Organometallics 1992, *11*, 3242–3248

Applications of Two-Dimensional ^{31}P CP/MAS NMR Techniques for Studying Metal Phosphine Complexes in the Solid State

Gang Wu and Roderick E. Wasylishen*

Department of Chemistry, Dalhousie University, Halifax, Nova Scotia, Canada B3H 4J3

Received April 1, 1992

The general utility of two-dimensional (2D) spin-echo correlation (SECSY), COSY, and homonuclear *J*-resolved ^{31}P CP/MAS NMR techniques in studying metal phosphine complexes in the solid state is discussed. The cross peaks in the ^{31}P 2D CP/MAS SECSY and COSY correlation spectra provide valuable homonuclear *J* connectivity information, even when small *J* splittings are unresolved in standard 1D CP/MAS spectra. The homonuclear *J*-resolved experiment can be used to reveal small unresolved *J* couplings such as $^2J(P,P)_{cis}$ in square planar and octahedral transition-metal phosphines. The advantages of applying the 2D SECSY experiment in the solid state are discussed, and the results of the SECSY and COSY experiments are compared.

Introduction

Two-dimensional (2D) NMR techniques have become powerful tools for chemists in studying molecular structures and dynamics during the last decade.[1] The application of 2D techniques has been limited mainly to solution samples; however, there have been a few recent applications of various 2D methods, such as exchange,[2] COSY,[3] INADEQUATE,[3c,i,4] and *J*-resolved experiments,[3e,5] to study homonuclear spin systems in rigid solids under conditions of cross-polarization (CP) and magic-angle spinning (MAS). For example, Kentgens et al. studied the ultraslow molecular motion in polyoxymethylene using a 2D exchange NMR technique.[2b–d] Fyfe et al. demonstrated the general application of 2D ^{29}Si MAS COSY and INADEQUATE techniques to investigate lattice connectivity in zeolites.[3f–k,4] Kubo, Root, and McDowell showed that both *J* coupling and dipolar coupling could provide an effective mechanism for coherence transfer in 2D spectra.[3l] They further determined the relative orientation of the two ^{31}P chemical shift tensors in $Ph_2PP(O)Ph_2$ by analyzing the cross peaks in the 2D ^{31}P COSY spectrum.

The combination of ^{1}H, ^{31}P cross-polarization, magic-angle spinning, and high-power proton decoupling has become a routine ^{31}P NMR tool for characterizing transition-metal phosphine compounds in the solid state.[6] The "high-resolution" ^{31}P CP/MAS spectra of such systems are often complicated by both homonuclear and heteronuclear *J* couplings. The spectra may also exhibit a doubling of all peaks due to the presence of two nonequivalent molecules in the unit cell (of course higher order splittings are possible if the unit cell contains more than two nonequivalent molecules).[7] The presence of a mixture of two or more polymorphs can also lead to difficulties in unraveling complex overlapping spectra. Obviously, it would be advantageous to implement 2D NMR techniques which have been so successful in solution NMR studies to help simplify 1D CP/MAS ^{31}P NMR spectra.

In this paper, we demonstrate the application of ^{31}P 2D techniques involving spin-echo correlation (SECSY), COSY, and homonuclear *J*-resolved experiments to investigate several metal phosphine compounds under conditions of cross-polarization, magic-angle spinning, and high-power proton decoupling. To the best of our knowledge, the application of the ^{31}P 2D CP/MAS SECSY experiment has not been described in the literature. In a previous study, we reported the first determination of $^2J(P,P)_{cis}$ in a solid square planar rhodium(I) phosphine complex using the 2D *J*-resolved technique.[5c] Here, we extend this technique to investigate other typical metal phosphine complexes. Finally, the advantages of applying the 2D SECSY experiment in the solid state are summarized and compared with information obtained using the COSY experiment.

Experimental Section

In order to study rotating solids, two modifications were made to the conventional spin-echo correlation (SECSY), COSY, and *J*-resolved pulse sequences:[8] (1) the first ^{31}P 90° pulse was replaced by the cross-polarization segment and (2) high-power proton

---

* To whom all correspondence may be addressed. Telephone: 902-494-2564 (office); 902-494-3722 (lab). Fax line: 902-494-1310. Electronic mail: RODW@AC.DAL.CA.

(1) (a) Ernst, R. R.; Bodenhausen, G.; Wokaun, A. *Principles of Nuclear Magnetic Resonance in One and Two Dimensions*; Oxford University Press: Oxford, England, 1987. (b) Sanders, J. K. M.; Hunter, B. K. *Modern NMR Spectroscopy: A Guide for Chemists*; Oxford University Press: Oxford, England, 1987. (c) *Pulse Methods in 1D and 2D Liquid-Phase NMR*; Brey, W. S., Ed.; Academic Press: San Diego, CA, 1988. (d) Martin, G. E.; Zektzer, A. S. *Two-Dimensional NMR Methods for Establishing Molecular Connectivity: A Chemist's Guide to Experiment Selection, Performance, and Interpretation*; VCH Publishers, Inc.: New York, 1988.

(2) (a) de Jong, A. F.; Kentgens, A. P. M.; Veeman, W. S. *Chem. Phys. Lett.* 1984, *109*, 337. (b) Kentgens, A. P. M.; de Jong, A. F.; de Boer, E.; Veeman, W. S. *Macromolecules* 1985, *18*, 1045. (c) Kentgens, A. P. M.; de Boer, E.; Veeman, W. S. *J. Chem. Phys.* 1987, *87*, 6859. (d) Kentgens, A. P. M. Ph.D. Thesis, University of Nijmegen, The Netherlands, 1987. (e) Hagemeyer, A.; Schmidt-Rohr, K.; Spiess, H. W. *Adv. Magn. Reson.* 1989, *13*, 85.

(3) (a) Menger, E. M.; Vega, S.; Griffin, R. G. *J. Am. Chem. Soc.* 1986, *108*, 2215. (b) Raleigh, D. P.; Harbison, G. S.; Neiss, T. G.; Roberts, J. E.; Griffin, R. G. *Chem. Phys. Lett.* 1987, *138*, 285. (c) Benn, R.; Grondey, H.; Brevard, C.; Pagelot, A. *J. Chem. Soc., Chem. Commun.* 1988, 102. (d) Bjorholm, T. *Chem. Phys. Lett.* 1988, *143*, 259. (e) Allman, T. *J. Magn. Reson.* 1989, *83*, 637. (f) Fyfe, C. A.; Gies, H.; Feng, Y. *J. Chem. Soc., Chem. Commun.* 1989, 1240. (g) Fyfe, C. A.; Gies, H.; Feng, Y. *J. Am. Chem. Soc.* 1989, *111*, 7702. (h) Fyfe, C. A.; Gies, G.; Feng, Y.; Kokotailo, G. T. *Nature* 1989, *341*, 223. (i) Fyfe, C. A.; Feng, Y.; Gies, H.; Grondey, H.; Kokotailo, G. T. *J. Am. Chem. Soc.* 1990, *112*, 3264. (j) Fyfe, C. A.; Grondey, H.; Feng, Y.; Kokotailo, G. T. *J. Am. Chem. Soc.* 1990, *112*, 8812. (k) Fyfe, C. A.; Gies, H.; Feng, Y. Grondey, H. *Zeolites* 1990, *10*, 278. (l) Kubo, A.; Root, A.; McDowell, C. A. *J. Chem. Phys.* 1990, *93*, 5462. (m) Kolodziejski, W.; Barrie, P. J.; He, H.; Klinowski, J. *J. Chem. Soc., Chem. Commun.* 1991, 961. (n) Han, X.; Rüegger, H.; Sonderegger, J. *Chin. Sci. Bull.* 1991, *36*, 382. (o) Kolodziejski, W.; Klinowski, J. *Solid State Nucl. Magn. Reson.* 1992, *1*, 41.

(4) Fyfe, C. A.; Feng, Y.; Grondey, H.; Kokotailo, G. T.; Mar, A. *J. Phys. Chem.* 1991, *95*, 3747.

(5) (a) Kubo, A.; McDowell, C. A. *J. Chem. Phys.* 1990, *92*, 7156. (b) Challoner, R.; Nakai, T.; McDowell, C. A. *J. Chem. Phys.* 1991, *94*, 7038. (c) Wu, G.; Wasylishen, R. E. *Inorg. Chem.* 1992, *31*, 145.

(6) Fyfe, C. A. *Solid State NMR for Chemists*; CFC Press: Guelph, Ontario, Canada, 1983.

(7) Davies, J. A.; Dutremez, S. *Coord. Chem. Rev.* 1992, *114*, 61.

(8) Bax, A. *Two Dimensional Nuclear Magnetic Resonance in Liquids*; Delft University Press: Delft, The Netherlands, 1982.

0276-7333/92/2311-3242$03.00/0

decoupling was performed during both the evolution (t_1) and the detection (t_2) periods.

The pulse sequence used in the SECSY experiment was CP-(ϕ_1)–t_1/2–90°(^{31}P,ϕ_2)–t_1/2–ACQ(ϕ_3,t_2). The basic phase cycling scheme for choosing the N-type peaks[9] was then extended to a 32-step phase cycling with the initial ^{1}H 90° pulse in the CP segment altering between +*y* and −*y*: $\phi_1 = 8(+x), 8(+y), 8(-x), 8(-y)$; $\phi_2 = +x, +x, +y, +y, -x, -x, -y, -y$; $\phi_3 = 4(+x, -x), 4(+y, -y), 4(-x, +x), 4(-y, +y)$. The phase of the ^{1}H spin lock pulse in the CP segment was −*x*. The t_1 increment was synchronized with the rotor spinning period, i.e., $t_1 = 2nT_R$, where *n* is an integer and T_R is the rotor period. Since the refocusing pulse and acquisition are always started at the top of rotational echoes, all spinning sidebands in the f_1 dimension are coincident, enhancing the signals in the 2D SECSY spectra.

The COSY pulse sequence used in this study was CP-(ϕ_1)–t_1–90°(^{31}P,ϕ_2)–ACQ(ϕ_3,t_2). The coherence transfer antiecho phase cycling generally used in the solution state COSY experiment[10] was extended to a 32-step phase cycling scheme with the initial ^{1}H 90° pulse in the CP segment alternating between +*y* and −*y*: $\phi_1 = +x, +x, +y, +y, -x, -x, +x, +x$; $\phi_2 = 8(+x), 8(+y), 8(-x), 8(-y)$; $\phi_3 = 4(+x, -x, +y, -y, -x, +x, -y, +y)$. The phase of the ^{1}H spin lock pulse in the CP segment was −*x*. Typically, $t_1 = nT_R$.

In the homonuclear *J*-resolved experiment, the pulse sequence was CP(ϕ_1)–t_1/2–180°(^{31}P,ϕ_2)–t_1/2–ACQ(ϕ_3,t_2) and a simple eight-step phase cycling was employed: $\phi_1 = \phi_2 = +y, +y, +x, +x, -y, -y, -x, -x$; $\phi_3 = +y, -y, +x, -x, -y, +y, -x, +x$. The initial ^{1}H 90° pulse in the CP segment alternated between +*y* and −*y* and the phase of the ^{1}H spin lock pulse was −*x*. The t_1 increment was synchronized with the rotor, i.e., $t_1 = 2nT_R$. Again, all spinning sidebands become coincident in the f_1 dimension, enhancing the 2D signals.

Samples of the red polymorph of chlorotris(triphenylphosphine)rhodium(I), RhCl(PPh$_3$)$_3$ (**1**), (bicyclo[2.2.1]hepta-2,5-diene)bis(triphenylphosphine)rhodium(I) hexafluorophosphate, [Rh(PPh$_3$)$_2$(NBD)]$^+$PF$_6^-$ (**2**), *cis*-dichlorobis(triphenylphosphine)platinum(II), *cis*-PtCl$_2$(PPh$_3$)$_2$ (**4**), and bromotris(triphenylphosphine)rhodium(I), RhBr(PPh$_3$)$_3$ (**5**), were purchased from the Aldrich Chemical Co. and used without further purification. A sample of the orange polymorph of RhCl(PPh$_3$)$_3$ (**6**) was prepared according to the literature method.[11] Samples of tetracarbonyl[1,5-bis(diphenylphosphino)pentane]tungsten, (OC)$_4$W(dpppe) (**3**), and tetracarbonyl[bis(diphenylphosphino)methane]tungsten, (OC)$_4$W(dppm) (**7**), were kindly provided by Dr. Klaus Eichele. The preparations of these tungsten complexes are described elsewhere.[12]

All ^{31}P CP/MAS NMR spectra were recorded on a Bruker MSL-200 NMR spectrometer operating at 81.033 MHz and referenced with respect to 85% H$_3$PO$_4$(aq) by setting the ^{31}P NMR peak of solid NH$_4$H$_2$PO$_4$ to +0.81 ppm. The Hartmann–Hahn match was set by using solid NH$_4$H$_2$PO$_4$, and a typical 90° pulse width was 4.5 μs. All samples were packed into zirconium oxide rotors (7-mm o.d.). All 2D spectra were obtained in the absolute-value mode. Sine-bell window functions were applied in both dimensions prior to the 2D Fourier transformation (2D FT). The ^{13}C{^{1}H} spectrum of **2** was recorded in CD$_2$Cl$_2$ solution on a Bruker AMX 400 NMR spectrometer operating at 100.62 MHz.

Results and Discussion

The isotropic region of the 1D ^{31}P CP/MAS spectrum of the red polymorph of RhCl(PPh$_3$)$_3$ (**1**) is shown in Figure 1. In the solid state, this compound has a distorted square planar structure in which the three phosphorus atoms are nonequivalent.[13] Therefore, the ^{31}P NMR spectrum gives rise to the ABM part of an ABMX spectrum (X = ^{103}Rh, $I = ^1/_2$; 100%); the ^2J(P,P)$_{cis}$ couplings are unresolved. The AB part of the spectrum is due to the two mutually trans ^{31}P nuclei, since ^2J(P,P)$_{trans}$ couplings are usually found to be much larger than ^2J(P,P)$_{cis}$. Analysis of the 1D CP/MAS spectrum of **1** yields the following parameters: δ(P$_1$) = 50.5 ppm, δ(P$_2$) = 32.3 ppm, δ(P$_3$) = 24.8 ppm, $|^1J(\text{Rh},\text{P}_1)|$ = 191 Hz, $|^1J(\text{Rh},\text{P}_2)|$ = 139 Hz, $|^1J(\text{Rh},\text{P}_3)|$ = 146 Hz, and $|^2J(\text{P}_2,\text{P}_3)|$ = 365 Hz. Here, P$_1$ denotes the phosphorus atom trans to Cl; P$_2$ and P$_3$ are the two mutually trans phosphorus atoms which are each cis to Cl.

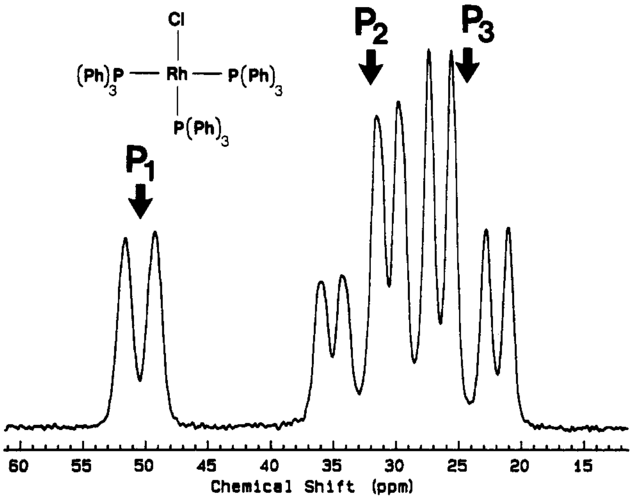

Figure 1. Isotropic region of the ^{31}P CP/MAS spectrum of the red polymorph of RhCl(PPh$_3$)$_3$. The sample spinning frequency was 4000 Hz, and the recycle time was 10 s. The contact time was 5 ms, and a total of 360 transients were recorded.

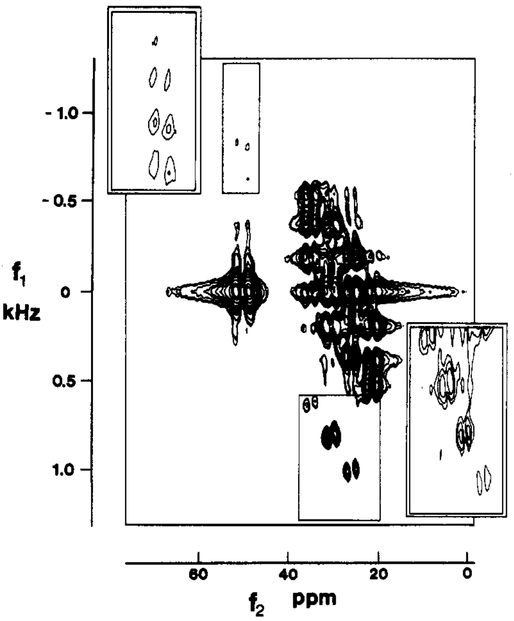

Figure 2. Isotropic part of the ^{31}P 2D SECSY spectrum of RhCl(PPh$_3$)$_3$. The double-sided inserts are lower contours and expansions of the indicated regions. The sample spinning frequency was 5400 Hz, and the recycle time was 5 s. A contact time of 5 ms was used, and the t_1 increment was 0.37 ms. A total of 64 t_1 increments were acquired and zero-filled to 128 words in the t_1 dimension prior to the 2D Fourier transformation. The digital resolution in the f_1 dimension was 20 Hz/pt. The total time to acquire the 2D FID was 2.8 h.

---

[9] (a) Nagayama, K.; Wüthrich, K.; Ernst, R. R. *Biochem. Biophys. Res. Commun.* **1979**, *90*, 305. (b) Nagayama, K.; Kumar, A.; Wüthrich, K.; Ernst, R. R. *J. Magn. Reson.* **1980**, *40*, 321.

[10] Bodenhausen, G.; Kogler, H.; Ernst, R. R. *J. Magn. Reson.* **1984**, *58*, 370.

[11] Osborn, J. A.; Jardine, F. H.; Young, J. F.; Wilkinson, G. *J. Chem. Soc. A* **1966**, 1711.

[12] (a) Eichele, K. Ph.D. Thesis, Universität Tübingen, Germany, 1991. (b) Lindner, E.; Fawzi, R.; Mayer, H. A.; Eichele, K.; Hiller, W. *Organometallics* **1992**, *11*, 1033.

[13] (a) Bennett, M. J.; Donaldson, P. B. *Inorg. Chem.* **1977**, *16*, 655. (b) Diesveld, J. W.; Menger, E. M.; Edzes, H. T.; Veeman, W. S. *J. Am. Chem. Soc.* **1980**, *102*, 7935. (c) Naito, A.; Sastry, D. L.; McDowell, C. A. *Chem. Phys. Lett.* **1985**, *115*, 19.

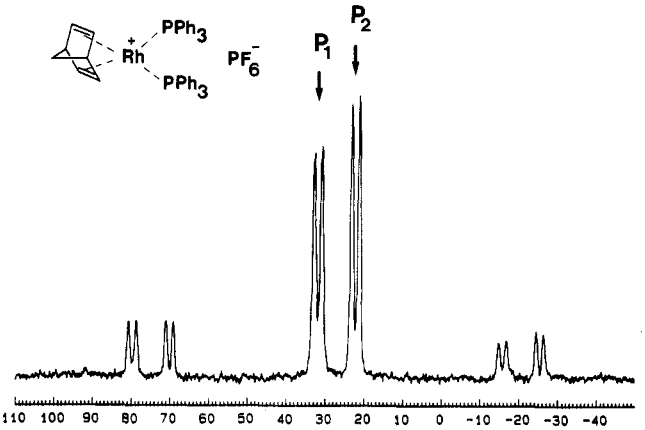

Figure 3. ^{31}P 1D CP/MAS spectrum of $[Rh(PPh_3)_2(NBD)]^+PF_6^-$. For the sake of clarity the low-frequency septet centered at −143.3 ppm due to PF_6^- with $^1J(P,F)$ = 712 Hz is not displayed. The isotropic peaks are indicated by arrows. The sample spinning frequency was 3872 Hz. The contact time was 5 ms, and the recycle time was 10 s. A total of 64 transients were recorded.

Recently, we found that one of the $^2J(P,P)_{cis}$ couplings, $^2J(P_1,P_2)_{cis} = 58 \pm 5$ Hz, is clearly resolved in the ^{31}P 2D CP/MAS homonuclear *J*-resolved spectrum of this compound.[5c] Although a nonzero $^2J(P_1,P_3)_{cis}$ is also evident from the 2D/*J*-resolved spectrum, it is too small to be resolved (<30 Hz).

The 2D ^{31}P CP/MAS SECSY spectrum of 1 is shown in Figure 2. The spectral presentation and interpretation of the CP/MAS SECSY spectra are directly analogous to those in the solution cases. Along the $f_1 = 0$ axis resides the normal 1D spectrum, which is equivalent to the diagonal line in a COSY spectrum. Cross peaks revealing *J* connectivity between nuclei at two different chemical shifts appear above and below the $f_1 = 0$ axis. A straight line that connects the related cross peaks makes an angle of 135° relative to the $f_1 = 0$ axis when both the f_1 and f_2 dimensions are equally scaled. Although the two $^2J(P,P)_{cis}$ couplings are not resolved in the normal 1D CP/MAS spectrum, the cross peaks between P_1, P_2, and P_3 are clearly observed in Figure 2. The cross peaks between P_1 and P_2 and between P_1 and P_3 are weak compared with those between P_2 and P_3. It is interesting to note that the cross peaks between P_1 and P_2 are more intense than those between P_1 and P_3, indicating $|^2J(P_1,P_2)_{cis}| > |^2J(P_1,P_3)_{cis}|$. The weaker cross peaks are only visible in the double-sided inserts of Figure 2. This is consistent with our results from the ^{31}P homonuclear *J*-resolved experiment.[5c] As is well-known from solution state NMR, 2D experiments are capable of providing *J* connectivity information even when the *J* coupling constants are too small to be resolved in 1D spectra. Similarly, the 2D SECSY spectrum of 1 demonstrates that one can also take advantage of the 2D experiment in the solid state to obtain correlation information between NMR signals via *J* coupling, even when such *J* splittings are unresolved in the normal 1D CP/MAS spectra.

The 1D ^{31}P CP/MAS NMR spectrum of $[Rh(PPh_3)_2(NBD)]^+PF_6^-$ (2) is shown in Figure 3. In the isotropic region, there are two doublets centered at 32.0 and 22.4 ppm. The half-height line widths of these peaks are about 80 Hz. Since the ^{31}P chemical shift anisotropy is large compared with the sample spinning frequency, the central isotropic peaks are flanked by first-order sidebands. The splittings of 154 and 157 Hz for the high- and low-frequency doublets, respectively, arise from the one-bond *J* coupling between ^{31}P and ^{103}Rh. The solution ^{31}P NMR parameters of the same cation[14] are $\delta(^{31}P)$ = 29.8 ppm and $^1J(P,Rh)$ = 157 Hz.

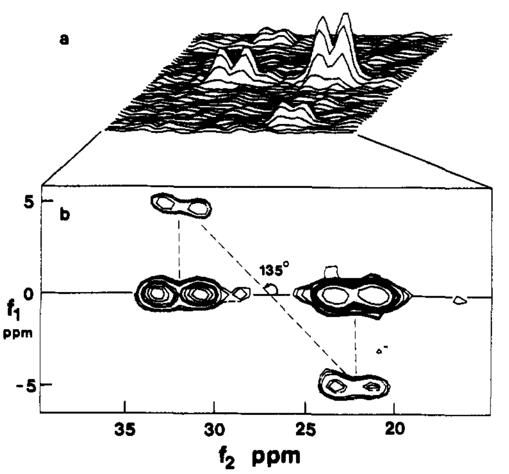

Figure 4. Stack plot (a) and contour plot (b) of the isotropic region of the 2D SECSY spectrum of $[Rh(PPh_3)_2(NBD)]^+PF_6^-$. The sample spinning frequency was 3200 Hz, and the recycle time was 5 s. The contact time was 5 ms, and the t_1 increment was 0.625 ms. A total of 32 t_1 increments were acquired and zero-filled to 64 words in the t_1 dimension prior to the 2D FT. The digital resolution in the f_1 dimension was 8 Hz/pt. The total time to record the 2D FID was only 1.4 h.

It is well-known that ^{31}P CP/MAS spectra are sensitive to the crystallographic equivalence of ^{31}P nuclei in the solid state.[6,15] However, it is not possible in the case of 2 to determine whether the two resonances at 32.0 and 22.4 ppm originate from two crystallographically nonequivalent molecules with two equivalent ^{31}P nuclei in each or from one molecule in which the two ^{31}P nuclei are nonequivalent. In principle, the ^{31}P homonuclear correlation experiment is capable of answering this question provided $^2J(P,P)_{cis} \neq 0$. The crystal structure of 2 is apparently unavailable in the literature.

The isotropic region of the 2D ^{31}P CP/MAS SECSY spectrum of 2 is shown in Figure 4. It is clear from the cross peaks that the two resonances at 32.0 and 22.4 ppm are coupled to each other via an unresolved $^2J(P,P)_{cis}$ coupling. Thus, the 2D SECSY spectrum of 2 provides one with definite evidence that the asymmetric unit contains one complete molecule with two nonequivalent nuclei.

Another 2D experiment that can provide homonuclear correlation information is the COSY experiment. In order to compare the SECSY and COSY experiments, the ^{31}P CP/MAS COSY experiment was also performed on compound 2. In the COSY experiment, it is unnecessary to synchronize the t_1 increment with the rotor period. By analyzing the cross peaks between different order spinning sidebands in such spectra, it is possible to obtain information on the relative orientation of the two corresponding chemical shift tensors.[31] However, if one is only interested in the correlation between different peaks, it is advantageous to synchronize the t_1 increment with the rotor period, i.e., $t_1 = nT_R$. Although a mismatch of the t_1 increment with the rotor period could introduce line broadening in the f_1 dimension, the stability of sample spinning frequency can be easily controlled within ±5 Hz, which is much

---

[14] Smith, R. T.; Ungar, R. K.; Sanderson, L. J.; Baird, M. C. *Organometallics* **1983**, *2*, 1138.

[15] (a) Harris, R. K.; Merwin, L. H.; Hägele, G. *J. Chem. Soc., Faraday Trans. 1* **1987**, *83*, 1055. (b) Harris, R. K.; Merwin, L. H.; Hägele, G. *J. Chem. Soc., Faraday Trans. 1* **1989**, *85*, 1409. (c) Penner, G. H.; Wasylishen, R. E. *Can. J. Chem.* **1989**, *67*, 1909. (d) Attar, S.; Bearden, W. H.; Alcock, N. W.; Alyea, E. C.; Nelson, J. H. *Inorg. Chem.* **1990**, *29*, 425. (e) Davies, J. A.; Dutremez, S.; Pinkerton, A. A. *Inorg. Chem.* **1991**, *30*, 2380.

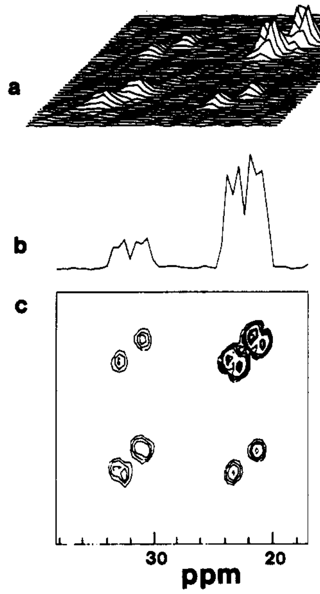

Figure 5. (a) Stack plot of the isotropic region of the 2D COSY spectrum of $[Rh(PPh_3)_2(NBD)]^+PF_6^-$. (b) Projection of the 2D COSY spectrum along the f_2 dimension. (c) Contour plot of the 2D ^{31}P CP/MAS COSY spectrum. The sample spinning frequency was 3086 Hz, and the recycle time was 5 s. A total of 256 t_1 increments were acquired and zero-filled to 512 words prior to the 2D FT. The digital resolution in the f_1 dimension was 25 Hz/pt. The total time to acquire the 2D FID was 10 h.

smaller than the observed line widths in the present study (70–150 Hz). The stack and contour plots of the 2D COSY spectrum of 2 are displayed in Figure 5. In the isotropic region, the cross peaks are apparent, indicating that the two doublets centered at 22.4 and 32.0 ppm are indeed coupled to each other via *J* coupling. Interestingly, small splittings are resolved in the projection of the 2D COSY spectrum along the f_2 dimension (see Figure 5b). Although the splitting of the antiphase multiplet in the 2D COSY spectrum is not exactly equal to the *J* coupling constant, the observation of a splitting provides definite evidence for *J* connectivity.

In order to obtain an accurate value for $^2J(P,P)_{cis}$ in 2, a ^{31}P 2D *J*-resolved CP/MAS experiment was carried out. The isotropic part of the 2D *J*-resolved spectrum of 2 is shown in Figure 6. While the *J* couplings to ^{103}Rh remain along the f_2 dimension, the homonuclear *J* couplings between the two ^{31}P nuclei appear along the f_1 dimension. The line width along the f_1 dimension was found to be reduced by a factor of 2 compared with that along the f_2 dimension, and the splitting due to $^2J(P,P)_{cis}$ is clearly resolved. The value of $^2J(P,P)_{cis}$ was estimated to be 45 ± 5 Hz from the 2D spectrum, which is similar to that observed in compound 1.

From the intensity distribution of the spinning sidebands in the 1D CP/MAS spectrum of 2, one can also obtain the principal components of the two ^{31}P chemical shift (CS) tensors using the Herzfeld–Berger approach.[16] Since the dipolar coupling constant between the two mutually cis ^{31}P nuclei is small (<500 Hz), the dipolar modulation of the spinning sidebands was assumed to be small and hence is neglected. Analysis of the spinning sidebands in the 1D CP/MAS spectrum yields the following principal components for the chemical shift tensors: δ_{11} = 88 ppm, δ_{22} = 49 ppm, and δ_{33} = −42 ppm for P_1; δ_{11} = 81 ppm, δ_{22} = 30 ppm and δ_{33} = −44 ppm for P_2. The errors in each of these values may be as large as ±5 ppm. Their values

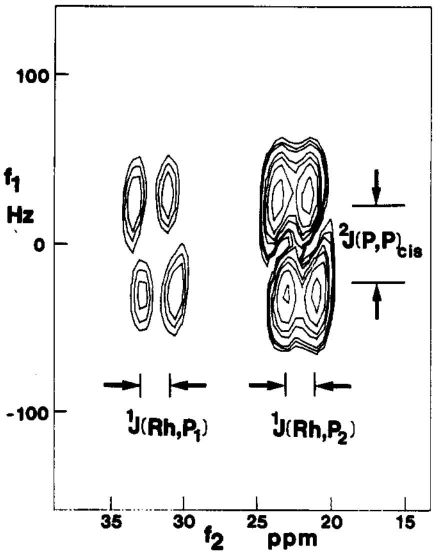

Figure 6. ^{31}P *J*-resolved 2D spectrum of $[Rh(PPh_3)_2(NBD)]^+PF_6^-$. The sample spinning frequency was 4000 Hz, and the t_1 increment was 0.50 ms. A total of 128 t_1 increments were recorded and zero-filled to 256 words prior to the 2D FT. The digital resolution in the f_1 dimension was 4 Hz/pt.

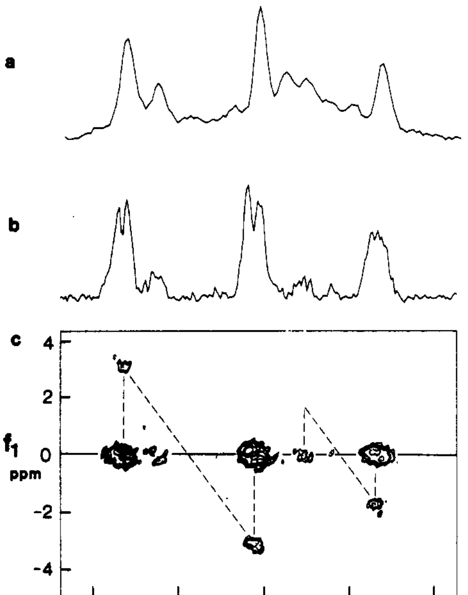

Figure 7. (a) Isotropic region of the 1D ^{31}P CP/MAS spectrum of $(OC)_4W(dpppe)$. (b) Projection of the 2D SECSY spectrum along the f_2 dimension. (c) Contour plot of the isotropic region of the 2D SECSY spectrum. The sample was spun at 3540 Hz, and the t_1 increment was 0.56 ms. A total of 128 t_1 increments were recorded and zero-filled to 256 words prior to the 2D FT. The digital resolution in the f_1 dimension was 8 Hz/pt.

were then confirmed from an analysis of the ^{31}P NMR powder line shape obtained using a static sample. It is noted that the difference between the two isotropic ^{31}P chemical shifts arises mainly from differences in δ_{22}. The X-ray crystal structure of a related compound, $[Rh(norphos)(NBD)]^+ClO_4^-$, norphos = (−)-(*R*,*R*)-2-*exo*-3-*endo*-bis(diphenylphosphino)bicyclo[2.2.1]heptene, reveals that the nonequivalence of the two ^{31}P nuclei is mainly due to different orientations of the phenyl groups attached to the phosphorus atoms; the two Rh-P bond lengths are essentially the same.[17] In a trigonal bipyramidal compound,

---

[16] Herzfeld, J.; Berger, A. E. *J. Chem. Phys.* **1980**, *73*, 6021.

[17] Kyba, E. P.; Davis, R. E.; Juri, P. N.; Shirley, K. R. *Inorg. Chem.* **1981**, *20*, 3616.

RhH(CO)(PPh$_3$)$_3$, we also found that the δ_{22} component of the ^{31}P CS tensor is sensitive to the local orientation of the phenyl groups.[18] Presumably, the variation of δ_{22} in 2 also reflects such orientational information.

The 1D ^{31}P CP/MAS spectrum of (OC)$_4$W(dpppe) (**3**) exhibits a complicated pattern;[12] see Figure 7a. On the basis of results obtained for the related compound, (OC)$_4$W(dppb), dppb = 1,4-bis(diphenylphosphino)butane, it might be argued that the two ^{31}P nuclei in **3** may be nonequivalent in the solid state.[12] However, the assignment of this pattern is impossible from the 1D spectrum. To shed some light on this problem, a 2D SECSY experiment was employed and the result is shown in Figure 7c. It is quite clear that the peaks at 16.8 and 10.5 ppm are due to two ^{31}P nuclei in the same molecule, while the peaks at 8.0 and 4.8 ppm are due to coupled ^{31}P nuclei in another nonequivalent molecule. Since the purity of **3** was confirmed by solution ^{31}P NMR, the multiplet observed in the solid state implies that the asymmetric unit cell contains more than one molecule or that there are polymorphs present in the sample. From the projection on the f_2 dimension of the 2D SECSY spectrum of **3**, one of the ^2J(P,P)$_{cis}$ couplings is well resolved, while the others are too small. However, the ^2J(P,P)$_{cis}$ coupling in **3** is readily resolved in the ^{31}P 2D *J*-resolved spectrum. While ^2J(P,P)$_{cis}$ for the two ^{31}P nuclei at 16.8 and 10.5 ppm was estimated to be 30 ± 5 Hz, which is larger than the value found in solution, 20 Hz,[12] the value of ^2J(P,P)$_{cis}$ for peaks at 8.0 and 4.8 ppm was found to be 25 ± 5 Hz. The large difference between the ^2J(P,P)$_{cis}$ couplings observed in the solid and solution states may reflect the conformational differences in the two phases. It is of interest to note that as the difference between the two ^{31}P isotropic shifts decreases and as both the isotropic shifts approach the solution shift, 7.1 ppm, ^2J(P,P)$_{cis}$ decreases.

In the ^{31}P 1D CP/MAS spectrum of *cis*-PtCl$_2$(PPh$_3$)$_2$ (**4**), there are three isotropic peaks centered at 12.7, 10.9, and 7.8 ppm.[19] The integrated area of the peaks at 12.7 ppm and 10.9 ppm was found to be half that of the peak at 7.8 ppm. They were tenatively assigned to be due to two nonequivalent crystallographic sites in the unit cell of **4**. While the two ^{31}P nuclei at one site are nonequivalent, those at the other site may have a higher symmetry so that the two ^{31}P nuclei are unresolved.

The 2D ^{31}P SECSY spectrum of **4** showed no evidence of cross peaks, indicating that ^2J(P,P)$_{cis}$ must be zero or very small. The absence of cross peaks is not surprising if one closely examines the 1D CP/MAS spectrum of **4**. The three peaks have essentially the same line widths, 120 Hz. Furthermore, since the separation between the peaks at 12.7 and 10.9 ppm is only 1.8 ppm (146 Hz at B_0 = 4.7 T) and the peak separation along the f_1 dimension is scaled by a factor of $^1/_2$ in the SECSY spectrum, overlaps between cross peaks, if there should be any, and the peaks along f_1 = 0 are likely.

To extend our previous work,[5c] we applied the 2D ^{31}P *J*-resolved technique to study other typical metal phosphine compounds. The power of this technique is beautifully demonstrated in the 2D *J*-resolved spectrum of RhBr(PPh$_3$)$_3$ (**5**), shown in Figure 8b, where the two ^2J(P,P)$_{cis}$ couplings are well resolved. In the 1D CP/MAS spectrum, Figure 8a, these small ^2J(P,P)$_{cis}$ couplings are unresolved. Analysis of the 1D ^{31}P CP/MAS spectrum of **5** yields: δ(P$_1$) = 52.7 ppm, δ(P$_2$) = 39.0 ppm, δ(P$_3$) = 29.7 ppm, |^1J(Rh,P$_1$)| = 182 Hz, |^1J(Rh,P$_2$)| = 142 Hz, |^1J(Rh,P$_3$)| = 137 Hz, and |^2J(P$_2$,P$_3$)$_{trans}$| = 357 Hz. From the 2D spectrum, ^2J(P$_1$,P$_2$)$_{cis}$ and ^2J(P$_1$,P$_3$)$_{cis}$ were found to be 53 and 29 Hz, respectively. It is interesting to compare the values of ^2J(P,P)$_{cis}$ observed in the solid state with that found in solution, 37 Hz.[20] While one of the ^2J(P,P)$_{cis}$ couplings is significantly larger than the solution value, the other one is much smaller. It is also worth noting in the 2D spectrum that the peak at 52.7 ppm is much less intense than the peaks at 39.0 ppm and 29.7 ppm. This is because of the destructive interference between the two antiphase doublets due to the two ^2J(P,P)$_{cis}$ couplings.

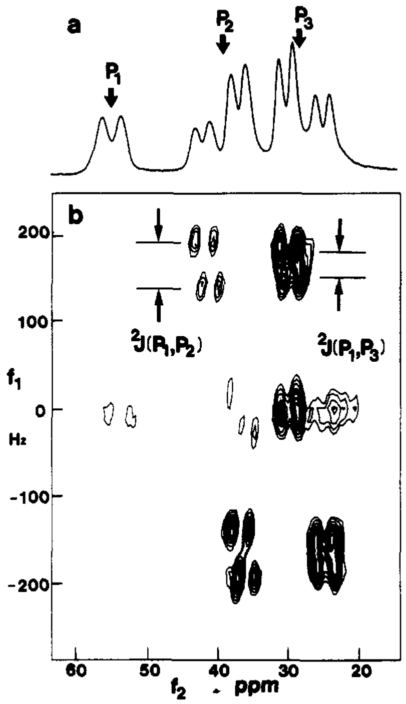

Figure 8. (a) Isotropic region of the 1D ^{31}P CP/MAS spectrum of RhBr(PPh$_3$)$_3$. (b) ^{31}P *J*-resolved 2D spectrum. The sample spinning frequency was 4000 Hz, and the t_1 increment was 0.50 ms. A total of 64 t_1 increments were acquired and zero-filled to 128 words prior to the 2D FT. The digital resolution in the f_1 dimension was 7 Hz/pt.

Table I. Values of ^2J(P,P)$_{cis}$ for Rhodium and Tungsten Phosphine Compounds in the Solid State

compd	$\Delta\nu_{1/2}$/Hz[a]	|^2J(P,P)$_{cis}$|/Hz solid[b]	|^2J(P,P)$_{cis}$|/Hz solution
RhCl(PPh$_3$)$_3$ (red) (**1**)	90–125	58, <30	38[c]
[Rh(PPh$_3$)$_2$(NBD)]$^+$PF$_6^-$ (**2**)	80	45	32[d]
(OC)$_4$W(dpppe) (**3**)	77	30, 25	19.7[e]
RhBr(PPh$_3$)$_3$ (**5**)	91–127	43, 29	37[c]
RhCl(PPh$_3$)$_3$ (orange) (**6**)	97–146	48, <30	38[c]
(OC)$_4$W(dppm) (**7**)	75	31	30.9[e]

[a] Half-height line width in the 1D ^{31}P CP/MAS spectra. [b] Error was estimated to be ±5 Hz. [c] From ref 20. [d] Obtained by analyzing the ^{13}C{^{1}H} spectrum in CD$_2$Cl$_2$ solution. [e] From ref 12.

Values of ^2J(P,P)$_{cis}$ in four square planar rhodium phosphine compounds and two octahedral tungsten phosphine compounds measured in the solid state using the 2D *J*-resolved technique are given in Table I. The corresponding values obtained in the solution state are also given. There seems to be no clear correlation between the ^2J(P,P)$_{cis}$ values found in the solid state and those observed in solutions. However, it can be seen that the value of ^2J(P,P)$_{cis}$ is quite sensitive to the crystallographic non-

---

(18) Wu, G.; Wasylishen, R. E.; Curtis, R. D. *Can. J. Chem.* **1992**, *70*, 863.

(19) (a) Harris, R. K.; McNaught, I. J.; Reams, P.; Packer, K. J. *Magn. Reson. Chem.* **1991**, *29*, S60. (b) Power, W. P.; Wasylishen, R. E. *Inorg. Chem.* **1992**, *31*, 2176.

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

equivalence of ^{31}P nuclei in the solid state. Presumably, the value of $^{2}J(\mathrm{P,P})_{cis}$ may be correlated with the local geometry about the two ^{31}P nuclei. In the normal 1D ^{31}P CP/MAS spectra of these metal phosphine compounds, the half-height line width ranges from 75 to 146 Hz and splitting due to $^{2}J(\mathrm{P,P})_{cis}$ cannot be resolved. We have found that homonuclear J coupling constants greater than one-third of the half-height line width in 1D ^{31}P CP/MAS NMR spectra can usually be resolved using the 2D J-resolved experiment. The errors in the $^{2}J(\mathrm{P,P})_{cis}$ values given in Table I were estimated to be ±5 Hz on the basis of the digital resolution along the f_1 dimension and the antiphase nature of these J-splittings. The signs of $^{2}J(\mathrm{P,P})_{cis}$ cannot be derived from the 2D J-resolved spectra.

In solution-state NMR, the advantage of employing the spin-echo 2D technique is to improve the resolution in the f_1 dimension by refocusing the magnetization dephased due to an inhomogeneous magnetic field. In the solid state, however, there are several intrinsic mechanisms of line broadening[21] which contribute more significantly to line width in the MAS spectra than the field inhomogeneity does. In fact, the magnetic field inhomogeneity contributes less than 4 Hz to the ^{31}P NMR line widths on our spectrometer, compared with the observed line width of 70–150 Hz in the metal phosphine compounds in the present study. The homonuclear dipolar interaction between the ^{31}P nuclei, the residual heteronuclear dipolar interaction between the ^{31}P and ^{1}H nuclei due to inefficient proton decoupling, the anisotropic ^{31}P chemical shifts, and magnetic susceptibility play more important roles in broadening the lines of an MAS spectrum. The spin-echo techniques used in SECSY and J-resolved 2D experiments take advantage of the fact that, at the top of each echo, the heteronuclear dipolar and anisotropic chemical shift interactions are refocused. Thus superior resolution is achieved in the f_1 dimension of a 2D spectrum. In principle, this resolution in the f_1 dimension is merely determined by the magnitude of the ^{31}P homonuclear dipolar interaction (here we ignore those factors that an experimentalist can control, e.g., rotor stability and magic-angle setting, etc.). Since the line widths in the MAS spectra are often linear with applied magnetic fields,[21c] resolution improvement by using spin-echo techniques will be more important at higher applied magnetic fields. A similar improvement in resolution can also be achieved by 1D rotor-synchronization CPMG spin-echo experiments for solid samples.[22] The resolution of ^{31}P MAS spectra can be further improved by combining the ^{31}P CRAMPS technique with cross-polarization and high-power proton decoupling.[23] In the latter experiment, line broadening due to both homonuclear ^{31}P dipolar interactions and anisotropic chemical shifts is reduced. Possibly, the combination of ^{31}P CRAMPS and 2D techniques could further increase the power of 2D techniques to study solid materials.

Conclusions

Since $^{2}J(\mathrm{P,P})_{cis}$ values are generally small in transition metal phosphines, they usually cannot be resolved in the normal 1D CP/MAS spectra of solids.[24] As we have demonstrated, the 2D experiments are of importance in providing information on spectral assignment via J connectivity, especially when there is more than one crystallographically nonequivalent site or polymorphism.

Although the 2D SECSY experiment is less popular than the COSY experiment in solution NMR studies, it does have some definite advantages over COSY in the solid state. (1) The line broadening in the MAS spectra is mainly due to residual anisotropic interactions in the solid state. With use of the spin-echo technique, line broadening mechanisms due to anisotropic chemical shifts, heteronuclear dipolar, and first-order quadrupolar interactions can be partially refocused in the 2D SECSY experiment, providing superior resolution along the f_1 dimension. This improvement in resolution enhances the sensitivity of the 2D SECSY experiment in detecting small J coupling constants, which may cause complete cancellation of the antiphase cross peaks in the COSY spectra. This problem may become more important at high applied fields. Although the chemical shift differences are scaled by a factor of $^{1}/_{2}$ in the f_1 dimension of SECSY spectra, the J-splittings in the antiphase cross peaks remain invariant. Recently, Kolodziejski and Klinowski[3c] have demonstrated that the SUPERCOSY sequence can enhance the sensitivity of the COSY experiment in the solid state; however, this sequence is severely limited to materials with very long T_2 relaxation times, i.e., $T_2 > 1/(2J)$, which requires a T_2 on the order of 20 ms to resolve a $^{2}J(\mathrm{P,P})_{cis}$ coupling of 30 Hz. For the metal phosphine compounds investigated in the present study the T_2 values are less than 5 ms. (2) Since the spectral width of the f_1 dimension of the SECSY spectra is determined only by the isotropic chemical shift difference between coupled nuclear spins, it has the potential to reduce the 2D data size. The smaller spectral width required for the f_1 dimension also has the advantage of shortening the total experimental time. (3) The usual disadvantage of the SECSY experiment in solution NMR is its poor sensitivity compared with COSY. This can be compensated for in the solid state by the rotation–synchronization of the t_1 increment. All spinning sidebands along the f_1 dimension become coincident, thereby enhancing the cross peaks in the 2D SECSY spectra.

Since the spin-echo technique used in the 2D J-resolved experiment has the potential to reduce the line width along the f_1 dimension,[5c] it is also an important experiment for systems where small J couplings cannot be resolved in the 1D spectra. Not only does the resolution of such small J couplings provide information for spectral assignment but the value of the J coupling constant itself may also reflect structural information in the solid state. Since small unresolved J couplings between ^{31}P nuclei exist in many inorganic solids, the application of the 2D ^{31}P CP/MAS homonuclear J-resolved experiment is of general importance.

The above examples clearly demonstrate that 2D ^{31}P CP/MAS experiments can be used as routine methods for studying metal phosphine compounds in the solid state. Obviously, they are also applicable to other systems. Other 2D pulse sequences frequently used in solution-state NMR can also be extended to study solid materials under conditions of cross-polarization, magic-angle spinning, and

---

(21) (a) Maricq, M. M.; Waugh, J. S. *J. Chem. Phys.* **1979**, *70*, 3300. (b) VanderHart, D. L.; Earl, W. L.; Garroway, A. N. *J. Magn. Reson.* **1981**, *44*, 361. (c) Alla, M.; Lippmaa, E. *Chem. Phys. Lett.* **1982**, *87*, 30. (d) Maciel, G. E. In *Magnetic Resonance. Introduction, Advanced Topics and Applications to Fossil Energy*; Petrakis, L., Fraissard, J. P., Eds.; D. Reidel Publishing Co.: Boston, MA, 1984; Vol. 124, p 71. (e) Hemminga, M. A.; de Jager, P. A.; Krüse, J.; Lamerichs, R. M. J. N. *J. Magn. Reson.* **1987**, *71*, 446. (f) Brunner, E.; Freude, D.; Gerstein, B. C.; Pfeifer, H. *J. Magn. Reson.* **1990**, *90*, 90.

(22) Harris, R. K.; Sebald, A. *Magn. Reson. Chem.* **1989**, *27*, 81.

(23) Harris, R. K.; Jackson, P.; Wilkes, P. J.; Belton, P. S. *J. Magn. Reson.* **1987**, *73*, 178.

(24) (a) Pregosin, P. S.; Kunz, R. W. In *NMR Basic Principles and Progress*; Diehl, P., Fluck, E., Kosfeld, R., Eds.; Springer-Verlag: Berlin, 1979; Vol. 16. (b) Maciel, G. E.; O'Donnell, D. J.; Greaves, R. In *Advances in Chemistry Series*; Alyea, E. C., Meek, D. W., Eds.; American Chemical Society: Washington, DC, 1982; Vol. 196, p 389.

high-power heteronuclear decoupling. Implementation of these techniques to solid-state problems is under active investigation in our laboratory.

Acknowledgment. We wish to thank Dr. Klaus Eichele for providing compounds 3 and 7 and for helpful discussions concerning this work. We are grateful to the NSERC of Canada for financial support.

OM920184T

Photoelectron Spectroscopy of f-Element Organometallic Complexes. 8.[†] DV–Xα and Gas-Phase UV Photoelectron Spectroscopic Investigation of the Electronic Structure of Tris(η^5-cyclopentadienyl)uranium(IV) Complexes[‡]

Antonino Gulino, Enrico Ciliberto, Santo Di Bella, and Ignazio Fragalà*

Dipartimento di Scienze Chimiche, Università di Catania, Viale A. Doria 6, 95125 Catania, Italy

Afif M. Seyam[§] and Tobin J. Marks*

Department of Chemistry, Northwestern University, Evanston, Illinois 60208-3113

Received April 22, 1992

The electronic structures of a series of closely related $U(\eta^5\text{-}C_5H_5)_3L$ (L = $-CH_3$, $-NH_2$, $-BH_4$, $-NCS$) complexes has been studied using the SCF Hartree–Fock–Slater first-principles discrete variational Xα method in combination with He I and He II UV photoelectron spectroscopy. The theoretical results reproduce the experimental He I and He II photoelectron spectroscopic data, thus providing a reliable description of the metal–ligand bonding. Symmetry considerations render the 5f elements well-suited templates for coordination of the Cp_3 ligand cluster. Interactions not restricted by symmetry appear partially or entirely modulated by the angular properties of π_2-related MO's. Bonding interactions with ancillary L ligands involve either $5f_{z^3}$ or $6d_{z^2}$ metal orbitals, depending upon the energies of the unperturbed ligand orbital counterparts. Metal–ligand interactions cause the energies of 5f orbitals to split into a narrow manifold with a remarkable "ligand field" energy shift associated only with the $5f_{y(3x^2-y^2)}$ orbital. The L→M charge donation results in an electronic configuration of the uranium atom which is almost constant throughout the $U(C_5H_5)_3L$ series and similar to that found in a fully relativistic SCF Dirac–Slater calculation on the simpler uranium atom. The stringent necessity of maintaining the uranium center in a particularly stable electronic configuration causes greater donation (hence larger covalency in the bonding) from ancillary L ligands to be compensated for by an increasing (L = $-NH_2 < -CH_3 < -NCS < BH_4^-$) ionic character of the U–Cp bonds. The present results show that nonrelativistic DV–Xα calculations, optimized for basis set and potential representation, reproduce experimental photoelectron spectroscopic data, including He I/He II relative intensity changes.

Introduction

Actinide organometallic chemistry today represents a large and active research area.[1] Among the variety of new molecules that have been reported since the earliest synthesis of UCp_3Cl (Cp = $\eta^5\text{-}C_5H_5$),[2] Cp–actinide complexes still represent a cornerstone because of their rich chemistry and structural variety. The important problem associated with understanding actinide molecular electronic structures has, conversely, received considerable attention only recently[1,3] and, in addition to classical 5f coordination complexes,[4] a number of reports have focused on organometallic molecules, including $Cp_{4-x}AnL_x$ complexes.[3,5] Theoretical as well as experimental studies have shown that the metal–ligand bonding involves donation of ligand electron density into both metal 5f and 6d atomic orbitals.[5] Evidence has also been provided for metal→ligand back-donation for those ancillary L ligands having π-acidic character.[6] Nevertheless, details of 5f vs 6d metal contributions to the bonding still remain an open question. The variation of the He I vs He II relative photoelectron (PE) spectroscopic peak intensities[3b,7] has provided experimental evidence of metal 5f involvement because of

---

[†] Part 7: Reference 5j.

[‡] Abstracted in part from the Ph.D. Thesis of A. Gulino, Università di Catania, 1989.

[§] On leave from the Department of Chemistry, University of Jordan, Amman, Jordan.

(1) (a) Bursten, B. E.; Strittmatter, R. J. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 1069–1085. (b) Marks, T. J.; Streitwieser, A., Jr. In *The Chemistry of the Actinide Elements*; Katz, J. J., Seaborg, G. T., Morss, L. R., Eds.; Chapman and Hall: London, 1986; Vol. 2, pp 1547–1587. (c) Marks, T. J. In *The Chemistry of the Actinide Elements*, 2nd ed.; Katz, J. J., Seaborg, G. T., Morss, L. R., Eds.; Chapman and Hall: London, 1986; Vol. 2, pp 1588–1627. (d) *Fundamental and Technological Aspects of Organo-f-Element Chemistry*; Marks, T. J., Fragalà, I. L., Eds.; D. Reidel: Dordrecht, Holland, 1985. (e) Marks, T. J.; Ernst, R. D. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon Press: Oxford, U.K., 1982; Chapter 21, and references therein. (f) Marks, T. J. *Science* **1982**, *217*, 989 and references therein. (g) *Actinides in Perspective*; Edelstein, N. M., Ed.; Pergamon Press: Oxford, U.K., 1981. (h) Marks, T. J.; Manriquez, J. M.; Fagan, P. J.; Day, V. W.; Day, C. S.; Vollmer, S. H. *ACS Symp. Ser.* **1980**, *No. 131*, 1. (i) Marks, T. J. *Prog. Inorg. Chem.* **1979**, *25*, 224–333 and references therein. (j) *Organometallics of f-Elements*; Marks, T. J., Fischer, R. D., Eds.; D. Reidel: Dordrecht, Holland, 1979, and references therein.

(2) Reynolds, L. T.; Wilkinson, G. *J. Inorg. Nucl. Chem.* **1956**, *2*, 246–253.

(3) (a) Fischer, R. D. *Angew. Chem., Int. Ed. Engl.* **1965**, *4*, 972. (b) Fragalà, I. In ref 1j, pp 421–466. (c) Fragalà, I.; Gulino, A. In ref 1d, pp 327–360. (d) Burns, C. J.; Bursten, B. E. *Comments Inorg. Chem.* **1989**, 2, 61–93. (e) Pepper, M.; Bursten, B. E. *Chem. Rev.* **1991**, *91*, 719–741.

(4) (a) Fragalà, I.; Condorelli, G.; Tondello, E.; Cassol, A. *Inorg. Chem.* **1978**, *17*, 3175–3179. (b) Casarin, M.; Ciliberto, E.; Fragalà, I.; Granozzi, G. *Inorg. Chim. Acta* **1982**, *64*, L247–L249. (c) Bursten, B. E.; Casarin, M.; Ellis, D. E.; Fragalà, I.; Marks, T. J. *Inorg. Chem.* **1986**, *25*, 1257–1261.