High-Resolution Solid-State Phosphorus-31 Nuclear Magnetic Resonance of Some Triphenylphosphine Transition-Metal Complexes

Sir:

Triphenylphosphine is a widely used ligand in coordination chemistry. ^{31}P NMR of its complexes in solution has become a standard technique. To our knowledge high-resolution solid-state ^{31}P NMR spectra of phosphine-metal complexes have not been reported in the literature. Employing high-resolution solid-state NMR techniques, so far mainly used for ^{13}C spectroscopy but also for ^{31}P NMR in biological membranes,[1] in phosphates,[2] and in polyphosphates,[3] we were able to obtain high-resolution ^{31}P NMR spectra of triphenylphosphine-metal complexes. Some representative spectra are shown in Figures 1-4.

All spectra are obtained by combining proton dipolar decoupling, magic angle spinning, and ^{1}H-^{31}P cross polarization. ^{1}H-^{31}P cross polarization greatly enhances the sensitivity over conventional ^{31}P NMR (i.e., using ^{31}P 90° pulses), since the repetition rate in the proton-enhanced experiment is governed by the proton spin-lattice relaxation time (1-5 s) instead of the ^{31}P spin-lattice relaxation time (several minutes for the solid compounds studied here).

The spectrometer is home built, operating at 72.862 MHz for ^{31}P and 180 MHz for protons. The magic angle spinner will be described elsewhere.[4]

Wilkinson's catalyst, $RhCl(PPh_3)_3$, has in first approximation a square-planar coordination around the Rh atom, but there is a definite distortion toward tetrahedral geometry.[5] The unit cell has four, crystallographically equivalent molecules.[5] The total spectrum of $RhCl(PPh_3)_3$ shows a large number of spinning sidebands, spanning about 30 kHz. Figure 1 shows only the center bands; the spinning sidebands are merely replicas of the center bands. The large number of sidebands, however, demonstrate the existence of a large ^{31}P chemical shift anisotropy.

The low-field doublet, $\delta = +50.2$,[6] results from the coupling of the phosphorus atom trans to chlorine with rhodium ($I = {}^1/_2$, abundance 100%) with coupling constant $J(\text{Rh-P}) = 185$ Hz. The spinning sidebands of this doublet are more intense than those of the high-field multiplet, indicating a larger chemical shift anisotropy. This results in a loss of intensity of the doublet relative to the multiplet. The high-field multiplet was analyzed as the AB part of an ABX spin system (A and B are the magnetically nonequivalent, mutually trans phosphorus atoms and X is Rh), with $\delta_A = +24.6$, $\delta_B = +32.0$, $J(\text{Rh-P}_A) \approx J(\text{Rh-P}_B) = 139$ Hz, and $J(\text{P}_A\text{-P}_B) = 365$ Hz. The coupling of the cis phosphorus atoms, normally in the range 0-50 Hz, is too small to be observed. The large trans coupling and the absence of a resolved cis coupling confirms that solid $RhCl(PPh_3)_3$ has a more square-planar than tetrahedral geometry. The parameters found for solid $RhCl(PPh_3)_3$ agree reasonably well with those derived from the solution spectrum in CH_2Cl_2:[7] $\delta_{\text{P trans Cl}} = +48.0$, $J(\text{Rh-P}) = 189$ Hz, $\delta_{\text{P cis Cl}} = +31.5$, $J(\text{Rh-P}) = 142$ Hz. In solution the mutually trans phosphorus atoms are equivalent. However, couplings of nonequivalent trans phosphorus atoms in rhodium compounds have been reported in the range 300-350 Hz.[8]

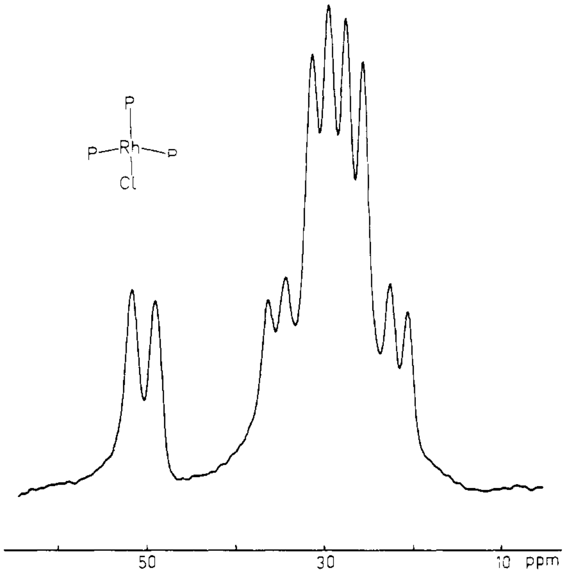

Figure 1. ^{31}P NMR spectrum of $RhCl(PPh_3)_3$ (cross polarization time (CP) 5 ms, pulse interval 1 s, 52 000 accumulations, magic angle spinning rate 4.2 kHz).

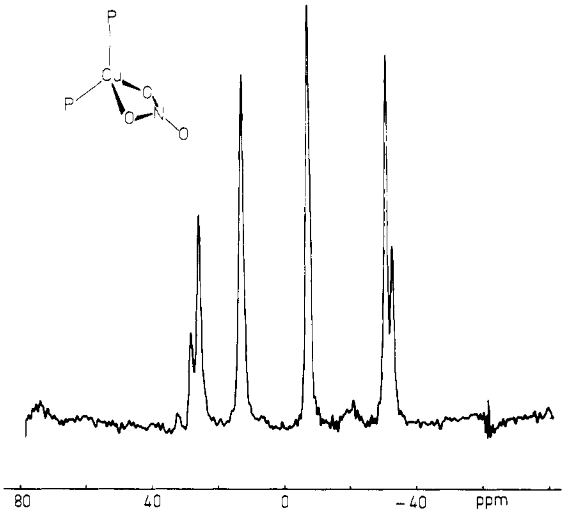

Figure 2. ^{31}P NMR spectrum of $(Ph_3P)_2CuNO_3$ (CP time 5 ms, pulse interval 5 s, 1277 accumulations, spinning rate 3.5 kHz).

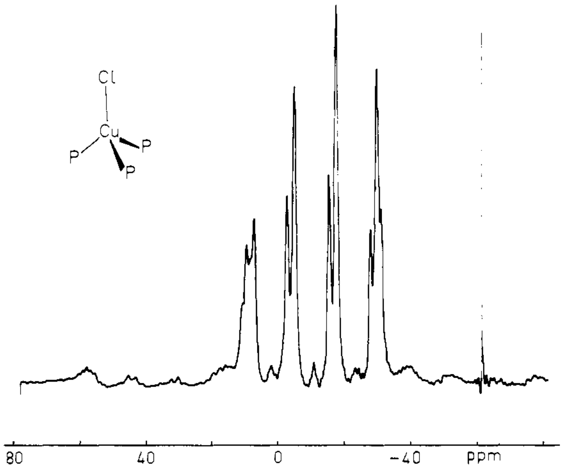

Figure 3. ^{31}P NMR spectrum of $(Ph_3P)_3CuCl$ (CP time 5 ms, pulse interval 5 s, 375 accumulations, spinning rate 3.5 kHz).

Only a few copper-phosphine complexes have been studied by ^{31}P NMR in solution,[9] investigations being hampered by disso-

---

(1) R. A. Haberkorn, J. Herzfeld, and R. G. Griffin, *J. Am. Chem. Soc.,* **100,** 1296 (1978).

(2) W. R. Rothwell, J. S. Waugh, and J. P. Yesinowski, *J. Am. Chem. Soc.,* **102,** 2637 (1980).

(3) W. M. Ritchey, A. Wong, T. Carr, A. N. Garroway, and W. S. Veeman, 4th EENC, Grenoble, 1979; T. Carr, W. M. Ritchey, and W. S. Veeman, in preparation.

(4) P. A. S. van Dijk, W. Schuı, J. W. M. van Os, E. M. Menger, and W. S. Veeman, to appear in *J. Phys. E:.*

(5) M. J. Bennet and P. B. Donaldson, *Inorg. Chem.,* **16,** 655 (1977). The red form was used in our study.

(6) All chemical shifts are reported in ppm, relative to external 85% H_3PO_4. Low-field shifts are taken positive.

(7) T. H. Brown and P. J. Green, *J. Am. Chem. Soc.,* **92,** 2359 (1970).

(8) (a) A. W. Gal, J. W. Gosselink, and F. A. Vollenbroek, *J. Organomet. Chem.,* **142,** 357 (1977); (b) D. H. M. W. Thewissen and H. L. M. van Gaal, *ibid.,* **172,** 69 (1979); (c) D. H. M. W. Thewissen, H. P. M. Ambrosius, H. L. M. van Gaal, and J. J. Steggerda, *J. Organomet. Chem.* **192,** 101 (1980).

0002-7863/80/1502-7935$01.00/0

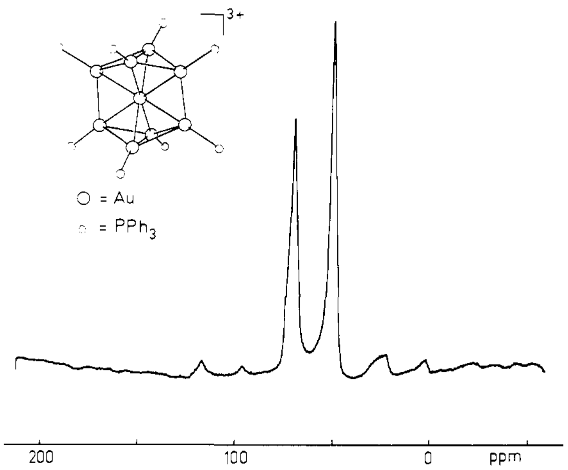

Figure 4. ^{31}P NMR spectrum of $[Au_9(PPh_3)_8][NO_3]_3$ (CP time 5 ms, pulse interval 5 s, 4710 accumulations, spinning rate 3.5 kHz).

ciation reactions.[9c] The only well-studied compound is $[\{(MeO)_3P\}_4Cu]^+$.[9a,b,d]

The Cu atom in $(Ph_3P)_2CuNO_3$ is tetrahedrally coordinated to the two phosphorus atoms and two oxygen atoms of the NO_3^- group.[10] The two triphenylphosphine groups are equivalent. The solid-state ^{31}P NMR spectrum of $(Ph_3P)_2CuNO_3$, Figure 2, shows four main peaks at +26.0, +13.1, -7.0, and -31.1 ppm, the outer peaks accompanied by satellite peaks at +28.3 and -33.1 ppm. The ^{65}Cu isotope (abundance ^{63}Cu 69.09%, ^{65}Cu 30.91%) seems to be responsible for these satellite peaks.

Because the crystal structure[10] shows that all phosphine groups are equivalent, the splitting of the phosphorus resonance line into four peaks has to be caused by coupling of the phosphorus spin ($I = {}^1/_2$) to the Cu spin ($I = {}^3/_2$ for both isotopes). Surprisingly, the splitting between the lines of this quartet increases to higher field. An explanation of this effect may be that due to the presence of a Cu quadrupole interaction not small compared to the Cu Zeeman interaction, the Cu-P dipolar and **J** tensor interactions are not averaged out by magic angle spinning. Then, in addition to the isotropic J coupling, also the dipolar and **J** tensor interactions contribute to the splitting. Analogous effects for ^{13}C-^{14}N couplings have been reported by Lippmaa and co-workers.[11] However, in their case also a broadening of the ^{13}C lines is found, while the ^{31}P lines of Figure 2 are only 2-ppm wide. In the absence of the Cu quadrupole interaction and without magic angle spinning, the Cu-P dipolar interaction would result in a more than 3-kHz-wide powder pattern, assuming the Cu-P distance to be 2.3 Å.[12] In this communication no attempt will be made to explain the unequal splittings together with the absence of severe line broadening. Both theoretical and further experimental work is under way to clarify this point.

In another copper complex, $(Ph_3P)_3CuCl$, the situtation is different. Here the crystal structure of $(Ph_3P)_3CuCl$ indicates that there are three molecules per unit cell, two are crystallographically identical, the third molecule being different.[13] The solid-state ^{31}P NMR spectrum of $(Ph_3P)_3CuCl$, Figure 3, shows resonances from the two different molecular sites at +9.9, -2.4, -15.3, and -27.9 ppm and at +7.6, -4.7, -17.2, and -29.9 ppm. Also ^{65}Cu satellite peaks appear on the outer signals. Here the splittings within one quartet are not very different, between 900 and 940 Hz. This indicates a smaller Cu quadrupole interaction as compared to $(Ph_3P)_2CuNO_3$, which is reasonable in view of the higher local symmetry (C_{3v}) around Cu in $(Ph_3P)_3CuCl$.

Of the few known gold cluster compounds the spectrum of one of the more interesting clusters, $[Au_9(PPh_3)_8][NO_3]_3$, is given in Figure 4. The spectrum shows two lines, the low-field one asymmetric, at +48.0 and +68.7 ppm.

Because the splitting is too large for a dipolar splitting (for a Au-P distance of 2.3 Å[12] the rigid lattice dipolar line width is calculated to be only 200 Hz), these lines must result from two inequivalent P sites, either in one molecule or in two, crystallographically inequivalent, molecules of the unit cell.

Unfortunately, the crystal structure is not known and no choice between these two possibilities can be made. In solution all phosphine groups are equivalent: in CD_2Cl_2 one sharp resonance is found at +57.1 ppm.[12]

We have now investigated 30 metal-phosphine complexes by high-resolution solid-state ^{31}P NMR. In this preliminary report only four representative spectra are shown, but it seems clear that NMR studies with solid-state line-narrowing techniques can provide valuable information about the structure of such complexes in powders.

Acknowledgment. This work was carried out partly under the auspices of The Netherlands Foundation of Chemical Research (SON) and with the aid of The Netherlands Organization for the Advancement in Pure Research (ZWO). We thank the Department of Inorganic Chemistry for providing us with the samples. Stimulating discussions with Dr. H. L. M. van Gaal are gratefully acknowledged. We thank Professors J. J. Steggerda and E. de Boer for their interest in this work.

J. W. Diesveld, E. M. Menger
H. T. Edzes, W. S. Veeman*
Department of Physical Chemistry
University of Nijmegen
Toernooiveld, 6525 ED Nijmegen
The Netherlands

Received June 11, 1980

---

[9] (a) R. W. King, T. J. Hutteman, and J. G. Verkade, *Chem. Commun.*, 561 (1965); (b) K. J. Coskram, R. D. Bertrand, and J. G. Verkade, *J. Am. Chem. Soc.*, **89**, 4535 (1967); (c) E. L. Muettertles and C. W. Alegranti, *ibid.*, **92**, 4114 (1970); (d) W. MacFarlane and D. S. Rycroft, *J. Magn. Reson.*, 24, 95 (1976).

[10] G. G. Messmer and G. J. Palenik, *Inorg. Chem.*, **8**, 2750 (1969).

[11] (a) E. Lippmaa, M. Alla, H. Raude, R. Teeäär, I. Heinmaa, and E. Kundla, Proceedings of the XXth Congress Ampere, Tallinn, 1978, E. Kundla, E. Lippmaa, and T. Saluvere, Eds., Springer Verlag, Berlin, Heidelberg, New York, 1979, p 87. (b) E. Kundla and M. Alla, *ibid.*, p 92.

[12] F. A. Vollenbroek, Thesis, Nijmegen, 1979. F. A. Vollenbroek, J. P. van den Berg, J. W. A. van der Velden, and J. J. Bour, *Inorg. Chem.*, **19**, 2685 (1980). Data are corrected with respect to 85% H_3PO_4.

[13] J. T. Gill, J. J. Mayerle, P. S. Welcker, D. F. Lewis, O. A. Ucko, D. J. Barton, D. Stowens, and S. J. Lippard, *Inorg. Chem.*, **15**, 1155 (1976).

Deactivation of the Fluorescent State of 9-*tert*-Butylanthracene. 9-*tert*-Butyl-9,10-(Dewar anthracene)

Sir:

The fluorescence quantum yields of 9-alkyl-substituted anthracenes in solution at room temperature slightly increase from 0.29 for methyl to 0.39 for isobutyl.[1] Surprisingly, 9-*tert*-butylanthracene in *n*-heptane shows at room temperature a fluorescence quantum yield of only 0.011.[2] Besides the typical temperature dependence of the fluorescence quantum yield of meso-substituted anthracenes[3] in solution, 9-*tert*-butylanthracene exhibits a dramatic viscosity dependence of its fluorescence quantum yield. At room temperature the fluorescence quantum yield in glycerol increases to 0.10 and in the matrix of poly(methyl methacrylate) (PMMA) even to 0.43. Since, contrary to most of the meso-substituted anthracenes, we do not observe any triplet-triplet absorption within the resolution time of our microsecond flash photolysis apparatus, the strong decrease of the fluorescence in solution must be accompanied by a concomitant increase in radiationless deactivation of the fluorescent state of 9-*tert*-butylanthracene. Consequently, this can be an increased internal conversion by the *tert*-butyl group,[4] operating as a "loose

---

[1] A. S. Cherkasov, *Bull. Acad. Sci. USSR, Phys. Ser.*, **20**, 436 (1956).

[2] S. Schoof, H. Güsten, and C. von Sonntag, *Ber. Bunsenges. Phys. Chem.*, **82**, 1068 (1978).

[3] S. Schoof, H. Güsten, and C. von Sonntag, *Ber. Bunsenges. Phys. Chem.*, **81**, 305 (1977).

0002-7863/80/1502-7936$01.00/0