Inorganica Chimica Acta, *143* (1988) 109–117

Fast Atom Bombardment, Electron Impact and Chemical Ionization Mass Spectrometry of the Neutral 18-Electron Species $M(CO)_2(CNR)_2(PR'_3)_2$ (M = Mo or W)

LISA D. DETTER, KAY A. CONNER, ARLENE P. ROTHWELL and RICHARD A. WALTON*
Department of Chemistry, Purdue University, West Lafayette, Ind. 47907, U.S.A.

(Received May 27, 1987)

Abstract

The molybdenum(0) and tungsten(0) complexes of the type $M(CO)_2(CNR)_2(PR'_3)_2$ have been studied using a variety of mass spectral techniques, *viz.* fast atom bombardment (FAB), electron impact (EI), and both positive- and negative-ion chemical ionization (PICI and NICI) mass spectrometry. The FAB-MS technique gave the most structurally informative spectra with the observation of the molecular ions M^+ (100% relative abundance in the case of M = W) and in some instances the pseudomolecular ion $(M + H)^+$. Fragmentation ions arising from competitive ligand loss (CO *versus* RNC *versus* PR'_3) were observed, as well as those formed by loss of H from fragment ions and dealkylation of RNC ligands. The EI and PICI spectra were not especially useful due to the relatively low thermal stability of these complexes, while the NICI spectra gave an abundance of ions that resulted from ligand redistribution reactions. Of special note were anions that contained $M(CO)_4$ and $M(CO)_3$ fragments. Dealkylation of the RNC ligands to give cyanometallate anions was also prevalent.

Introduction

A growing interest in mass spectrometry has been to use an array of ionization modes to collect molecular weight and fragmentation data for volatile and non-volatile species [1, 2]. During the past decade, several new 'soft ionization' methods have been developed which permit direct desorption of gas phase analyte ions without the need for sample vaporization; these techniques include field desorption (FD) [3, 4], plasma desorption (PD) [5], laser desorption (LD) [6], secondary ion (SIMS) [1, 7], and fast atom bombardment (FAB-MS) [8, 9] mass spectrometry. Very few studies have employed a selection of these techniques in concert to assess their relative value in the characterization of inorganic and organometallic complexes. We recently began to examine the implications of such a strategy by employing SIMS, EI, positive-ion chemical ionization (PICI) and negative-ion chemical ionization (NICI) mass spectrometry to characterize 18-electron species of the type $Cr(CO)_3(CNR)(R'–DAB)$ (R'-DAB = R'N=CH–CH=NR') [1].

In the present report we describe the results of a similar comparative FAB, EI, PICI, and NICI mass spectral study of a selection of mixed carbonyl–isocyanide–phosphine complexes of molybdenum and tungsten of stoichiometry $M(CO)_2(CNR)_2(PR'_3)_2$. The molybdenum complexes have recently been the subject of a detailed study [10] dealing with their electrochemical and spectroscopic properties in solution. The tungsten analogues, with the exception of $W(CO)_2(CNxylyl)_2(PPr^n_3)_2$, are reported here for the first time.

The 'soft ionization' method used herein is FAB-MS. Although SIMS capabilities are available in our laboratory, the method could not be used here since the molecular weight of each compound exceeded the high mass limit imposed by our quadrupole (*ca.* m/z = 500). However, based on the results of other comparative SIMS and FAB-MS studies [9, 11] similar spectral results are expected for these two techniques.

Experimental

Starting Materials

$Mo(CO)_6$ and $W(CO)_6$ were purchased from Pressure Chemical Company, allyl chloride from Aldrich, phosphine ligands and cyclohexyl, isocyanide from Strem, and xylyl isocyanide from Fluka Chemical Co. The RNC ligands, where R = methyl, isopropyl, tert-butyl, mesityl, and 2,4,6-tri-tert-butylphenyl were prepared by the cited methods [12, 13].

The acetonitrile intermediates $(\eta^3\text{-}C_3H_5)MCl(CO)_2(NCCH_3)_2$ (M = Mo or W) [14, 15] and the molybdenum complexes of $Mo(CO)_2(CNR)_2(PR'_3)_2$ [10] were prepared as described in the literature.

---

*Author to whom correspondence should be addressed.

0020-1693/88/$3.50

Synthetic Procedures for New Complexes

While the electrochemical and spectroscopic properties of $W(CO)_2(CNxylyl)_2(PPr^n{}_3)_2$ were described in an earlier report [10], the preparative details for this complex were not reported and are now described. A mixture comprising 0.55 g of $(\eta^3\text{-}C_3H_5)WCl(CO)_2(NCCH_3)_2$ and 0.38 g of xylylNC was stirred in 20 ml of CH_2Cl_2 for 30 min. An immediate color change from yellow to red indicated that the isocyanide had displaced the nitrile ligands. Approximately 0.7 ml of $PPr^n{}_3$ was added and the solution stirred overnight. At the end of this period, the reaction mixture was reduced in volume to about 5 ml, placed on a 15 × 2 cm alumina column, and eluted with a 6:1 CH_2Cl_2:hexane mixture. A large orange band was collected and the solvent stripped off. The resulting orange oil was triturated with methanol to yield an orange powder which was recrystallized from CH_2Cl_2/methanol; yield 62%. *Anal.* Calc. for $C_{38}H_{60}N_2O_2P_2W$: C, 55.48; H, 7.35. Found: C, 54.23; H, 7.03%. The microanalytical data were in accord with the presence of a small amount of CH_2Cl_2 of crystallization. The electrochemical and IR spectral properties of this sample agreed with those reported previously [10].

The following complexes were prepared by a similar procedure with suitable modifications:

$W(CO)_2(CNxylyl)_2(PEt_2Ph)_2$. A sticky orange solid was obtained after trituration with a 1:1 mixture of petroleum ether:diethyl ether. The mustard yellow solid was recrystallized twice from CH_2Cl_2/diethyl ether/petroleum ether; yield 38%. *Anal.* Calc. for $C_{40.5}H_{49}ClN_2O_2P_2W$: C, 55.46; H, 5.63. Found: C, 55.53; H, 5.79%.

$W(CO)_2(CNxylyl)_2(PEt_2Ph)_2\cdot\frac{1}{2}CH_2Cl_2$. A sticky orange solid was obtained after trituration with a 1:1 band was reduced in volume to *ca.* 3 ml. The resulting oily residue was treated with 25 ml of a 1:1 petroleum ether:diethyl ether mixture and cooled to 0 °C for 4 days. This afforded a yellow solid; yield 13%. The identity of this complex was based upon its electrochemical and IR spectral properties.

$W(CO)_2(CNBu^t)_2(PPr^n{}_3)_2$. The yellow oily residue that was obtained after column chromatography was mixed with 10 ml of petroleum ether and cooled to 0 °C. The yellow crystals that resulted were recrystallized from CH_2Cl_2/petroleum ether; yield 47%. *Anal.* Calc. for $C_{30}H_{60}N_2O_2P_2W$: C, 49.58; H, 8.32. Found: C, 48.13; H, 7.64%. This microanalysis is in accord with the presence of a trace of lattice CH_2Cl_2 (calc. for $W(CO)_2(CNBu^t)_2(PPr^n{}_3)_2\cdot\frac{1}{4}CH_2Cl_2$: C, 48.58; H, 8.15).

$W(CO)_2(CNBu^t)_2(PMePh_2)_2$. This complex crystallized as small yellow crystals upon evaporation of the eluate following column chromatography. Further crystallization was induced upon the addition of *ca.* 10 ml of methanol; yield 74%. *Anal.* Calc. for $C_{38}H_{44}N_2O_2P_2W$: C, 56.59; H, 5.50. Found: C, 56.12; H, 5.86%.

Physical Measurements

Infrared spectra were recorded as Nujol mulls with an IBM IR/32 Fourier Transform spectrometer (4000–400 cm^{-1}). Electrochemical measurements were obtained with a Bioanalytical Systems, Inc. model CV-1A instrument in conjunction with a Hewlett-Packard model 7035B x-y recorder. Measurements were carried out on dichloromethane solutions that contained 0.1 M tetra-n-butylammoniumhexafluorophosphate (TBAH) as the supporting electrolyte. $E_{1/2}$ potentials were referenced to the Ag/AgCl electrode at room temperature. Elemental microanalyses were performed by Dr H. D. Lee of the Purdue University Microanalytical Laboratory.

Mass Spectrometry Instrumentation

The EI and CI experiments were performed utilizing a Finnigan model 4000 mass spectrometer with an INCOS data system. The source temperature was maintained at 250 °C for the Mo and W complexes, the average probe temperature was 150 °C, and the primary ion beam was 70 eV. The reagent gas for PICI and NICI was isobutane at 0.3 torr. The FAB mass spectra were recorded in S-glycerol and/or 3:1 dithiothreitol/dithioerythreitol matrices using a Kratos MS-50 spectrometer.

Results and Discussion

(a) Syntheses and Preliminary Characterization of $W(CO)_2(CNR)_2(PR'_3)_2$

Tungsten(0) complexes of this type, which were needed for the mass spectral studies described herein, were synthesized by the use of a procedure similar to that reported for the analogous molybdenum compounds [10], *viz.* eqns. (1) and (2).

$$(\eta^3\text{-}C_3H_5)WCl(CO)_2(NCCH_3)_2 \xrightarrow{RNC} (\eta^3\text{-}C_3H_5)WCl(CO)_2(CNR)_2 + 2RCN \qquad (1)$$

$$(\eta^3\text{-}C_3H_5)WCl(CO)_2(CNR)_2 \xrightarrow{PR'_3} W(CO)_2(CNR)_2(PR'_3)_2 + C_3H_5Cl \qquad (2)$$

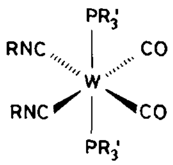
The electrochemical and IR spectral properties of these complexes (Table I) closely resembled those of their molybdenum analogues. The Nujol mull IR spectra are consistent with the *cis* isomer (I) or a mixture of *cis* isomers (up to three are possible),

TABLE I. Electrochemical and IR Spectroscopic Data for $W(CO)_2(CNR)_2(PR'_3)_2$

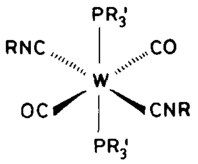
Complex	IR spectra (Nujol mulls) (cm^{-1})		CV data[a]		
	ν(CO)	ν(CN)	$E_{p,a}^{(1)}$	$E_{p,c}^{(1)}$	$E_{p,c}^{(2)}$
$W(CO)_2(CNxylyl)_2(PPr^n_3)_2$[b]	1858s, 1844s, 1831s	2056m, 2016w, 1983m, 1966m, 1927w	+0.07	−0.05	−0.18
$W(CO)_2(CNxylyl)_2(PEt_2Ph)_2$	~1865sh, 1844s, 1821s, ~1795sh	2054m, 2019w, 1941s, br	+0.15	+0.02	−0.15
$W(CO)_2(CNBu^t)_2(PEt_3)_2$	1858s, 1825s, 1794s	~2100m−w, 2050w, 2033s	−0.15	−0.27	−0.48
$W(CO)_2(CNBu^t)_2(PPr^n_3)_2$	1842s, 1802s	2100m, ~2090w?, 2002vs	0.00	−0.14	−0.33
$W(CO)_2(CNBu^t)_2(PMePh_2)_2$	1849s, 1801s	2110m, 2087m−w, 2052m	+0.14	−0.08	−0.28

[a] Single scan cyclic voltammograms; data in volts *vs.* Ag/AgCl. Recorded on solutions in 0.1 M TBAH/CH_2Cl_2 at a Pt-bead working electrode. [b] Data for this complex taken from ref. 10.

as is known to be the case for complexes of the type $Mo(CO)_2(CNR)_2(PR'_3)_2$ [10].



I



II

Single-scan cyclic voltammetric (CV) measurements on solutions of these complexes in 0.1 M TBAH/CH_2Cl_2 show behavior strikingly similar to that reported for their molybdenum analogues [10]. A scan starting at a potential of *ca.* −0.6 V and sweeping to more positivie potentials shows an oxidation ($E_{p,a}^{(1)}$) between +0.15 and −0.15 V and a coupled reduction wave ($E_{p,c}^{(1)}$) between +0.02 and −0.27 V (all potentials *versus* Ag/AgCl) when a switching potential of *ca.* +0.5 V is used. Continuation of the sweep to more negative potentials revealed a product wave ($E_{p,c}^{(2)}$) that corresponded to the reduction of the all *trans* isomer of $[W(CO)_2(CNR)_2(PR'_3)_2]^+$. This species (**II**) is formed in a rapid chemical (isomerization) step that follows oxidation of *cis*-$W(CO)_2(CNR)_2(PR'_3)_2$ to *cis*-$[W(CO)_2(CNR)_2(PR'_3)_2]^+$. These electrochemical data, which are presented in Table I, demonstrate that the tungsten systems display redox behavior in solution that is essentially identical to that of their molybdenum analogues [10]. Furthermore, the accessibility and relative stability of the 17-electron $[W(CO)_2(CNR)_2(PR'_3)_2]^+$ is clearly established. Trends in the $E_{p,a}$ and $E_{p,c}$ values (Table I) are very close to those observed for the molybdenum complexes upon varying the nature of R and R′.

(b) Mass Spectral Studies

Measurements were carried out on a total of nine neutral $Mo(CO)_2(CNR)_2(PR'_3)_2$ compounds and five neutral $W(CO)_2(CNR)_2(PR'_3)_2$ compounds. The techniques to be compared are FAB, EI, and PICI and NICI mass spectrometry. A summary of key data is presented in Tables II and III. The last three mass spectral procedures require sample vaporization prior to mass analysis. Molecular weight data and the useful fragmentation information that can be obtained were considered for each method. Competitive ligand eliminations (*i.e.* CO *versus* RNC *versus* PR'_3) for each series of complexes were also compared. Although relative bond strengths can be important in determining which ligand is lost initially from a large molecular ion, the ability of the smaller ions to delocalize charge can become a dominant factor in determining the remaining relative abundances [16].

TABLE II. Summary of Key FAB-MS Data for Complexes of the Type $M(CO)_2(CNR)_2(PR'_3)_2$[a]

Fragment	$Mo(CO)_2(CNR)_2(PR'_3)_2$			$W(CO)_2(CNR)_2(PR'_3)_2$		
	R = Cy R' = PPh_3[b]	R = xylyl		R = Bu^t		R = xylyl R' = PEt_2Ph
		R' = PEt_2Ph	PPh_3[c]	R' = PEt_3	R' = $PMePh_2$	
$[M(CO)_2(CNR)_2(PR'_3)_2 + H]^+$		7		93	49	55
$[M(CO)_2(CNR)_2(PR'_3)_2]^+$	8	5	7	100	100	100
$[M(CO)_2(CNR)_2(PR'_3) + H]^+$				13	9	5
$[M(CO)_2(CNR)_2(PR'_3)]^+$	6				5	5
$[M(CO)_2(CNR)(PR'_3)_2]^+$	5	1		9		12
$[M(CO)(CNR)_2(PR'_3)_2 + H]^+$		3		17	11	15
$[M(CO)(CNR)_2(PR'_3)_2]^+$	6	3	5		8	13
$[M(CO)(CNR)_2(PR'_3) + H]^+$		5			9	
$[M(CO)(CNR)_2(PR'_3)]^+$	12	5		13	21	19
$[M(CO)(CNR)(PR'_3)_2]^+$	4	2	3			
$[M(CO)(CNR)(PR'_3)]^+$	6			11		
$[M(CNR)_2(PR'_3)_2 + H]^+$					8	11
$[M(CNR)_2(PR'_3)_2]^+$	6	2				10
$[M(CNR)_2(PR'_3)]^+$	9			10		18
$[M(CO)(PR'_3)_2]^+$				10		5
$[M(CO)(PR'_3)]^+$					23	12
$[M(CO)(CNR)]^+$				15		
$[M(CNR)_2]^+$				17		
$[M(PR'_3)]^+$					64	

[a] Numbers in the table refer to the relative abundances of the identified positive ions in the FAB-MS, where 100 represents the maximum relative abundance. [b] Base peak in this spectrum was at m/z 359 and corresponds to $[Mo(PPh_3)-H]^+$. A peak at m/z 157 (66%) is due to an organic fragment. [c] Base peak in this spectrum was at m/z 157. An intense peak at m/z 359 (84%) corresponds to $[Mo(PPh_3)-H]^+$.

(i) FAB mass spectra

This technique has been used to obtain a wealth of spectral data for metal-containing complexes which are thermally unstable in conventional EI or CI mass spectrometry. There have been several reports in the literature that demonstrate the applicability of FAB-MS for the study of transition metal carbonyl-containing compounds [1, 9, 17–21]. The key FAB mass spectral features of a selection of four $Mo(CO)_2(CNR)_2(PR'_3)_2$ complexes and four $W(CO)_2(CNR)_2(PR'_3)_2$ complexes were compared. In all cases except one, the molecular ion (M^+) was observed and in most instances also the pseudomolecular ion $(M + H)^+$. The one exception was $W(CO)_2(CNBu^t)_2(PPr^n_3)_2$, which under our experimental conditions gave as the only significant metal-containing ions those associated with peaks at *m/z* 649 and *m/z* 621. These correspond to the decomposition products $[W(CO)_2(CNBu^t)_3(PPr^n_3)]^+$ (100%) and $[W(CO)(CNBu^t)_3(PPr_3)]^+$ (44%) which arise from a ligand redistribution reaction. For this complex we did not observe $[W(CO)_2(CNBu^t)_2(PPr^n_3)_2]^+$. These observations presumably reflect the low thermal stability of $W(CO)_2(CNBu^t)_2(PPr^n_3)_2$. Of the other complexes studied, only $Mo(CO)_2(CNxylyl)_2(PPr^n_3)_2$ did not give a very satisfactory FAB-MS; structurally informative metal-containing ions were present in very low relative abundance. With both S-glycerol and dithiothreitol/dithioerythritol as matrices, the molecular ion $[Mo(CO)_2(CNxylyl)_2(PPr^n_3)_2]^+$ (M^+, *m/z* 736) and the fragment ion $(M - CO)^+$ (*m/z* 708) were observed in less than 1% abundance relative to the base peak $[Pr^n_3POH]^+$ (*m/z* 177).

Details of the FAB-MS of six of the eight complexes studied are summarized in Table II where relative abundances (relative to 100 as the maximum) are compared. A representative spectrum (of $W(CO)_2(CNBu^t)_2(PMePh_2)_2$) is shown in Fig. 1. Abundant organic-fragment ions are seen at low *m/z* values. In some instances, these are the most abundant ions in the FAB-MS and include ions such as $[R'_3P + H]^+$ and $[P(C_6H_4)_2]^+$ (in the case of the PPh_3 ligand). The base peaks for $W(CO)_2(CNxylyl)_2(PEt_2Ph)_2$, $W(CO)_2(CNBu^t)_2(PMePh_2)_2$, and $W(CO)_2(CNBu^t)_2(PEt_3)_2$ were the M^+ ions. Large pseudomolecular ions $[M + H]^+$ were also seen for each of these complexes at 55%, 49%, and 93% relative abundance, respectively. Characteristic molecular weight information was also observed for each of the Mo species. However, the relative abundances of the molecular ions M^+ were less than 10%. Several characteristic fragmentation sequences were observed in the FAB-MS spectra for the Mo and W analogues (albeit the

TABLE III. Summary of NICI Mass Spectral Data for Complexes of the Type $M(CO)_2(CNR)_2(PR'_3)_2$[a]

Fragment	$Mo(CO)_2(CNR)_2(PR'_3)_2$								$W(CO)_2(CNR)_2(PR'_3)_2$			
	R = Me R' = PPh_3	Pr^i PPh_3	Cy PPh_3	xylyl			mesityl PPr^n_3	Bu^t_3Ph PPh_3	Bu^t		xylyl	
				PPr^n_3	PEt_2Ph	PPh_3			PPr^n_3[b]	$PMePh_2$	PPr^n_3	PEt_2Ph
$[M(CO)_4(PR'_3)]^-$		1		14								2
$[M(CO)_4(CN)(CNR)]^-$			23									
$[M(CO)_4(CN)(PR'_3)]^-$		4	6									
$[M(CO)_4(CNR)]^-$				94	84	68	100				2	4
$[M(CO)_4(CN)]^-$	100	59	100									
$[M(CO)_3(CN)(CNR)(PR'_3)]^-$			1							5		1
$[M((CO)_3(CN)(CNR)]^-$			5		61							
$[M(CO)_3(CN)(PR'_3)]^-$		2	1									
$[M(CO)_3(CNR)_2]^-$				100	100	100	59	100			3	100
$[M(CO)_3(CNR)(PR'_3)]^-$							73					
$[M(CO)_3(CN)]^-$	49	100	31									
$[M(CO)_2(CNR)_3]^-$				7	17	11		18				8
$[M(CO)_2(CNR)_2(PR'_3)]^-$	6			4			21				100	58
$[M(CO)_2(CN)(CNR)(PR'_3)_2]^-$										100		
$[M(CO)_2(CN)(CNR)(PR'_3)]^-$									1	8	1	
$[M(CO)_2(CN)_2(PR'_3)_2]^-$										3		
$[M(CO)_2(CN)_2(PR'_3)]^-$		1					4			1		
$[M(CO)_2(CN)(PR'_3)]^-$	11	4							2			
$[M(CO)_2(CN)(CNR)_2]^-$									2			
$[M(CO)_2(CN)(CNR)]^-$			1				1			1		
$[M(CO)_2(CNR)_2]^-$	100					1	6	3				1
$[M(CO)_2(CNR)(PR'_3)]^-$	4											
$[M(CO)(CN)(CNR)_2(PR'_3)]^-$									3			
$[M(CO)(CN)(NR)(PR'_3)]^-$		1	2									
$[M(CO)(CNR)_2(PR'_3)_2]^-$	3											
$[M(CO)(CNR)(PR'_3)-H]^-$											4	
$[M(CNR)_2(PR'_3)]^-$	1											
$[M(CN)(PR'_3)_2]^-$				8							30	

---

[a] Numbers in the Table refer to the relative abundances of the identified negative ions in the NICI mass spectra, where 100 represents the maximum relative abundance. [b] The base peak in this spectrum is associated with a cluster of peaks at *m/z* 592; possibilities are *m/z* 592 $[W(CO)_3(CNBu^t)_2(PPr^n_3)-2H]^-$ and *m/z* 591 $[W(CO)_3(CNBu^t)_2(PPr^n_3)-3H]^-$.

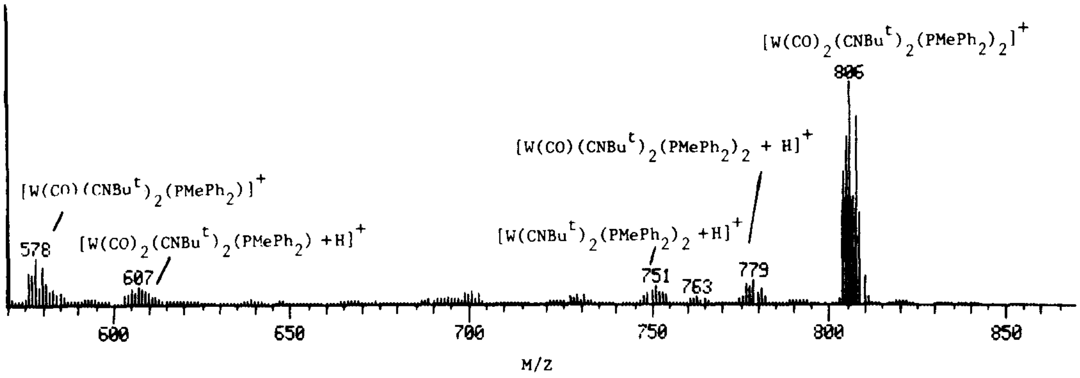


Fig. 1. FAB-MS (high mass region only) of $W(CO)_2(CNBu^t)_2(PMePh_2)_2$ from a 1:1 dithiothreitol/dithioerythritol matrix. The cluster of peaks at *m/z* 806 is probably due to a combination of $[W(CO)_2(CNBu^t)_2(PMePh_2)_2]^+$ (*m/z* 806) and $[W(CO)_2(CNBu^t)_2(PMePh_2)_2 + H]^+$ (*m/z* 807) ions.

Mo species were of much lower intensity). Competitive fragmentation is seen to occur by loss of a CO ligand, an RNC ligand, or a PR'_3 ligand. The ions $[M(CO)(CNR)_2(PR'_3)_2]^+$, $[M(CO)_2(CNR)(PR'_3)_2]^+$, and $[M(CO)_2(CNR)_2(PR'_3)]^+$ are present in various relative abundances but in only two spectra, *viz.* those of $Mo(CO)_2(CNCy)_2(PPh_3)_2$ and $W(CO)_2(CNxylyl)_2(PEt_2Ph)_2$, are all three of these fragment ions seen to be present in comparable abundances. While we observe no discernible trends in these fragmentation patterns (Table II), it is apparent that unlike our previous results on the SIMS of a series of complexes of the type $Cr(CO)_3(CNR)(R'\text{-DAB})$ [1], there is not a preferred loss of CO ligands. For these chromium complexes, the most abundant metal-containing species result from the sequential loss of three carbonyl ligands to give in most instances $[Cr(CNR)(R'\text{-DAB})]^+$ as a very abundant species. However, note that SIMS studies on mixed nitrosyl–isocyanide complexes of type $[Cr(NO)(CNR)_4L]^+$, where L = RNC, an amine, or a phosphine, and some closely related compounds, showed that loss of NO is competitive with loss of RNC [16, 22]. Further fragmentation of the $[M(CO)_2(CNR)_2(PR'_3)_2]^+$ ions occurs by the loss of intact isocyanide and phosphine ligands but this does not lead to any signficant amounts of the bare Mo^+ or W^+ ions.

As already mentioned, other peaks commonly encountered in the FAB-MS experiments result from fragmentations within the intact phosphine ligands. Such fragmentations have been reported in previous EI, FAB-MS and SIMS studies of alkyl and aryl phosphines [17, 19, 23]. The general trend is for alkyl phosphines to lose intact R′ groups (from PR'_3) or in the case of aryl phosphines either the loss of intact phenyl groups or skeletal rearrangement to form stable 9-phosphafluorenyl ions such as $[P(C_6H_4)_2]^+$ and $[P(C_6H_5)_2]^+$. Similar phosphine fragmentations were observed for the Mo and W compounds. For example, the FAB-MS of $W(CO)_2(CNBu^t)_2(PEt_3)_2$ contained peaks at *m/z* 613 $[W(CO)_2(CNBu^t)_2(PEt_3)(PEt_2)]^+$ (25%), *m/z* 557 $[W(CNBu^t)_2(PEt_3)(PEt_2)]^+$ (11%), *m/z* 439 $[W(CNBu^t)_2(PEt_2)]^+$ (12%), *m/z* 384 $[W(CO)(CNBu^t)(PEt_2)]^+$ (13%) and *m/z* 298 $[W(CNBu^t)(P)]^+$ (12%) which, formally at least, arise from loss of C_2H_5 from PEt_3. For $Mo(CO)_2(CNxylyl)_2(PPh_3)_2$ phosphine fragmentation with loss of phenyl groups gave peaks at *m/z* 862 $[Mo(CO)_2(CNxylyl)_2(PPh_3)(PPh_2)]^+$ (1%), *m/z* 834 $[Mo(CO)(CNxylyl)_2(PPh_3)(PPh_2)]^+$ (5%), *m/z* 806 $[Mo(CNxylyl)_2(PPh_3)(PPh_2)]^+$ (3%) and *m/z* 675 $[Mo(CNxylyl)(PPh_3)(PPh_2)^+]$ (5%). Note that the extent of phosphine fragmentation is less than that encountered in EI and CI mass spectrometry (*vide infra*).

In the case of some of the Mo complexes we observed the loss of H from certain of the fragment ions. For instance, the base peak in the FAB-MS of $Mo(CO)_2(CNCy)_2(PPh_3)_2$ corresponds to *m/z* 359 $[Mo(PPh_3)\text{–}H]^+$, while low abundance ions (*ca.* 1%), corresponding to $[Mo(CO)_2(CNxylyl)_2(PPr^n_3)\text{–}H]^+$ (*m/z* 575) and $[Mo(CO)(CNxylyl)_2(PPr^n_3)\text{–}H]^+$ (*m/z* 547) were seen in the spectrum of $Mo(CO)_2(CNxylyl)_2(PPr^n_3)_2$. A much more extensive series of such peaks were found in the FAB-MS of $Mo(CO)_2(CNxylyl)_2(PPh_3)_2$, namely, at *m/z* 883 $[Mo(CNxylyl)_2(PPh_3)_2\text{–}H]^+$ (4%), *m/z* 780 $[Mo(CO)(CNxylyl)(PPh_3)_2\text{–}H]^+$ (3%), *m/z* 752 $[Mo(CNxylyl)(PPh_3)_2\text{–}H]^+$ (2%), *m/z* 675 $[Mo(CNxylyl)(PPh_3)(PPh_2)\text{–}H)]^+$ (5%), *m/z* 649 $[Mo(CO)(CNxylyl)_2(PPh_3)\text{–}H]^+$ (10%), *m/z* 621 $[Mo(CNxylyl)_2(PPh_3)\text{–}H]^+$ (10%), *m/z* 544 $[Mo(CNxylyl)_2(PPh_2)\text{–}H]^+$ (4%), *m/z* 518 $[Mo(CO)(CNxylyl)(PPh_3)\text{–}H]^+$ (2%), and *m/z* 359 $[Mo(PPh_3)\text{–}H]^+$ (84%). This loss of hydrogen, which, incidentally, has been observed in the FAB-MS of other phosphine-containing complexes [17], may reflect the occurrence of favored cyclometallation reactions. The higher relative abundance of such ions in the EI spectra suggests that higher temperatures or greater internal energies facilitate orthometallation.

The dealkylation of the coordinated RNC ligands is seen in the FAB-MS of two of the complexes. Both complexes, $W(CO)_2(CNBu^t)_2(PEt_3)_2$ and $W(CO)_2(CNBu^t)_2(PMePh_2)_2$, contain the Bu^tNC ligand which has been shown from previous SIMS and FD mass spectral studies to be susceptible to quite facile dealkylation [1, 16, 24–26]. For these complexes we observe the following ions: *m/z* 548 $[W(CO)(CNH)(PMePh_2)(PHPh)]^+$ (8%), *m/z* 493 $[W(CN)(CNBu^t)(PMePh_2)]^+$ (8%), *m/z* 439 $[W(CO)(CNH)(PMePh_2)]^+$ (19%), and *m/z* 467 $[W(CO)_2(CN)(CNBu^t)(PEt_3)]^+$ (10%). Note that as before [1, 24] we write ions that contain (CNH) in this isocyanic acid form although we cannot of course distinguish them from the alternative hydrocyanic acid form (NCH). The presence of cyanide (CN) units has been previously encountered in field desorption mass spectrometric studies of $[M(CNBu^t)_6X]PF_6$ and $[M(CNBu^t)_5(CN)X]PF_6$ (M = Tc or Re, X = Cl or Br) where dealkylation occurred easily [25]. Either (CNH) or (CN) units have been observed in the EI mass spectra of a series of complexes $Cr(CO)_{3+n}(CNBu^t)_{3-n}$ ($n = 0$, 1, or 2) [26]. In the SIMS study of $[Cr(CO)_3(CNR)(R'\text{-}DAB)]$, dealkylation occurred to give fragment ions that contained $[Cr(CNH)]^+$ in quite high abundance [1].

(ii) EI mass spectra

A total of nine Mo complexes and four W complexes of the type $M(CO)_2(CNR)_2(PR'_3)_2$ were studied, *viz.* M = Mo for R = Me, Pr^i, Cy or $Bu^t{}_3Ph$ when $PR'_3 = PPh_3$, R = xylyl when $PR'_3 = PPr^n{}_3$, PMe_2Ph, PEt_2Ph or PPh_3, and R = mesityl when $PR'_3 = PPr^n{}_3$; M = W for $R = Bu^t$ when $PR'_3 = PPr^n{}_3$ or $PMePh_2$, and R = xylyl for $PR'_3 = PPr^n{}_3$ or PEt_2Ph. Overall, the EI spectra provided little in the way of useful structural information compared to the FAB-MS data. Generally, the abundances of metal-containing fragments were lower and those of organic fragments much higher than in the case of FAB-MS. These observations are not unexpected based on the high internal energies encountered in EI mass spectrometry and from the relatively low thermal stability of the $M(CO)_2(CNR)_2(PR'_3)_2$ complexes analyzed. Extensive thermal decomposition of metal–phosphines in EI mass spectrometry is not an uncommon problem.

Molecular weight information was limited to very few of the complexes and even in these instances the abundances of the molecular cations were generally very low (≲1%). The one exception was $W(CO)_2(CNxylyl)_2(PPr^n{}_3)_2$ for which M^+ (*m/z* 822) was present in 25% relative abundance. A peak at *m/z* 794 was due to $[W(CO)(CNxylyl)_2(PPr^n{}_3)_2]^+$ (19%).

Some resemblances to FAB-MS were seen in the loss of intact CO, RNC and PR'_3 ligands, fragmentation of the bound RNC and PR'_3 ligands, and loss of H atoms. As a case in point consider $W(CO)_2(CNBu^t)_2(PPr^n{}_3)_2$, whose FAB-MS was not recorded (*vide supra*), but for which the following ions were observed in its EI mass spectrum: *m/z* 578 $[W(CO)(CNBu^t)_3(PPr^n{}_2)]^+$ (5%); *m/z* 537 $[W(CO)(CNBu^t)_2(PPr^n{}_3)-H]^+$ (4%); *m/z* 508 $[W(CNBu^t)_2(PPr^n{}_3)-2H]^+$ (9%); *m/z* 479 $[W(CO)(CN)(CNBu^t)(PPr^n{}_3)-2H]^+$ (4%); *m/z* 464 $[W(CO)_2(CN)(CNBu^t)(PPr^n{}_2)-2H]^+$ (5%); *m/z* 452 $[W(CO)(CNBu^t)(PPr^n{}_3)-3H]^+$ (5%); *m/z* 436 $[W(CO)(CN)(CNBu^t)(PPr^n{}_2)-2H]^+$ (3%); *m/z* 408 $[W(CN)(CNBu^t)(PPr^n{}_2)-2H]^+$ (3%); *m/z* 381 $[W(CO)(CN)_2(PPr^n{}_2)]^+$ (4%); *m/z* 379 $[W(CO)(CN)_2(PPr^n{}_2)-2H]^+$ (4%) and *m/z* 351 $[W(CN)_2(PPr^n{}_2)-2H]^+$ (7%). Dealkylation from the Bu^tNC ligands gave only (CN), there being no direct evidence for fragments that contained (CNH).

In some of the spectra there was evidence for thermal decomposition leading to ligand distribution reactions. In FAB-MS, only the spectrum of $W(CO)_2(CNBu^t)_2(PPr^n{}_3)_2$ contained peaks attributable to thermolysis, *viz.* prominent ions $[W(CO)_n(CNBu^t)_3(PPr^n{}_3)]^+$ (n = 2 or 1), whereas the EI measurements showed such results in several of the spectra e.g. *m/z* 649 $[W(CO)_2(CNBu^t)_3(PPr^n{}_3)]^+$ (15%) and *m/z* 621 $[W(CO)(CNBu^t)_3(PPr^n{}_3)]^+$ (11%) from $W(CO)_2(CNBu^t)_2(PPr^n{}_3)_2$; *m/z* 610 $[Mo(CO)_4(PMe_2Ph)_2]^+$ (1%), *m/z* 582 $[Mo(CO)_3(CNxylyl)_2(PMe_2Ph)]^+$ (1%) and *m/z* 337 $[Mo(CO)_2(CN)_2(CNxylyl)]^+$ (2%) from $Mo(CO)_2(CNxylyl)_2(PMe_2Ph)_2$.

(iii) CI mass spectra

In the CI measurements, the ionization gas employed was isobutane. The internal energy imparted to the analytes of interest is known to be much less if compared to EI ionization. Nonetheless, the PICI measurements gave little useful molecular weight information. As with the EI mass spectral measurements, the most abundant ions were those of organic fragments with $[R'_3P + H]^+$ usually being the base peak. Of the eight Mo and four W complexes studied, all of which were the same as those whose EI mass spectra were recorded (*vide supra*), only two gave the molecular cations in appreciable abundance, *viz.* *m/z* 806 $[W(CO)_2(CNBu^t)_2(PMePh_2)_2]^+$ (35%) and *m/z* 822 $[W(CO)_2(CNxylyl)_2(PPr^n{}_3)_2]^+$ (11%). Ions arising from thermal decomposition, e.g. $[M(CO)_3(CNR)_3]^+$, are present in several of the PICI spectra but in low relative abundance as is the case for almost all metal-containing fragment ions.

The NICI spectra are quite different from either the FAB, EI, or PICI spectra in that the spectra are dominated by ions that contain tricarbonyl or tetracarbonyl fragments and either (CN) or (CNR) units (Table III and Fig. 2). While some such 'carbonyl-rich' fragments are seen in the EI and PICI

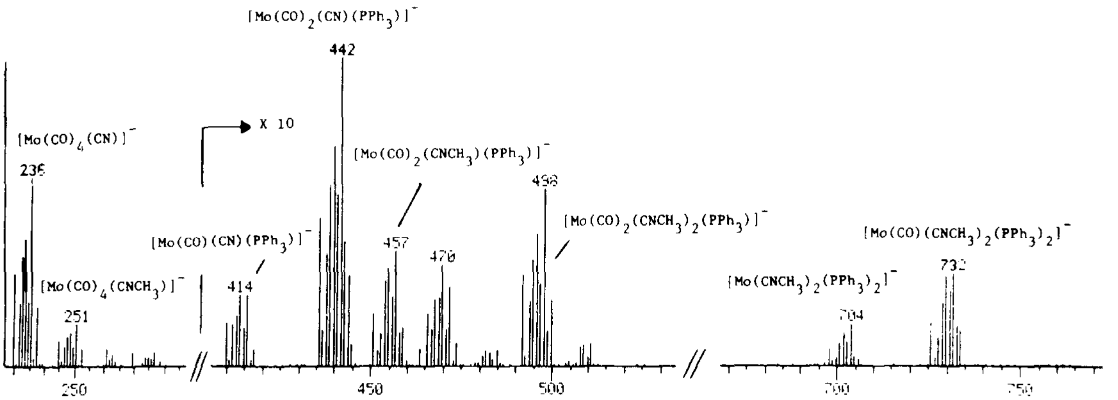


Fig. 2. NICI spectrum of $Mo(CO)_2(CNCH_3)_2(PPh_3)_2$ with 0.3 torr of isobutane reagent. The base peak in the spectrum at *m/z* 236 results from the overlap of the $[Mo(CO)_2(CNCH_3)_2]^-$ and $[Mo(CO)_4(CN)]^-$ ions. The region from *m/z* 400 to 750 is shown as a 10-fold intensity scale expansion.

mass spectra, they are present in low relative abundance. The stability of tricarbonyl and tetracarbonyl products in the NICI mass spectra is reasonable since CO ligands are very effective at removing electron density from the metal center via metal-to-CO π-back-bonding in the comparatively electron-rich anions. Another feature of special interest is the large number of peaks which contain between one and three carbonyl units in conjunction with various combinations of intact isocyanide or cyano groups, e.g. $[M(CO)_2(CNR)_3]^-$ (Table III). The high abundance of isocyanide-containing ions indicates competitive eliminations of CO, *versus* intact RNC loss, *versus* dealkylation of RNC to yield cyanide-containing products. The fact that isocyanide is lost competitively with CO, indicates that the isocyanide ligands display similar π-backbonding capabilities as compared to CO in these species.

The high abundances of peaks due to the 17-electron ions $[M(CO)_4(CNR)]^-$ and $[M(CO)_3(CNR)_2]^-$ in the case of the aryl isocyanide ligands (Table III) attest to their superior π-accepting ability compared to the alkyl isocyanide analogues. In the case of the two tungsten complexes that contained aryl isocyanide ligands, the 17-electron species $[W(CO)_2(CNR)_2(PR'_3)]^-$ were also abundant ions in the NICI mass spectra (Table III). We saw no evidence for 19-electron $[M(CO)_2(CNR)_2(PR'_3)_2]^-$, although in our previous study on the mass spectra of $Cr(CO)_3(CNBu^t)(Bu^t\text{–}DAB)$, the monoanion $[Cr(CO)_3(CNBu^t)(Bu^t\text{–}DAB)]^-$ was observed in low relative abundance (2%) in the NICI spectrum. Clearly, such 19-electron species are unstable.

Loss of intact PR'_3 ligands is facile as compared to CO and RNC loss, in accord with the superior π-accepting properties of the latter ligands. This is especially true in the case of the higher mass ions (Table III), of which few that contain PR'_3 ligands occur in relatively high abundance. For example, in the case of tetracarbonyl and tricarbonyl anions, only $[Mo(CO)_3(CNmesityl)(PPr^n_3)]^-$ occurs in high abundance (73%).

In the case of ions that arise from fragmentation of coordinated ligands, dealkylation of RNC is common (Table III) but hydrogen loss is not and neither is fragmentation of PR'_3. Loss of hydrogen atoms in NICI mass spectral studies has been observed for other systems, e.g. (η^6-arene)$Cr(CO)_3$ type molecules [27].

Conclusions

In this comparative mass spectral study a series of $M(CO)_2(CNR)_2(PR'_3)_2$ complexes (where M = Mo or W) was analyzed. The techniques employed were fast atom bombardment, electron impact, and positive and negative chemical ionization mass spectrometry. FAB-MS is the only technique which yielded abundant molecular ions and a wealth of information concerning the fragmentation of $[M(CO)_2(CNR)_2(PR'_3)_2]^+$ ions. This is in contrast to our earlier study on carbonyl complexes of the type $Cr(CO)_3(CNR)(R'\text{–}DAB)$ where only the PICI spectra gave abundant molecular ions. The absence of intense 17-electron molecular cations $[M(CO)_2(CNR)_2(PR'_3)_2]^+$ in the EI and PICI mass spectra accords with the relatively low thermal stability of these complexes and the higher internal energies imparted by these techniques. Thermolysis of the compounds on the probe tip prior to ionization can account for much of the observed decomposition. It is also apparent that the tungsten complexes were generally more stable towards decomposition compared to their molybdenum analogues. Competitive ligand loss involving CO, RNC and PR'_3 was observed within each series.

While fragmentation of coordinated phosphine ligands was quite prevalent in the EI and PICI spectra, intact loss of PR'_3 occurred readily in the NICI spectral measurements. These latter spectra showed that decomposition (ligand redistribution reactions) predominates. The NICI spectra contained abundant tetracarbonyl and tricarbonyl-containing anions.

Acknowledgement

This work was supported by the NSF-MRL Program, Grant DMR83-16988. We are most grateful to Professor R. Graham Cooks for his encouragement in carrying out these investigations.

References

1 L. D. Detter and R. A. Walton, *Polyhedron, 5,* 1321 (1986), and ref. therein.
2 H. M. Schiebel and H. R. Schulten, in M. L. Gross (ed.), 'Mass Spectrometry Reviews', Vol. 5, Wiley, New York, 1986.
3 H. R. Schulten, *Int. J. Mass Spectrom. Ion Phys., 32,* 97 (1979), and refs. therein.
4 (a) H. D. Beckey and H. R. Schulten, *Angew. Chem., Int. Ed. Engl., 12,* 425 (1975); (b) H. D. Beckey, *Int. J. Mass Spectrom. Ion Phys., 2,* 500 (1969); (c) H. U. Winkler and H. D. Beckey, *Org. Mass Spectrom., 6,* 655 (1972); (d) H. Budzikiewicz and M. Linscheid, *Biomed. Mass Spectrom., 4,* 103 (1977).
5 B. Sundqvist and R. D. McFarlane, *Mass Spectrom. Rev., 4,* 421 (1985).
6 (a) M. A. Posthumus, P. G. Kistemaker, H. L. C. Meuzelaar and M. C. Ten Noever de Brauw, *Anal. Chem., 50,* 985 (1978); (b) J. L. Pierce, K. L. Busch, R. G. Cooks and R. A. Walton, *Inorg. Chem., 21,* 2597 (1982).
7 R. J. Day, S. E. Unger and R. G. Cooks, *Anal. Chem., 52,* 557A (1980).
8 M. Barber, R. S. Bordoli, R. D. Sedgwick and A. N. Tyler, *Nature, 293,* 270 (1981).
9 J. M. Miller, *Adv. Inorg. Chem. Radiochem., 28,* 1 (1984); R. L. Cochran, *Appl. Spectros. Rev., 22,* 137 (1986).
10 K. A. Conner and R. A. Walton, *Inorg. Chem., 25,* 4422 (1986).
11 J. E. Campana, *Int. J. Mass Spectrom. Ion Phys., 51,* 133 (1983).
12 W. D. Weber, G. W. Gokel and I. K. Ugi, *Angew. Chem., Int. Ed. Engl., 11,* 530 (1972).
13 Y. Yamamoto, K. Aoki and H. Yamakazi, *Inorg. Chem., 18,* 1681 (1979).
14 R. G. Hayter, *J. Organomet. Chem., 13,* C1 (1968).
15 B. J. Brisdon, M. Cartwright, D. A. Edwards and K. E. Paddick, *Inorg. Chim. Acta, 40,* 191 (1980).
16 J. L. Pierce, D. E. Wigley and R. A. Walton, *Organometallics, 1,* 1328 (1982).
17 R. Davis, I. F. Groves, J. L. A. Durrant, P. Brooks and I. Lewis, *J. Organomet. Chem., 241,* C27 (1983).
18 E. Tolun, C. J. Proctor, J. F. J. Todd, J. M. A. Walshe and J. A. Connor, *Org. Mass. Spectrom., 19,* 294 (1984).
19 T. Blumenthal, M. I. Bruce, O. B. Shawkataly, B. N. Green and I. Lewis, *J. Organomet. Chem., 269,* C10 (1984).
20 B. Gregory, C. R. Jablonski and Y.-P. Wang, *J. Organomet. Chem., 269,* 75 (1984).
21 B. J. Brisdon and A. J. Floyd, *J. Organomet. Chem., 288,* 305 (1985).
22 D. E. Wigley and R. A. Walton, *Inorg. Chem., 22,* 3138 (1983).
23 J. L. Pierce, D. DeMarco and R. A. Walton, *Inorg. Chem., 22,* 9 (1983).
24 L. D. Detter, R. G. Cooks and R. A. Walton, *Inorg. Chim. Acta, 115,* 55 (1986).
25 J. P. Farr, M. J. Abrams, A. D. Costello and S. J. Lippard, *Organometallics, 4,* 139 (1985).
26 J. A. Connor, E. M. Jones, G. K. McEwen, M. K. Lloyd and J. A. McCleverty, *J. Chem. Soc., Dalton Trans.,* 1246 (1972).
27 I. K. Gregor and M. Gilhaus, *Mass Spectrom. Rev., 3,* 39 (1984).