Journal of Organometallic Chemistry
Elsevier Sequoia S.A., Lausanne
Printed in The Netherlands

NOTE

Mass spectra of transition metal carbonyl derivatives of tris(dimethylamino)phosphine and trimethylphosphite[1]

Despite considerable interest in the mass spectra of phosphorus compounds[2-7], and also of metal carbonyls and their derivatives[8-14], there is little literature on the mass spectra of metal carbonyl phosphines. In view of current interest in this field[14-15] we wish to report our findings for the following carbonyl phosphines:

(I) $Fe(CO)_3[P(NMe_2)_3]_2$
(II) $Fe(CO)_4P(NMe_2)_3$
(III) *trans*-$Cr(CO)_4[P(NMe_2)_3]_4$
(IV) $Cr(CO)_5P(NMe_2)_3$
(V) $Fe(CO)_3[P(OMe)_3]_2$
(VI) $Fe(CO)_4P(OMe)_3$
(VII) *trans*-$Cr(CO)_4[P(OMe)_3]_2$

Experimental

Spectra were obtained with a double focussing MS-9 mass spectrometer, at a nominal ionising electron energy of 70 eV.

(I) and (II) were prepared by the room temperature reaction of $Fe_2(CO)_9$ magnetically stirred with $P(NMe_2)_3$ in toluene under nitrogen for 24 h. The products were separated by fractional crystallisation from pentane at −80°. The monosubstituted product decomposed extensively on the probe of the mass spectrometer, to give the disubstituted derivative.

(III) and (IV) were prepared by the method of King[16], and separated and purified by fractional sublimation at 0.1 mm between 60 and 100°.

(VI) was prepared by the reaction of $Fe_2(CO)_9$ magnetically stirred with $P(OMe)_3$ in refluxing heptane under nitrogen for 24 h, and crystallised from pentane at −80°. It decomposed extensively on the probe to give the disubstituted product (V).

(VII) was prepared from resublimed $Cr(CO)_6$ and freshly distilled with $P(OMe)_3$ by refluxing in heptane (N_2, magnetic stirring) for 60 h, resublimed $Cr(CO)_6$ being returned mechanically to the reaction flask. After removal of solvent, the product was purified by low-temperature crystallisation from pentane. The procedure gave the *trans*-isomer exclusively, as expected from the preparation of the molybdenum analogue[17].

Results and discussion

(a) Free ligands

Our results for $P(OMe)_3$ (which agree with other workers[7]) and for $P(NMe_2)_3$ (to be discussed elsewhere[18]) are summarised in eqn. (1), for purposes of comparison.

$$\begin{tikzcd} & \underset{(93)}{P(OMe)_2^+} \arrow[r, "*"] & \underset{(63)}{HPOMe^+}\ * \\ \underset{(124)}{P(OMe)_3^+} \arrow[ur] \arrow[r] \arrow[dr] & \underset{(109)}{O{=}P(OMe)_2^+} \arrow[r, "*"] & \underset{(79)}{HOPOMe^+} \\ & \underset{(94)}{HP(OMe)_2^+} \arrow[r, "*"] & \underset{(79)}{HP(O)OMe^+} \end{tikzcd} \qquad (1a)$$

$$\underset{(163)}{P(NMe_2)_3^+} \xrightarrow{*} \underset{(119)}{P(NMe_2)_2^+} \xrightarrow{*} \underset{(76)}{HPNMe_2} \qquad (1b)$$

(*b*) *Complexes*

Full data for these are obtainable from the author on request.

In addition to the expected loss of CO groups and of complete ligands, we note the following decomposition pathways:

(*i*) *Radical loss from the ligand system* [loss of $^{\bullet}NMe_2$ from $(I)^{+*}$, $(III)^{+*}$ and $(IV)^{+*}$, which may be preceded by loss of CO, and of $^{\bullet}OMe$ from $(V)^+$, $(VI)^+$ and $(VII)^+$] This is the only ligand fragmentation observed in the fully carbonylated ions, although the free $P(OMe)_3$ ligand shows several fragmentation pathways. This suggests that the process should be regarded as a phosphine to phosphide conversion, with oxidation of the metal:

$$[M^IPR_3]^+ \longrightarrow [M^{II}PR_2]^+ + R^{\bullet}$$

(*ii*) *Rearrangement, with hydrogen transfer to metal* [loss of $CH_3N{=}CH_2$ from $[(Me_2N)_3P]_2Fe^{+*}$, $(Me_2N)_3PFe^{+*}$, $[(Me_2N)_3P]_2Cr^+$, $(Me_2N)_3PCr^{+*}$, and of CH_2O from $[(MeO)_3P]_2Fe^+$, $(MeO)_3PFe^+$, $(MeO)_3PCr^+$]. This rearrangement is not observed in $(Me_2N)_3P^+$ itself, nor in any part of the parent ions. It occurs in all four of the ions ML^+ (metastable observed in three cases), in which inter-ligand transfer is impossible. We therefore regard it as a 1–4 hydrogen shift, of which there are many known examples[19]. The metal is the acceptor, *e.g.*:

$$Fe^IP(NMe_2)_3^+ \longrightarrow H{-}Fe^{III}P(NMe_2)_2^+ + CH_2{=}NCH_3$$

and its coordination number is increased by one unit. The formal oxidation number is raised by two units, since ligand hydrogen is conventionally regarded as hydridic.

A change in oxidation number of the metal in the cracking of complexes has been suggested by other workers[20]. Rearrangements in which the metal acts as an acceptor are known, but in these the formal oxidation number of the metal is unaltered [$M(C_5H_4{-}CO{-}R)^+ \longrightarrow MR^+$], or increased by one unit [$Cr(Ar{-}CO{-}R)^+ \longrightarrow CrR^+$][21]. Such rearrangements, of type $M{-}CO{-}R \longrightarrow M{-}R + CO$, are known in solution chemistry, being the reverse of the insertion reaction[22]. An increase of two in formal oxidation without rearrangement has been observed in other carbonyl phosphine cracking patterns [$Ph_2PCH_2CH_2PPh_2Mo^+ \longrightarrow Mo(PPh_2)_2^+$ (ref. 14), $Ph_2P{-}NRPPh_2W^+ \longrightarrow W(PPh_2)_2^+$ (ref. 23)]. The failure of the parent ions to undergo the rearrangement is predictable from steric and electronic considerations.

(*iii*) *Methyl loss*. This we have found with all the $P(OMe)_3$ complexes and in

---

* Asterisk indicates throughout that there is metastable evidence for the transition being described.

them only. It takes place after all CO's have been lost. It may perhaps be a metal-assisted process:

$$(M^I)^+ \cdot P(OMe)_3 \rightarrow (M^{II})^+\text{–O–}P(OMe)_2 + Me^\bullet$$

The alternatives are to formulate the product as $(M^{II})^+\text{–}P(O)(OMe)_2$ (which seems chemically unreasonable) or to place positive charge and/or unpaired spins on the ligands at some stage (in which case there is no good reason for the failure of the parent ions to show this loss).

(*iv*) *Hydrogen transfer between ligands.* While the ions $(Me_2N)_3PFe^+$ and $(Me_2N)_3PCr^+$ lose only one $CH_3N{=}CH_2$ unit, $[(Me_2N)_3P]_2Fe^+$ shows two such losses in direct succession (metastables observed), while $(Me_2N)_3PFe(CO)P(NMe_2)_2^+$ undergoes successively loss of $CH_3N{=}CH_2$*, CO and a second $CH_3N{=}CH_2$*.

$CH_3N{=}CH_2$ loss involves hydrogen transfer. It does not occur from the parent ion, from $P(NMe_2)_3^+$ itself or from $HFeP(NMe_2)_2^+$. It therefore seems unlikely that the hydrogen transfer is taking place within either a $P(NMe_2)_3$ or a $P(NMe_2)_2$ ligand. Hydrogen transfer to metal certainly operates in some cases [see (*i*) above], but here would lead to an implausible accumulation of hydrogen on a metal in high formal oxidation state. In any case, the ion of mass (Fe + 196) could not be generated in this way*.

The only remaining possibility is hydrogen transfer between ligands;

$$(Me_2N)_2P\text{–}M \cdot P(NMe_2)_3^+ \rightarrow (Me_2N)_2PH \cdot M\text{–}P(NMe_2)_2^+ + CH_2{=}NCH_3$$

This rearrangement, a 1–5 shift, can be shown from models to be sterically facile, provided the ligands can adopt the *cis*-configuration (as they readily can when all, or nearly all, the CO groups have been lost). The phosphorus atoms exchange roles; the phosphide ligand becomes a phosphine, while the phosphine ligand is converted to phosphide. The reaction may be regarded as a consequence of the high basicity of the uncoordinated lone pair of the phosphide ligand, which may be independently inferred from its readiness to act as a bridging group[24–28].

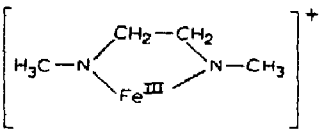
The $CH_3N{=}CH_2$ loss from $[(Me_2N)_3P]_2Fe^+$, discussed in (*ii*) above, may also be followed by loss of methylamine*. This indicates either a 1–6 shift with hydrogen transfer between ligands $[(Me_2N)_2P(N^+HMe_2) \cdot FeP(NMe_2)_2$ being formed as a minor isomer of the main product], or hydrogen transfer from metal to nitrogen in $(Me_2N)_3PFe(H)P(NMe_2)_2^+$.

Formaldehyde loss* from $(MeO)_3PCrP(OMe)_2^+$ seems a similar reaction, as is perhaps the second of the successive loss of two CH_2O groups (metastables observed) from the ion $\{[(MeO)_3P]_2Cr-CH_3\}^+$ $\{[(MeO)_3PCr-CH_3]^+$ shows one loss* of $CH_2O\}$.

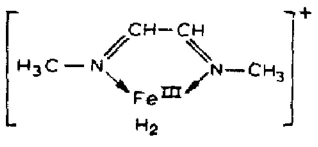
(*v*) *Other rearrangements.* An intense ion $FeN_2C_4H_{10}^+$ is formed by phosphine loss* from $HFeP(NMe_2)_2^+$. There is no analogous product with Cr, nor with the $FeP(OMe)_3$ complexes. There is also an ion of moderate abundance corresponding to $FeN_2C_4H_8^+$. The strong peak is peculiar to the $FeP(NMe_2)_3$ system. Possible structures are (A) or (B) for Fe + 86, and (C) for Fe + 84.

---

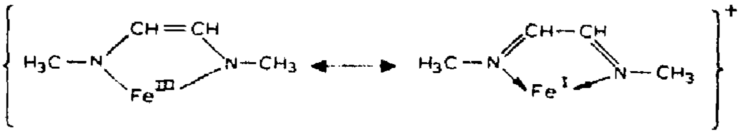
* The detailed structures of Fe + 240 and Fe + 267 would be $H_2Fe^V[P(NMe_2)_2]_2^+$ and $HFe^{IV}(CO)[P(NMe_2)_2]_2^+$. Fe + 239 would be $HFe^{IV}[P(NMe_2)_2]_2^+$, and Fe + 196 would have to be $H_2Fe^{VI}[P(NMe_2)_2]{=}PNMe_2^+$.



(A)



(B)



(C)

Rearrangements with amide transfer to metal must be responsible for the production of (Me$_2$N)$_3$PFeNMe$_2^+$, and also for its decay* to P(NMe$_2$)$_2^+$, with, presumably, loss of neutral Fe^{II}(NMe$_2$)$_2$. Similar migrations to metal of groups originally bound to phosphorus give rise to ions FeN$_2$C$_3$H$_4^+$, FeNMe$_2^+$, (Me$_2$N)$_3$PCrNMe$_2^+$, Cr(NMe$_2$)$_2^+$, CrNC$_2$H$_5^+$, (MeO)$_3$PFeOMe$^+$ {from (MeO)$_3$PFe^{+*} or [(Me$_2$N)$_3$P]$_2$FeMe^{+*}}, (Me$_2$N)$_3$PCrOMe$^+$.

These rearrangements may be compared with the migration of hydroxides to metal reported in metallocene carbinols[29].

Conclusions

The cracking pattern of both ligands is modified by complexing, and it is possible to rationalise the observations by assuming that the positive charge resides on the metal throughout, but that the valency of the metal may change. Rearrangements may occur with hydrogen transfer or transfer of larger groups to metal. The details of the cracking pattern depend on the nature of both ligand and metal.

Acknowledgements

The author wishes to thank Dr. F. J. Preston for helpful discussions.

Department of Chemistry, P. S. Braterman
University of Glasgow, Glasgow, W. 2 (Great Britain)

1 Material presented in part at *Chemical Society, Autumn Meeting*, Brighton, 1966.
2 Y. Wada and R. Kiser, *Inorg. Chem.*, 3 (1964) 174.
3 Y. Wada and R. Kiser, *J. Phys. Chem.*, 68 (1964) 2290.
4 J. Occolowitz and G. L. White, *Anal. Chem.*, 35 (1963) 1179.
5 F. W. McLafferty, *Anal. Chem.*, 28 (1956) 314.
6 A. Quayle, *Advan. Mass Spectrometry, Proc. Conf. London*, 1 (1959) 365.
7 D. A. Bafus, E. J. Gallegos and R. W. Kiser, *J. Phys. Chem.*, 70 (1966) 2614.
8 A. Foffani, S. Pignataro, B. Cantone and F. Grasso, *Z. Physik. Chem. (Frankfurt)*, 45 (1965) 79.
9 R. W. Kiser and R. E. Winters, *Inorg. Chem.*, 4 (1965) 157.
10 R. B. King, *J. Am. Chem. Soc.*, 88 (1966) 2075.
11 R. E. Winters and J. H. Collins, *J. Phys. Chem.*, 70 (1966) 2057.
12 W. F. Edgell and W. M. Risen Jr., *J. Am. Chem. Soc.*, 88 (1966) 5451.
13 B. F. G. Johnson, J. Lewis, I. G. Williams and J. M. Wilson, *J. Chem. Soc., A.*, (1967) 341.

14 J. Lewis, A. R. Manning, J. R. Miller and J. M. Wilson, *J. Chem. Soc., A.*, (1966) 1663.
15 R. B. King, *Am. Chem. Soc., 153rd meeting, Miami Beach*, 1967.
16 R. B. King, *Inorg. Chem.*, 2 (1963) 936.
17 R. Poilblanc and M. Bigorgne, *Bull. Soc. Chim. France*, (1962) 1301.
18 P. S. Braterman, W. Sim and K. Crosbie, in preparation.
19 C. Djerassi and C. Fenselau, *J. Am. Chem. Soc.*, 87 (1965) 5747, 5752.
20 C. G. Macdonald and J. S. Shannon, *Australian J. Chem.*, 19 (1966) 1545.
21 A. Mandelbaum and M. Cais, *Tetrahedron Letters*, 51 (1964) 3847.
22 R. J. Mawby, F. Basolo and R. G. Pearson, *J. Am. Chem. Soc.*, 86 (1964) 5043.
23 A. P. Walker, private communication.
24 J. Chatt and D. A. Thornton, *J. Chem. Soc.*, (1964) 1005.
25 J. Chatt and D. T. Thompson, *J. Chem. Soc.*, (1964) 2713.
26 R. G. Hayter, *J. Am. Chem. Soc.*, 86 (1964) 823.
27 R. G. Hayter, *Inorg. Chem.*, 3 (1964) 711.
28 R. G. Hayter and L. F. Williams, *Inorg. Chem.*, 3 (1964) 717.
29 H. Egger, *Monatsh. Chem.*, 97 (1966) 602.

Received May 19th, 1967; in revised form June 15th, 1967.