Niobium–phosphorus coupling constants

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Abstract

Magic-angle spinning ^{31}P NMR spectra of solid niobium half-sandwich compounds are shown to yield values of $(^{93}$Nb, ^{31}P) coupling constants not accessible from solution-state spectra, and also to provide more accurate values of chemical shifts. Results are reported and discussed for eight compounds and the general value of NMR spectra of solids for these and similar cases is emphasized.

Key words: Niobium; Phosphorus; Coupling; Nuclear magnetic resonance; Magic-angle spinning

1. Introduction

There has been considerable interest recently in the chemistry of half-sandwich complexes containing multiply-bonded alkylimido ligands. Convenient synthetic entries have been established into niobium systems [1,2], and these routes have been exploited to develop an extensive derivative chemistry [2–5]. Traditionally, structural characterization has been carried out by X-ray crystallography, when suitable single crystals are available, and by solution-state NMR spectroscopy. However, two problems arise: (a) there may be structural changes between solid and solution, and (b) niobium-93 (in common with many transition-metal nuclei) is quadrupolar, so that in the solution state it relaxes rapidly and is self-decoupled from nearby spin-$\frac{1}{2}$ nuclei such as ^{31}P. Solid-state phosphorus-31 NMR, using the magic-angle spinning (MAS) technique, can overcome both problems. In the first place, it can act as a bridge between solid-state (X-ray) and solution-state (NMR) measurements. Secondly, the relaxation rate of a central metal such as ^{93}Nb is slowed in the

solid state, so that, for example, splittings arising from $(^{93}$Nb, ^{31}P) coupling become visible in the ^{31}P spectra.

The aim behind the work reported here is to derive data for $(^{93}$Nb, ^{31}P) coupling constants in a number of half-sandwich niobium compounds containing a single phosphine ligand, and to establish how they may be related to chemical structure.

Since ^{93}Nb has a spin quantum number $I = \frac{9}{2}$ and is present at 100% natural abundance, the ^{31}P spectra (ignoring other types of nuclei) should consist of simple decets, the lines all being of equal intensity and equally spaced. The spacings should be a direct measure of $|J_{NbP}|$. There is, however, complication in obtaining accurate values of J_{NbP}, which occurs because frequently the quadrupole coupling constant of the niobium nucleus is sufficiently high that it becomes significant with respect to the Zeeman interaction. In such circumstances, a first-order approach to simulation of the spectra (which is necessary to predict simple decet splitting) is inadequate. Second-order terms become of importance, and the effects of these are transferred from the quadrupolar nucleus $(^{93}$Nb) to the spectrum of the spin-$\frac{1}{2}$ nucleus $(^{31}$P) via the dipolar interaction — giving rise to a phenomenon usually called residual dipolar splitting. Since the second-order terms do not have the simple $(3 \cos^2\theta - 1)$ geometric factors associated with magic-angle spinning, they cannot be entirely

TABLE 1. Solid-state NMR data for the half-sandwich niobium complexes

	Compound [a]	δ_P/ppm	$|J_{NbP}|$/Hz	Oxidation state	Synthesis reference
1a	CpNb(NMe)Cl$_2$(PMe$_3$)	7.7	490	V	1,2
1b	CpNb(NMe)Cl$_2$(PMePh$_2$)	12.3	476	V	1,2
1c	CpNb(NMe)Cl$_2$(PPh$_3$)	32.7	446	V	1,2
2a	CpNb(N^{t}Bu)Cl$_2$(PMe$_3$)	5.0	508	V	2
2b	CpNb(NAr)Cl$_2$(PMe$_3$)	7.7	471	V	1,2
3	Cp*Nb(NMe)Cl$_2$(PMe$_3$)	3.1	523	V	2
4	Cp*Nb(NAr)(CO)(PMe$_3$)	10.1	913	III	3
5	Cp*Nb(NAr)(PhC $\equiv$ CPh)(PMe$_3$)	11.7	696	III	3
6	Cp*Nb(NAr)(H)$_2$(PMe$_3$)	ca. −5	ca. 260	V	3
7	Cp*NbCl$_2$(CO)$_2$(PMe$_3$)	ca. −16	ca. 240	III	8

[a] Ar $\equiv$ 2,6-Pr$_2^i$C$_6$H$_3$; Cp* $\equiv$ C$_5$Me$_5$.

eliminated by MAS, though they are averaged to a certain extent. Such effects have recently been reviewed [6].

Fortunately, in the case of ^{93}Nb it would appear that, for the magnetic field used in the present work (7.4 T), the controlling ratio, K = $| \chi_{Nb}/4S(2S - 1)\nu_{Nb} |$ (where χ_{Nb} and ν_{Nb} are the quadrupole coupling constant and Zeeman frequency of niobium respectively),

is sufficiently low that perturbation theory can be applied to the problem. Then, although the splittings in the ^{31}P spectra become unequal, their average remains precisely equal to the (Nb, P) coupling constant in magnitude. Strictly speaking, this has only been proved when the quadrupolar and indirect (J) coupling tensors are axially symmetrical and are both coaxial with the Nb,P internuclear vector, but significant errors in
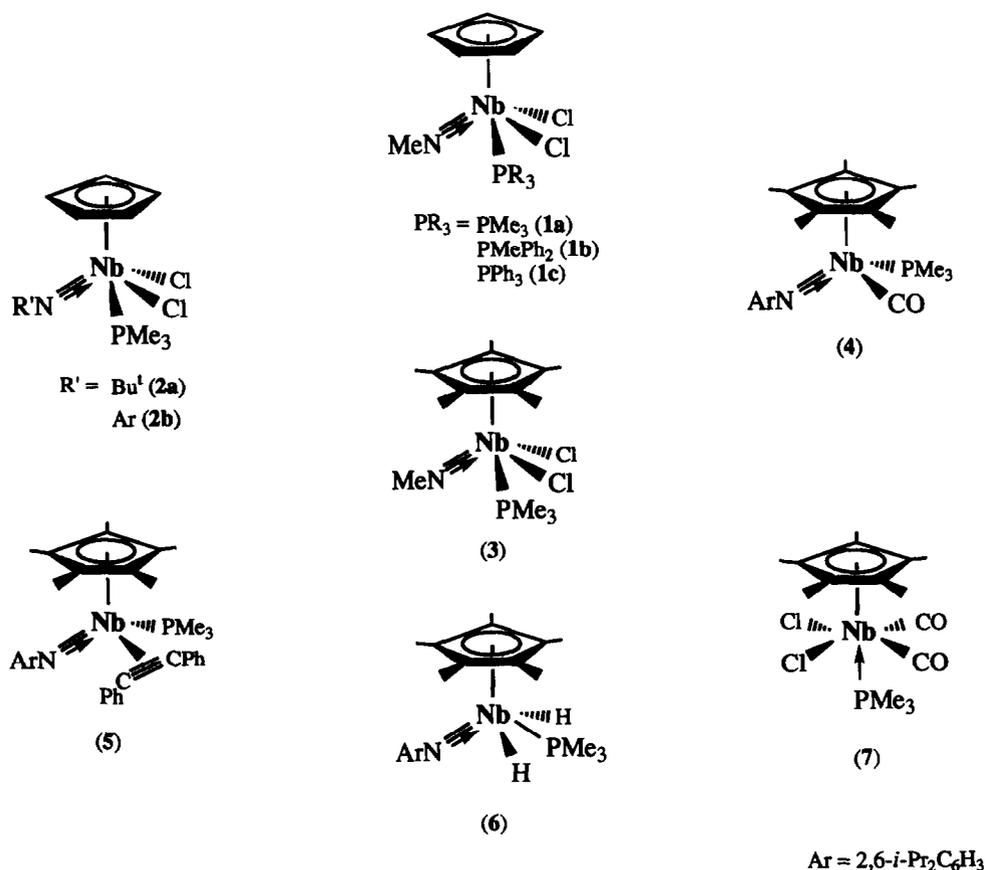

Fig. 1. Molecular structures of the compounds examined.

measurement of J are not expected if there are departures from these criteria.

We have illustrated [7] the application of the spectral analysis methods outlined above for several complexes of transition metals involving phosphine ligands, including one compound of niobium, so the technique itself will not be described in detail here.

2. Results and discussion

The ten compounds examined are listed in Table 1, with the structures illustrated in Fig. 1. Seven of them involve niobium in its highest (+V) oxidation state, whereas three are in oxidation state +III. Solution-state ^{31}P NMR spectra are difficult to obtain and are relatively uninformative. A typical example is illustrated in Fig. 2a, which shows that no splittings arising from (Nb, P) coupling are visible, and even the ^{31}P chemical shift cannot be obtained with any accuracy, since the resonance band is ca. 70 ppm in width at half height. By contrast, the ^{31}P MAS spectrum of the solid (Fig. 2b) contains relatively sharp lines clearly forming a simple decet with apparently equal spacings. Of the compounds examined, the one (4) referred to in Fig. 2 has the lowest quadrupole coupling constant, therefore giving the sharpest lines, with the most equal spacings. In consequence, the ^{31}P chemical shift and the value of $|J_{NbP}|$ are the most accurately measured. In contrast, the spectra of two compounds (6 and 7) contain an anomalous distribution of linewidths for which no convincing explanation is yet available, and consequently the NMR parameters are least well-defined. A more typical ^{31}P spectrum is that for compound 1b, illustrated in Fig. 3, where the modest nature of both linewidths and splitting asymmetry can be seen. The asymmetry is a consequence of the transferred second-order quadrupolar effects mentioned in the Introduction.

The splitting patterns were analysed using the perturbation theory approach outlined in ref. [6] and used in ref. [7], though it should be noted that certain assumptions are made which are unlikely to be strictly valid for the cases discussed here (this is not expected to affect the reported derived parameters significantly). The results for the ^{31}P chemical shifts and (^{93}Nb, ^{31}P) coupling constants are given in Table 1. Both are clearly sensitive to the chemical structure of the compounds. Replacement of methyl groups by phenyl in molecules of type 1 causes deshielding, as expected, and also leads to a small but significant decrease in $|J_{NbP}|$. A wider variation in both shifts and couplings is apparent for the remaining systems. The niobium–phosphorus coupling constants range from ca. 240 to 913 Hz, which shows this parameter to have potential
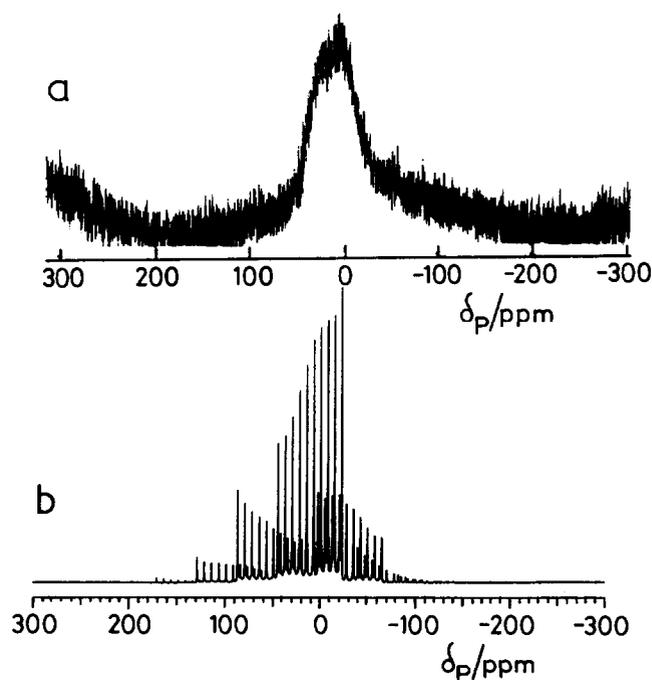

Fig. 2. Phosphorus-31 NMR spectra of $Cp^*Nb(NAr)(CO)(PMe_3)(4)$: (a) In solution in C_6D_6, at 100 MHz; (b) in the solid state, at 121.4 MHz. The ten central lines in (b) represent isotropic transitions. The remaining lines are spinning sidebands.

value for structural correlations. The formal oxidation state of niobium is not a dominant influence — indeed, the smallest and largest values of $|J_{NbP}|$ occur for two of the compounds of O.S. III. Clearly more work is needed to establish useful relations to structure, but there is little doubt that $|J_{NbP}|$ can be chemically useful, nor that this requires NMR spectra of solids.

Spin–spin coupling from other quadrupolar metals to phosphorus can be evaluated similarly, and Table 2 gives a few examples (not an exhaustive list) for comparison. Obviously there are substantial variations, but all the values are hundreds of Hz (ranging up to nearly 2 kHz in the case of copper) and are chemically significant, underlining the value of solid-state (MAS) NMR as compared to more-traditional solution-state work. However, in some cases (see, for example, ref. [17]), splittings arising from (metal, phosphorus) coupling can be observed in solution-state spectra, both of ^{31}P and of the metal.

3. Experimental section

3.1. Nuclear magnetic resonance

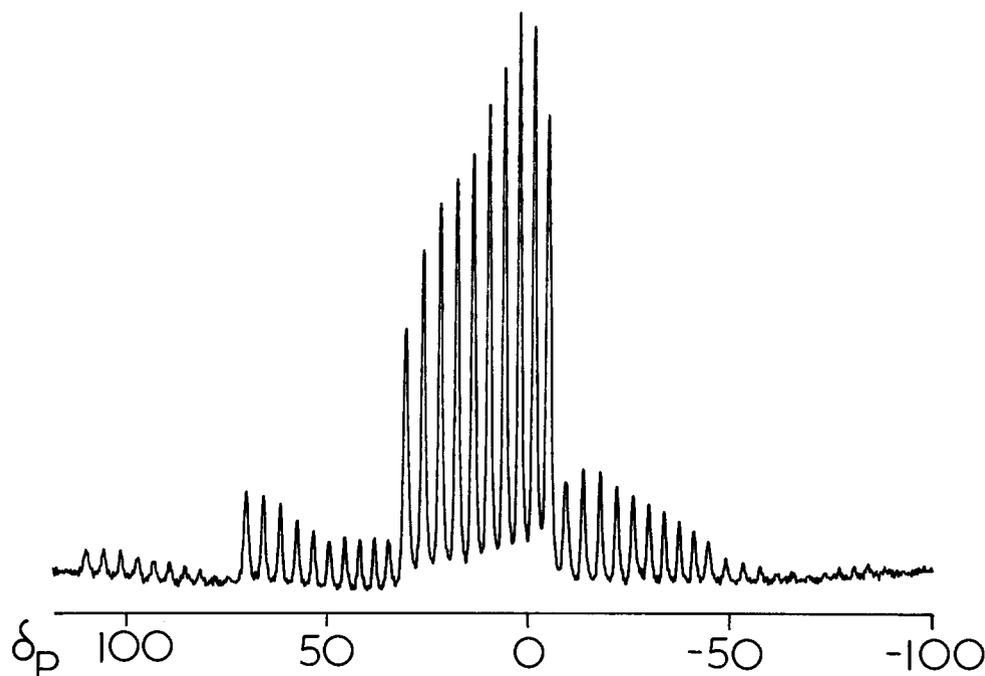Phosphorus-31 NMR spectra were obtained at 121.4 MHz using a Varian VXR 300 spectrometer at ambi-

Fig. 3. 121.4 MHz ^{31}P CPMAS spectrum of CpNb(NMe)Cl$_2$(PMePh$_2$)(**1b**): The ten central lines are isotropic transitions, the remaining peaks being spinning sidebands. The unequal spacings of the decet arise from transferred second-order quadrupolar effects [7]. The intensity variations are produced by the interplay of dipolar, indirect coupling and shielding tensors [7]. Spectrometer conditions: contact time 2.5 ms; recycle delay 1.0 s; number of transients 600; spinning rate 4.82 kHz.

ent probe temperature under conditions of ^{1}H → ^{31}P cross-polarization, high-power proton decoupling and magic-angle spinning. Contact times varied from 1 to 8

ms, the recycle delay was 1 s (except in the case of **6** where it was 2 s), and between 500 and 3000 transients were acquired for each spectrum. A Doty 7 mm o.d.

TABLE 2. Some metal–phosphorus coupling constants obtained by MAS NMR

Compound	Coupling	$|J_{iso}|$/Hz	Literature reference
Me$_3$P-AlCl$_3$/zeolite	^{27}Al, ^{31}P	300	9
Mn$_2$(CO)$_9$PPh$_3$	^{55}Mn, ^{31}P	297	7
Mn$_2$(CO)$_8$(PPh$_3$)$_2$		335 [a]	7
(OC)$_4$BrMnPPh$_2$R [b]		197 to 210	10
(OC)$_4$MnPPh$_2$(CH$_2$)$_n$SO$_2$ [c]		206 to 214	10
Co$_4$(CO)$_{11}$PPh$_3$	^{59}Co, ^{31}P	425	7
Co$_2$(CO)$_6$(PPh$_3$)$_2$		324 [a]	7
HFeCo$_3$(CO)$_{11}$PPh$_3$		472	7
Co$_4$(CO)$_8$(C$_2$H$_2$)(PPh$_3$)$_2$		522 [a]	7
(Ph$_3$P)$_2$CuNO$_3$	^{63}Cu, ^{31}P	1450	11
[Cu$_2$(^{t}BuHPCH$_2$PH^{t}Bu)$_3$]$^{2+}$2BF$_4^-$		956	12
Cu(PPh$_3$)$_2$X [d,e]		1160 to 1440	13
Cu(PPh$_3$)$_3$X [d,e]		890 to 980	14
[L$_n$CuX]$_m$ [d,f]		1358 to 1865	15
Cp(OC)$_2$MoPPh$_2$(CH$_2$)$_m$	$^{95/97}$Mo, ^{31}P	190 (m = 3)	10
		157 (m = 4)	
all-trans-Ru(PEt$_3$)$_2$(CO)$_2$(C ≡ CPh)$_2$	^{99}Ru, ^{31}P	104	16
(μ-H)Ru$_4$(CO)$_{10}$(μ-PPh$_2$)[μ_4-PPh(C$_6$H$_4$)] [g]		129 and 159	16

[a] Average for different ^{31}P sites; [b] R = Et, Pr, Bu, Pe; [c] n = 2,3,4; [d] X = halide. [e] There are a number of other papers by Healy and co-workers giving (Cu, P) coupling constants derived from solid-state MAS ^{31}P NMR. [f] L = 1-phenyl-3,4-dimethylphosphole or 1-phenyldibenzophosphole. [g] Data for the PPh$_2$ group (two nonequivalent sites).

MAS probe was employed with spinning rates between 4.8 and 5.3 kHz. Phosphorus chemical shifts are quoted relative to the signal from aqueous (85%) phosphoric acid, using the high-frequency-positive convention. They were actually measured using a sample of brushite ($\delta_P = 1.1$ ppm) by replacement. The second-order quadrupolar effects were analysed according to ref. [7] to yield isotropic chemical shifts and coupling constants. The compounds are air- and moisture-sensitive, so it was necessary to use airtight inserts in the MAS rotors, as described previously [18]. The solution-state ^{31}P spectrum shown in Fig. 2a was obtained using a Bruker AC250 spectrometer. Carbon-13 CPMAS spectra at 75.43 MHz were also obtained for all the compounds. They served to confirm the molecular structures but were otherwise unremarkable.

3.2. Half-sandwich niobium imido complexes

Preparations of compounds **1a, 2a,b** and **3** have been reported [2]. The syntheses of compounds **4–7** have been outlined in preliminary reports [3,5,8] and full accounts will be published elsewhere. Compounds **1b** and **1c** were prepared by a procedure analogous to that used for **1a** [1,2].

Acknowledgments

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