Mass Spectra of Organometallic Compounds. I. Metal Carbonyl Complexes of Tris(dimethylamino)phosphine[1]

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Abstract: The mass spectra of the compounds $[(CH_3)_2N]_3PM(CO)_5$ (M = Cr and Mo), $[(CH_3)_2N]_3PM(CO)_4P[N(CH_3)_2]_3$ (M = Cr, Mo, and W), $[(CH_3)_2N]_3PFe(CO)_4$, $[(CH_3)_2N]_3PFe(CO)_3P[N(CH_3)_2]_3$, and $C_5H_5V(CO)_3P[N(CH_3)_2]_3$ are reported. The cracking pattern and metastable ions of these spectra have been analyzed. Competing with the usual stepwise loss of metal carbonyl groups is the loss of a single dimethylamino group from the complexed $[(CH_3)_2N]_3P$ ligand. A measure of the relative tendencies for parent ions of these complexes to lose one carbonyl group and to lose one dimethylamino group is suggested as a novel qualitative and semiquantitative means for estimating the metal–carbonyl bond strength. Metastable ion evidence is presented for the simultaneous loss of two carbonyl groups in two cases. The carbonyl-free ions of the type $[(CH_3)_2N]_3PM^+$ are major ions in the mass spectra and break down further by elimination of an azapropene (CH_3NCH_2) fragment. Ions with metal–nitrogen bonds such as $(CH_3)_2NFe^+$ and $[(CH_3)_2N]_3PMN(CH_3)_2{}^+$ (M = Cr, Mo, W, and Fe) are also observed. In at least one case such ions appear to arise by elimination of PH_3 from an ion containing one more phosphorus atom.

Over the past few years numerous novel transition-metal organometallic compounds have been synthesized. These compounds, mostly metal carbonyl derivatives, often have novel structures with relatively unusual ligands including π-bonded olefins and acetylenes, σ-bonded hydrocarbon and fluorocarbon groups, tricovalent nitrogen, phosphorus, arsenic, and antimony ligands, organosulfur ligands, and various halogens. Furthermore, many such compounds contain metal–metal and metal–hydrogen bonds.

The availability of such an extensive series of transition-metal organometallic compounds and the recent improved availability of appropriate mass spectrometers make of interest a general study of the mass spectra of transition-metal organometallic compounds. At the outset of this work a few investigations of relatively simple metal carbonyl derivatives had been made,[4] particularly by Winters and Kiser. These studies clearly established the stepwise loss of carbonyl groups in the mass spectra of metal carbonyls.[5,6] Furthermore these initial studies suggested that in the mass spectra of metal carbonyl derivatives containing ligands other than carbonyl, loss of carbonyl ligands appears to occur in preference to loss of other ligands. Thus mass spectra of cyclopentadienylmetal carbonyl derivatives of the type $C_5H_5M(CO)_n$ contain $C_5H_5M^+$ ions in large abundance but negligible amounts of $M(CO)_n{}^+$ ions.[4d,e]

In an attempt to explore further the nature of mass spectra of the many available transition-metal organometallic compounds, the spectra of about 150 such compounds have been investigated using the Mellon Institute MS-9 mass spectrometer. In order to permit the investigation of a maximum number of compounds within the limited amount of time available on the spectrometer, the investigation of a given compound has been limited to one or more scans of the entire mass range at 70-ev electron energies. However, in almost all cases the mass number of each ion can be clearly established by simple counting. In almost all cases the chemistry of the compound studied and the characteristic isotope patterns of many of the metals in the compounds permit unequivocal assignment of a given ion once its mass number is known. In some particularly favorable cases, further information may be obtained by observation of metastable ions.[7] These indicate fragmentation patterns of the observed ions by the relationship $m^* = m_2{}^2/m_1$, where m^* is the mass of the metastable ion, m_1 is the mass of the parent ion, and m_2 is the mass of the daughter ion. In a few unusually favorable cases, enough metastable ions are observed to indicate the complete fragmentation processes in a given compound.

The present paper is the first of a series of papers discussing the results from this exploratory mass spectral study.[8] It discusses the mass spectra of metal carbonyl complexes of tris(dimethylamino)phosphine, a typical tricovalent phosphorus ligand capable of replacing carbonyl groups in metal carbonyls. Complexes of this particular tricovalent phosphorus ligand were selected not only because samples remained from a previous synthetic study[9] but also because the fairly

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(1) This work was presented in part at the 153rd National Meeting of the American Chemical Society, Miami Beach, Fla., April 1967, Paper L-156.

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(4) (a) R. E. Winters and R. W. Kiser, *Inorg. Chem.*, 3, 699 (1964); (b) *ibid.*, 4, 157 (1965); (c) A. Foffani, S. Pignataro, B. Cantone, and F. Grasso, *Z. Physik. Chem.* (Frankfurt), 45, 79 (1965); (d) R. E. Winters and R. W. Kiser, *J. Organometal. Chem.* (Amsterdam), 4, 190 (1965); (e) R. E. Winters and R. W. Kiser. *J. Phys. Chem.*, 69, 3198 (1965).

(5) Very recently a study by Schildcrout, Pressley, and Stafford[6] using a magnetic sector spectrometer capable of distinguishing the molecular beam (zero ion-source contact) mass spectrum from possible contributions of pyrolysis intermediates has confirmed the stepwise loss of carbonyl groups in tetracarbonylnickel by analysis of the metastable ions.

(6) S. M. Schildcrout, G. A. Pressley, Jr., and F. E. Stafford, *J. Am. Chem. Soc.*, 89, 1617 (1967).

(7) For a further discussion of metastable ions see H. Budzikiewicz, C. Djerassi, and D. H. Williams, "Interpretation of Mass Spectra of Organic Compounds," Holden-Day, Inc., San Francisco, Calif., 1964, p xiii, or R. I. Reed, "Applications of Mass Spectrometry to Organic Chemistry," Academic Press Inc., New York, N. Y., 1966, pp 30–33.

(8) Some of these mass spectral results dealing with polynuclear metal carbonyl derivatives were presented in the preliminary communication: R. B. King, *J. Am. Chem. Soc.*, 88, 2075 (1966).

(9) R. B. King, *Inorg. Chem.*, 2, 936 (1963).

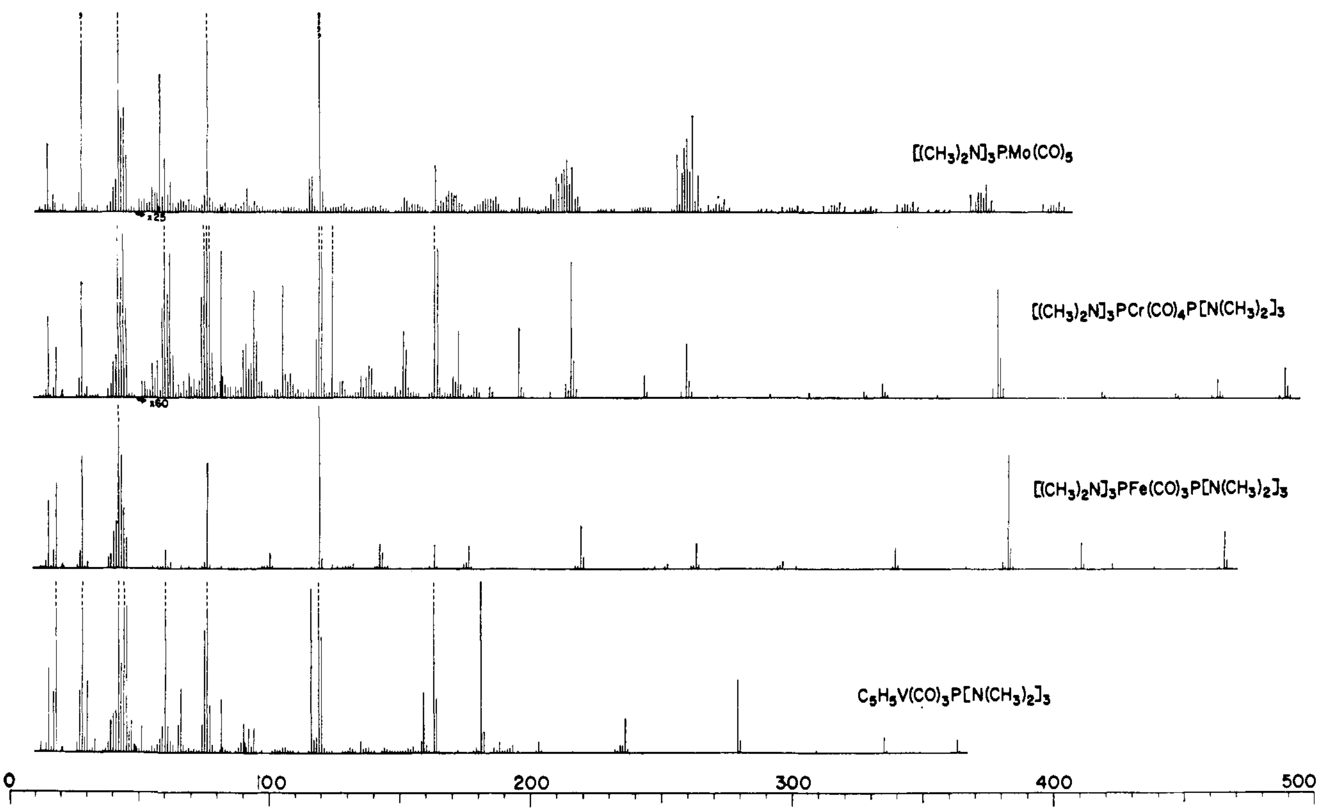

Figure 1. Mass spectra of four of the compounds discussed in this paper (peaks terminating with dotted lines are off-scale with the scale used in this drawing).

low molecular weight of the tris(dimethylamino)phosphine makes the complexes reasonably volatile, a requirement for successful mass spectroscopy. When this work was begun, no mass spectral studies of metal carbonyl complexes of tricovalent phosphorus ligands had been reported. However, after this work was complete a report by Braterman[10] appeared which also discusses certain metal carbonyl complexes of tris(dimethylamino)phosphine such as $[(CH_3)_2N]_3PFe(CO)_4$ and $[(CH_3)_2N]_3PFe(CO)_3P[N(CH_3)_2]_3$. A recent study by Lewis and coworkers[11] included some metal carbonyl derivatives of other tricovalent phosphorus ligands.

Experimental Section

The mass spectra were run on a standard MS-9 mass spectrometer located at the Mellon Institute. They are reported in Tables I–V, inclusive. In addition, Figure 1 depicts the mass spectra of four representative compounds. The operating conditions were a 70-ev electron energy, 200–230° inlet temperature,[12] resolution of 1000, and 8 kv accelerating voltage. Samples were introduced directly into the ion source using a metal probe. The standard galvanometer recorder was used to measure the output signal from the electron multiplier. The relative peak intensities were estimated by measurement of the heights of the peaks on the galvanometer recorder chart with a millimeter rule. Values relative to an arbitrary value of 100.0 for the strongest peak containing a metal atom (generally $[(CH_3)_2N]_3PM^+$) are reported in the tables.

Natural vanadium, chromium, and iron contain primarily or entirely the isotopes ^{51}V, ^{52}Cr, and ^{56}Fe, respectively. The *m/e* values reported for ions containing any of these three particular metals are for ions containing these three particular isotopes. Natural molybdenum and tungsten contain a mixture of isotopes forming characteristic patterns that are diagnostic of the presence of these metals in a given ion. The *m/e* values for ions containing molybdenum or tungsten are given in the tables just for the ions containing ^{96}Mo and ^{184}W, respectively,[13] although in all cases the characteristic multiline pattern containing the ions with the several isotopes of these metals was observed. The reported relative intensity data for the molybdenum and tungsten ions are based on the heights of the ions containing ^{98}Mo and ^{184}W, respectively.[13] In the mass spectra of the molybdenum and tungsten compounds the relative intensities of the ions containing the metals and of the ions not containing the metals are not directly comparable due to the many isotopes of the metals.

For transitions not involving ions of the multiisotopic metals molybdenum and tungsten, metastable ions were observed as much weaker and broader peaks often at nonintegral *m/e* values. These metastable ions provide excellent corroboratory evidence regarding suggested modes of fragmentation of certain of the observed ions.[7] Because of the weakness and breadth of the metastable ions, they were only unequivocally observed for transitions involving the strongest ions of the spectrum and for those involving only essentially monoisotopic elements.

Discussion

The stepwise loss of carbonyl groups from metal carbonyl ions previously[4] noted has now also been observed for the metal carbonyl complexes of tris(dimethylamino)phosphine. In the case of the iron carbonyl complex $[(CH_3)_2N]_3PFe(CO)_4$ (Table III),

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[10] P. S. Braterman, private communication, April 1967. See also P. Braterman, *J. Organometal. Chem.* (Amsterdam), 11, 198 (1968).

[11] J. Lewis, A. R. Manning, J. R. Miller, and J. M. Wilson, *J. Chem. Soc., Sect. A*, 1663 (1966).

[12] Because of the relatively high inlet temperature, it is necessary to consider the possibility of thermal decomposition of the compounds introduced into the mass spectrometer. This may account for the presence of ions obviously arising from the compounds $[(CH_3)_2N]_3PM(CO)_5$ in the mass spectra of the $[(CH_3)_2N]_3PM(CO)_4P[N(CH_3)_2]_3$ (M = Cr, Mo, and W) compounds and for the presence of the ion $(C_5H_5)_2V^+$ in the mass spectrum of $C_5H_5V(CO)_3P[N(CH_3)_2]_3$.

[13] Ions containing the isotopes ^{96}Mo and ^{184}W rather than other isotopes of these metals were arbitrarily selected as those reported in the tables because the values 96 and 184 most closely approximate the atomic weights of molybdenum and tungsten, respectively. Ions containing the isotopes ^{98}Mo and ^{184}W were selected for the relative intensity measurements because these are the most abundant isotopes of these metals.

Table I. Mass Spectra of $[(CH_3)_2N]_3PM(CO)_5$ Complexes

Ion	Relative intensities: M = Cr[a]	Relative intensities: M = Mo[b]
$[(CH_3)_2N]_3PM(CO)_5^+$	15	11
$[(CH_3)_2N]_3PM(CO)_4^+$	24	28
$[(CH_3)_2N]_2PM(CO)_5^+$	1.6	1.9
$[(CH_3)_2N]_3PM(CO)_3^+$	0.6	11
$[(CH_3)_2N]_2PM(CO)_4^+$	2.0	5.0
$[(CH_3)_2N]_3PM(CO)_2^+$	8.2	8.1
$[(CH_3)_2N]_2PM(CO)_3^+$	2.2	5.0
$[(CH_3)_2N]_3PMCO^+$	25	1.9
$[(CH_3)_2N]_2PM(CO)_2^+$	2.9	10
$[(CH_3)_2N]_3PM^+$	100	100
$[(CH_3)_2N]_2PMCO^+$	4.3	3.7
$[(CH_3)_2N]_2PHM^+$	58	<3
$(CH_3)_2NP(CH_2NCH_2)M^+$	<1	42
$PCH_2NCH_2M^+$	<1	16
$(CH_3)_2NMCH_2NCH_3^+$	1.6	~7
$(CH_3NCH_2)_2M^+$	0.9	~7
$CH_3NCH_2MCH_2NCH_2^+$	1.0	~3
$(CH_3)_2NM^+$	1.3	~5
$CH_3NCH_2M^+$	41	~4
M^+	23	<2
$[(CH_3)_2N]_3PO_2^+$ (?)	2.2	13
$[(CH_3)_2N]_3P^+$	39	44
$[(CH_3)_2N]_2P^+$	170	290
$[(CH_3)_2N]_3P^{2+}$	0.4	4.4
$(CH_3)_2NPH^+$	180	240
CH_3NP^+	36	51

Metastable transitions in the mass spectrum of $[(CH_3)_2N]_3PCr(CO)_5$

m/e	Process	Neutral fragment lost
301.7	$355 \xrightarrow{-28} 327$	CO
273.5	$355 \xrightarrow{-44} 311$	$(CH_3)_2N$
190.1	$243 \xrightarrow{-28} 215$	CO
137.7	$215 \xrightarrow{-43} 172$	CH_3NCH_2
86.8	$163 \xrightarrow{-44} 119$	$(CH_3)_2N$
48.5	$119 \xrightarrow{-43} 76$	CH_3NCH_2

[a] Source pressure = 2.7×10^{-6} mm. [b] Source pressure = 1.8×10^{-6} mm.

the stepwise loss of the four carbonyl groups is further supported by observation of metastable transitions at *m/e* 277, 249.3, 222, and 194.3 corresponding to each of the four successive steps in going from the parent ion $[(CH_3)_2N]_3PFe(CO)_4^+$ to the carbonyl-free ion $[(CH_3)_2N]_3PFe^+$.

Two examples were also noted of the loss of two carbonyl groups from a metal carbonyl ion in one step.[14] Thus the metastable ion at *m/e* 233 in the mass spectrum of $C_5H_5V(CO)_3P[N(CH_3)_2]_3$ (Table V) can only correspond to the following process.

$$\underset{m/e\ 335}{C_5H_5V(CO)_2P[N(CH_3)_2]_3^+} \longrightarrow \underset{m/e\ 279}{C_5H_5VP[N(CH_3)_2]_3^+} + 2CO$$

Also in the mass spectrum of this vanadium complex, no detectable concentration of the monocarbonyl ion $C_5H_5V(CO)P[N(CH_3)_2]_3^+$ was observed. Thus the one carbonyl group in $C_5H_5V(CO)P[N(CH_3)_2]_3^+$ is lost at least as easily as one of the two carbonyl groups in $C_5H_5V(CO)_2P[N(CH_3)_2]_3^+$.

The mass spectrum of $[(CH_3)_2N]_3PFe(CO)_3P[N(CH_3)_2]_3$ provides another example of the loss of the two carbonyl groups from a metal carbonyl ion in one step. The metastable ion at *m/e* 361 in the mass spectrum of this compound (Table IV) corresponds to the following process.

Table II. Mass Spectra of $[(CH_3)_2N]_3PM(CO)_4P[N(CH_3)_2]_3$Complexes

Ion	Relative intensities: M = Cr[a]	Relative intensities: M = Mo[b]	Relative intensities: M = W[c]
$[(CH_3)_2N]_3PM(CO)_4P[N(CH_3)_2]_3^+$	28	6.8	130
$[(CH_3)_2N]_3PM(CO)_3P[N(CH_3)_2]_3^+$	16	3.6	9.2
$[(CH_3)_2N]_2PM(CO)_4P[N(CH_3)_2]_3^+$	2.9	1.0	160
$[(CH_3)_2N]_3PM(CO)_2P[N(CH_3)_2]_3^+$	<0.3	0.4	4.3
$[(CH_3)_2N]_2PM(CO)_3P[N(CH_3)_2]_3^+$	3.9	2.1	30
$[(CH_3)_2N]_3PMCOP[N(CH_3)_2]_3^+$	<0.2	2.6	6.5
$[(CH_3)_2N]_2PM(CO)_2P[N(CH_3)_2]_3^+$	<0.2	1.6	4.3
$[(CH_3)_2N]_3PMP[N(CH_3)_2]_3^+$	120	17	100
$[(CH_3)_2N]_3PM(CO)_5^+$	1.6	8.6	6.5
$[(CH_3)_2N]_2PMP[N(CH_3)_2]_3^+$	12	7.6	53
$[(CH_3)_2N]_3PM(CO)_4^+$	3.9	19	5.4
$[(CH_3)_2N]_2PMPH[N(CH_3)_2]_2^+$	2.6	<1	
$[(CH_3)_2N]_2PMP[N(CH_3)_2]_2^+$	<1	2.6	17
$[(CH_3)_2N]_2PM(CO)_5^+$	<0.5	~1	4.3
$[(CH_3)_2N]_3PM(CO)_3^+$	<0.5	7.6	4.3
$[(CH_3)_2N]_2PM(CO)_4^+$	<0.5	3.4	3.3
$[(CH_3)_2N]_3PM(CO)_2^+$	2.3	7.4	3.3
$[(CH_3)_2N]_4PM^+$	39	6.0	49
$[(CH_3)_2N]_2PMPN(CH_3)_2^+$	<0.7	~1	9.8
$[(CH_3)_2N]_2PM(CO)_3^+$	<0.7	~1	<2
$[(CH_3)_2N]_3PMCO^+$	14	~2	11
$[(CH_3)_2N]_2PM(CO)_2^+$	<0.7	8.0	5.4
$[(CH_3)_2N]_3PM^+$	100	100	100
$[(CH_3)_2N]_2PHM^+$	50	<1	<2
$[(CH_3)_2N]_2PMNHCH_3^+$	<0.7	~3	12
$(CH_3)_2NPCH_2NCH_2M^+$	<3	~70	74
$[(CH_3)_2N]_3PO_2^+$ (?)	53	750	9
$[(CH_3)_2N]_3P^+$	1500	1300	1330
$[(CH_3)_2N]_2P^+$	5100	5500	2900
$(CH_3)_2NPH^+$	6300	5000	2900
CH_3NP^+	1100	1200	810
$[(CH_3)_2N]_3P^{2+}$	110	77	110

[a] Source pressure = 2.3×10^{-6} mm. [b] Source pressure = 5.0×10^{-7} mm. [c] Source pressure = 1.6×10^{-6} mm.

$$\underset{m/e\ 466}{[(CH_3)_2N]_3PFe(CO)_3P[N(CH_3)_2]_3^+} \longrightarrow \underset{m/e\ 410}{[(CH_3)_2N]_3PFe(CO)P[N(CH_3)_2]_3^+} + 2CO$$

In this case the intermediate dicarbonyl ion $[(CH_3)_2N]_3PFe(CO)_2P[N(CH_3)_2]_3^+$ (*m/e* 438) is also observed as well as a metastable ion at *m/e* 412 corresponding to the formation of the dicarbonyl ion from the tricarbonyl ion. The relatively low concentration of the dicarbonyl ion supports further the tendency for the tricarbonyl ion to lose two carbonyl groups in one step forming the monocarbonyl ion and bypassing the dicarbonyl ion. Thus two competing modes of fragmentation of the ion $[(CH_3)_2N]_3PFe(CO)_3P[N(CH_3)_2]_3^+$ are loss of one carbonyl group to form the corresponding dicarbonyl ion and simultaneous loss of two carbonyl groups to form directly the corresponding monocarbonyl ion.

Another process occurring in the fragmentation of tris(dimethylamino)phosphine–metal carbonyl complexes is the loss of a $(CH_3)_2N$ group (mass 44) from a $[(CH_3)_2N]_3PM(CO)_x^+$ ion to form the corresponding $[(CH_3)_2N]_2PM(CO)_x^+$ ion. This process competes effectively with the loss of carbon monoxide from the same ion. Similar processes were noted in the study of Braterman.[10]

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[14] For other examples of the loss of two carbonyl groups from a metal carbonyl in one step, see ref 11.

Table III. Mass Spectrum of $[(CH_3)_2N]_3PFe(CO)_4$[a,b]

m/e	Ion	Rel intensity
331	$[(CH_3)_2N]_3PFe(CO)_4^+$	18
303	$[(CH_3)_2N]_3PFe(CO)_3^+$	14
287	$[(CH_3)_2N]_2PFe(CO)_4^+$	2.2
275	$[(CH_3)_2N]_3PFe(CO)_2^+$	41
247	$[(CH_3)_2N]_3PFeCO^+$	39
231	$[(CH_3)_2N]_2PFe(CO)_2^+$	26
219	$[(CH_3)_2N]_3PFe^+$	100
203	$[(CH_3)_2N]_2PFeCO^+$	2.3
195	$[(CH_3)_2N]_3PO_2^+$?	1.9
176	$[(CH_3)_2N]_2PHFe^+$	84
163	$[(CH_3)_2N]_3P^+$	7.3
142	$(CH_3NCH_2)_2Fe^+$	89
132	$(CH_3)_2NPHFe^+$	15
119	$[(CH_3)_2N]_2P^+$	57
100	$(CH_3)_2NFe^+$	28
76	$(CH_3)_2NPH^+$	54
60	CH_3NP^+	15
56	Fe^+	7.7

Metastable transitions

m/e	Process	Neutral fragment lost
277	$331 \xrightarrow{-28} 303$	CO
249.3	$303 \xrightarrow{-28} 275$	CO
222	$275 \xrightarrow{-28} 247$	CO
194.3	$247 \xrightarrow{-28} 219$	CO
141.6	$219 \xrightarrow{-43} 176$	CH_3NCH_2
114.6	$176 \xrightarrow{-34} 142$	PH_3
92.2	$219 \xrightarrow{-77} 142$	$(CH_3)_2NPH_2$
48.5	$119 \xrightarrow{-43} 76$	CH_3NCH_2

[a] Ions observed in this $[(CH_3)_2N]_3PFe(CO)_4$ mass spectrum, because of the $[(CH_3)_2N]_3PFe(CO)_3P[N(CH_3)_2]_3$ impurity, have been excluded from the listing in this table. Also the relative intensities have been corrected for the presence of $[(CH_3)_2N]_3PFe(CO)_3P[N(CH_3)_2]_3$. [b] Source pressure = 2.2×10^{-6} mm.

A rough indication of the relative tendencies for the parent tris(dimethylamino)phosphine–metal carbonyl ion (P^+) to lose carbon monoxide and to lose a dimethylamino group is provided by the ratio $[P - 44]/([P - 44] + [P - 28])$, where $[P - 44]$ and $[P - 28]$ correspond to the relative intensities of the ions 44 and 28 mass units less than the parent ion, respectively.[15,16] Table VI lists the values of this ratio for the tris(dimethylamino)phosphine–metal carbonyl complexes studied.[17]

Table IV. Mass Spectrum of $[(CH_3)_2N]_3PFe(CO)_3P[N(CH_3)_2]_3$[a]

m/e	Ion	Rel intensity
466	$[(CH_3)_2N]_3PFe(CO)_3P[N(CH_3)_2]_3^+$	90
438	$[(CH_3)_2N]_3PFe(CO)_2P[N(CH_3)_2]_3^+$	3.8
422	$[(CH_3)_2N]_2PFe(CO)_3P[N(CH_3)_2]_3^+$	13
410	$[(CH_3)_2N]_3PFeCOP[N(CH_3)_2]_3^+$	130
394	$[(CH_3)_2N]_2PFe(CO)_2P[N(CH_3)_2]_3^+$	0.6
382	$[(CH_3)_2N]_3PFeP[N(CH_3)_2]_3^+$	290
366	$[(CH_3)_2N]_2PFeCOP[N(CH_3)_2]_3^+$	5.1
339	$[(CH_3)_2N]_3PFePH[N(CH_3)_2]_2^+$	51
323	$[(CH_3)_2N]_2PFe(CO)PH[N(CH_3)_2]_2^+$	2.6
296	$[(CH_3)_2N]_2PHFePH[N(CH_3)_2]_2^+$	13
295	$[(CH_3)_2N]_2PFePH[N(CH_3)_2]_2^+$	9.0
294	$[(CH_3)_2N]_2PFeP[N(CH_3)_2]_2^+$	5.1
263	$[(CH_3)_2N]_4PFe^+$	60
252	$(CH_3)_2NPHFePH[N(CH_3)_2]_2^+$	9.0
251	$(CH_3)_2NPHFeP[N(CH_3)_2]_2^+$	6.4
247	$[(CH_3)_2N]_3PFeCO^+$	6.4
219	$[(CH_3)_2N]_3PFe^+$	100
176	$[(CH_3)_2N]_2PHFe^+$	51
163	$[(CH_3)_2N]_3P^+$	57
143	$(CH_3)_2NFeCH_2NCH_3^+$	33
142	$(CH_3NCH_2)_2Fe^+$	56
119	$[(CH_3)_2N]_2P^+$	400
100	$(CH_3)_2NFe^+$	33.4
76	$(CH_3)_2NPH^+$	260
60	CH_3NP^+	44

Metastable transitions

m/e	Process	Neutral fragment lost
412	$466 \xrightarrow{-28} 438$	CO
361	$466 \xrightarrow{-56} 410$	2CO
355.9	$410 \xrightarrow{-28} 382$	CO
301	$382 \xrightarrow{-43} 339$	CH_3NCH_2
258.5	$339 \xrightarrow{-43} 296$	CH_3NCH_2
184.2	$263 \xrightarrow{-44} 219$	$(CH_3)_2N$
141.5	$219 \xrightarrow{-43} 176$	CH_3NCH_2
114.6	$176 \xrightarrow{-34} 142$	PH_3
48.5	$119 \xrightarrow{-43} 76$	CH_3NCH_2

[a] Source pressure = 1.2×10^{-6} mm.

The tendency for the parent ions to lose carbon monoxide to form the $(P - 28)^+$ ion is negatively correlated with the metal–carbon bond strength since this process involves rupture of a metal–carbon bond. However, the loss of a dimethylamino group from the parent ion to form the $(P - 44)^+$ ion does not involve rupture of a direct metal–ligand bond but instead rupture of a phosphorus–nitrogen bond. Thus the tendency for the parent ion to lose a dimethylamino group is much less affected by variations in the metal–carbon bond strength than the tendency for the parent ion to lose a carbonyl group. For this reason higher values of the ratio $[P - 44]/([P - 44] + [P - 28])$ as given in Table VI can be taken to mean a higher metal–carbon bond strength at least for closely similar compounds.

Of interest is the much higher value of the ratio $[P - 44]/([P - 44] + [P - 28])$ for the tungsten carbonyl derivatives than for the completely analogous molybdenum and chromium carbonyl derivatives. This

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(15) This ratio is meaningful only when the fragmentation products $(P - 44)^+$ and $(P - 28)^+$ from the *parent* ion P^+ are considered. Similar fragmentation products coming from other ions M^+ which are themselves fragments of the parent ion P^+ have more than one possible origin which prevents this ratio from being meaningful. For example, the ions $[(CH_3)_2N]_2PM(CO)_4^+$ found in the mass spectra of the $[(CH_3)_2N]_3PM(CO)_5$ compounds (Table I) can arise either by loss of CO (28 mass units) from the ions $[(CH_3)_2N]_2PM(CO)_5^+$ or by loss of $(CH_3)_2N$ (44 mass units) from the ions $[(CH_3)_2N]_3PM(CO)_5^+$.

(16) Calculation of a meaningful $[P - 44]/([P - 44] + [P - 28])$ ratio for $[(CH_3)_2N]_3PFe(CO)_3P[N(CH_3)_2]_3$ is complicated by the tendency for the parent ion to decompose not only by losses of 28 mass units (one carbonyl group) and 44 mass units (one dimethylamino group) but also by loss of 56 mass units (two carbonyl groups). Thus the meaningful ratio for this iron complex to compare with the other values given in Table VI lies between $[P - 44]/([P - 44] + [P - 28])$ (=0.77) and $[P - 44]/([P - 44] + [P - 28] + [P - 56])$ (=0.18), depending upon how much of the observed $(P - 56)^+$ ion arises from loss of two carbonyl groups from the parent ion P^+ and how much of the observed $(P - 56)^+$ ion arises from the loss of only one carbonyl group from the $(P - 28)^+$ ion.

(17) No pure $[(CH_3)_2N]_3PW(CO)_5$ was available for this study. However, some of the available $[(CH_3)_2N]_3PW(CO)_4P[N(CH_3)_2]_3$ apparently decomposed in the mass spectrometer to give enough $[(CH_3)_2N]_3PW(CO)_5$ (footnote 12) to provide sufficient concentrations of the appropriate ions to calculate the ratio in Table VI.

Table V. Mass Spectrum of $C_5H_5V(CO)_3P[N(CH_3)_2]_3$[a]

m/e	Ion	Rel intensity
363	$C_5H_5V(CO)_3P[N(CH_3)_2]_3^+$	6.0
335	$C_5H_5V(CO)_2P[N(CH_3)_2]_3^+$	3.0
319	$C_5H_5V(CO)_3P[N(CH_3)_2]_2^+$	0.7
279	$C_5H_5VP[N(CH_3)_2]_3^+$	33
236	$C_5H_5VPH[N(CH_3)_2]_2^+$	16
203	$C_5H_5V(CH_2NCH_3)N(CH_3)_2^+$	5.7
181	$(C_5H_5)_2V^+$	110
163	$[(CH_3)_2N]_3P^+$	280
159	$C_5H_5V(CH_2NCH_3)_2^+$	28
135	$[(CH_3)_2N]_2P(H)CH_3^+$	7.3
119	$[(CH_3)_2N]_2P^+$	830
116	$C_5H_5V^+$	100
90.5	$(C_5H_5)_2V^{2+}$	5.7
81.5	$[(CH_3)_2N]_3P^{2+}$	24
76	$(CH_3)_2NPH^+$	830
66	$C_5H_6^+$	37
65	$C_5H_5^+$	15
60	CH_3NP^+	210

Metastable transitions

m/e	Process	Neutral fragment lost
309	$363 \xrightarrow{-28} 335$	CO
233	$335 \xrightarrow{-56} 279$	2CO
199.5	$279 \xrightarrow{-43} 236$	CH_3NCH_2
86.9	$163 \xrightarrow{-44} 119$	$(CH_3)_2N$
64.5	$66 \xrightarrow{-1} 65$	H
48.5	$119 \xrightarrow{-43} 76$	CH_3NCH_2

[a] Source pressure = 1.2×10^{-6} mm.

Table VI. Values of [P − 44]/([P − 44] + [P − 28]) for Various Tris(dimethylamino)phosphine Complexes

Complexes	[P − 44]/ ([P − 44] + [P − 28])
$C_5H_5V(CO)_3P[N(CH_3)_2]_3$	0.09
$[(CH_3)_2N]_3PCr(CO)_5$	0.06
$[(CH_3)_2N]_3PMo(CO)_5$	0.09
$[(CH_3)_2N]_3PW(CO)_5$	0.44
$[(CH_3)_2N]_3PFe(CO)_4$	0.13
$[(CH_3)_2N]_3PFe(CO)_3P[N(CH_3)_2]_3$	0.77
$[(CH_3)_2N]_3PCr(CO)_4P[N(CH_3)_2]_3$	0.16
$[(CH_3)_2N]_3PMo(CO)_3P[N(CH_3)_2]_3$	0.22
$[(CH_3)_2N]_3PW(CO)_4P[N(CH_3)_2]_3$	0.94

indicates the greater strength of tungsten–carbon bonds as compared with similar molybdenum–carbon bonds and chromium–carbon bonds. This is in accord with prior indications both from nmr studies on $C_8H_8M(CO)_3$ (M = Cr, Mo, and W) compounds[18] and from kinetic studies on substitution reactions of (bipy)-$M(CO)_4$ (bipy = 2,2′-bipyridyl; M = Cr, Mo, or W) compounds.[19] The mass spectrometric technique of comparing the tendency for loss of a carbonyl group with the tendency for a process nearly independent of the metal–carbon bond strength (such as loss of the dimethylamino group in a tris(dimethylamino)phosphine ligand) provides a novel and independent qualitative to semiquantitative method for estimating metal–carbon bond strengths.

Common to all of the mass spectra reported in this paper were ions at *m/e* 163, 119, 76, and 60 corresponding to the ions $[(CH_3)_2N]_3P^+$, $[(CH_3)_2N]_2P^+$, $(CH_3)_2NPH^+$, and CH_3NP^+, respectively. These ions are rational ionization and fragmentation products of tris(dimethylamino)phosphine and were also observed by Braterman.[10] Their presence appears to be indicative of a complex of this ligand. The presence of metastable ions at *m/e* 86.8–86.9 (Tables I and V) and at *m/e* 48.5 (Tables I and III–V) corresponds to the following two reactions **A** and **B**, respectively. The

$$\underset{m/e\ 163}{[(CH_3)_2N]_3P^+} \longrightarrow \underset{m/e\ 119}{[(CH_3)_2N]_2P^+} + (CH_3)_2N \qquad (A)$$

$$\underset{m/e\ 119}{[(CH_3)_2N]_2P^+} \longrightarrow \underset{m/e\ 76}{(CH_3)_2NPH^+} + CH_3NCH_2 \qquad (B)$$

elimination of a CH_3NCH_2 (azapropene) fragment corresponding to a mass loss of 43 has also been observed for other ions containing 3d (first-row) transition metal atoms but no carbonyl groups found in the spectra of various tris(dimethylamino)phosphine–metal carbonyl complexes. Examples of such eliminations of CH_3NCH_2 fragments are given by reactions 1–5.

$$\underset{m/e\ 215}{[(CH_3)_2N]_3PCr^+} \longrightarrow \underset{m/e\ 172}{[(CH_3)_2N]_2PHCr^+} + CH_3NCH_2 \qquad (1)$$

(Table I: metastable ion at *m/e* 137.7)

$$\underset{m/e\ 219}{[(CH_3)_2N]_3PFe^+} \longrightarrow \underset{m/e\ 176}{[(CH_3)_2N]_2PHFe^+} + CH_3NCH_2 \qquad (2)$$

(Tables III and IV: metastable ion at *m/e* 141.5–141.6)

$$\underset{m/e\ 382}{[(CH_3)_2N]_3PFeP[N(CH_3)_2]_3^+} \longrightarrow \underset{m/e\ 339}{[(CH_3)_2N]_2PHFeP[N(CH_3)_2]_3^+} + CH_3NCH_2 \qquad (3)$$

(Table IV: metastable ion at *m/e* 301)

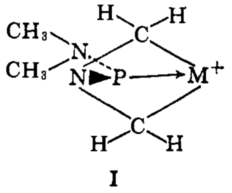
$$\underset{m/e\ 339}{[(CH_3)_2N]_2PHFeP[N(CH_3)_2]_3^+} \longrightarrow \underset{m/e\ 296}{[(CH_3)_2N]_2PHFePH[N(CH_3)_2]_2^+} + CH_3NCH_2 \qquad (4)$$

(Table IV: metastable ion at *m/e* 258.5)

$$\underset{m/e\ 279}{C_5H_5VP[N(CH_3)_2]_3^+} \longrightarrow \underset{m/e\ 236}{C_5H_5VPH[N(CH_3)_2]_2^+} + CH_3NCH_2 \qquad (5)$$

(Table V: metastable ion at *m/e* 199.5)

Such eliminations of CH_3NCH_2 (mass 43) fragments appear to be restricted to ions containing first-row transition metals but no carbonyl groups. As already discussed, ions containing carbonyl groups eliminate CO (mass 28) fragments and possibly also $(CH_3)_2N$ (mass 44) fragments. A third mode of elimination occurs with the carbonyl-free tris(dimethylamino)-phosphine ions of the heavier transition metals molybdenum and tungsten of the type[$(CH_3)_2N]_3PM^+$ which appear (Tables I and II) to decompose by loss of 46 mass units forming ions probably of the type $(CH_3)_2NP(CH_2NCH_2)M^+$ possibly with structure I involving the formation of new metal–carbon bonds. The failure to observe metastable ions for these processes resulting from the multiisotopic nature of molybdenum and tungsten precludes any reliable conclusions regarding the mechanism of loss of the $(CH_3)_2NH_2$ (mass 46) fragment.



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[18] R. B. King, *J. Organometal. Chem.* (Amsterdam), 8, 129 (1967).

[19] R. J. Angelici and J. R. Graham, *J. Am. Chem. Soc.*, 87, 5586 (1965); J. R. Graham and R. J. Angelici, *ibid.*, 87, 5590 (1965).

In the case of the tungsten system, an ion, probably $[(CH_3)_2N]_2PWNHCH_3^+$, is observed at 14 mass units less than the $[(CH_3)_2N]_3PW^+$ ion, suggesting that the first step involves loss of a CH_2 fragment. This may be followed by loss of the methyl group to give the ion $[(CH_3)_2N]_2PWNH^+$ which is unstable with respect to loss of ammonia by means of the NH group attached to the tungsten atom abstracting two protons from the remaining methyl groups. The net result of these successive losses of methylene, methyl, and ammonia fragments would be loss of 46 mass units and formation of the $(CH_3)_2NP(CH_2NCH_2)W^+$ ion (I, M = W).

Despite the well-established presence[9] of metal–phosphorus rather than metal–nitrogen bonds in the metal carbonyl complexes of tris(dimethylamino)phosphine, some fragments in the mass spectra of these compounds clearly contain metal–nitrogen bonds. These include the ions $(CH_3)_2NCrCH_2NCH_3^+$ (Table I), $(CH_3)_2NCr^+$ (Table I), $(CH_3NCH_2)_2Fe^+$ (Tables III and IV), $(CH_3)_2NFe^+$ (Tables III and IV), and $C_5H_5V(CH_2NCH_3)N(CH_3)_2^+$ (Table V). In addition the ions of the type $[(CH_3)_2N]_4PM^+$ (M = Cr, Mo, W, and Fe) observed in the metal carbonyl complexes containing two tris(dimethylamino)phosphine ligands probably are $[(CH_3)_2N]_3PMN(CH_3)_2^+$ with one metal–nitrogen bond, since bonding of four dimethylamino groups *and* a metal atom to a single phosphorus atom appears unlikely.

Such ions containing metal–nitrogen bonds appear to be formed by elimination of the phosphorus as phosphine, PH_3, since the metastable ion at *m/e* 114.6 in the mass spectrum of the tris(dimethylamino)phosphine complexes of the iron carbonyls corresponds to the reaction

$$\underset{m/e\ 176}{[(CH_3)_2N]_2PHFe^+} \longrightarrow \underset{m/e\ 142}{(CH_3NCH_2)_2Fe^+} + PH_3$$

Substituted phosphines may also be eliminated to form ions with metal–nitrogen bonds as demonstrated by the metastable ion at *m/e* 92.2 in the mass spectrum of $[(CH_3)_2N]_3PFe(CO)_4$ corresponding to the reaction

$$\underset{m/e\ 219}{[(CH_3)_2N]_3PFe^+} \longrightarrow \underset{m/e\ 142}{(CH_3NCH_2)_2Fe^+} + (CH_3)_2NPH_2$$

Metastable peaks corresponding to the formation of the other ions believed to contain metal–nitrogen bonds have not been observed.

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Mass Spectra of Organometallic Compounds. II. Some Cyclopentadienylmetal Carbonyl Derivatives[1]

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Abstract: Mass spectra of cyclopentadienylmetal carbonyl derivatives exhibit not only stepwise loss of their carbonyl groups but also extrusion of C_2H_2 from the $C_5H_5M^+$ ions to give $C_3H_3M^+$ ions. Compounds of the type $RFe(CO)_2C_5H_5$ also exhibit ions in their mass spectra arising from ferrocene and substituted ferrocene pyrolysis products. Sufficient metastable ions have been observed in the mass spectra of the iron compounds $CH_3COFe(CO)_2C_5H_5$ and $CH_3OCOCH_2Fe(CO)_2C_5H_5$ to establish degradation pathways from the molecular ion down to the bare metal ion Fe^+. The mass spectra of the latter iron compound and of the related molybdenum compound $C_2H_5OCOCH_2Mo(CO)_3C_5H_5$ exhibit processes involving fragmentation of ketene (CH_2CO, mass 42). This molybdenum compound as well as the iron compound $C_6H_5COFe(CO)_2C_5H_5$ and the tungsten compound $CH_2{=}CHCOW(CO)_3C_5H_5$ do not exhibit the parent ions in their mass spectra. Instead, the highest mass ion in their mass spectra occurs 28 mass units below the expected value for their parent ions, suggesting facile decarbonylation within the mass spectrometer. The mass spectrum of the π-allyl derivative $C_3H_5Mo(CO)_2C_5H_5$ exhibits the carbonyl ions $C_3H_5Mo(CO)_nC_5H_5^+$ (n = 1 or 2) but not the carbonyl-free allyl ion $C_3H_5MoC_5H_5^+$. Instead, the carbonyl-free cyclopropenyl ion $C_3H_3MoC_5H_5^+$ is observed in high abundance.

A major portion of the recent synthetic work in transition-metal organometallic chemistry has dealt with cyclopentadienylmetal carbonyl derivatives. However, the mass spectra of relatively few such compounds have been studied. Winters and Kiser[3] report the mass spectra of the simple mononuclear cyclopentadienylmetal carbonyls of the first transition series $C_5H_3M(CO)_n$ (M = V, n = 4; M = Mn, n = 3, M = Co, n = 2). Schumacher and Taubenest[4] describe the mass spectra of a few other cyclopentadienylmetal carbonyls including the binuclear $[C_5H_5Mo(CO)_3]_2$ and $[C_5H_5Fe(CO)_2]_2$; the trinuclear $(C_5H_5)_3Ni_3(CO)_2$; and the bromides $C_5H_5Fe(CO)_2Br$ and $C_5H_5Mo(CO)_3Br$.

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(1) For part I of this series, see R. B. King, *J. Am. Chem. Soc.*, 90, 1412 (1968).

(2) Department of Chemistry, University of Georgia, Athens, Ga; Fellow of the Alfred P. Sloan Foundation, 1967–1969.

(3) R. E. Winters and R. W. Kiser, *J. Organometal. Chem.* (Amsterdam), 4, 190 (1965).

(4) E. Schumacher and R. Taubenest, *Helv. Chim. Acta*, **49**, 1447 (1966).