Iminophosphorane-substituted Proton Sponges. Part 5.[1] Structures in the Solid State. Correlation Between Solid State ^{31}P MAS NMR Spectra and Crystal Structures

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The ^{31}P NMR spectra of protonated iminophosphorane-substituted proton sponges of known crystal structure have been recorded in the solid state under the conditions of magic angle spinning (MAS) and ^{1}H-decoupling. Variable temperature experiments and a comparison with the averaged ^{31}P chemical shifts in solution show that no proton transfer occurs in the crystal, even when strong intramolecular hydrogen bonds are present. Good agreement between the NMR results and the X-ray structures gives weight to structural predictions based on solid state ^{31}P MAS NMR spectroscopy, for compounds which do not yield suitable monocrystals.

In a series of previous papers we have described the X-ray structures of iminophosphorane-substituted proton sponges derived from 1,8-diaminonaphthalene,[1-4] and from *o*-phenylenediamine,[5-7] where strong intramolecular hydrogen bonds (IMHB) are present. Since our primary research interests are the dynamics of proton exchange in crystals,[8,9] we decided to study some representative examples by ^{31}P MAS NMR spectroscopy in order to check the possible prototropic behavior.

Results and Discussion

Summary of the Crystallographic Results.—In Table 1 the crystallographic data relevant for the following discussion are gathered. After many unsuccessful attempts, the X-ray determination of the structure of the fluorene derivative **7** was abandoned since the crystals were too small and of too poor quality to determine even the space group and the cell dimensions.

The relevant information of ^{31}P chemical shifts in solution and the results of the MAS experiments are summarized in Table 2.

^{31}P Chemical Shifts in the Solid State.—The iminophosphorane fragments of compounds **1**–**12** give rise to signals in the ^{31}P NMR spectra from which relevant information concerning the hydrogen bonds can be obtained. Compounds **2**, **4**, **6** and **7** also contribute with a signal arising from the counter anions PF_6^- which will be discussed later. Naphthalene derivatives **1** and **2**, both showing intramolecular hydrogen bonds in the X-ray structure and differing only in the anions, present two signals at 13.8 and 10.6 ppm and 23.5 and 20.3 ppm, assigned to the neutral (Ph_3PN) and protonated (Ph_3PNH^+) iminophosphorane fragments, respectively. We will comment later on the effect of the counter anions. Benzene derivatives **3** and **4**, which differ not only in the nature of the anion but also in that of the hydrogen bond, intermolecular for **3** and intramolecular for **4** (see Table 1), show also the signals for the neutral fragment, 13.8 and 9.4 ppm, and those of the cation, 33.1 ppm, in both cases. An unexpected third ^{31}P signal at 25.7 ppm is also observed in the solid state NMR spectrum of compound **3**, which cannot be due to an impurity since the crystals used in the X-ray study were also used for the MAS NMR study. (Lines at 33.1 and 13.8 ppm are of similar intensities, but due to possible differences in the T_1 relaxation times those intensities cannot be used to estimate the populations.)

The reason why compound **3** presents two signals at 25.7 and 33.1 ppm in the Ph_3PNH^+ spectral range could not be determined. Three hypotheses were examined and ruled out: (i) the splitting, ~900 Hz ($\Delta\delta = 7.4$ ppm) is caused by a dipolar coupling to the quadrupolar ^{14}N nucleus; (ii) the existence in the crystal of two different types of hydrogen bonds; and (iii) the simultaneous obtention of two types of crystals in the crystallization process. The first explanation can be ruled out since the calculated splitting should be ~160 Hz.† The possible existence in the unit cell of two kinds of molecules, one with the proton intramolecularly bonded to the other N atom, as in compound **4**, and responsible for the signal at 33.1 ppm, and the other with the proton intermolecularly bonded to the Br^- anion, signal at 25.7 ppm, which is the situation found by X-ray analysis, is also inconsistent. The structure refined exceedingly well ($R = 0.033$),[6] and even assuming that the N–H···N proton could have been lost, the geometrical disposition of the iminophosphorane groups rules out such possibility. Finally, the crystallization crop was carefully examined under the microscope, and although all the individual crystals appeared very similar, a dozen of them (those most different in aspect) were mounted in the diffractometer and proved to be identical.

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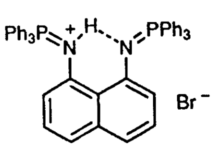
† According to Olivieri *et al.*,[11] the maximum quadrupolar line splitting is given by D_χ/Z_N, where D is the dipolar coupling constant of the $\frac{1}{2}$ spin nucleus (for ^{31}P, $D = 3510/r^3$, where $r = 1.6$ Å is the P–N distance), χ is the quadrupolar coupling constant (here chosen to be 4 MHz as maximum value) and Z_N is the Larmor frequency of ^{14}N ($Z_N = 21.6$ MHz at 7 T). With these data, we obtain a maximum splitting of ~160 Hz.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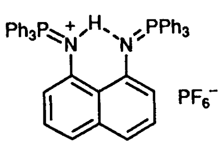
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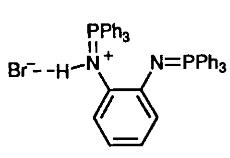
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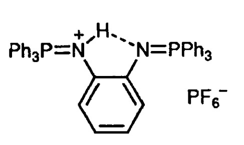
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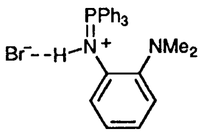
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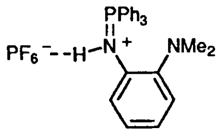
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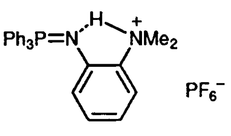
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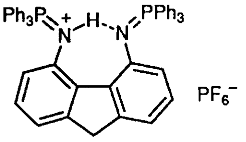
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Table 1 Summary of crystallographic data pertaining to compounds **1**–**6**

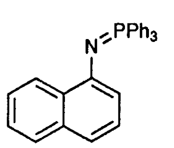
Compound	N-H/Å	N···N/Å	H···N/Å	N-H···N/°	N=P[a]/°	N$^+$=P[a]/°	PF$_6^-$
1	0.85(8)	2.584(4)	1.78(8)	159(9)	−65.5(2)	−37.8(2)	—[b]
2	0.83(5)	2.606(4)	1.90(5)	143(5)	−44.3(2)	−57.9(2)	Ordered
3	0.74(6)	2.794(4)	—[c]	—[c]	71.8(2)	−48.0(2)	—[b]
4	0.88(2)	2.584(3)	2.05(3)	118(3)	63.9(1)	−46.4(1)	Ordered
5	0.81(4)	2.810(3)	—[c]	—[c]	—[e]	43.8(1)	—[b]
6a[d]	0.87(5)	2.746(5)	—[c]	—[c]	—[e]	126.7(2)	Disordered
6b[d]	0.88(5)	2.627(5)	2.10(4)	120(3)	68.8(2)	—[f]	Disordered

[a] The average twist of the PPh$_3$ fragment with respect to the C–N bond. [b] These compounds are bromides. [c] No IMHB. [d] Two independent molecules, **6a** and **6b** in the asymmetric unit. [e] No neutral N=PPh$_3$ present in these molecules. [f] No cationic NH$^+$=PPh$_3$ group present in this molecule.

Table 2 ^{31}P Chemical shifts of iminophosphoranes **1**–**13**[a]

Compound	Anion	Solvent	δ_P	δ(Solid state)
1	Br$^-$	CDCl$_3$	20.57	13.8, 23.5
2	PF$_6^-$	CDCl$_3$	20.45	10.6, 20.3
3	Br$^-$	CDCl$_3$	22.26	13.8, 25.7, 33.1[d]
4	PF$_6^-$	CDCl$_3$	22.15	9.4, 33.1
5	Br$^-$	CDCl$_3$	26.38	34.5
6	PF$_6^-$	CDCl$_3$	27.08	7.2, 37.1
7	PF$_6^-$	CDCl$_3$	24.41	10.2, 12.8[c], 15.9, 24.6, 28.2, 30.9[c]
8	—	CDCl$_3$	3.68	
9	BF$_4^-$	CDCl$_3$	37.08	
10	PF$_6^-$	CDCl$_3$	24.52	
11	—	CDCl$_3$[d]	3.73	
12	BF$_4^-$	CDCl$_3$	33.13	

[a] External references, solution 85% H$_3$PO$_4$; solid (NH$_4$)$_2$HPO$_4$ {δ_P[85% H$_3$PO$_4$] = δ_P[(NH$_4$)$_2$HPO$_4$] + 1.6}. [b] Relative intensities 1:2:1. [c] These signals are twice as intense as the two others. [d] From ref. 10.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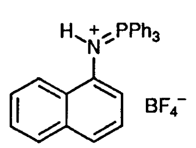
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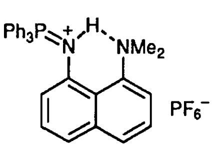
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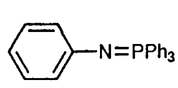
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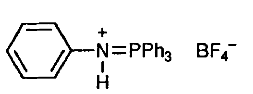
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It might be that during the grinding process used to prepare the sample for the NMR experiments, a chemical reaction occurs which partly transforms the structure of compound **3** into a structure similar to that of compound **4** (but that will not only imply a proton transfer but also a spatial reorganization of one of the N=PPh$_3$ groups which is highly unlikely).

Compound **5** having only a protonated iminophosphorane group shows a signal at 34.5 ppm. Compound **6** clearly illustrates the usefulness of solid state NMR for confirming X-ray structures. According to the crystallographic results,[5] there are two species present in the crystal: **6a** protonated on the iminophosphorane and **6b** protonated on the dimethylamino group. In the ^{31}P MAS NMR spectrum these two species can be clearly identified: **6a** with a ^{31}P chemical shift of 37.1 ppm and **6b** which gives a ^{31}P signal at 7.2 ppm, showing again the complementary relationship of these two techniques.

A more complicated case arises in the fluorene derivative **7** where suitable monocrystals cannot be obtained, although the compound is crystalline since it gives a diffraction pattern. At room temperature, there are three signals for each iminophosphorane group: δ_P 10.2, 12.8 and 15.9 for the neutral part and δ_P 24.6, 28.2 and 30.9 for the cation (Fig. 1). This result leads to the assumption that three different species

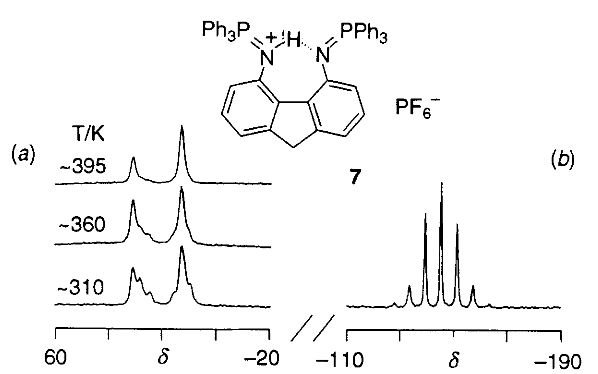


Fig. 1 Variable temperature ^{31}P MAS NMR spectra of compound **7**, 4 μs ^{31}P 90° pulses, 50 kHz sweep width, 5 s recycle delay, ^{1}H decoupling during acquisition. (*a*) Signals of the iminophosphorane fragments at different temperatures. (*b*) Signal of the counterion PF_6^-

Table 3 Estimated ^{31}P chemical shifts of neutral and protonated iminophosphorane fragments in $CDCl_3$ solution and experimental ^{31}P chemical shifts in the solid state (both in ppm and referred to H_3PO_4 85%)

	Naphthalene		Benzene	
	Neutral	Cation	Neutral	Cation
Solution	3.7	37.1	7.5	36.9
Solid[a]				
1	15.4 (11.7)	25.1 (−12.0)	—	—
2	12.2 (8.5)	21.9 (−15.2)	—	—
3	—	—	15.4 (7.9)	34.7 (−2.2)
4	—	—	11.0 (3.5)	34.7 (−2.2)
5	—	—	—	36.1 (−0.8)
6a	—	—	—	38.7 (1.8)
6b	—	—	8.8 (1.3)	—

[a] In brackets $\Delta\delta_P$ values = δ_P (solid) − δ_P (solution).

Table 4 Geometrical characteristics of the IMHB (in Å, from Table 1) and $\Delta\delta_P$ effects (in ppm, from Table 3)

	Neutral		Cation	
Compound	H···N	$\Delta\delta_P$	N–H	$\Delta\delta_P$
1	1.78	11.7	0.85	−12.0
2	1.90	8.5	0.83	−15.2
4	2.05	3.5	0.88	−2.2

could be present in the solid in different sites, differing in the nature of the hydrogen bond network and/or in the conformation of the iminophosphorane fragments. As temperature is increased, the lines at 10.2, 15.9, 24.6 and 28.2 ppm broaden (Fig. 1). A complete coalescence was not reached at 395 K. The lines at 12.8 and 30.9 are not altered substantially. These results indicate a moderately slow exchange of the species whose lines broaden. The nature of this process could not be clarified in this study. It could involve site exchange or conformational exchange, possibly coupled with proton transfer.

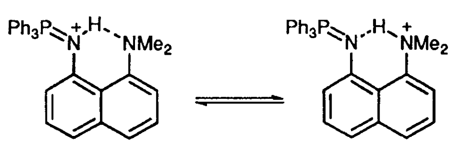
Finally, it is interesting to note that the hexafluorophosphate anion of compounds **2**, **4**, **6** and **7** [Fig. 1(*b*)] shows a septuplet centred at −145.5 ppm with a scalar coupling constant of $^{1}J(^{19}F-^{31}P)$ = 730 Hz, which may be indicative of a high isotropic mobility, probably rotation, just like in solution (δ_P = −145, ^{1}J = 706–770 Hz).[12,13] The nature, ordered (**2**, **4**) or disordered **6** of hexafluorophosphate (Table 1) has no influence on its appearance in ^{31}P MAS NMR (this problem has been studied in the solid state by ^{19}F and ^{31}P variable-temperature NMR,[14] and the authors conclude to a random reorientation of the PF_6^- octahedron).

^{31}P *Chemical Shifts in Solution.*—The results reported in Table 2 for the ^{31}P NMR spectra in $CDCl_3$ solution can now be discussed. A first observation is that the anion has no effect: **1** and **2** (average value, 20.5 ppm); **3** and **4** (average value, 22.2 ppm); and **5** and **6** (average value, 26.7 ppm).

The question now arises as to whether information concerning the nature of the hydrogen bonds in the iminophosphorane sponges can be obtained from the chemical shifts listed in Table 2. Assuming that the proton transfer in the sponges can be described as an equilibrium between two tautomers, the averaged chemical shift can be expressed as eqn. 1 where x_a and

$$\delta = x_a\delta_a + x_b\delta_b \qquad (1)$$

x_b represent the mole fractions of the fragments Ph_3PN and Ph_3PNH^+ and δ_a and δ_b, the corresponding intrinsic chemical shifts. They can be approximated in the naphthalene series from those of model compounds **8** and **9**. Setting $x_a = x_b = 0.5$ we obtain from eqn. (1) a calculated value of δ = 20.4 which is in good agreement with the experimental value of 20.5 ppm found for **1** and **2**. In the case of **10** we can reproduce the experimental chemical shift value of 24.5 ppm by setting $x_a = 0.62$ and $x_b = 0.38$. This result is consistent with an independent estimation based on pK_a measurements (58 ± 2% of protonation on the iminophosphorane)[4] and with the greater basicity of $N{=}PPh_3$ with regard to NMe_2.[4]



10a **10b**

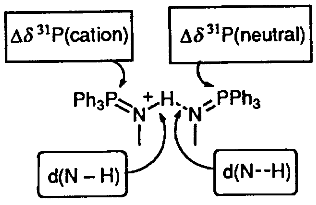
In the benzene series, we calculated from eqn. (1), using the chemical shifts from **11** and **12** as intrinsic values, the average chemical shift of 18.4 ppm for the symmetric molecules **3** and **4**, whereas the value of 22.2 ppm is found experimentally. We assign the difference of 3.8 ppm to a proximity effect and used it as a correction factor for the interpretation of the chemical shifts of **5** and **6**, *i.e.* we set $\delta_a = \delta\mathbf{11} + 3.8$ and $\delta_b = \delta\mathbf{12} + 3.8$ in eqn. (1). With these values we reproduced the chemical shifts of **5** and **6** assuming that $x_a = 0.65$ and $x_b = 0.35$, *i.e.* the proton is preferentially located on the iminophosphorane fragment and only to a minor extent on the dimethylamino group.

All these results indicate that we have obtained evidence that the tautomerism of the iminophosphorane sponges can be described in terms of an equilibrium between two tautomers rather than with a proton motion in a single minimum potential.

Comparison of the ^{31}P *Chemical Shifts in Solution and in the Solid State.*—We have gathered in Table 3 the values we have previously discussed.

It appears that $\Delta\delta_P$ values are much larger for naphthalenes than for benzenes. A reasonable assumption is that $\Delta\delta_P$ is related to the strength of the hydrogen bond. We have three compounds **1**, **2** and **4**, for which we have determined by X-ray crystallography the N–H and H···N distances of the IMHB (Table 1) and calculated the $\Delta\delta_P$ increments, these data being reported in Table 4.

Not only is there a regular variation in the sense that the stronger the IMHB, (the shorter the N···H distance and the longer the N–H distance) the larger the $\Delta\delta_P$ value of the



IMHB

neutral part and the weaker the $\Delta\delta_P$ of the cation, but also a linear relationship exists between these values.

$$\text{Neutral: } \Delta\delta_P(\text{ppm}) = 66.1 \text{ ppm } -30.5d(\text{N}\cdots\text{H/Å}) \quad r^2 = 0.996 \quad (2)$$

$$\text{Cation: } \Delta\delta_P(\text{ppm}) = -243.3 \text{ ppm } + 263.2d(\text{N–H/Å}) \quad r^2 = 0.97 \quad (3)$$

To confirm that the strength of the IMHB affects the ^{31}P chemical shifts of the neutral and cationic iminophosphorane fragments in the direction we have assumed (these IMHBs make the neutral part to resemble the cation and the cationic part to resemble the neutral moiety) the ^{31}P NMR spectra of compounds **11** and **12** were recorded in three solvents with different acidities: $CDCl_3$ (Table 2), CH_3OH (11.80 and 34.04 ppm, respectively) and CF_3CH_2OH (28.72 and 35.46 ppm, respectively). These values show that an intermolecular hydrogen bond with the solvent shifts the ^{31}P signals to higher frequencies (in the case of trifluoroethanol, the very large effect corresponds probably to partial protonation) and that these shifts are not due to solvent effects since the cation is only slightly affected.

The absence of proton transfer in compound **1** where there is a very strong IMHB (see Table 4) may be related to the different conformations of the protonated and neutral iminophosphoranes in the crystal (see Table 1 under N=P and $N^+ = P$): if these conformations correspond to the energy minimum, then the transfer of the proton would involve the reorientation of the $NPPh_3$ groups, which is not possible in the crystal since the rotations would involve contacts between phenyl groups.

Experimental

All compounds have been described in previous papers.[1–7]

^{31}P *NMR solution spectroscopy*. The spectra were recorded on a Varian Unity 300 spectrometer (U. Murcia) working at 121.42 MHz, using an external reference 85% H_3PO_4 in water. The ^{31}P MAS NMR spectra were recorded with a Bruker MSL300 spectrometer (F.U. Berlin) working at 121.49 MHz for ^{31}P and 300.13 MHz for ^{1}H. The spectrometer was equipped with a 5 mm high speed CPMAS probehead from Doty-Scientific, Columbia, USA. Recording conditions on all spectra: no cross polarization (CP), ^{1}H 90° pulses of 4 μs, ^{1}H decoupling during acquisition, recycle delays of 5 s, rotation frequencies of 8.5 kHz. A Bruker B VT 1000 temperature unit was used to control the temperature of the bearing nitrogen gas stream. Line widths of 100–200 Hz were observed due to the coupling with the quadrupolar ^{14}N atom, which cannot be resolved at this field (7 T).

^{31}P *NMR solid state spectroscopy*. All solid state ^{31}P chemical shifts are given related to external $(NH_4)_2HPO_4$. Conversion from δ values related to $(NH_4)_2HPO_4$ to δ values related to 85% H_3PO_4 is given in Table 2. To determine this conversion, solid $(NH_4)_2HPO_4$ and liquid H_3PO_4 contained in a sealed capsule were measured under the same MAS conditions.

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References

1 Part 4. J. Laynez, M. Menéndez, J. L. Saiz, A. L. Llamas-Saiz, C. Foces-Foces, J. Elguero, P. Molina, M. Alajarín and A. Vidal, *J. Chem. Soc., Perkin Trans. 2*, 1993, 709.

2 A. L. Llamas-Saiz, C. Foces-Foces, P. Molina, M. Alajarín, A. Vidal, R. M. Claramunt and J. Elguero, *J. Chem. Soc., Perkin Trans. 2*, 1991, 1025.

3 A. L. Llamas-Saiz, C. Foces-Foces, J. Elguero, P. Molina, M. Alajarín and A. Vidal, *J. Chem. Soc., Perkin Trans. 2*, 1991, 1667.

4 A. L. Llamas-Saiz, C. Foces-Foces, J. Elguero, P. Molina, M. Alajarín and A. Vidal, *J. Chem. Soc., Perkin Trans. 2*, 1991, 2033.

5 A. L. Llamas-Saiz, C. Foces-Foces, J. Elguero, P. Molina, M. Alajarín and A. Vidal, *Acta Crystallogr., Sect. C*, 1992, **48**, 1940.

6 A. L. Llamas-Saiz, C. Foces-Foces, J. Elguero, P. Molina, M. Alajarín and A. Vidal, *Acta Chem. Hung., Models in Chemistry*, 1993, **130**, 467.

7 A. L. Llamas-Saiz and C. Foces-Foces, *Acta Crystallogr., Sect. C*, 1994, **50**, in the press.

8 J. A. S. Smith, B. Wehrle, F. Aguilar-Parrilla, H. H. Limbach, C. Foces-Foces, F. H. Cano, J. Elguero, A. Baldy, M. Pierrot, M. M. T. Khursid and J. B. Larcombe-McDouall, *J. Am. Chem. Soc.*, 1989, **111**, 7304.

9 F. Aguilar-Parrilla, G. Scherer, H. H. Limbach, C. Foces-Foces, F. H. Cano, J. A. S. Smith, C. Toiron and J. Elguero, *J. Am. Chem. Soc.*, 1992, **114**, 9657.

10 M. Pomerantz, B. T. Ziemnika, Z. M. Merchant, W. N. Chou, W. B. Perkins and S. Biiner, *J. Org. Chem.*, 1985, **50**, 1757; W. N. Chou and M. Pomerantz, *J. Org. Chem.*, 1991, **56**, 2762.

11 A. C. Olivieri, L. Frydman and L. E. Díaz, *J. Magn. Reson.*, 1987, **75**, 50.

12 G. Mavel, NMR Studies of Phosphorus Compounds, in *Annu. Rep. NMR Spectrosc.*, Ed. E. F. Mooney, Academic, London, 1973, vol. **5B**, pp. 23 and 99.

13 V. Wray, Fluorine-19 NMR Spectroscopy, in *Annu. Rep. NMR Spectrosc.*, Ed. G. A. Webb, Academic, London, 1983, vol. **14**, p. 347.

14 T. Rojo, M. I. Arriortua, J. Ruiz, J. Darriet, G. Villeneuve and D. Beltran-Porter, *J. Chem. Soc., Dalton Trans.*, 1987, 285.

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