^{31}P chemical shift anisotropies of trimethyl- and triphenylphosphine-substituted Group 6 metal pentacarbonyl complexes

Jordan H. Wosnick, Frederick G. Morin, and Denis F.R. Gilson

Abstract: The ^{31}P chemical shift tensor components and anisotropies of the trimethyl- and triphenylphosphine complexes of the group 6 metal pentacarbonyls, $M(CO)_5PR_3$ (M = Cr, Mo, W and R = Me, Ph), have been measured using solid-state CP-MAS ^{31}P NMR spectroscopy. For the trimethylphosphine derivatives, the chemical shift tensors have near axial symmetry and the shift tensor components are in reasonable agreement with the calculated values for the chromium and molybdenum complexes. In the triphenylphosphine complexes, the tensors are asymmetric due to the different torsion angles of the phenyl rings. The trend to higher shielding of the isotropic ^{31}P chemical shifts on descending group 6 arises from changes in the perpendicular components of the shift tensor. The one-bond coupling constants, $^1J(^{95/97}Mo–^{31}P)$, for the trimethyl- and triphenylphosphine complexes are 129 and 133 Hz, respectively.

Key words: chemical shift anisotropy, phosphines, chromium, molybdenum, tungsten.

Résumé : Faisant appel à la spectroscopie RMN «CP-MAS» à l'état solide du ^{31}P, on a mesuré les composantes du tenseur du déplacement chimique du ^{31}P et les anisotropies des complexes triméthyl- et triphénylphosphines de pentacarbonyles de métaux du groupe 6, $M(CO)_5PR_3$ (M = Cr, Mo, W et R = Me, Ph). Pour les dérivés de la triméthylphosphine, les tenseurs du déplacement chimique présentent une symétrie pratiquement axiale et les composantes du tenseur du déplacement sont en bon accord avec les valeurs calculées pour les complexes du chrome et du molybdène. Pour les dérivés de la triphénylphosphine, les tenseurs sont asymétriques à cause des différents angles de torsion des noyaux phényles. La tendance vers des blindages plus importants des déplacements chimiques isotropes du ^{31}P lorsqu'on descend dans le groupe 6 provient de changements dans les composantes perpendiculaires du tenseur du déplacement. Les constantes de couplage à travers une liaison, $^1J(^{95/97}Mo–^{31}P)$, des complexes triméthyl- et triphénylphosphines sont respectivement 129 et 133 Hz.

Mots clés : anisotropie du déplacement chimique, phosphines, chrome, molybdène, tungstène.

[Traduit par la Rédaction]

Introduction

^{31}P NMR spectroscopy has become a common tool in recent years for studying the structural and electronic properties of organometallic complexes containing phosphine ligands. Direct information about the tensor properties of the chemical shift is not available from solution spectra but can be regained from solid-state spectra under either non-spinning conditions or with magic-angle spinning, where the well-known "powder pattern" is replaced by a sharp isotropic peak surrounded by spinning side bands and the chemical shift tensor information can be recovered from the relative intensities of the spinning side-band manifolds at low spinning speeds (1). This is desirable because the components of the chemical shift tensor provide more information than do the isotropic chemical shifts.

Theoretical methods, particularly Density Functional Theory (DFT) approaches, are now capable of calculating the chemical shift tensors of molecules containing "heavy" nuclei (2), and the purpose of the present study was to determine the chemical shift tensor components for a series of phosphine-substituted group 6 metal pentacarbonyl complexes of the form $M(CO)_5PR_3$ (M = Cr, Mo, W and R = Me, Ph) and to compare these values with the results of the DFT predictions of Kaupp (3) and of Ruiz-Morales and Ziegler (4). The known trend (5) of the ^{31}P isotropic chemical shifts in the direction of increased shielding on going from chromium to tungsten was interpreted by Kaupp as arising from changes in the perpendicular components of the shift tensor. Supporting evidence for this has been reported recently for Group 6 metal pentacarbonyl complexes with the ligand 5-phenyldibenzophosphole (PhDBP) (5). Wasylishen and co-workers (6, 7) have suggested that PhDBP resembles triphenylphosphine as a ligand except that two of the phenyl groups are constrained to one plane and the ^{31}P chemical shift anisotropy reflects this difference in local symmetry. We have examined the ^{31}P chemical shift anisotropies of the triphenylphosphine complexes for

Received March 23, 1998.

J.H. Wosnick, F.G. Morin, and D.F.R. Gilson.[1] Department of Chemistry, McGill University, 801 Sherbrooke Street West, Montreal, QC H3A 2K6, Canada.

[1] Author to whom correspondence may be addressed. Telephone: (514) 398-6908. Fax: (514) 398-3797. E-mail: gilson@omc.lan.mcgill.ca

Table 1. Solid state ^{31}P chemical shift tensor components and anisotropies,[a] isotropic chemical shifts, and coupling constants for the complexes $M(CO)_5PR_3$ (M = Cr, Mo, W; R = Me, Ph). Chemical shift values are in ppm, referenced to 85% H_3PO_4, and all coupling constants are in Hz.

	δ_{iso} soln	δ_{iso} solid	δ_{11}	δ_{22}	δ_{33}	$\Delta\delta$[a]	$^1J_{MP}$
$Cr(CO)_5PMe_3$	10	8	38	29	–42	–75.5	
$Cr(CO)_5PMe_3$ [b]	0.3		32	32	–63	–95	
$Cr(CO)_5PMe_3$ [c]	15.0		45.1	45.1	–45.1	–90.2	
$Mo(CO)_5PMe_3$	14	–15	13	–6	–52	–55.5	128
		–17	13	–6	–56	–59.5	129
$Mo(CO)_5PMe_3$ [b]	–22		1	1	–68	–69	
$Mo(CO)_5PMe_3$ [c]	–10.9		6.1	6.1	–45	–69	
$W(CO)_5PMe_3$	–35	–36	–31	–36	–42	–8.5	220
$W(CO)_5PMe_3$ [b]	–22		0	0	–67	–67	
$Cr(CO)_5PPh_3$	55	54	100	75	–14	–102	
$Cr(CO)_5PPh_3$ [c]	64.5		106.8	94.2	–7.4	–107.8	
$Mo(CO)_5PPh_3$	38	36	78	49	–20	–83.5	133
$Mo(CO)_5PPh_3$ [c]	50.4		85.5	71.1	–7.9	–86.2	
$W(CO)_5PPh_3$	22	19	52	22	–17	–54	236, 244[e]
$Cr(CO)_5PhDBP$ [c]		46.8	127	41	–28	–112	
$Mo(CO)_5PhDBP$ [d]		28.0	104	24	–44	–108	120
$W(CO)_5PhDBP$ [d]		7.7	69	–13	–36	–64	
$Mo(CO)_5MeDBP$ [f]		16.5	112	–23	–40	–84.5	123

[a] $\Delta\delta$ is defined as $\delta_{33} - (\delta_{11} + \delta_{22})/2$.

[b] Calulated values from ref. 3.

[c] Calculated values from ref. 4.

[d] From ref. 6.

[e] Solution value from ref. 17.

[f] From ref. 7.

comparison with the PhDBP results and the calculations of Ruiz-Morales and Ziegler (4).

Experimental

The complexes $M(CO)_5PPh_3$ (M = Cr, Mo, W) were prepared by the trimethylamine – N-oxide promoted substitution of the triphenylphosphine on the metal hexacarbonyl (8), and purified by recrystallization from a 2:1 ethanol–chloroform mixture. The trimethylphosphine complexes were prepared by displacement of the bromide ion from the tetraethylammonium bromopentacarbonylmetallate salt (9, 10) using trimethylphosphine – silver iodide adduct as the source of phosphine (11, 12). These complexes were purified by repeated sublimations or by crystallization from hexane solution at –20°C, the isolation of the compounds being complicated by their low melting points and tendency to form oils. Infrared and solution ^{31}P and ^1H nmr spectroscopy were used to confirm the identity and purity of the products by comparison with the literature spectra (5, 13, 14).

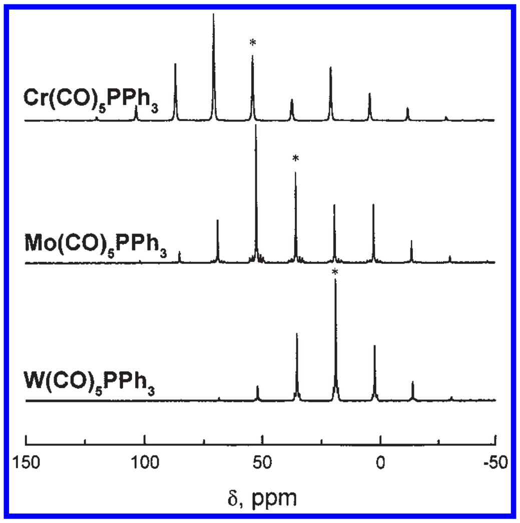
CP-MAS nmr spectra were recorded on a Chemagnetics CMX-300 spectrometer operating at 121.279 MHz, using high-power proton decoupling, contact times of 2 ms, and recycle delays of 2–180 s, depending on the complex studied. Samples were packed into 7.5 mm bullet-type zirconia rotors. Different spinning rates, ranging from 0.3 to 2.5 kHz, were used to locate isotropic peaks and the chemical shifts were referenced to 85% H_3PO_4. Line broadenings of between 0 and 25 Hz were applied to the spectra. The spectra were curve-fitted using the program Peakfit (Jandel Scientific) and the chemical shift tensor components were calculated from the spinning side-band intensities using the Herzfeld–Berger Analysis program of Eichele and Wasylishen (15).

Results and discussion

The phosphine complexes of the Group 6 metals are especially easy to study via ^{31}P NMR because, while each metal has nmr-active isotopes, none are present in a natural abundance large enough to seriously complicate the ^{31}P spectra with scalar coupling or quadrupole–dipole effects. The chemical shift tensor values, isotropic chemical shifts, and coupling constants for the six complexes studied are presented in Table 1, together with the calculated shift tensor values (3, 4) and the results reported for the PhDBP and MeDBP complexes (6, 7). The standard deviations in the δ_{ii} values, from the measurements at different spinning rates, were ±2 ppm.

The CP-MAS spectra showed only one chemical shift for all compounds except the trimethylphosphine(pentacarbonyl)molybdenum complex, where two shifts were observed separated by about 2 ppm. This difference is probably due to the presence of two crystallographically nonequivalent phosphorus atoms in the asymmetric unit cell, although the reported X-ray crystal structure (16) indicated only one molecule in the asymmetric unit. Unfortunately,

Fig. 1. ^{31}P CP-MAS spectra of the triphenylphosphine complexes of Group 6 metal pentacarbonyls. Spinning speed: 1600 Hz for all spectra. Asterisks indicate the isotropic shift position.



decomposition of the sample prevented the determination of the crystal structure of this polymorph.

The molybdenum and tungsten complexes showed additional splittings due to couplings from the isotopes with spin, ^{95}Mo (15.7%, I = 5/2), ^{97}Mo (9.46%, I = 5/2), and ^{183}W (14.4%, I = 1/2), but no splitting from ^{53}Cr (9.55%, I = 3/2) was observed in the spectra of either of the chromium complexes. The solid state value for ^1J(P–W) in the tungsten triphenylphosphine complex was slightly lower than the value in solution (17).

Couplings to quadrupolar nuclei are not always observed in solution state spectra, due to rapid relaxation, but can be observed in solid state spectra under magic-angle-spinning conditions (18). There is an additional line displacement that depends upon the residual dipole–quadrupole coupling interaction, d, given by eq. [1].

$$[1] \qquad d = -(3\chi D'/20\nu_s)(3\cos^2\beta - 1 + \eta\sin^2\beta\cos(2\alpha))$$

where $D' = (D - \Delta J/3)$, D is the dipolar coupling constant, $-(\mu_0/4\pi)\gamma_I\gamma_S h/(2\pi r^3)$, ΔJ is the anisotropy in the spin coupling, χ is the nuclear quadrupole coupling constant, and η is the asymmetry in the electric field gradient. The angles β and α are the polar and azimuthal angles relating the internuclear vector and the principal axes of the electric field gradient. The local symmetry around the metal–phosphorus bond is such that η is assumed to be zero and β and α are taken to be 0° and 90°, respectively, and eq. [1] is much simplified. The two molybdenum isotopes have very similar magnetogyric ratios and, therefore, have spin–spin coupling constants that cannot be easily distinguished, but the nuclear quadrupole moment of ^{97}Mo is much greater, 0.255×10^{-28} m^2 versus -0.022×10^{-28} m^2 for ^{95}Mo, and so, in principle, the second-order splittings can be analysed to give the quadrupole coupling constants and the anisotropy in J. The direct dipole coupling constants, calculated using a bond length of 2.508 Å (16), are –202 and –206 Hz for ^{97}Mo and ^{95}Mo, respectively. The quadrupole coupling constants of triphenylphosphine(pentacarbonyl)molybdenum have been measured (19) to be 1.972 MHz and 22.783 MHz for ^{95}Mo and ^{97}Mo, respectively, and the former is probably negative in sign (20). These values were obtained at 77 K and the room temperature quadrupole coupling constants would be lower in frequency. Thus, neglecting ΔJ and using the low-temperature χ values, the calculated second-order splittings would be –70 and 6.1 Hz for ^{97}Mo and ^{95}Mo, respectively, compared with the experimental values of –55 and 4.5 Hz. The differences could be due to the lower quadrupole coupling constants at high temperature and a finite anisotropy in the spin–spin coupling constant. The splittings in the spectra of the trimethylphosphine complex were not sufficiently well resolved for a full analysis and only the J value could be determined.

The experimentally determined chemical shift tensors for the trimethylphosphine complexes show near-axial symmetry ($\delta_{11} \approx \delta_{22}$), the deviations being attributable to solid state effects, and the values are in quite good agreement with the theoretical predictions (3) if the δ_{11} and δ_{22} values are averaged and compared with the calculated perpendicular component. The lack of agreement for the tungsten complex is not unexpected and was attributed by Kaupp to the neglect of spin-orbit contributions in the calculations (3). The agreement between the observed and calculated shift tensor components confirms the assignment of δ_{33} as lying along the bond direction in both the trimethyl- and triphenylphosphine complexes. The chemical shift tensors of the triphenylphosphine compounds deviate from axial symmetry, in contrast to free triphenylphosphine, which has an axially symmetric chemical shift tensor (21, 22). This asymmetry is attributed to the breakdown in local symmetry caused by the different torsional angles of the phenyl rings. For the chromium and molybdenum complexes, the δ_{22} component shows the largest difference between experimental and calculated values (4) but the spans and shift anisotropies, $\Delta\delta$, are in good agreement.

The influence of the metal atom on the phosphorus chemical shift anisotropy can be clearly seen in Table 1 and Fig. 1. The most noticeable trend is the marked decrease in the spans, ($\delta_{11} - \delta_{33}$), and anisotropies of the chemical shift tensors on moving from chromium to tungsten. This decrease is due almost entirely to changes in δ_{11} and δ_{22}. For example, in the trimethylphosphine complexes, where δ_{11} and δ_{22} change by nearly 70 ppm, δ_{33} varies by only 14 ppm. For the triphenylphosphine series, δ_{11} and δ_{22} decrease by about 20 ppm from Cr to Mo and by about 30 ppm from Mo to W. In contrast, δ_{33} for these complexes remains almost constant at –17 ± 3 ppm. It is this behaviour which results in the increased shielding observed for the solution chemical shift on going from chromium to tungsten. The DFT calculations of the shift tensor components for the series of trimethyl- and triphenylphosphine pentacarbonyl complexes the Group 6 metals showed good agreement with experiment, a result that should encourage further work, both experimental and theoretical.

Wasylishen and co-workers (6, 7) have suggested that the PhDBP ligand is analogous to triphenylphosphine and we are now able to compare the ^{31}P chemical shift tensor components of both ligands when bonded to the Group 6 metal carbonyls, Table 1. The changes in the δ_{ii} values are almost constant (within 5 ppm, and close to the experimental error) regardless of the metal atom; for PhDBP, the δ_{11} value is less shielded by 23 ppm and the δ_{22} and δ_{33} values more shielded by 30 and 19 ppm, respectively, than in the triphenylphosphine complexes.

Acknowledgements

This work was supported by grants from the Natural Sciences and Engineering Research Council of Canada and from Merck-Frosst. The authors are grateful to Dr Martin Kaupp for helpful discussions and to Drs R.E. Wasylishen and K. Eichele for the HBA program.

References

1. J. Herzfeld and A.E. Berger. J. Chem. Phys. **73,** 6021 (1980).
2. M. Kaupp, V.G. Malkin, and O.L. Malkina. *In* Encyclopedia of computational chemistry. *Edited by* P. v.R. Schleyer. Wiley Interscience, New York. 1997.
3. M. Kaupp. Chem. Ber. **129,** 535 (1996).
4. Y. Ruiz-Morales and T. Ziegler. J. Phys. Chem. A, **102**, 3970 (1998).
5. S.O. Grim, D.A. Wheatland, and W.J. McFarlane. J. Am. Chem. Soc. **89,** 5573 (1967).
6. K. Eichele, R.E. Wasylishen, J.M. Kessler, L. Solujic, and J.H. Nelson. Inorg. Chem. **35**, 3904 (1996).
7. K. Eichele, R.E. Wasylishen, K. Maitra, J.H. Nelson, and J.F. Britten. Inorg. Chem. **36**, 3539 (1997).
8. T.S.A. Hor. Inorg. Chim. Acta, **143,** 3 (1988).
9. E.W. Abel, I.S. Butler, and J.G. Reid. J. Chem. Soc. 2063 (1963).
10. M.J. Wovkulich and J.D. Atwood. Organometallics, **1**, 1316 (1982).
11. J.A. Connor, E.M. Jones, and G.K. McEwen. J. Organomet. Chem. **43**, 357 (1972).
12. K.J. Lee and T.L. Brown. Inorg. Chem. **31,** 289 (1992).
13. M.F. Guns, E.G. Claeys, and G.P. van der Kelen. J. Mol. Struct. **53,** 45 (1973).
14. R. Mathieu, M. Lenzi, and R. Poilblanc. Inorg. Chem. **9,** 2030 (1970).
15. K. Eichele and R.E. Wasylishen. HBA program. Dalhousie University, Halifax, N.S.
16. M.S. Davies, R.K. Pierans, and M.J. Aroney. J. Organomet. Chem. **458**, 141 (1993); M.S. Davies, M.J. Aroney, I.E. Buys, T.W. Hambley, and J.L. Calvert. Inorg. Chem. **34**, 330 (1995).
17. R.L. Keiter and D.G. Vander Velde. J. Organomet. Chem. **258**, C34 (1983).
18. R.K. Harris and A.C. Olivieri. Prog. NMR Spectrosc. **24**, 435 (1992).
19. J.D. Blumer, C.P. Cheng, and T.L. Brown. Chem. Phys. Lett. **51**, 473 (1977).
20. K. Eichele, R.E. Wasylishen, and J.H. Nelson. J. Phys. Chem. A, **101**, 5463 (1997).
21. G.H. Penner and R.E. Wasylishen. Can. J. Chem. **67**, 1909 (1989).
22. Y. Huang, H.L. Uhm, D.F.R. Gilson, and I.S. Butler. Inorg. Chem. **36**, 435 (1997).

This article has been cited by:

1. Cecil Dybowski, Shi Bai. 2000. %Solid-State Nuclear Magnetic Resonance. *Analytical Chemistry* **72**:12, 1-8. [CrossRef]