10654 *J. Am. Chem. Soc.* **1996,** *118,* 10654−10655

Unusual ^{31}P Chemical Shielding Tensors in Terminal Phosphido Complexes Containing a Phosphorus−Metal Triple Bond

Gang Wu,[†,‡] David Rovnyak,[†,‡] Marc J. A. Johnson,[‡]
Nadia C. Zanetti,[‡] Djamaladdin G. Musaev,[§]
Keiji Morokuma,[*,§] Richard R. Schrock,[*,‡]
Robert G. Griffin,[*,†,‡] and Christopher C. Cummins[*,‡]

Francis Bitter Magnet Laboratory
and Department of Chemistry
Massachusetts Institute of Technology
77 Massachusetts Avenue
Cambridge, Massachusetts 02139-4307
Cherry L. Emerson Center for Scientific
Computation and Department of Chemistry
Emory University, Atlanta, Georgia 30322

Received February 27, 1996

Phosphorus-31 NMR data for one-coordinate phosphorus compounds are extremely scarce in the literature.[1,2] Until recently, the only stable compounds with a terminal phosphorus atom involved in a triple bond were phosphaalkynes, $RC{\equiv}P$,[3,4] and the isoelectronic iminophosphenium cations, $[RN{\equiv}P]^+$.[5] The isotropic ^{31}P chemical shift range for these compounds extends from 96 to −207 ppm. In general, phosphaalkynes and iminophosphenium ions are found to have their ^{31}P chemical shifts at lower frequency (more shielded) compared to phosphaalkenes and iminophosphines, respectively. This trend is analogous to the relationship between ^{13}C chemical shifts in alkynes and alkenes. Recently, the first terminal phosphido (P^{3-}) complexes containing a phosphorus-metal triple bond were successfully synthesized.[6,7] Surprisingly, ^{31}P NMR signals in these complexes were found above 1000 ppm. Observation of such unusual ^{31}P chemical shieldings suggests that phosphorus−metal triple-bonding schemes may differ substantially when compared to phosphorus−carbon and phosphorus−nitrogen triple-bonding schemes.

Here we report the ^{31}P chemical shielding tensors for the terminal phosphido ($M{\equiv}P$) complexes $Mo(P)[N(^tBu)Ar]_3$ (**1**, Ar = C_6H_5; **2**, Ar = 3,5-$C_6H_3Me_2$) and $M(P)(NN_3)$ (NN_3 = $[Me_3SiNCH_2CH_2)_3N]^{3-}$; **3**, M = Mo; **4**, M = W). The anisotropies are all in excess of 2000 ppm, which is by far the largest ^{31}P chemical shielding anisotropy (CSA) ever observed.

A typical solid-state ^{31}P NMR spectrum[8] of the terminal phosphido complexes obtained with magic-angle-spinning (MAS) is shown in Figure 1. In addition to the isotropic peak, a large number of rotational sidebands extend over a range of ca. 2000 ppm. From the rotational sideband intensities, it is possible to compute the principal components of the chemical shielding tensor.[9,10] For complexes **1**−**4**, orientations of the principal components of the ^{31}P chemical shielding tensor are constrained by crystallographic symmetry. For example, complex **1** crystallizes in the space group $I\bar{4}3d$ with its $Mo{\equiv}P$ bond lying along the crystallographic C_3 axis.[11] Therefore, the ^{31}P chemical shielding tensor in **1** must be axially symmetric with the unique axis lying along the $Mo{\equiv}P$ direction. Similarly, complexes **2** and **4** crystallize in the space groups $P6_3$ and $Pa\bar{3}$, respectively; each complex has its $M{\equiv}P$ vector lying along a cystallographic C_3 axis.[6,7] The structure of **3**, although not yet determined, is expected to be identical to **4**. Our NMR results also confirmed that the ^{31}P chemical shielding tensor in **3** is axially symmetric, suggesting the presence of an axis with C_3 or greater symmetry.

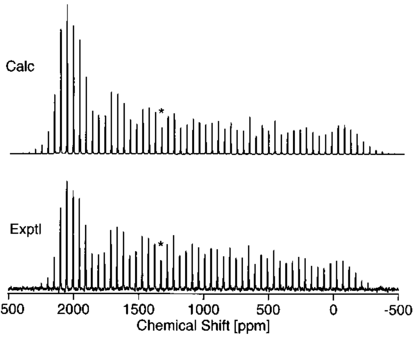

Figure 1. Observed and calculated ^{31}P MAS NMR spectra of $Mo(P)(NN_3)$ (**3**) at 128.489 MHz. The sample spinning frequency was 6.16 kHz. The isotropic peak is indicated by an asterisk. Slight deviations between the experimental and calculated spectra are noticeable in the wings of the spectra because the excitation pulse does not uniformly excite the 300 kHz wide powder spectrum.

Table 1. Experimental Phosphorus Chemical Shift Tensors for Compounds Containing Terminal Phosphorus Involved a Triple Bond[a,b]

compd	δ_{iso}	δ_{11} ($\delta_\perp$)	δ_{22} ($\delta_\perp$)	δ_{33} ($\delta_\parallel$)	Ω[c]
1	1217 (1224)	1987	1987	−324	2311
2	1208 (1216)	1978	1978	−330	2308
3	1328 (1346)	2125	2125	−267	2392
4	1059 (1080)	1728	1728	−280	2008
$P{\equiv}N$	275	734	734	−642	1376[d]
$[P{\equiv}N(Mes^*)]^+$	77	308	196	−273	581[e]
$P{\equiv}C(Mes^*)$	31	229	140	−274	503[f]

[a] All ^{31}P chemical shifts are in ppm with respect to 85% aqueous H_3PO_4. [b] Chemical shifts observed in solutions are given in parentheses. [c] Span of the chemical shift tensor, $\Omega = \delta_{11} - \delta_{33}$. [d] References 12−14. [e] Reference 15. [f] Reference 16.

---

[*] Authors to whom correspondence may be addressed.

[†] Francis Bitter Magnet Laboratory, Massachusetts Institute of Technology.

[‡] Department of Chemistry, Massachusetts Institute of Technology.

[§] Emory University.

(1) Fluck, E.; Heckmann, G. In *Phosphorus-31 NMR Spectroscopy in Stereochemical Analysis-Organic Compounds and Metal Complexes*; Verkade, J. G., Quin, L. D., Eds.; VCH Publishers, Inc.: Deerfield Beach, FL, 1987; pp 61−113.

(2) Niecke, E.; Gudat, D. In *Phosphorus-31 NMR Spectral Properties in Compound Characterization and Structural Analysis*; Quin, L. D., Verkade, J. G., Eds.; VCH Publishers, Inc.: New York, 1994; pp 159−174.

(3) Appel, R.; Westerhaus, A. *Tetrahedron Lett.* **1981**, *22*, 2159−2160.

(4) Becker, G.; Gresser, G.; Uhl, W. *Z. Naturforsch.* **1981**, *36b*, 16−19.

(5) Niecke, E.; Nieger, M.; Reichert, F. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 1715−1716.

(6) Laplaza, C. E.; Davis, W. M.; Cummins, C. C. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 2042−2044.

(7) Zanetti, N. C.; Schrock, R. R.; Davis, W. M. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 2044−2046.

(8) All solid-state ^{31}P NMR spectra were obtained on a custom designed NMR spectrometer operating at 317 MHz for ^1H nuclei. MAS probe was equipped with a 5-mm spinner assembly (Doty Scientific, Inc.). Typically the samples were spun at 5−10 kHz. Solid $NH_4H_2PO_4$ was used as a secondary chemical shift reference sample, which has a ^{31}P NMR signal at 0.8 ppm with respect to 85% aqueous H_3PO_4. For each sample, ^{31}P MAS NMR spectra were obtained at several different sample spinning speeds in order to identify isotropic peaks. As expected, the extremely large CSA in **1**−**4** makes the MAS NMR spectra of them very sensitive to the setting of the magic angle. It was noted that a deviation of 0.01° from the magic angle can cause observable broadenings or even splittings of the peaks in the MAS spectra.

(9) Maricq, M. M.; Waugh, J. S. *J. Chem. Phys.* **1979**, *70*, 3300−3316.

(10) Herzfeld, J.; Berger, A. E. *J. Chem. Phys.* **1980**, *73*, 6021−6030.

(11) Crystal data pertaining to **1** are as follows: $a = b = c = 22.8595(9)$ Å, $V = 11945.4(8)$ Å^3, space group $I\bar{4}3d$, $Z = 16$. $M_r = 571.58$, and $\rho_{calcd} = 1.271$ mg/m^3; full details to appear in an upcoming full paper by Johnson, M. J. A.; Odom, A. L.; and Cummins, C. C.

(12) Lazzeretti, P.; Tossell, J. A. *J. Phys. Chem.* **1987**, *91*, 800−804.

(13) Raymonda, J.; Klemperer, W. *J. Chem. Phys.* **1971**, *55*, 232−233.

(14) Appleman, B. R.; Dailey, B. P. *Adv. Magn. Reson.* **1974**, *7*, 231−320.

(15) Curtis, R. D.; Schriver, M. J.; Wasylishen, R. E. *J. Am. Chem. Soc.* **1991**, *113*, 1493−1498.

(16) Duchamp, J. C.; Pakulski, M.; Cowley, A. H.; Zilm, K. W. *J. Am. Chem. Soc.* **1990**, *112*, 6803−6809.

S0002-7863(96)00639-7 CCC: $12.00

Table 2. Theoretical ^{31}P Chemical Shift Tensors, HOMO and LUMO Energies, P−X Bond Length, and Binding Energies of Some Compounds Having a Terminal Phosphorus Triple Bond

property		P_2	PN	PCH	$PMo(NH_2)_3$
NMR shielding (ppm)[a]	δ_{iso}	586 (635)	278 (344)	−74 (−20)	1463
	$\delta_{11} = \delta_{22}$	1200 (1273)[b]	736 (835)	209 (290)	2228
	δ_{33}	−641 (−642)	−638 (−638)	−639 (−640)	−67
	Ω	1841 (1915)	1374 (1473)	848 (930)	2295
orbital energy: ϵ_i (au)	HOMO-1, σ	−0.301	−0.329	−0.368	−0.248
	HOMO, π	−0.293	−0.339	−0.291	−0.231
	LUMO, π^*	−0.105	−0.087	−0.056	−0.061
r(P−X) (Å) calcd		1.904	1.489	1.539	2.108
exptl[c]		1.8937	1.4909	1.5421	
Δ_e(P−X) (kcal/mol) calcd[d]		109.9	141.6	188.1	81.1
exptl[e]		117.0 ± 2.5	147.5 ± 5.0		

[a] Defined in the same way as in Table 1. [b] Values in parentheses are results of the previous ab initio studies from ref 23. [c] Reference 24. [d] Zero-point correction included. [e] Reference 25.

The experimentally determined principal values of the ^{31}P chemical shielding tensors for **1**−**4** are given in Table 1. Also listed in Table 1 are ^{31}P chemical shielding tensors for other compounds containing terminal phosphorus involved in a triple bond. From Table 1, three major trends are immediately apparent. First, the ^{31}P chemical shielding tensors for **1-4** are significantly anisotropic. To our knowledge, the ^{31}P CSA of 2392 ppm in **3** is the largest value reported in the literature. Second, the least shielded component of the ^{31}P chemical shielding tensor, δ_{11}, varies dramatically, from 229 ppm in P≡C-(Mes*) to 2125 ppm in **3**. To fully appreciate the magnitude of this chemical shielding range, one should consider that the entire ^{31}P chemical shielding range for all phosphorus-containing compounds is approximately 2000 ppm. Third, the most shielded component, δ_{33}, remains similar for all compounds listed in Table 1. This last trend can be understood readily. For linear molecules paramagnetic shielding vanishes along the molecular axis, so the ^{31}P chemical shielding along P≡N and P≡P is close to the shielding found for a free phosphorus atom, $\delta = -633$ ppm.[17] However, breaking the C_∞ symmetry by the ligands in other compounds listed in Table 1 introduces an additional paramagnetic shift of 300−400 ppm. Nevertheless, the variation of the most shielded component, δ_{33}, is much smaller than that of the least shielded component, δ_{11}.

The most striking observation for complexes **1**−**4** is the enormous paramagnetic shielding at the ^{31}P nucleus when the external magnetic field is oriented perpendicular to the phosphorus−metal triple bond (i.e., the $\delta_\perp$ component of the ^{31}P chemical shielding tensor. In order to assess the electronic structures of the present systems, we performed MO calculations on the model complex $PMo(NH_2)_3$ (**5**) as well as on P_2, PN, and PCH with the B3LYP density functional method.[18] As shown in Table 2, the calculated ^{31}P chemical shielding tensor and CSA for **5** agree well with the experimental values for **1**−**4** in Table 1. Results given in Table 2 also confirm much larger paramagnetic shielding in both perpendicular and parallel components for **5**, compared to those for other compounds with a terminal phosphorus triple bond. The highest occupied MOs (HOMOs) of these systems are nearly degenerate P−X σ and π bonding orbitals and the lowest unoccupied MOs (LUMOs) are P−X antibonding π^* orbitals.[26] Therefore, when the applied magnetic field is oriented along directions perpendicular to the the P≡X bond, σ(P−X) → π^*(P−X) MO mixing should make the primary contribution to the ^{31}P paramagnetic shieldings. Interestingly, the perpendicular component of the ^{31}P chemical shielding tensors, **5** > P_2 > PN > PCH, correlates very well with the calculated $\sigma-\pi^*$ energy gap. Concerning the spatial distribution of the MOs, the σ(P−X) HOMO for **5** is found to be more localized on the P atom than on the other atoms. One should also note in Table 2 that the decrease in the HOMO−LUMO energy gap is associated with the decrease in the calculated P≡X binding energy.

In summary, the extreme ^{31}P deshielding and CSA effects found for compounds containing a phosphorus−metal triple bond have been investigated by both experimental and quantum chemical methods. Both effects arise from the significant paramagnetic shielding at directions perpendicular to the phosphorus−metal triple bond. This paramagnetic shielding is interpreted as primarily due to the field-induced mixing between σ(M−P) and π^*(M−P) MOs. The energy gap between σ(M−P) and π^*(M−P) is remarkably small in the present terminal phosphido complexes, consistent with the predicted low M≡P binding energy.

Acknowledgment. G.W. wishes to thank the Natural Sciences and Engineering Research Council (NSERC) of Canada for a postdoctoral fellowship. We are grateful to Dr. Klaus Eichele and Professor Rod Wasylishen (Dalhousie University) for helpful discussions. This research was supported by grants from the National Institutes of Health (GM-23403 and RR-00995). C.C.C. is grateful for support from the National Science Foundation (CAREER Award CHE-9501992), DuPont (Young Professor Award), the Packard Foundation (Packard Foundation Fellowship), Union Carbide (Innovation Recognition Award), and 3M (Innovation Fund Award). M.J.A.J. is grateful for an NSERC graduate research fellowship. R.R.S. thanks the NIH (GM 31978) for support. K.M. is grateful for support from the National Science Foundation (CHE-9409020).

JA960639W

---

(17) Flygare, W. H. *Chem. Rev.* **1974**, *74*, 653−687.

(18) We used the B3LYP3 density functional[19] with the lanl2dz+f and 6-311G** basis sets for Mo and the other atoms, respectively, for geometry optimization and the GIAO method[20] with the (17s13p9d3f/8s7p5d1f)[21] and 6−311G** basis sets, respectively, for NMR chemical shift calculation using the GAUSSIAN94 package.[22]

(19) (a) Becke, A. D. *Phys. Rev. A: At., Mol., Opt. Phys.* **1988**, 38, 3098. (b) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B: Condens. Matter* **1988**, 37, 785. (c) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648.

(20) Ditchfield, R. *Mol. Phys.* **1974**, *27*, 789.

(21) Blomberg, M. R. A.; Siegbahn, P. E. M.; Svensson, M. *Inorg. Chem.* **1993**, *32*, 4218.

(22) *GAUSSIAN94/Version-D.3*; Fresch, M. J.; Trucks, G. W.; Schlegel, H. B.; Gill, P. M. W.; Johnson, B. G.; Robb, M. A.; Cheesemen, J. R.; Keith, T. A.; Petersson, J. A.; Montgomery, J. A.; Raghavachari, K.; Al-Laham, M. A.; Zakrzewski, V. G.; Ortiz, J. V.; Foresman, J. B.; Cioslowski, J.; Stefanov, B. B.; Nanayakkara, A.; Challacombe, M.; Peng, C. Y.; Ayala, P. Y.; Chen, W.; Wong, M. W.; Andres, J. L.; Replogle, E. S.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Binkley, J. S.; DeFrees, D. J.; Baker, J.; Stewart, J. J. P.; Head-Gordon, M.; Gonzales, C.; Pople, J. A.; Gaussian, Inc.: Pittsburgh, PA, 1995.

(23) Chesnut, D. B.; Rusiloski, B. E. *Chem. Phys.* **1991**, *157*, 105.

(24) For P_2 and PN, see: *International Tables of Selected Constants. 17. Spectroscopic Data Relative to Diatomic Molecules.* Rosen, B. N. Y., Ed.; Pergamon Press: Oxford, 1970. For PCH, see: Johns, J. W. C.; Shurvell, H. F.; Tyler, J. K. *Can. J. Phys.* **1969**, *47*, 893.

(25) *CRC Handbook of Chemistry and Physics*, 72nd ed. Lide, D. L., Ed. CRC Press: Boca Raton−Ann Arbor−Boston, 1992.

(26) There is an occupied MO of higher energy strongly localized on the N atoms, which is irrelevant to the present study. The P 3s lone pair MOs are lower in energy and need not be considered.