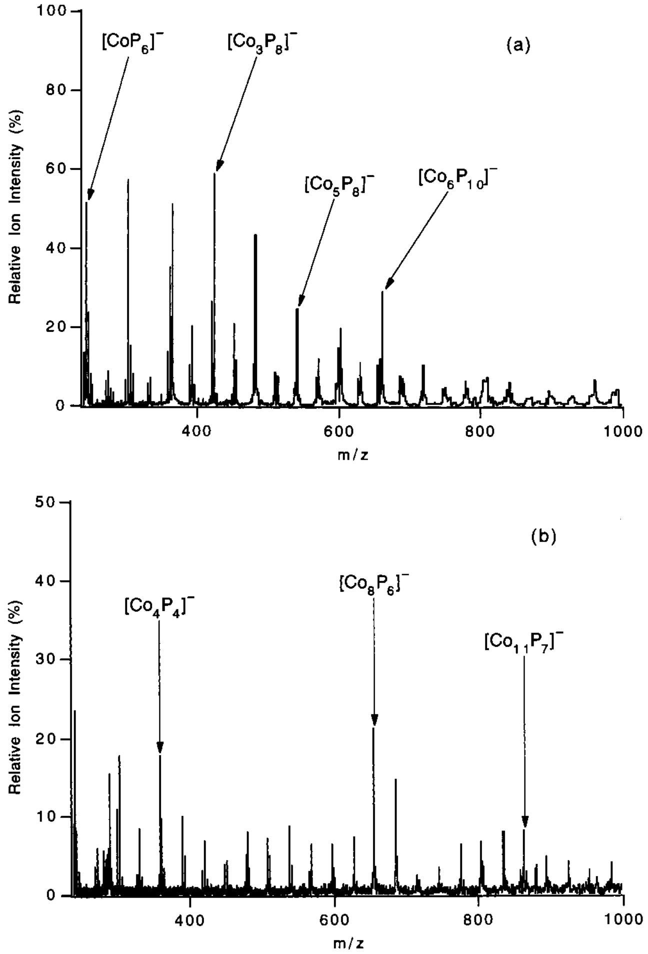
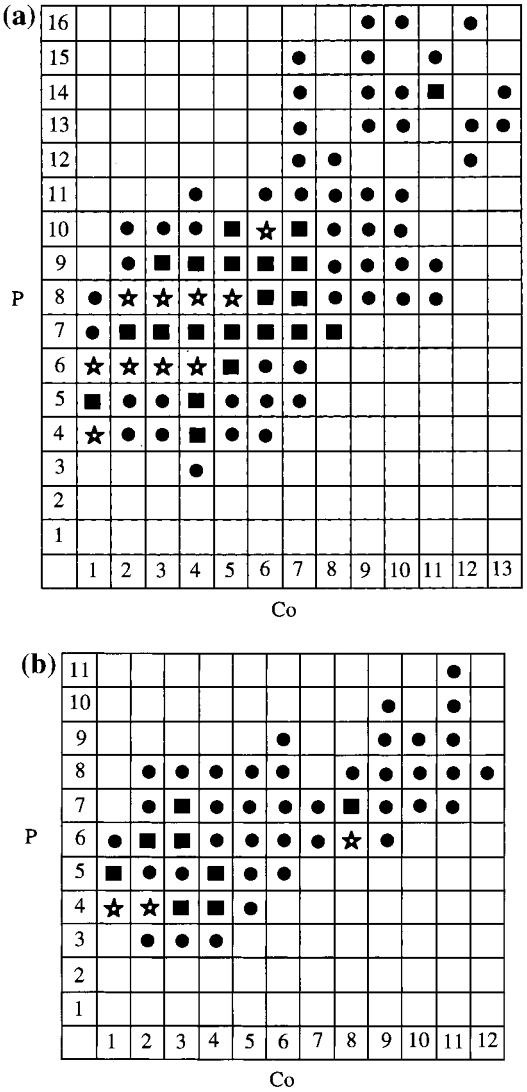


Figure 4. Negative ion spectra of mixtures of cobalt and red phosphorus: (a) A 1:1 (w/w) mixture irradiated at a laser power of 1400 MW cm^{-2}. (b) A 2:1 (w/w) mixture irradiated at a laser power of 1900 MW cm^{-2}. Note the relative ion intensities in (a) and (b) are related to the base peak $[CoP_4]^-$.



(a)

P

16									●	●		●	
15							●		●		●		
14							●		●	●	■		●
13							●		●	●		●	●
12							●	●				●	
11				●		●	●	●	●	●			
10		●	●	●	■	☆	■	●	●	●			
9		●	■	■	■	■	■	●	●	●	●		
8	●	☆	☆	☆	☆	■	■	●	●	●	●		
7	●	■	■	■	■	■	■	■					
6	☆	☆	☆	☆	■	●	●						
5	■	●	●	■	●	●	●						
4	☆	●	●	■	●	●							
3				●									
2													
1													
	1	2	3	4	5	6	7	8	9	10	11	12	13

Co

(b)

P

11											●	
10									●		●	
9						●			●	●	●	
8		●	●	●	●	●		●	●	●	●	●
7		●	■	●	●	●	●	■	●	●	●	
6	●	■	■	●	●	●	●	☆	●			
5	■	●	●	■	●	●						
4	☆	☆	■	■	●							
3		●	●	●								
2												
1												
	1	2	3	4	5	6	7	8	9	10	11	12

Co

Figure 5. Maps of observed $[Co_xP_y]^-$ anions: ● <10%, ■ 10−20%, ☆ >20% relative intensity. (a) From a 1:1 (w/w) mixture of cobalt metal and red phosphorus at a laser power of 1400 MW cm^{-2}. (b) From a 2:1 (w/w) mixture of cobalt metal and red phosphorus at a laser power of 1900 MW cm^{-2}.

interference in the localized pressure conditions required for optimum formation of ions. Fluctuation of the intensities of the positive ions observed with Ni was often quite pronounced after only 10 laser shots, and caused some difficulties with the CID experiments. Defocused laser pulses reduced the diminution of ion yields with number of laser pulses, and allowed ion signals to be maintained for at least 20 laser pulses, sufficient for completion of the MS−MS experiments.

Associative Formation of $[MP_y]^+$. The positive ions $[MP_y]^+$ obtained from single laser pulses of samples Co+P and Ni+P are shown in Figures 1 and 2, respectively. In both spectra the most abundant ions contain an even number of phosphorus atoms, $y = 2, 4, 6, 8$. No positive ions containing more than one M atom were detected. The $[NiP_6]^+$ ion is always of lower intensity than either $[NiP_4]^+$ or $[NiP_8]^+$. In some spectra low-intensity $[NiP_{10}]^+$ was apparent. The ion populations produced were dependent upon the irradiance conditions and the M/P ratio, with differing conditions for the optimum formation of particular species. In general the larger ions such as $[MP_8]^+$ were favored at higher irradiances ($\geq$1400 MW cm^{-2}) and lower M/P ratios, and the smaller ions such as $[MP_2]^+$ predominated at lower irradiances ($\leq$600 MW cm^{-2}) and high M/P ratios. Positive ions were also observed when the laser was used in the long-pulse low-power mode as shown in Figure 2. In addition to the $[MP_y]^+$ clusters, elemental species such as M^+ and P_n^+ ($n = 1-5$) were detected. However, the odd numbers of P atoms in the P_n^+ clusters are not observed in the $[MP_y]^+$ clusters: for example, $[MP_3]^+$ is not detected while $[P_3]^+$ is often formed in abundance.

Therefore, to better understand the associative processes in the gas phase, the positive ions formed by laser ablation of red phosphorus were investigated. The ions P_n^+ ($n = 3, 4, 5, 6, 7, 10, 12$) were observed, with the distribution dependent on the laser power. At the lower power of 110 MW cm^{-2}, the ions with $n = 3, 4, 5, 7, 10$ were observed, but at 600 MW cm^{-2} the observed ions had $n = 3, 4, 6, 12$. P_4^+ was prominent at all laser powers.

In view of the contrasting distributions of y in $[MP_y]^+$ and n in P_n^+ we conclude that that processes which lead to $[MP_y]^+$ are not the same as the clustering processes which generate P_n^+. In separate experiments we have shown that Co^+ and Ni^+ react with P_4 vapor produced from white phosphorus to produce the ions $[MP_2]^+$, $[MP_4]^+$, and $[MP_8]^+$, and so it is likely that the $[MP_y]^+$ ions arise from the reactions of M^+ ions with neutral P_4 molecules in the plume.

Dissociation of $[MP_y]^+$. Collisionally induced dissociation of all $[MP_y]^+$ ions ($y = 2, 4, 6, 8$) was examined, using argon at 1×10^{-5} Pa, excitation pulses typically 20−40 μs, and

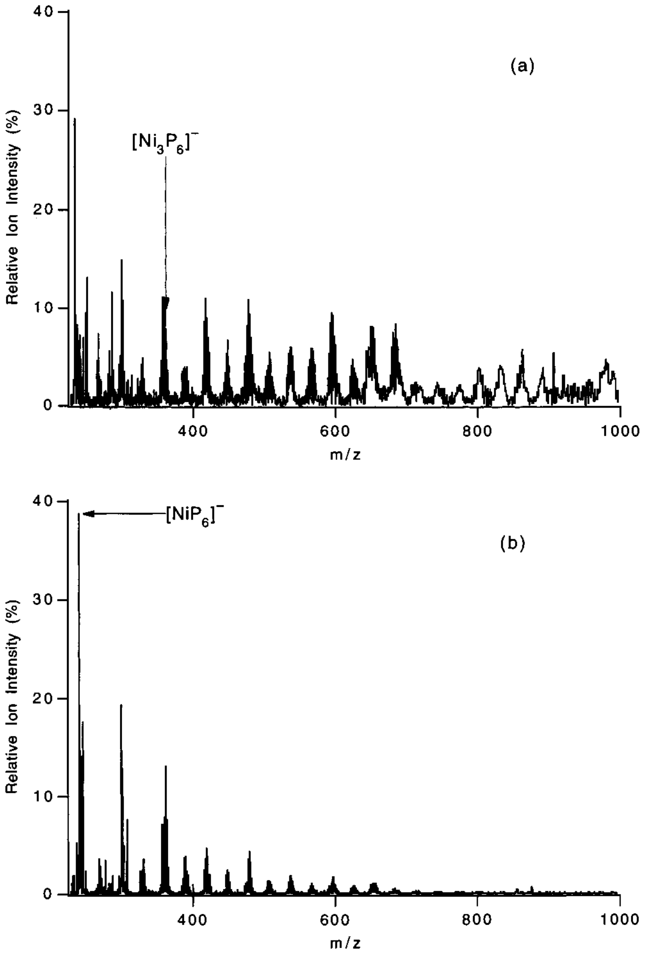


Figure 6. Negative ion spectra of mixtures of nickel metal and red phosphorus. (a) From a 10:1 mixture irradiated at a laser power of 1400 MW cm^{-2}. (b) From a 2:1 mixture irradiated at a laser power of 3600 MW cm^{-2}. Note that the relative ion intensities in (a) and (b) are related to the base peak [NiP$_4$]$^-$.

collision periods ranging from 0.01 to 0.05 s to allow single or few collisions. Major and minor dissociation products were identified. A representative CID spectrum, for [CoP$_8$]$^+$, is shown in Figure 3. The initial dissociation products of [CoP$_8$]$^+$ after a collision time allowing one collision were [CoP$_4$]$^+$, [CoP$_2$]$^+$, and Co$^+$. Dissociation experiments of [CoP$_8$]$^+$ using center-of-mass energies in the range 14−56 eV gave similar products to those shown in Figure 3. With increased collision times other products such as [CoP$_3$]$^+$ and [CoP]$^+$ were observed. Table 1 presents the products from CID experiments with all of the [MP$_y$]$^+$ clusters.

Loss of a P$_2$ unit is a common process, and loss of P$_4$ occurs for [MP$_4$]$^+$, [MP$_6$]$^+$, and [MP$_8$]$^+$. Significantly, [MP$_6$]$^+$ is not a product of dissociation of [MP$_8$]$^+$. The results in Table 1 suggest that the structures of [MP$_y$]$^+$ where $y = 2$, 4, and 6 consist of a metal with P$_2$ coordinated ligands, and that [MP$_8$]$^+$ could be either [M(P$_4$)$_2$]$^+$ or [M(P$_4$)(P$_2$)$_2$]$^+$ with P$_2$ bound more tightly than P$_4$.

Odd-y ions, [MP]$^+$ and [MP$_3$]$^+$, are generated by dissociation but not by association. For instance [NiP$_3$]$^+$ is formed when [NiP$_4$]$^+$ collides with argon, but not in the plume where Ni$^+$ and P$_3$$^+$ are known to be present. There is insufficient information to know whether [NiP$_3$]$^+$ could be formed from Ni$^+$ and P$_3$.

Reactions of [MP$_y$]$^+$. The reactants chosen for investigation of reactions were methane, acetylene, benzene, ammonia, methanol, dimethylaniline, diethylaniline, and fluorobenzene, spanning a range of ligand or charge-transfer properties. The ions [MP$_y$]$^+$ ($y = 2$, 4, 8; M = Co, Ni) had sufficient intensity to allow reactions with them to be investigated, but insufficient ion intensity did not allow the study of [MP$_6$]$^+$. With reactant pressures of ca. 1×10^{-5} Pa in the ion trap, the reactions were monitored typically for up to 10 s, and in some cases up to 60 s.

Five types of reactions with reactant L were observed, namely charge transfer (eq 1), complete (eq 2) or partial (eq 3) substitution of the bound P atoms by L, addition of L (eq 4), and CID (eq 5). Some of the reagents undergo two or three types of reaction:

charge transfer from L

$$[\mathrm{MP}_y]^+ + \mathrm{L} \rightarrow [\mathrm{MP}_y] + \mathrm{L}^+ \qquad (1)$$

complete substitution of P$_y$

$$[\mathrm{MP}_y]^+ + \mathrm{L} \rightarrow [\mathrm{ML}]^+ + \mathrm{P}_y \qquad (2)$$

partial substitution of P$_y$

$$[\mathrm{MP}_y]^+ + \mathrm{L} \rightarrow [\mathrm{MP}_{y-x}\mathrm{L}]^+ + P_x \qquad (3)$$

addition of L

$$[\mathrm{MP}_y]^+ + \mathrm{L} \rightarrow [\mathrm{MP}_y\mathrm{L}]^+ \qquad (4)$$

collisional dissociation

$$[\mathrm{MP}_y]^+ + \mathrm{L} \rightarrow [\mathrm{MP}_{y-x}]^+ + \mathrm{P}_x + \mathrm{L} \qquad (5)$$

With methane, the [MP$_y$]$^+$ gave only dissociation products, similar to the CID with argon. With dimethylaniline, diethylaniline, and fluorobenzene, all of the [CoP$_y$]$^+$ ions undergo charge transfer. In the case of dimethyaniline the high-resolution mode was required to resolve the reagent and [CoP$_2$]$^+$ − both having a nominal mass of 121 amu. [CoP$_8$]$^+$ reacting with benzene gave some C$_6$H$_6$$^+$ by charge transfer. These charge-transfer results indicate that the [CoP$_y$]$^+$ species all have higher ionization energies than 9.2 eV, and that [CoP$_8$]$^+$ may have an ionization energy close to 9.2 eV.

The patterns of the other four reaction types according to the identities of [MP$_y$]$^+$ and L are presented in Table 2. In general the reactions of [MP$_2$]$^+$ are dominated by substitution processes, while the reactions of [MP$_4$]$^+$ involve addition as well as part and complete substitution: [CoP$_2$NH$_3$]$^+$ is a minor product of addition by [CoP$_2$]$^+$. The complete substitution of [MP$_2$]$^+$ or [MP$_4$]$^+$ by L = NH$_3$ or C$_6$H$_6$ generates the bis-ligand products [ML$_2$]$^+$.

The general observation that the [MP$_2$]$^+$ ions show less evidence of addition than do [MP$_4$]$^+$ is unexpected since [MP$_2$]$^+$ is expected to be more coordinatively incomplete.

The larger [MP$_8$]$^+$ ions are involved in partial substitution reactions or CID processes, while two NH$_3$ molecules can totally substitute the P$_8$ group. These results suggest that the [MP$_8$]$^+$ ions are composed of readily displaced groups such as P$_4$.

Density functional calculations of the structures and reactions of the [MP$_y$]$^+$ ions are to be reported in a separate paper.[64]

Negative Ions [M$_x$P$_y$]$^-$. Formation. In constrast with the positive ions, extensive ranges of anionic clusters [M$_x$P$_y$]$^-$ were observed after laser ablation of both cobalt and nickel phosphides. Sample mixtures of various ratios were investigated to optimize cluster formation, and the best results for the negative ions were often obtained with a 10:1 mix for Ni/P, with less dependence on the composition of the solid for cobalt. Ions

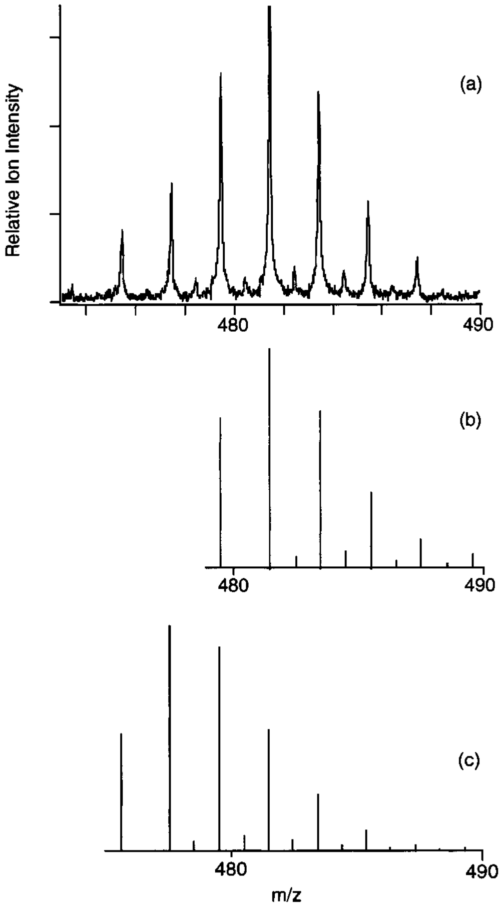


Figure 7. (a) High-resolution laser ablation (1400 MW cm^{-2}) mass spectrum of $[Ni_xP_y]^-$ ions in the mass range 474−489. (b) Calculated isotopomer pattern for $[Ni_5P_6]^-$. (c) Calculated isotopomer pattern for $[Ni_4P_8]^-$.

$[Co_xP_y]^-$ comprised a more extensive series of compositions x/y than the $[Ni_xP_y]^-$ ions. In contrast with the positive ions, many polymetal negative ions were observed, with x ranging up to 13 for Co and 9 for Ni. A typical mass spectrum derived from a Co+P mixture irradiated at a laser power density of 1400 MW cm^{-2} is presented in Figure 4. Below $m/z \sim 170$ the spectra are often populated by $[P_xO_y]^-$ ions, formed by adventitious exposure of the solid sample (see Experimental). Anaerobic preparation of the samples allowed detection of a more extensive collection of $[Co_xP_y]^-$ clusters. The $[Co_xP_y]^-$ ions observed are mapped in Figure 5. Assignments have been confirmed by high-resolution measurements (mass discrepancy <25 ppm). Many of these ions, particularly those of higher mass, were present in very low concentrations with some detected only with the high-resolution mode of the mass spectrometer. The single isotopes for Co and P simplified the task of peak identification, and there are no ambiguities in the assignment of ion compositions.

In general, $[Co_xP_y]^-$ clusters with x even are favored, and in particular the series $[Co_xP_6]^-$, $[Co_xP_8]^-$, and $[Co_xP_{10}]^-$ ($x \geq 5$) are present with greater intensity than neighboring compositions with odd numbers of P atoms. A greater range of $[Co_7P_y]^-$ species is produced relative to clusters with $x \leq 6$.

Figure 6 presents a typical distribution of $[Ni_xP_y]^-$ ions, obtained at an irradiance of 1400 MW cm^{-2}. $[P_xO_y]^-$ ions were again detected at low mass and were observed to cause even more pronounced inhibition of formation of $[Ni_xP_y]^-$ than of $[Co_xP_y]^-$. In contrast to the simplicity of the $[Co_xP_y]^-$ spectra, the $[Ni_xP_y]^-$ spectra are more complex because nickel has five naturally occurring isotopes. Further complexity in the spectra is observed at high mass, where it is apparent that several large clusters with similar masses contribute to the broad manifold of isotopomer peaks. Peaks were assigned to cluster ions by detailed examination of the isotopomer patterns as measured in the narrow band mode. For example, the distribution of peaks from m/z 475−488 shown in Figure 7 can be assigned as the overlap of the patterns of $[Ni_5P_6]^-$ and $[Ni_4P_8]^-$, with the latter slightly more abundant. The assignments of all $[Ni_xP_y]^-$ clusters were based on similar analyses of the narrow-band spectra, and the identified $[Ni_xP_y]^-$ ions are mapped in Figure 8.

	11									●	●
	10					●			●	●	
	9					●			●	●	
	8				●	●			●		
	7			●	●	●		●			
	6	☆	■	■	●	●	●				
P	5	■	●	●	●		●				
	4	☆		●			●	●	●		
	3			●				●	●		
	2						●	●	●		
	1										
		1	2	3	4	5	6	7	8	9	10

Ni

Figure 8. The ion map of all the $[Ni_xP_y]^-$ anions observed by laser ablation of nickel + phosphorus mixtures, ● <10%, ■ 10−20%, ☆ >20%.

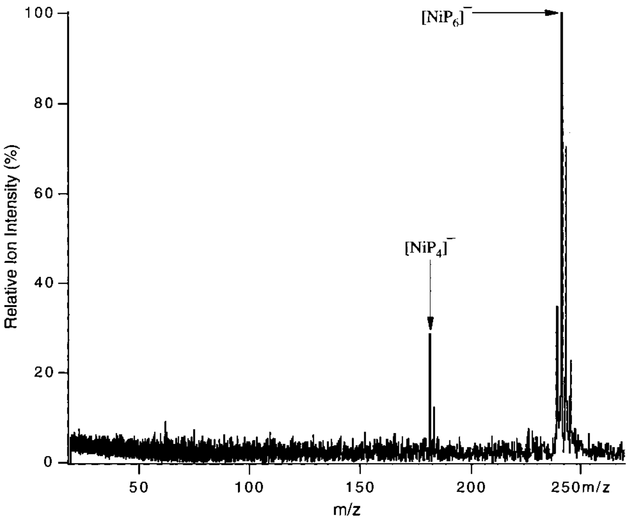


Figure 9. CID of $[NiP_6]^-$ (20.5 eV) showing $[NiP_4]^-$ as the only product ion.

We draw attention to several features of the distribution of $[M_xP_y]^-$ compositions in Figures 5 and 8:

(1) Most of the ions have $y \geq x$, including all of the more abundant ions except $[Co_6P_8]^-$.

(2) For each value of x there are many values of y. The breadth in y of the distribution for $[Co_xP_y]^-$ is in contrast to the narrower distribution of sulfide ions $[Co_xS_y]^-$,[10] while the distribution of $[Ni_xP_y]^-$ is more comparable with the distribution of $[Ni_xS_y]^-$.[4]

(3) All of the $[Ni_xP_y]^-$ compositions are observed also for $[Co_xP_y]^-$, except for an unusual group of six $[Ni_xP_y]^-$ ions $[Ni_6P_2]^-$, $[Ni_7P_2]^-$, $[Ni_7P_3]^-$, $[Ni_8P_2]^-$, $[Ni_8P_3]^-$, and $[Ni_8P_4]^-$ with $x \gg y$.

Collision-Induced Dissociation of $[M_xP_y]^-$ Ions. Some of the smaller $[M_xP_y]^-$ ions were successfully subjected to CID measurements. Figure 9 shows the CID of $[NiP_6]^-$ (center-of-mass energy 20 eV), and Figure 10 shows the CID of $[Co_2P_8]^-$ (center-of-mass energy 10 eV).

The CID results can be summarized as follows:

$$[CoP_4]^- \rightarrow [CoP_2]^-$$

$$[Co_2P_6]^- \rightarrow [Co_2P_4]^-, [CoP_4]^-$$

$$[Co_2P_8]^- \rightarrow [Co_2P_6]^-, [Co_2P_4]^-\ [CoP_4]^-$$

$$[Co_3P_8]^- \rightarrow [Co_3P_6]^- \rightarrow [Co_2P_4]^-$$

$$[NiP_4]^- \rightarrow [NiP_2]^-\ P_2^-$$

$$[NiP_6]^- \rightarrow [NiP_4]^-$$

The loss of P_2 is a common process for all the anions studied. The loss of a CoP_4 unit was also a process for two of the $[Co_xP_y]^-$ anions.

The P_2 loss from the anions is comparable with the dissociation of P_2 from the $[MP_y]^+$ cations, and supports structures containing P_2 ligands. Our investigations of the structures and structural principles for $[MP_y]^+$ and $[M_xP_y]^-$ by density functional methods[64] use this experimental information.

Summary and Conclusions

Monometallic cations $[MP_y]^+$ and polymetallic anions $[M_xP_y]^-$ are generated by association in the plume formed by laser ablation of a mixture of M and elemental P. More than 80 $[Co_xP_y]^-$ ions for $x \leq 13$ can be identified. There is a predominance of clusters with y even. The clusters are relatively easily dissociated by collision with inert gas, and again loss of P_{even} is the principal process, although some clusters with y odd can be generated by dissociation. The compositions of the ions formed by associative and dissociative processes strongly indicate that P_2 structural units exist in these clusters. This view is supported by the observation of $[Co_xP_y]^-$ clusters with $y \gg x$, in comparison with $[Co_xS_y]^-$ clusters where $y \approx x$,[10] with the hypothesis that P_2 in $[Co_xP_y]^-$ could be structurally equivalent to S in $[Co_xS_y]^-$. On exposure to σ-donor and π-donor molecules the $[MP_y]^+$ species undergo partial or complete substitution of the phosphide ligands, as well as addition: simple collisional dissociation also occurs with these reactants.

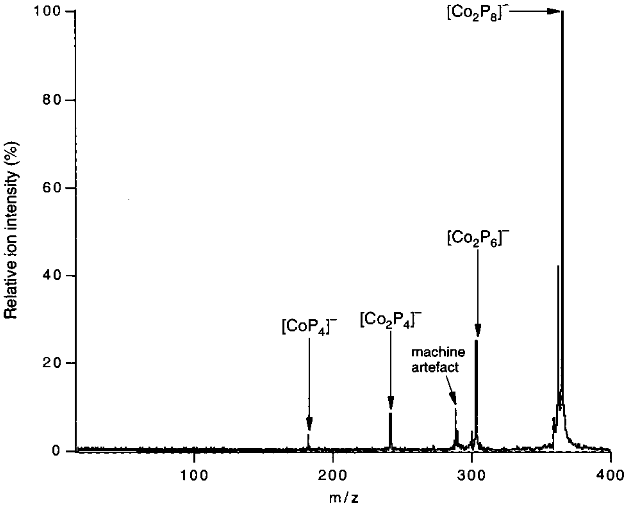


Figure 10. CID of $[Co_2P_8]^-$ (10 eV) showing $[Co_2P_6]^-$, $[Co_2P_4]^-$ and $[CoP_4]^-$ as the product ions.

The formation of few monometallic cations $[MP_y]^+$ and many polymetallic anions $[M_xP_y]^-$ is similar to the ranges of positive and negative ions obtained by laser ablation of metal sulfides.[2−5,10,11,13,15] The results for $[MP_y]^+$ are also comparable and consistent with the reactions of $M^+_{(g)}$ with $P_{4(g)}$[64] and with $S_{8(g)}$.[9,12,17] Although we have no definitive data, it is suggested that the wider range of anions $[M_xP_y]^-$ could be due to the favorability of electron attachment during the formation processes: this can be investigated with calculations of electron affinity, in progress.[64]

Acknowledgment. This research is supported by the Australian Research Council. K.J.F. acknowledges the award of a National Research Fellowship during this investigation.

IC980699Y