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Solid-State ^{31}P NMR Studies of Mercury(II) Phosphonates. Anisotropies of the ^{31}P Chemical Shift and the ^{31}P–^{199}Hg Indirect Spin–Spin Coupling

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The ^{31}P powder NMR line shapes of a number of solid mercury(II) phosphonates are analyzed in order to determine the anisotropies in both the ^{31}P chemical shift and the ^{31}P–^{199}Hg indirect spin–spin coupling. The magnitudes and orientation of the principal components of the ^{31}P chemical shift tensor are determined for diethyl *N*-phenylphosphoramidate, $(EtO)_2P(O)NHPh$, by using dipolar–chemical shift NMR spectroscopy. Spectral simulations indicate that the most shielded component of the ^{31}P chemical shift tensor lies along the P=O bond, while the intermediate component, δ_{22}, lies perpendicular to the N—P=O plane. This information is used to interpret the ^{31}P NMR line shapes for a series of mercury phosphonate complexes. These spectra indicate the presence of substantial anisotropies in the ^{31}P–^{199}Hg indirect spin–spin (J) coupling, ranging from 1500 to 2700 Hz. The large anisotropies in J indicate that mechanisms other than the Fermi contact contribute to the electron-mediated communication between ^{31}P and ^{199}Hg.

Introduction

The isotropic values of chemical shifts and indirect spin–spin or J coupling constants have been used for many years to derive information concerning the molecular structure of transition-metal compounds from high-resolution NMR spectra. Modern solid-state high-resolution NMR techniques,[1] using high-power proton decoupling, cross-polarization, and magic-angle spinning, have been applied recently to metal complexes[2-4] to provide a more exact comparison between spectroscopic data and the molecular structure as determined by X-ray diffraction. It has become apparent from these NMR investigations, as well as NMR studies of many other compounds in solid or oriented phases, that substantially more information can be obtained from the three-dimensional nature of the various interactions which are manifested in the NMR spectrum.[5-9] In this fashion, various values of the chemical shift or the J coupling may be found to correspond with specific orientations of a molecule in the magnetic field, providing a more complete picture of the anisotropic nature of the molecule under investigation.

While numerous studies of this type have been performed to determine chemical shift anisotropies,[10] relatively little is known about the anisotropy in the indirect spin–spin coupling. Although much theoretical effort has been placed on calculating anisotropies in J coupling (ΔJ),[11-13] the experimental difficulties in measuring this parameter precisely have discouraged its study. In the solid state, the Hamiltonian containing the anisotropy in J is mathematically linked with that of the direct dipolar coupling between two nuclei.[11,14] Thus, in practice, the two interactions cannot be measured independently. For light nuclei, there is usually some uncertainty in the magnitude of the direct dipolar coupling due to librational motion.[15] The propagation of this error into estimates of ΔJ has often led to uncertainties on the order of, or even greater than, the actual magnitude of ΔJ quoted.

Despite the difficulties in determining the anisotropy in J coupling, the importance of its measurement cannot be diminished. The indirect spin–spin coupling between two nuclei was originally described by Ramsey[16] in terms of several mechanisms that allow electron-mediated communication between the nuclear spins.[11,17-19] The terms that contribute to the second-rank indirect coupling tensor are given by eq 1, where $\mathbf{J}^{(1a)}$ is the diamagnetic orbital

$$\mathbf{J} = \mathbf{J}^{(1a)} + \mathbf{J}^{(1b)} + \mathbf{J}^{(2)} + \mathbf{J}^{(3)} + \mathbf{J}^{(4)} \qquad (1)$$

contribution, $\mathbf{J}^{(1b)}$ is the paramagnetic orbital contribution, $\mathbf{J}^{(2)}$ is the spin–dipolar contribution, $\mathbf{J}^{(3)}$ is the Fermi contact term, and $\mathbf{J}^{(4)}$ is a cross-term between the spin–dipolar and contact Hamiltonians. The most important of these, and the one most commonly mentioned in the interpretation of isotropic values of $\mathbf{J}$, is the Fermi contact mechanism ($\mathbf{J}^{(3)}$). The Fermi contact contribution is completely isotropic, depending on the electron density precisely at the nuclei involved. The other terms $\mathbf{J}^{(1b)}$, $\mathbf{J}^{(2)}$, and $\mathbf{J}^{(4)}$ contribute to the anisotropy of the coupling tensor, while $\mathbf{J}^{(1)}$ and $\mathbf{J}^{(2)}$ also contribute to the isotropic value of $\mathbf{J}$. For heavier nuclei, it has been recognized that relativistic effects influence the electronic interactions.[20] The relativistic treatment of indirect spin–spin coupling incorporates the four terms of Ramsey's formalism[16] into a single expression.[13] However, it is possible to separate the relativistic expression into two terms, one of which is analogous to the Fermi contact, $\mathbf{J}^{(3)}$, depending on the electron density at the two nuclei.[13] The anisotropy in $\mathbf{J}$ remains in the other relativistic term. Thus, if experiments indicate any anisotropy in $\mathbf{J}$, it is clear that interpretations based solely on the Fermi contact mechanism may need to be reevaluated. Lucid descriptions of computational schemes for calculating $\mathbf{J}$ have recently been reviewed by Jameson.[11,18]

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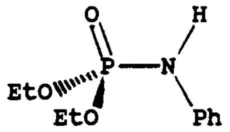
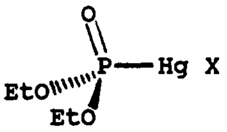
In order to provide both experimental evidence of the existence of ΔJ and some idea of the magnitudes that can be expected, we have undertaken a study of a number of mercury–phosphorus compounds,[21] in this case concentrating on the mercury phosphonates. These compounds have been well characterized by both solution NMR spectroscopy and X-ray diffraction.[22] Previous NMR studies have shown that the indirect spin–spin couplings between ^{199}Hg and ^{31}P are some of the largest couplings yet measured.[23] The theoretical calculations also indicate that the anisotropic terms of the J coupling Hamiltonian contribute more for the heavier nuclei, due to relativistic effects.[13] The effects of any librational motion should be quite minimal for these large, heavy molecules; thus estimates of the ^{199}Hg–^{31}P direct dipolar coupling based on Hg–P bond lengths determined by X-ray diffraction should be quite accurate. In the process of this investigation, we have determined the orientation of the ^{31}P chemical shift tensor for the phosphonate group in diethyl *N*-phenylphosphoramidate (**1**), making it one of the few ^{31}P chemical shift tensor orientations determined for P=O compounds that have not relied on symmetry arguments. We then proceeded to analyze the ^{31}P line shapes from a series of (diethyl phosphonato)mercury(II) complexes (**2**) and establish the presence of any anisotropy in the ^{31}P–^{199}Hg indirect spin–spin coupling of these compounds.



1

a ^{15}N

b ^{14}N



2

a X = CH_3COO

b SCN

c Cl

d Br

e I

Experimental Section

Preparation of Compounds. $(EtO)_2P(O)^{14/15}NHPh$ (1). These compounds were prepared according to literature methods,[24] by reacting diethyl phosphite with aniline-^{15}N (99%) (for **1a**) or aniline (for **1b**), to yield a yellow oil. White crystals were obtained by adding a small amount of ethanol to the oil, followed by cooling in an ice bath. The crystals were isolated by filtration and washed with H_2O.

$(EtO)_2P(O)Hg(OOCCH_3)$ (2a) and $(EtO)_2P(O)Hg(SCN)$ (2b). These were prepared as described by Fox and Venezky.[25]

$(EtO)_2P(O)HgX$ (X = Cl, Br, I) (2c–e). The compounds were prepared as described by Fox and Venezky.[25] The products were recrystallized from a benzene–hexane mixture. The iodide salt was found to turn yellow with the appearance of elemental Hg upon prolonged exposure to air and/or light.

NMR Spectra. The purity of all compounds prepared was analyzed by ^{31}P solution NMR spectroscopy at 146.3 MHz on a Nicolet NT-360 NB NMR spectrometer, with the compounds dissolved in dichloromethane (0.4 M), except compound **2b**, which was dissolved in dimethylformamide (0.4 M). Solution spectra were obtained with acquisition times of 0.606 s at a temperature of 293 K. All solid-state ^{31}P NMR spectra were obtained at 81.0 MHz on a Bruker MSL-200 NMR spectrometer under conditions of cross-polarization (CP) and high-power proton decoupling. Typical ^{1}H–^{31}P times for the CP sequence were 3 ms. The pulse widths for the Hartmann–Hahn matching condition were 4 μs, corresponding to a ^{1}H decoupling field of 62.5 kHz (14.7 G). Magic-angle spinning (MAS) spectra were obtained at spinning rates between 2 and 4 kHz in a Bruker double-air-bearing MAS probe. Acquisition times for the solid-state NMR experiments were 65.57 ms, during which 4096 data points were collected. The resulting free-induction decays were zero-filled to 8192 data points prior to Fourier transformation. All spectra were obtained at 293 K and were referenced with respect to 85% H_3PO_4(aq); for the solid-state NMR spectra, this was accomplished by using $NH_4H_2PO_4$(s), which has a ^{31}P chemical shift of +0.81 ppm with respect to 85% H_3PO_4(aq).

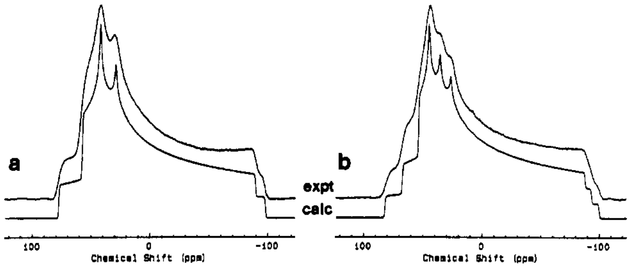


Figure 1. Experimental and calculated ^{31}P CP static NMR spectra of $(EtO)_2P(O)NHPh$: (a) ^{15}N-enriched (**1a**); (b) ^{14}N (**1b**). The calculated spectra were generated by using the following parameters: δ_{11} = 67.9 ppm, δ_{22} = 36.1 ppm, δ_{33} = −93.5 ppm, $R(^{31}P,^{15}N)$ = −1010 Hz, $R(^{31}P,^{14}N)$ = +720 Hz, $^1J_{iso}(^{31}P,^{15}N)$ = −42 Hz, $^1J_{iso}(^{31}P,^{14}N)$ = +30 Hz, α = 0°, β = 110°. The calculated spectra were convoluted with 100-Hz Gaussian broadening.

Simulated spectra were generated by using a FORTRAN-77 program developed in this laboratory incorporating the POWDER simulation routine,[26] and all calculations were performed on a 80286/287 microcomputer.

Results and Discussion

$(EtO)_2P(O)^{14/15}NHPh$ (1). The ^{31}P static powder NMR spectra for compounds **1a** and **1b** are given in Figure 1. The detailed line shapes result from the orientation dependence of the ^{31}P chemical shift and ^{31}P–^{15}N or ^{31}P–^{14}N dipolar coupling. The dipolar coupling causes the anisotropic ^{31}P chemical shift powder pattern to be split into two and three subspectra for the ^{15}N ($I = {}^1/_2$) and ^{14}N (I = 1) compounds, respectively.[27] The magnitude of the splittings at the shoulders and peaks of the ^{31}P spectra can be analyzed to provide the orientation of the ^{31}P chemical shift tensor with respect to the dipolar vector,[14,28,29] which in this case is the P–N bond. For compound **1b**, the ^{31}P line shape was analzyed under the high-field approximation, where it is assumed that the quadrupolar interaction of the ^{14}N nucleus does not distort the ^{31}P–^{14}N dipolar splittings.[27c] The parameters used to generate these best-fit line shapes shown in Figure 1 are given in the figure caption. The excellent agreement between the ^{31}P powder NMR spectrum for compound **1b**, calculated by using the parameters from the best-fit simulation for **1a** without adjustment, and the experimental line shape indicates that the high-field approximation is valid in this case.

The ^{31}P chemical shift tensor is quite anisotropic, with the overall line shape spanning a spectral width of over 160 ppm, or 13 kHz at 81.0 MHz, the Larmor frequency for ^{31}P at a magnetic field strength of 4.70 T. With the use of standard convention for chemical shielding parameters,[6,10] the chemical shielding anisotropy, $\Delta\sigma$, is 145.5 ppm, with an asymmetry (η_σ) or deviation from axial symmetry of 0.33. This is typical for ^{31}P nuclei in phosphonates,[10] where on average $\Delta\sigma$ = 168 ppm and η_σ = 0.47.

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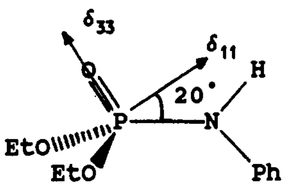
The values obtained here also agree very well with the results of Klose et al.[30] for a series of phosphonic acids and esters, especially for compounds that contained an alkoxy functionality in place of the anilino group in compound **1**.

The ^{31}P–^{15}N dipolar coupling constant, $R = 1010 \pm 30$ Hz for **1a**, is in good agreement with those reported for $(PhO)_2P(O)^{15}NHMe$ (950 and 1100 Hz) by Griffin et al.[31] using two separate MAS experiments that are sensitive to dipolar coupling. This value for the ^{31}P–^{15}N dipolar coupling constant (1010 ± 30 Hz) corresponds to a P–N bond length of 1.70 ± 0.02 Å, somewhat longer than the X-ray diffraction value of 1.62 Å reported for a similar compound, $(MeO)_2P(O)NHPh$.[32] This difference is not surprising, as librational motion would reduce the observed magnitude of R obtained from the NMR spectrum.[15] Molecular motion causes bond lengths derived from dipolar NMR studies to be longer, in general, than those determined by X-ray diffraction and can be expected to occur in molecules containing relatively light nuclei. This difference between X-ray diffraction and NMR-derived bond lengths is not expected to introduce substantial errors and should not influence the results of the analysis performed here. It is unlikely that this difference in bond lengths determined by X-ray diffraction and NMR spectroscopy is due to anisotropy in **J**, as such effects should be extremely minimal for indirect coupling between relatively light nuclei.[17]

The Euler angles, α and β, orient the principal components of the ^{31}P chemical shift tensor with respect to the P–N bond (dipolar vector), where β describes the angle between the most shielded component of the ^{31}P chemical shift tensor, δ_{33}, and the P–N vector and α is the angle between the projection of the P–N vector onto the δ_{11}–δ_{22} plane and δ_{11} itself.[27,29] These angles were varied until the splittings in the calculated spectra matched the splittings observed at the regions of the singularities of the ^{31}P NMR powder pattern, and the ones quoted here are those that provided a best-fit simulation of the experimental line shapes. The X-ray crystal structure for $(MeO)_2P(O)NHPh$ indicates that the N—P═O angle is approximately 111 ± 1°.[32] The optimum values for α and β of 0 ± 5 and 110 ± 2° (or, equivalently, 70 ± 2°), respectively, place δ_{33}, the most shielded component, along the P═O bond, as indicated in the following diagram:



This is in accord with ^{31}P chemical shift tensor orientations derived for other phosphorus(V) compounds containing the P═O moiety on the basis of symmetry considerations,[30,33,34] single-crystal NMR results,[35,36] and theoretical calculations,[37] although it differs from the orientation determined for the fluorophosphates.[38] The values of α and β for **1** place δ_{22} perpendicular to the N—P═O plane. We anticipate that the orientation of the ^{31}P chemical shift tensor will be similar in all phosphonates.

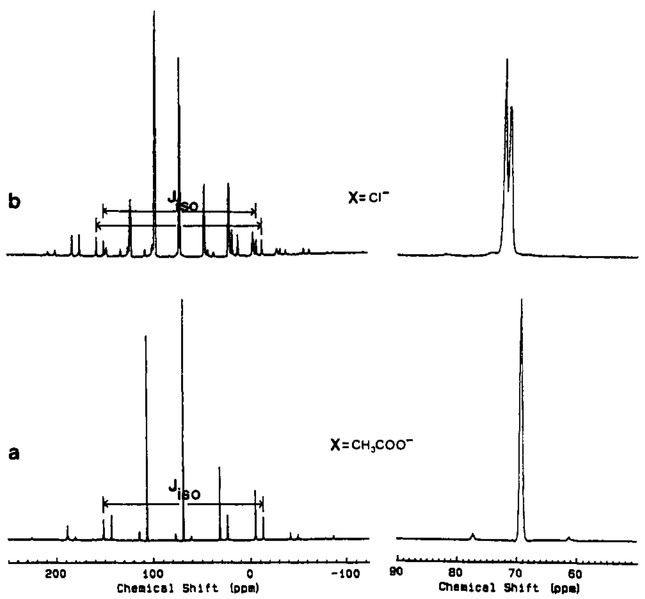


Figure 2. Phosphorus-31 CPMAS spectra of two mercury phosphonate compounds: (a) the acetate complex, **2a**; (b) the chloride complex, **2c**. The regions of the ^{31}P isotropic chemical shifts are expanded on the right, and splittings due to J coupling with ^{199}Hg nuclei are indicated in the full spectra.

Table I. Isotropic ^{31}P Chemical Shifts (ppm) and ^{31}P–^{199}Hg Indirect Spin–Spin Coupling Constants (Hz) for the Mercury Phosphonates $(EtO)_2P(O)HgX$ (**2**) in Dichloromethane Solution and in the Solid State, As Determined by ^{31}P Solution NMR Spectroscopy and ^{31}P CPMAS NMR Spectroscopy, Respectively[a]

		solution		solid	
X	compd	$\delta_{iso}(^{31}P)$	$^1J_{iso}(^{31}P,^{199}Hg)$	$\delta_{iso}(^{31}P)$	$^1J_{iso}(^{31}P,^{199}Hg)$
CH_3COO	**2a**	58.63	12868	69.4	13324
SCN[b]	**2b**	69.86	11948	76.9	12119
Cl	**2c**	65.19	12665	72.2	13784
				71.3	12708
Br	**2d**	68.64	11989	87.4	13496
I	**2e**	75.31	11085	88.9	12623

[a] All shifts are given with respect to external 85% H_3PO_4(aq). Uncertainties in the ^{31}P chemical shifts are ±0.02 ppm in solution and ±0.2 ppm in the solid state. Uncertainties in the indirect spin–spin coupling constants are ±2 Hz in solution and ±15 Hz in the solid state. [b] Dissolved in dimethylformamide.

The ^{31}P NMR powder pattern for **1a** could not be accurately simulated without including the indirect spin–spin coupling between ^{31}P and ^{15}N. The ^{31}P CPMAS NMR spectra of compound **1a** clearly showed a splitting of the isotropic ^{31}P signal that corresponded to $J_{iso}(^{31}P,^{15}N) = 42$ Hz, in excellent agreement with the solution value of 41.5 Hz. Simulations of the ^{31}P NMR powder pattern of **1a** also indicated that the sign of J_{iso} was the same as that of R; i.e., $J_{iso}(^{31}P,^{15}N)$ is negative, in accord with a previous study.[24] The isotropic ^{31}P chemical shift in the solid state of 3.6 ppm agrees well with the value obtained in solution, 3.1 ppm.

$(EtO)_2P(O)HgX$ Complexes (2). The ^{31}P CPMAS NMR spectrum of $(EtO)_2P(O)HgOAc$ (**2a**) shows three separate signals independent of the rotor frequency, one major peak at 69.4 ppm and two minor peaks at ±6662 Hz relative to the major one (151.6 ppm and −12.9 ppm), each of which is flanked by spinning sidebands (see Figure 2a). The major ^{31}P signal is due to ^{31}P nuclei that are bonded to Hg nuclei which do not possess nuclear magnetic moments. Thus the observed frequency for these ^{31}P nuclei is determined solely by the chemical shift interaction. The two minor components that lie to either side of the major peak arise from ^{31}P nuclei that are adjacent to ^{199}Hg nuclei ($I = 1/2$, natural abundance 16.84%). Their signals are split to either side of the ^{31}P isotropic shift by indirect spin–spin coupling, or J coupling, between ^{31}P and ^{199}Hg and are referred to as ^{199}Hg satellites of the ^{31}P signal. These couplings are extremely large;

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Table II. Phosphorus-31 Chemical Shift Tensor Components (ppm with Respect to 85% H_3PO_4(aq)) and Anisotropies in ^{31}P–^{199}Hg Indirect Spin–Spin Coupling (Hz) for the Mercury Phosphonates **2**, As Determined from the ^{31}P CP Static Powder NMR Spectra, with the Chemical Shift Tensor Data for **1** for Comparison[a]

compd	δ_{11}	δ_{22}	δ_{33}	$\Delta\sigma$	η_σ	ΔJ
2a	125.5	109.7	-27.0	144.6	0.16	2700
2b	147.5	105.7	-22.5	149.1	0.42	1600
2c	121.6	110.1	-13.6	129.5	0.13	
2d	143.7	122.6	4.2	129.0	0.25	
2e	144.9	116.1	7.2	123.3	0.35	1500
1	67.9	36.1	-93.5	145.5	0.33	

[a] Uncertainties in the chemical shift tensor components are ±1 ppm and in the values for ΔJ are ±250 Hz. Definitions for $\Delta\sigma$ and η_σ correspond to the convention used by Duncan.[10]

e.g., for **2a**, $J_{iso}(^{31}P,^{199}Hg)$ = 13 324 Hz, leading to the wide frequency range of the spectrum (over 25 kHz). There is no evidence of coupling to ^{201}Hg ($I = {}^3/_2$, 13.22% natural abundance) in the ^{31}P NMR spectra of compounds **2**; ^{31}P nuclei adjacent to ^{201}Hg may not be observed due to dipolar coupling to this isotope, which has a large quadrupole moment.

The ^{31}P CPMAS NMR spectra for compounds **2** allow determination of the isotropic values of the ^{31}P chemical shift and the ^{31}P–^{199}Hg indirect spin–spin coupling in the solid state. These values are given in Table I along with the values obtained for these compounds in dichloromethane solution, which agree with previous results.[22,39] The general trends in the ^{31}P chemical shift and ^{31}P–^{199}Hg J coupling constants are the same in the solid state as in solution for this group of compounds. However, in all cases, the ^{31}P chemical shift in the solid state occurs to high frequency of the value obtained in solution. The isotropic J coupling also increases in the solid state; e.g., in the case of the bromide (**2d**) and iodide (**2e**) complexes, $J_{iso}(^{31}P,^{199}Hg)$ is over 1500 Hz larger in the solid state than in solution. One possible explanation for this could be a difference in the solution and solid-state structures. In solution, these compounds exist predominantly as dimers,[40] whereas, in the solid state, the crystal structure for the chloride salt, **2c**,[22] indicates the molecules are not associated in a dimeric fashion. Crystal structures for the other salts, as yet not available in the literature, would prove interesting for comparison of the solution and solid-state isotropic chemical shift and J coupling values and the underlying structural influences on these parameters that they would imply. However, as these differences in isotropic chemical shift and coupling constants generally are small in magnitude, it would appear there are no gross differences in the P–Hg–X framework between the solution and solid-state structures.

One interesting feature of the ^{31}P CPMAS spectrum of the chloride, **2c**, is the presence of two distinct phosphorus sites in the crystal, giving rise to two signals separated by approximately 70 Hz (see Figure 2b and Table I). The isotropic J values for the two sites differ by over 1000 Hz. However, the crystal structure determined by X-ray diffraction[22] indicated that there were four crystallographically distinct molecules in the unit cell. Two of these molecules contained Hg atoms in a distorted trigonal-bipyramidal evironment, and in the remaining two molecules, the Hg atoms were in a distorted octahedral environment. On the basis of this crystal structure, one would expect to observe four distinct ^{31}P signals in the ^{31}P CPMAS spectrum for **2c**. It would be extremely coincidental that both the isotropic chemical shifts and $J(^{31}P,^{199}Hg)$ couplings would be identical in two separate cases in one crystal. Reinvestigation of the X-ray diffraction results may be necessary in light of the solid-state ^{31}P CPMAS NMR spectrum.

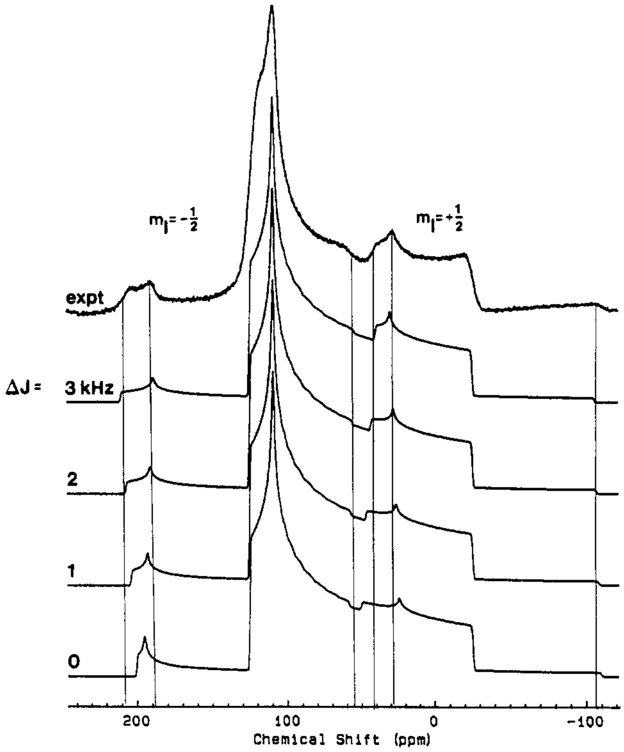

Figure 3. Phosphorus-31 static NMR spectra of $(EtO)_2P(O)HgO_2CCH_3$ (**2a**). At the top is the experimental spectrum, with vertical lines extending down from the critical frequencies of the satellite line shapes. The remaining four spectra were calculated by using values of ΔJ that vary from 0 to 3000 Hz, as indicated. All other parameters were held constant, as discussed in the text.

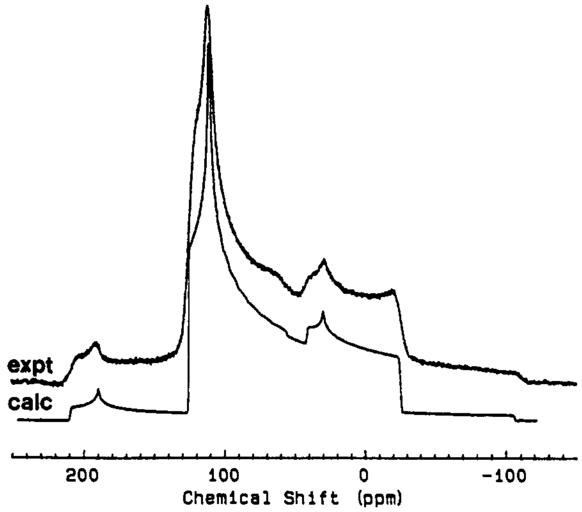

Figure 4. Phosphorus-31 CP static NMR spectrum of $(EtO)_2P(O)HgO_2CCH_3$ (**2a**) and the best-fit calculated spectrum, corresponding to a value of ΔJ = 2700 Hz.

The ^{31}P static powder NMR spectra of the mercury phosphonates are dominated by the effects of ^{31}P anisotropic chemical shifts; for the satellites, this is combined with both ^{31}P–^{199}Hg indirect J coupling and direct dipolar coupling. The experimental ^{31}P NMR powder pattern for **2a**, given in Figures 3 and 4, illustrates that, although the satellites overlap extensively with the central line shape, the three singulairites of each pattern can be discerned. Unobscured observation of the central line shape allows direct determination of the principal components of the ^{31}P chemical shift tensor. This has been performed for all of compounds **2**, with the results listed in Table II. Relative to the shift tensor components obtained for the phosphoramidate, **1**, each of the components has shifted, on average, 77 ppm to high frequency. We anticipate that the orientation of the ^{31}P chemical shift tensor in compounds **2** is similar to what was determined for **1** and has been observed for all other phosphonates, as mentioned previously.

The line shapes for the satellites, shifted from the isotropic ^{31}P chemical shift by $^1/_2J_{iso}$ in each direction, must be analyzed in

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terms of the ^{31}P anisotropic chemical shift, ^{31}P–^{199}Hg direct dipolar coupling, and any anisotropy that may exist in the ^{31}P–^{199}Hg indirect spin–spin coupling (ΔJ). Two of these three parameters can be evaluated independently of the ^{31}P satellite line shapes. The three principal components of the ^{31}P chemical shift tensor are available from the central line shape. The ^{31}P–^{199}Hg direct dipolar coupling constant, R, is calculated to be 677 ± 43 Hz on the basis of the known range of the Hg–P bond lengths for compound **2c**, 2.36 ± 0.04 Å, as determined by X-ray diffraction.[22] Although the ^{31}P MAS results for **2c** were not in agreement with the expectations based on this diffraction study in terms of the number of signals, we do not expect the Hg–P bond lengths to differ by more than ±0.04 Å. The orientation of the principal components of the ^{31}P chemical shift tensor relative to the P–Hg bond can be assumed to be similar (within 10°) to that determined with respect to the P–N bond in **1**. Any further influences on the ^{31}P satellite line shapes must arise from the effects of anisotropy in the J coupling.[21]

Simulations of the ^{31}P line shape for **2a** are given with the experimental spectrum in Figure 3. The simulations correspond to the spectra anticipated for $\Delta J = 0$, 1000, 2000, and 3000 Hz, with all other parameters held at their independently determined values. The vertical lines extending down from the experimental spectrum correspond to its critical frequencies, i.e., those frequencies, three for each of the two spin states of ^{199}Hg ($m_I = +^1/_2, -^1/_2$), that denote inflection points or peaks in the satellite line shapes. Clearly, a value for ΔJ between 2000 and 3000 Hz would provide a calculated spectrum that best fits the one observed. The best-fit simulation was obtained for $\Delta J = 2700$ Hz, and this calculated spectrum is given with the experimental spectrum in Figure 4. It should be noted that an identical calculated line shape was obtained for $\Delta J = 1300$ Hz, if the absolute sign of J_{iso}(^{31}P,^{199}Hg) was taken to be negative. This arises because absolute sign information is not available from the solid-state NMR spectrum; only the relative signs of the isotropic J coupling constant and the "effective" dipolar coupling constant, $R_{eff} = R - \Delta J/3$, can be determined. However, a negative sign for $^1J_{iso}$(^{31}P,^{199}Hg) would be contrary to all double-resonance NMR investigations of this coupling, as they have shown that the sign of this coupling constant is positive.[11,41,42]

In such a fashion, the ^{31}P NMR spectra for compounds **2a**, **2b**, and **2e** have been analyzed. The values of ΔJ for **2b** and **2e** correspond to the case where $^1J_{iso}$(^{31}P,^{199}Hg) was positive; identical line shapes were obtained for a negative J_{iso} if $\Delta J = 2400$ and 2500 Hz for **2b** and **2e**, respectively. Due to excessive line broadening introduced by dipolar coupling to the quadrupolar chlorine and bromine nuclei, the spectra of **2c** and **2d** were not sufficiently defined to allow determination of ΔJ. Also, the presence of two distinct ^{31}P nuclei in the ^{31}P NMR spectrum of the chloride salt, as indicated by the MAS results, further complicates any attempt to analyze its line shape. The error of ±250 Hz quoted for ΔJ in Table II is based on the sensitivity of the simulations to changes in its value, as well as to changes in the values of R (±43 Hz) and the angles α and β (±10°).

The quoted values for ΔJ assume that the indirect spin–spin coupling tensor, **J**, is axially symmetric. This should be a reasonable assumption, as the Hg and P atoms are essentially σ-bonded. Phosphorus-31 single-crystal NMR studies of two tetraalkyldiphosphine disulfides indicated that **J**(^{31}P,^{31}P) was axially symmetric along the P–P bond.[43] From the crystal structure for **2c**,[22] there appears to be fairly regular symmetry about the Hg–P bond. From the simulations, it is also evident that there are no substantial differences in the observed and calculated values of the splittings about the three principal components of the ^{31}P chemical shift tensor. Such distortions would be expected to influence the line shape if the asymmetry in **J** was significantly different from zero and would be clearly recognized as they would give rise to different asymmetries in the central and satellite line shapes.

It is quite clear that there is substantial anisotropy in the ^{31}P–^{199}Hg J coupling, i.e., that mechanisms other than the Fermi contact contribute to the transmission of nuclear spin information via the electrons between the two nuclei. The values for ΔJ determined here indicate that 10–20% of the total observed coupling is anisotropic in the mercury phosphonates; it appears that the Fermi contact still dominates the indirect spin–spin coupling. Significantly, the value of ΔJ determined in this study is much smaller than the anisotropy in J(^{31}P,^{199}Hg) of 5170 ± 250 Hz observed for a mercury phosphine, $[HgP(o\text{-tolyl})_3(NO_3)_2]_2$.[21] We have also recently studied the ^{31}P powder NMR line shapes of a number of other mercury phosphines, which indicate that anisotropies in **J** on the order of 5–6 kHz are present.[44] Apparently, the greater electron-donating ability of the phosphine ligand compared to that of the phosphonate influences the contributions of mechanisms other than the Fermi contact to the overall indirect spin–spin coupling.

Anisotropy in the indirect spin–spin coupling between ^{199}Hg and ^{13}C in dimethylmercury has been recently determined by Pulkkinen et al.[45] The isotropic J(^{13}C,^{199}Hg) coupling constant is 692.5 Hz; a value of $\Delta J = 864 \pm 15$ Hz was obtained for this compound dissolved in various liquid crystals. Santos et al.[46] also have reported anisotropy in **J** on the order of −450 Hz between ^{195}Pt and ^{15}N in a complex similar to *cis*-platin, where the isotropic J coupling constant between these nuclei is approximately −275 Hz. It has been suggested recently by Olivieri[47] that substantial anisotropies exist in the indirect spin–spin coupling between ^{119}Sn and ^{35}Cl and between ^{31}P and ^{63}Cu. We anticipate that such influences are present in many transition-metal complexes or compounds containing the heavier elements of the periodic table. It is quite clear that further study of J couplings in the solid state will be necessary before a complete understanding of the importance of the various mechanisms and a precise interpretation of metal–phosphorus J couplings, among others, are available.

Conclusions

Phosphorus-31 powder NMR line shapes of solid diethyl *N*-phenylphosphoramidate have been analyzed to obtain the magnitudes and orientation of the principal components of the ^{31}P chemical shift tensor. The most shielded component of this tensor has been found to lie along the P=O bond, without resorting to symmetry arguments. It is believed that this orientation is relatively constant for ^{31}P nuclei in all phosphonates. The orientation derived for the phosphoramidate has been used to interpret the ^{31}P powder NMR line shapes of a series of mercury phosphonate complexes. In the solid state, the isotropic values of the ^{31}P chemical shift and the ^{31}P–^{199}Hg indirect spin–spin coupling are observed to increase compared to those in solution, presumably because of slight structural changes. The ^{31}P NMR line shapes reveal substantial anisotropies in the J coupling between ^{31}P and ^{199}Hg, which indicates that mechanisms for J coupling other than the Fermi contact are important. It is anticipated that these mechanisms make significant contributions in mercury–phosphorus compounds and possibly other metal–phosphorus complexes. Such observations may compel reevaluation of interpretations of metal–phosphorus J couplings based on Fermi contact explanations and the s character of the bonding orbitals around the nuclei involved. We are continuing our investigations of anisotropies in **J** from solid-state NMR line shapes, as well as single-crystal NMR studies of these mercury phosphonates and other related compounds.

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Biomimetic Oxidation Studies. 5. Mechanistic Aspects of Alkane Functionalization with Fe, Fe_2O, and Fe_4O_2 Complexes in the Presence of Hydrogen Peroxide[1]

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The biomimetic oxidation reactions of a variety of hydrocarbons with iron complexes, $Fe_2O(OAc)_2(bpy)_2Cl_2$ (**1**), $Fe_4O_2(OAc)_7(bpy)_2(ClO_4)$ (**2**), $Fe_2O(OAc)(tmima)_2(ClO_4)_3$ (**3**) (tmima = tris[(1-methylimidazol-2-yl)methyl]amine), and $Fe(ClO_4)_3\cdot 6H_2O$ (**4**), using H_2O_2/O_2 as the oxidant were studied. Functionalization of cyclohexane gave cyclohexanol (CyOH) and cyclohexanone (CyONE). Complex **4** was the most effective and selective, 15–20 mmol of CyOH, 5–8 mmol of CyONE/mmol of Fe complex, and CyOH/CyONE ratios of ~2; however, the pseudo-first-order rate constants for the formation of CyOH and CyONE for **1** and **2** were ~1.4–1.6 times greater than those for **4**. Complexes **1–3** gave 2–7 and 3–8 mmol of product/mmol of Fe complex, respectively, with CyOH/CyONE ratios of 0.6–1.1. The presence of an oxidizing intermediate was suggested by iodometric titration in the functionalization of cyclohexane with complexes **1–4** and H_2O_2. This intermediate was isolated from the reaction mixture and identified by ^{13}C NMR as cyclohexyl hydroperoxide (CyOOH) as compared to an independently prepared sample. The decomposition of CyOOH by **1–4** and H_2O_2 gave CyOH/CyONE ratios of 0.7, 0.9, 0.7, and 2.8, respectively, in the ranges observed in the actual cyclohexane oxidation reactions. These hydrocarbon oxidation reactions were also inhibited by 2,4,6-tri-*tert*-butylphenol. Reactions run under a sweep of argon gave mmol of product/mmol of Fe complex 0–31% of the normal values. These results are consistent with a free-radical chain mechanism in which an initially formed cyclohexyl radical is trapped by oxygen gas to give a cyclohexyl peroxyl radical, which abstracts a hydrogen atom to give CyOOH and carry the chain. The tertiary hydrogen of adamantane was selectively abstracted with complexes **1–4** to obtain normalized C^3/C^2 values of 3.5, 3.3, 3.4, and 5.6, respectively. Toluene was transformed to a mixture of benzyl alcohol, benzaldehyde, and *o*; *m*; and *p*-cresols with benzylic/aromatic activation ratios of 3.4, 4.2, 0.9, and 20, respectively, and indicate that hydroxyl radicals (aromatic C–H functionalization) may also participate. Functionalization of methane, ethane, and propane was also observed.

Introduction

Recent spectroscopic studies on methane monooxygenases (MMO) have shown that the active center has a diiron-μ-oxo or diiron-μ-hydroxo structure [$Fe_2(\mu\text{-}O)$, $Fe_2(\mu\text{-}OH)$] and that histidine may be a terminal ligand.[2] These enzymes are active in the conversion of a variety of alkanes, including methane, to their respective alcohols.[3] This type of diiron-μ-oxo(hydroxo) structure has also been proposed for other iron-containing biomolecules such as hemerythrin,[4] purple acid phosphatase,[5] and ribonucleotide reductase.[6] More importantly, we have shown that this type of possible biomimetic structure, FeOFe, was capable of initiating hydrocarbon functionalization via the synthesis of a MMO active site model, $Fe_2O(OAc)_2(bpy)_2Cl_2$ (**1**), for the conversion of ethane, propane, and cyclohexane to their corresponding alcohols in the presence of *tert*-butyl hydroperoxide (TBHP).[1a]

Previous biomimetic oxidation studies with mononuclear and, more pertinently, Fe cluster complexes and hydrogen peroxide (H_2O_2), a monooxygen transfer reagent that can replace oxygen gas,[7] have shown functionalization of alkanes and other substrates,[8] but clearly, mechanistic details are still not totally defined with regard to the active Fe oxidant and the identity of any definitive organic intermediate that may provide both alcohol and ketone or aldehyde. In this paper, we report on kinetic and mechanistic aspects of the functionalization of several hydrocarbons by **1**, its synthetic precursor $[Fe_4O_2(OAc)_7(bpy)_2](ClO_4)$ (**2**), a polyimidazole complex, $[Fe_2O(OAc)(tmima)_2](ClO_4)_3$, (**3**) (tmima = tris[(1-methylimidazol-2-yl)methyl]amine),[9] and, for com-

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