Inorganica Chimica Acta, *142* (1988) 101–105

The Mass Spectrometric Behaviour of some Iridium(I) and Iridium(III) Pyrazolate Derivatives

ANNA LAURA BANDINI, GUIDO BANDITELLI
Dipartimento di Chimica Inorganica e Metallorganica, Via Venezian 21, 20133 Milan, Italy
GIOVANNI MINGHETTI
Dipartimento di Chimica, Via Vienna 2, 07100 Sassari, Italy
UMBERTO VETTORI
Centro C.N.R., Dipartimento di Chimica Analitica, Via Marzolo 1, 35100 Padua, Italy
and PIETRO TRALDI
C.N.R. Area di Ricerca, Corso Stati Uniti 4, 35100 Padua, Italy

(Received May 8, 1987)

Abstract

The mass spectrometric behaviour of a series of monomeric iridium(I) and iridium(III) pyrazolates, $Ir(PPh_3)_2(CO)(pz\text{-}N)$ (**1**–**3**) and $Ir(PPh_3)_2(CO)(H)_2(pz\text{-}N)$ (**4**–**6**) (**1** and **4**: pzH = 3,5-dimethylpyrazole; **2** and **5**: pzH = 3,5-bis(trifluoromethyl)pyrazole; **3** and **6**: pzH = 3,5-dimethyl-4-nitropyrazole), has been studied in detail with the aid of linked scans and mass analysed ion kinetic energy spectra. The differences observed as a function of the substituents on the pyrazolate ligands are described, and a comparison with the results previously reported for homologous rhodium(I) derivatives is made. The reactions leading, under the experimental conditions, to binuclear species or to orthometallated derivatives are discussed.

Introduction

In a previous paper [1] some of us described the synthesis and the behaviour in solution of several iridium(I) monohapto pyrazolates*, as well as the crystal structure of one of them, *trans*-$Ir(PPh_3)_2(CO)(pz''\text{-}N)$, as established by an X-ray diffraction analysis.

The iridium(I) compounds were shown to undergo reversible oxidative addition of dihydrogen, to give the corresponding iridium(III) *cis*-dihydrides, and protonation with acids (e.g. HBF_4) to afford mononuclear cationic species, *trans*-$[Ir(PPh_3)_2(CO)(pz\text{-}NH)]^+$ [2]. Quite recently the same iridium(I) compounds were shown to be sufficiently inert to be used as starting materials for assembling hetero-bimetallic molecules, e.g. $Ir(PPh_3)_2(CO)(\mu\text{-}pz\text{-}N,N')AuCl$ [3]. On the whole, the monomeric iridium(I) (and iridium(III)) species showed, in solution, a remarkable stability to dimerization: indeed: under our experimental conditions, no dimeric species, having bridging pyrazolato ligands, was isolated independently of the nature of the substituents on the heterocyclic ring. In contrast, a sharp propensity to give dinuclear species was observed in the chemistry of rhodium(I) [4].

As part of an investigation on the behaviour of the pyrazolate complexes [5], following a mass spectrometric study of several rhodium(I) derivatives carried out by means of different ionization techniques [6], here we report some results concerning the iridium complexes.

It is worth noting that in recent years the application of mass spectroscopy in the field of coordination and organometallic compounds has gained increasing importance thanks to the very many techniques which are now available, e.g. FAB, Laser Desorption [7], Direct Electron Impact [8]. The goal of this type of investigation is, eventually, to gain information on the reactivity of these systems in the vapour phase.

Experimental

All mass spectrometric measurements were obtained on a VG ZAB 2F instrument operating in EI conditions (70 eV, 200 μA). Samples were introduced in Direct Electron Impact (DEI) [8] conditions with a source temperature (unless specified) of 180 °C.

---

*Throughout this paper a generic pyrazole is indicated by pzH, 1-unsubstituted pyrazole ($C_3H_4N_2$) by PzH, 3,5-dimethylpyrazole by pz'H, 3,5-bis(trifluoromethyl)pyrazole by pz''H and 3,5-dimethyl-4-nitropyrazole by pz'''H.

0020-1693/88/$3.50

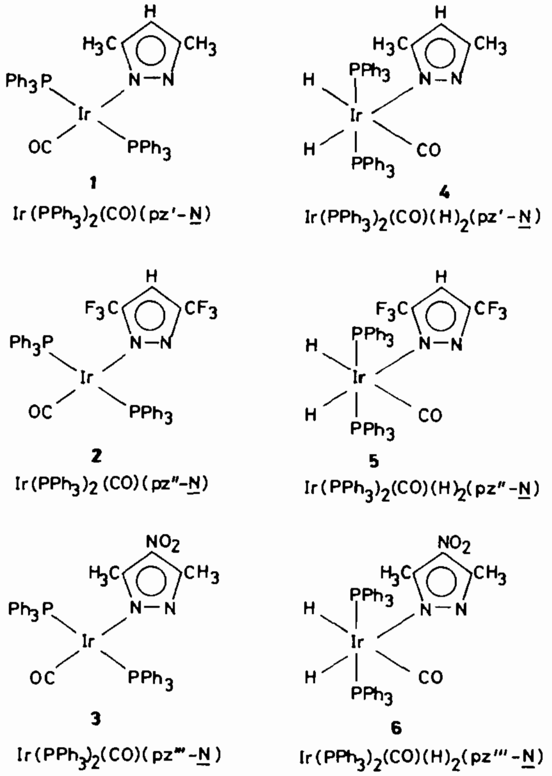


Fig. 1. Compounds 1–6.

Metastable transitions were detected by B/E linked scans [9] and by mass analysed ion kinetic energy spectrometry [10].

Compounds 1–6, Fig. 1, were analytically pure samples synthesized and purified according to the literature [2].

Results and Discussion

The title compounds give rise to spectra which are strongly influenced by the thermodynamic conditions (temperature and sample vapour pressure) of the ionic chamber and by the direct inlet probe temperature. For these reasons the spectra here discussed were obtained, unless specified, with the same ion source temperature and by introducing a comparable amount of sample in DEI conditions.

We never observed the molecular ions of the iridium(III) derivatives, **4–6**, which immediately give rise to **1–3** respectively. The condensed phase behaviour of the dihydrides **4–6** may account for this result. Indeed it is well known that the oxidative addition of dihydrogen by Vaska's compounds is reversible; in agreement, complexes **4–6** eliminate dihydrogen even at room temperature [2]. Furthermore the compounds **1–3** give rise to EI mass spectra which show very scarce or absent molecular species. By introducing about 0.1 mg of sample and with a ion source temperature of 100 °C, it was possible for compound **2** only to obtain mainly the mass spectrum corresponding to the 'monomeric' structure: small variations of the vapour pressure conditions were critical for the detection of the mononuclear species.

The most evident result of the above findings is that the EI mass spectra of the compounds **1–3** show well detectable ions corresponding to the binuclear molecules **1a–3a** respectively:

$$\underset{\mathbf{1-3}}{2\mathrm{Ir(PPh_3)_2(CO)(pz\text{-}}N)} \longrightarrow \underset{\mathbf{1a-3a}}{[\mathrm{Ir(PPh_3)(CO)}(\mu\text{-}\mathrm{pz}\text{-}N,N')]_2} + 2\mathrm{PPh_3}$$

An analogous behaviour has already been observed by us for a monomeric derivative of rhodium(I), $\mathrm{Rh(PPh_3)_2(CO)(pz''\text{-}}N)$ [6].

This 'dimerization' process can arise, in principle, either by a gas-phase ion–molecule reaction (a, b) leading to highly reactive species such as $[\mathrm{M\text{-}PPh_3}]^{+\cdot}$ or by a thermal process in the condensed phase (c), involving the formation of binuclear compounds followed by the ionization of the bimetallic complex (Scheme 1). The first two mechanisms proposed in Scheme 1 hypothesize the occurrence of a gas-phase ion–molecule reaction. We are inclined to mechanism (c) for the absence (or the low abundance) of the eventual reacting ions in the corresponding mass spectra; furthermore binuclear moieties are always present, also for very low sample vapour pressure and with the source in the 'open' configuration. Such 'dimerization' has been observed in the synthesis of rhodium(I) and iridium(I) pyrazolato derivatives and evidenced by the rearrangement of the complex $\mathrm{Rh(SC)(PPh_3)_2(pz'\text{-}}N)$, which is stable at −50 °C and dimerizes with loss of phosphine at higher temperatures [11]. As a further confirmation, when compound **1** was heated under vacuum (10^{-5} torr) for a few days white crystals sublimed, which were identified by infrared and melting point data as triphenylphosphine.

$$\text{(a)}\ \mathrm{M_{(s)}} \longrightarrow \mathrm{M_{(g)}} \xrightarrow{\mathrm{EI}} [\mathrm{M}]^{+\cdot} \xrightarrow{\mathrm{M_{(g)}}} [\mathrm{M_2}]^{+\cdot} \xrightarrow{-2\mathrm{PPh_3}} [\mathrm{M\text{-}PPh_3}]_2^{+\cdot}$$

$$\text{(b)}\ \mathrm{M_{(s)}} \longrightarrow \mathrm{M_{(g)}} \xrightarrow{\mathrm{EI,\ -PPh_3}} [\mathrm{M\text{-}PPh_3}]^{+\cdot} \xrightarrow{\mathrm{M_{(g)}}} [\mathrm{M\text{-}PPh_3}]_2^{+\cdot} + \mathrm{PPh_3}$$

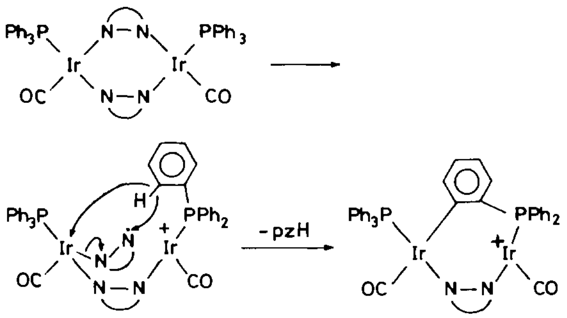
$$\text{(c)}\ 2\mathrm{M_{(s)}} \xrightarrow{-2\mathrm{PPh_3}} [\mathrm{M\text{-}PPh_3}]_2 \xrightarrow{\mathrm{EI}} [\mathrm{M\text{-}PPh_3}]_2^{+\cdot}$$

Scheme 1.

The more relevant fragments arising from EI of **1–3** are reported in Table I. All the examined binuclear ions, **1a–3a**, show some common EI

TABLE I. More Relevant Ions Observed in EI mass spectra of 1–3

Ions	**1a**		**2a**		**2**		**3a**		**3**	
	m/z	*I* (%)	*m/z*	*I* (%)	*m/z*	*I* (%)	*m/z*	*I* (%)	*m/z*	*I* (%)
M	1152	100	1368	4	946	0.05	1242	100		
M–CO	1124	3	1340	0.5	918	0.1				
M–pzH	1056	1	1164	0.5	742	2	1101	3	742	18
M– [Co + pzH]	1028	3	1136	0.2	714	2.5	1073	1.5	714	16
M – [H + CO + pzH + Ph]					636	3.4			636	15
M – [CO + pzH + PPh_3]	766	8	874	1						
PPh_3	262	50	262	100			262	98		
PzH	96	0.3	204	37			141	2		



Scheme 2.

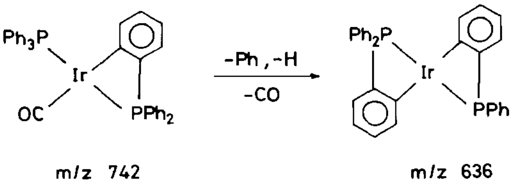
induced decomposition processes, the most relevant being the primary loss of a pyrazole (pzH) (see Table I). For such fragmentation we propose the concertated mechanism reported in Scheme 2. The pyrazole loss must necessarily implicate the cleavage of an Ir–N bond and a hydrogen transfer on the heterocycle. The only source of hydrogen in the molecule is the phenyl group: consequently it is reasonable to assume the formation of an orthometallated species. On the other hand in mass spectrometry the rarely observed H rearrangement from a phenyl group is always induced by the *ortho*-effect (*i.e.* the formation of an *ortho*-substituted phenyl group). Finally it is worth mentioning that an orthometallated system of the above type has been recently reported [12] for the stable two centers rhodium pyrazolate, $Rh_2(\mu\text{-Pz-}N,N')_2(\mu\text{-P}(C_6F_4)Ph_2)Br(CO)(pcBr)$ (pcBr = $P(o\text{-Br-}C_6F_4)Ph_2$).

The tendency to give stable ions through pzH loss and formation of an orthometallated species is further confirmed by the presence of the corresponding double charge ions. As for example, for compound **1a** ionic species at *m/z* 528, 514, 500, 461, 452 and 413, corresponding to $[P_2(C_6H_5)_5(C_6H_4)(CO)_2pz'Ir_2]^{2+}$, $[P_2(C_6H_5)_5(C_6H_4)COpz'Ir_2]^{2+}$, $[P_2(C_6H_5)_5(C_6H_4)pz'Ir_2]^{2+}$, $[P_2(C_6H_5)_3(C_6H_4)_2pz'Ir_2]^{2+}$, $[P_2(C_6H_5)_4(C_6H_4)_2Ir_2]^{2+}$, and $[P_2(C_6H_5)_2(C_6H_4)_3Ir_2]^{2+}$ respectively, are well detectable. For clearness the differences between these masses can be evidenced as follows:

$$\begin{tikzcd}
{[P_2(C_6H_5)_5(C_6H_4)(CO)_2pz'Ir_2]^{2+}} \\ \text{1056 u. } (m/z\ 528) \arrow[d, "-\mathrm{Co}"] & \\
{[P_2(C_6H_5)_5(C_6H_4)COpz'Ir_2]^{2+}} \\ \text{1028 u.} \arrow[d, "-\mathrm{Co}"] & \\
{[P_2(C_6H_5)_5(C_6H_4)pz'Ir_2]^{2+}} \arrow[r, "-\mathrm{pz'H}"] & {[P_2(C_6H_5)_4(C_6H_4)_2Ir_2]^{2+}} \\
\text{1000 u.} \arrow[d, "-\mathrm{PhH}"] & \text{904 u.} \\
{[P_2(C_6H_5)_3(C_6H_4)_2pz'Ir_2]^{2+}} \arrow[r, "-\mathrm{pz'H}"] & {[P_2(C_6H_5)_2(C_6H_4)_3Ir_2]^{2+}} \\
\text{922 u.} & \text{826 u.}
\end{tikzcd}$$

An EI induced orthometallation must be invoked also to explain the ions at *m/z* 742 arising from genuine 'monomeric' molecular moieties of **2** and **3** by primary pzH loss, metastable supported, in the case of compound **2**.

Further Ph, CO, H sequential losses lead to ionic species at *m/z* 636 for both **2** and **3**. The loss of another hydrogen is likely to result in the formation of a further Ir–C bond; thus the overall pattern may imply the existence of a phosphide ligand, e.g. Scheme 3.



Scheme 3.

The primary processes above observed in the gas-phase remind one of some relevant aspects of the reactivity, e.g. 'cyclometalation' or 'aryl transfer', of

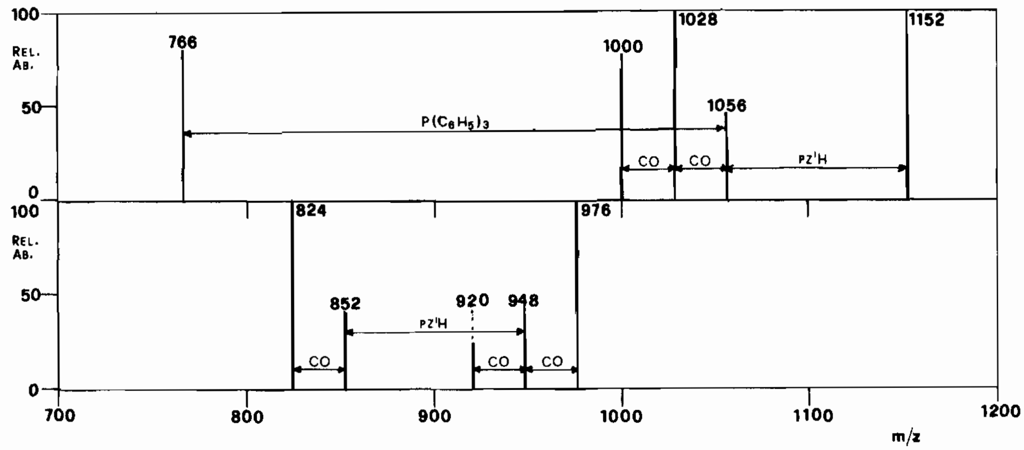


Fig. 2. B/E spectra of $[(CO)(Ph_3P)Ir(pz'\text{-}N,N')]_2^{+\bullet}$, *m/z* 1152, (up) and $[(CO)(Ph_3P)Rh(pz'\text{-}N,N')]_2^{+\bullet}$, *m/z* 976, (down).

mono- and polynuclear transition-metal phosphine complexes [13].

For compound **3a** only, $[Ir(\mu\text{-}pz'''\text{-}N,N')(PPh_3)(CO)]_2$, primary fragmentation products due to the cleavage of the NO_2 substituent on the pyrazolato group are evidenced. Thus primary O, NO and NO_2 losses were observed, leading to ionic species at *m/z* 1226, 1212 and 1196 respectively.

Finally all the examined compounds show the usual formation of phosphine molecular ions and related fragment ions.

Comparing the mass spectrometric behaviour of the iridium ions **1a**–**3a** with that, already described by us, of the analogous rhodium containing derivatives, it appears that the main differences lie in the primary fragmentation processes. While for the iridium derivatives primary losses of pzH and CO are observed, these decomposition pathways are absent for rhodium(I) compounds, for which a primary PPh_3 loss is found. This can be due either to different ionization energies of the fragment ions (Stevenson Audier rule [14]) or to a quite different stability of the ionic species so formed, containing a hexaatomic bimetallic $\overline{\text{M–N–N–M–N–N}}$ cycle, in agreement with the observed instability of the monomeric rhodium(I) pyrazole derivatives.

The case of 3,5-dimethylpyrazolate derivatives requires, however, further comment. In fact the neutral species loss of 152u from the molecular ion can originate either by loss of $2C_6H_4$ or by loss of 2CO and pzH. The former, typical of the mass spectrometric behaviour of PPh_3, was proposed in the case of the rhodium(I) derivative*, in assumption of the high stability of the metallocyclo product ions; the latter was recently observed in a synthetic study on some iridium(I) pyrazolylgallates [15].

To discriminate between these two hypotheses an exact mass measurement of these ions, [*M*-152], requires a resolution much higher (*ca.* 200 000) than that available (*ca.* 30 000); anyway metastable data can clarify this problem. B/E spectra allow us to obtain information about the mechanism and the energies involved in the fragmentation processes of the homologous Rh and Ir compounds. The B/E spectra of $[(CO)(Ph_3P)Rh(pz'\text{-}N,N')]_2^{+\bullet}$ and $[(CO)(Ph_3P)Ir(pz'\text{-}N,N')]_2^{+\bullet}$ are reported in Fig. 2. These spectra give evidence that the ionic species at *m/z* 824 for the rhodium derivative is due to losses of 2CO and pz'H as in the case of the iridium derivative (*m/z* = 1000).

It is noteworthy that the primary pz'H loss observed for **1a** in the first field-free region is present also in the usual mass spectrum. On the contrary the primary CO loss for **1a** is observed in the normal mass spectrum only. This difference between B/E and mass spectra data must be explained in terms of internal energies of reacting species: the CO loss is favoured by higher internal energy content, the pz'H by lower ones. For the Rh derivative the pz'H loss is always subsequent to the CO one, in agreement with the higher stability of hexatomic bimetallic cycle of Rh pyrazolate with respect to Ir pyrazolate. Finally it must be remembered that the pyrazole loss has never been observed in the case of the 3,5-bis(trifluoromethyl)pyrazolate Rh(I) derivative. Hence, while for Ir compounds the primary pyrazole loss always results in a favoured decomposition process, for Rh derivatives the result is strongly influenced by the pyrazole substituents and it is never a primary loss.

Also in the present case mass spectrometry has given clear information on either the stability of the product ions or the reactivity of ionic species. The

---

*The re-examination of $[Rh(\mu\text{-}pz'\text{-}N,N')(PPh_3)(CO)]_2$ EI induced decomposition has shown the presence of well detectable molecular species (*m/z* 976) leading to fragment ions at *m/z* 824 and 262.

presence of EI induced fragmentation ions somehow related to analogous species observed in condensed phase chemistry and the newest mass spectrometric techniques stimulate the use of mass spectrometry as a bench test in organometallic chemistry as well.

In any case, the comparison, through MIKE and collision spectroscopy, of the EI induced product ions with model compounds is always desirable; while this has become a routine procedure in organic chemistry, in organometallic chemistry the approach is more difficult due to the unavailability of the necessary models.

Acknowledgement

Financial support by the Ministero della Pubblica Istruzione (Rome) is gratefully acknowledged.

References

1 A. L. Bandini, G. Banditelli, F. Bonati, F. Demartin, M. Manassero and G. Minghetti, *J. Organomet. Chem., 238,* C9 (1982).

2 A. L. Bandini, G. Banditelli, F. Bonati, G. Minghetti, F. Demartin and M. Manassero, *J. Organomet. Chem., 269,* 91 (1984).

3 A. L. Bandini, G. Banditelli, F. Bonati, G. Minghetti, F. Demartin and M. Manassero, *Inorg. Chem., 26,* 1351 (1987).

4 G. Banditelli, A. L. Bandini, F. Bonati and G. Minghetti, *J. Organomet. Chem., 218,* 229 (1981).

5 (a) F. Bonati, *Chim. Ind., 62,* 323 (1980); (b) S. Trofimenko, *Prog. Inorg. Chem., 34,* 115 (1986).

6 P. Traldi, U. Vettori, G. Banditelli, A. L. Bandini and G. Minghetti, *Inorg. Chim. Acta, 69,* 207 (1983).

7 A. H. Verbueken, F. J. Bruynscel and R. E. Van Grieken, *Biomed. Mass Spectrom., 12,* 438 (1985).

8 P. Traldi, U. Vettori and F. Dragoni, *Org. Mass. Spectrom., 17,* 587 (1982).

9 A. P. Bruins, K. R. Jennings and S. Evans, *Int. J. Mass Spectrom. Ion Phys., 26,* 395 (1978).

10 R. G. Cooks, J. H. Beynon, R. M. Caprioli and G. R. Lester, 'Metastable Ions', Elsevier, Amsterdam, 1973.

11 R. Uson, L. A. Oro, M. A. Ciriano, D. Carmona, A. Tiripicchio and M. Tiripicchio-Camellini, *J. Organomet. Chem., 206,* C14 (1981).

12 F. Barcelo, P. Lahuerta, M. A. Ubeda, C. Fons-Fons, H. F. Cano and M. Martinez-Ripoll, *J. Chem. Soc., Chem. Commun.,* 43 (1985).

13 e.g.: P. E. Garrou, *Chem. Rev., 85, 171* (1985), and refs. therein.

14 D. P. Stevenson, *Discuss. Faraday Soc., 10,* 35 (1951); H. E. Audier, *Org. Mass Spectrom., 2,* 283 (1969).

15 S. Nussbaum, S. J. Rettig and J. Trotter, *Can. J. Chem., 63,* 692 (1985).