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A Theoretical Investigation of One-Bond Phosphorus−Phosphorus Indirect Nuclear Spin−Spin Coupling Tensors, ^{1}J(^{31}P,^{31}P), Using Density Functional Theory

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In the present study, one-bond ^{31}P,^{31}P indirect nuclear spin−spin coupling tensors, $^1\mathbf{J}(^{31}\mathrm{P},^{31}\mathrm{P})$, are calculated using nonrelativistic and relativistic zeroth-order regular approximation (ZORA) density functional theory (DFT) methods for the following model molecules and ions: P_2, *cis*-MeP═PMe, *trans*-RP═PR (R = H, Me, Ph), (*cis*-η^1-PhP═PPh)Cr(CO)$_5$, (*cis*- and *trans*-η^1-MeP═PMe)Cr(CO)$_5$, H_2P-PH_2, H_2P-PF_2, *cis*- and *trans*-diphosphetes, a phosphole tetramer, $[O_3P-PO_3]^{4-}$, $[HO_3P-PO_3H]^{2-}$, $[FO_2P-PO_2F]^{2-}$, $Me_2(S)P-P(S)Me_2$, $[MeN\equiv P-PMe_3]^+$, and Me_3P-PF_5. These compounds have been chosen because the values of $^1J(^{31}\mathrm{P},^{31}\mathrm{P})_{\mathrm{iso}}$ in these systems vary from approximately −480 to +770 Hz, thereby spanning the known range of experimentally measured one-bond ^{31}P,^{31}P indirect nuclear spin−spin coupling constants. However, in many cases, the sign of $^1J(^{31}\mathrm{P},^{31}\mathrm{P})_{\mathrm{iso}}$ has not been determined by experiment. Our DFT results for $^1J(^{31}\mathrm{P},^{31}\mathrm{P})_{\mathrm{iso}}$ and the anisotropy of **J** are in qualitative agreement with experimental values; furthermore, our calculations provide the absolute sign of $^1J(^{31}\mathrm{P},^{31}\mathrm{P})_{\mathrm{iso}}$ in cases where it is unknown experimentally. A number of empirical trends between $^1J(^{31}\mathrm{P},^{31}\mathrm{P})_{\mathrm{iso}}$ and various structural parameters have been reproduced by our calculations. Inspection of the mechanisms which contribute to $^1J(^{31}\mathrm{P},^{31}\mathrm{P})_{\mathrm{iso}}$ indicates that the Fermi contact (FC) mechanism dominates in all cases where formal single P,P bonds exist and that the paramagnetic spin−orbit mechanism is of equal or greater importance in comparison with the FC mechanism in cases where formal multiple P,P bonds exist. Results from relativistic ZORA DFT calculations differ from the nonrelativistic calculations by less than 10%, indicating that inclusion of relativistic effects is not crucial, as anticipated, given that the systems investigated herein contain relatively light atoms ($Z \leq 24$).

1. Introduction

Thousands of solution and solid-state ^{31}P nuclear magnetic resonance (NMR) studies have been carried out, and many one-bond ^{31}P,^{31}P indirect nuclear spin−spin coupling constants, $^1J(^{31}\mathrm{P},^{31}\mathrm{P})_{\mathrm{iso}}$, have been measured.[1−5] General empirical trends in $^1J(^{31}\mathrm{P},^{31}\mathrm{P})_{\mathrm{iso}}$ have been identified and are often used to elucidate structures of inorganic or organometallic compounds. On the basis of the known dependence of $^1J(^{31}\mathrm{P},^{31}\mathrm{P})_{\mathrm{iso}}$ on parameters such as oxidation state, coordination number, substituent electronegativity, the presence or absence of localized electron lone pairs, and stereochemistry, values of $^1J(^{31}\mathrm{P},^{31}\mathrm{P})_{\mathrm{iso}}$ in new systems may be qualitatively predicted.[6] For example, the reduction in the magnitude of $^1J(^{31}\mathrm{P},^{31}\mathrm{P})_{\mathrm{iso}}$ in a ligand upon coordination to a metal center is often used as a diagnostic tool to verify complexation.[2] Also, the sensitivity of $^1J(^{31}\mathrm{P},^{31}\mathrm{P})_{\mathrm{iso}}$ to various arrangements of ligands about the coupled phosphorus nuclei may be used to distinguish between stereoisomers: are the substituents bonded to phosphorus in a cis or a trans arrangement? For compounds where both the cis and trans isomers have been investigated, experimental evidence indicates that $^1J(^{31}\mathrm{P},^{31}\mathrm{P})_{\mathrm{iso}}$ values are generally larger in magnitude for the cis isomer, e.g., *cis*-MeP═PMe (297.5 Hz) vs *trans*-MeP═PMe (219.8 Hz).[2] In many cases, however, the sign of $^1J(^{31}\mathrm{P},^{31}\mathrm{P})_{\mathrm{iso}}$ is unknown, thereby hampering attempts to definitively establish trends in $^1J(^{31}\mathrm{P},^{31}\mathrm{P})_{\mathrm{iso}}$.

Recognizing simple relationships between NMR parameters and molecular structure based on empirical observations is a goal of the experimentalist. One of the first established and well-abided relationships involves ^{13}C,^{13}C spin pairs and the correlation between $^1J(^{13}\mathrm{C},^{13}\mathrm{C})_{\mathrm{iso}}$ and the hybridization of the two carbon atoms forming the C,C bond. To a first approximation, $^1J(^{13}\mathrm{C},^{13}\mathrm{C})_{\mathrm{iso}}$ increases with the s character of the C,C bond: 34.6 Hz for ethane, 67.6 Hz for ethene, 171.5 Hz for ethyne, and 57.0 Hz for benzene.[7,8] In 1963, Frei and Bernstein[9] proposed a formalism correlating $^1J(^{13}\mathrm{C},^{13}\mathrm{C})_{\mathrm{iso}}$ values for unsubstituted hydrocarbons with the product of the s character of the coupled carbon atoms, C and C′: $^1J(^{13}\mathrm{C},^{13}\mathrm{C}')_{\mathrm{iso}}/\mathrm{Hz} = 576 s_{\mathrm{C}} s_{\mathrm{C}'} - 3.4$. Variations of this empirical equation exist with slightly different coefficients.[10−12] Moreover, a number of trends correlating $^1J(^{13}\mathrm{C},^{13}\mathrm{C})_{\mathrm{iso}}$ with substituent electronegativities have been established.[9−13] Although these relationships seem to work for directly bonded ^{13}C,^{13}C spin pairs, they cannot generally be extended to other spin pairs. For example, attempts at correlating $^1J(^{31}\mathrm{P},^{31}\mathrm{P})_{\mathrm{iso}}$ and the P,P bond order have been made;[1] however, the sign of $^1J(^{31}\mathrm{P},^{31}\mathrm{P})_{\mathrm{iso}}$ was not considered. These arguments are therefore invalid since $^1J(^{31}\mathrm{P},^{31}\mathrm{P})_{\mathrm{iso}}$ values may be of either sign (vide infra). While definite trends involving the s character of the P,P bond and various mechanisms for $^1J(^{31}\mathrm{P},^{31}\mathrm{P})_{\mathrm{iso}}$ have been identified and will be discussed herein, no simple, general relationship has been found between $^1J(^{31}\mathrm{P},^{31}\mathrm{P})_{\mathrm{iso}}$ and P,P bond order.

The known range of $^1J(^{31}\mathrm{P},^{31}\mathrm{P})_{\mathrm{iso}}$ values covers approximately 1400 Hz, as shown in Table 1, with Mes*P═PC[Si(CH$_3$)$_3$]$_3$

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TABLE 1: Survey of Experimental Values of $^{1}J(^{31}P,^{31}P)_{iso}$ and the P−P Bond Length for Some Phosphorus-Containing Compounds[a]

molecule	$^{1}J(^{31}P,^{31}P)_{iso}$/Hz	ref (J)	r_{PP}/Å	ref (r_{PP})
$H_2P{-}PH_2$	-108.0 ± 0.2	115	2.2191	131
$Me_2P{-}PMe_2$	-179.9	132	2.1212	133
$Me_2P{-}P(t\text{-}Bu)_2$	-318 ± 5	134		
$Et_2P{-}P(c\text{-}C_6H_{11})_2$	± 282	135		
$(t\text{-}Bu)_2P{-}P(t\text{-}Bu)_2$	-451 ± 3	136		
MePhP−PPhMe	-215 ± 2[b]	109		
	-234 ± 2			
$Ph_2P{-}PPh_2$	-200 ± 100[c]	137	2.217	138
$H_2P{-}PF_2$	± 211	117	2.218	118
$F_2P{-}PF_2$	-227.1[d]	108		
$Me_2P{-}P(CF_3)_2$	± 252	139		
	-256	140		
	-226.5 to -230.3	108		
$[Ph_3P{-}PPh_2][GaCl_4]$	± 340[e]	141	2.220	141
	-323 ± 2[f]	24		
$[Mes^{*}N{\equiv}P{-}PPh_3][SO_3CF_3]$	-405	16	2.625	17
$Me_2P{-}P(S)Me_2$	-220	124		
$Me_2(S)P{-}P(S)Me_2$ (TMPS)	-18.7	124,125	2.214	22
$Et_2(S)P{-}P(S)Et_2$ (TEPS)	$+30$[g]	126		
$(MeO)_2(O)P{-}P(O)(MeO)_2$	*ca.* 200	142		
$(EtO)_2(S)P{-}P(O)(EtO)_2$	± 583	143		
$[HO_2P{-}PO_3]^{3-}$	± 465	119		
$K_2[FO_2P{-}PO_2F]$	$+766 \pm 1$	15		
$Ag_4[O_3P{-}PO_3]$	± 500	21		
$Me_3P{-}PF_5$	$+715$, $+720$[h]	123		
$Me_2HP{-}PF_5$	$+714$, $+723$[i]	123		
$Mes^{*}P{=}PMes^{*}$	$\pm(580 \pm 20)$[j]	101	2.034	86
$Mes^{*}P{=}PC[Si(CH_3)_3]_3$	-620	14		
$(\eta^5\text{-}C_5H_5)(CO)_2Fe{-}P{=}PMes^{*}$	± 600	144		
cis-$(\eta^1\text{-}Mes^{*}P{=}PMes)M(CO)_5$ (M=Cr, Mo, W)	$\pm(603.0, 585.9, 576.8)$	88	2.039[k]	88
trans-$(\eta^1\text{-}Mes^{*}P{=}PMes)M(CO)_5$ (M=Cr, Mo, W)	$\pm(517.6, 518.8, 528.8)$	88		
$ArP{=}PAr{\cdot}Mo(CO)_5$	± 510[l]	105		
$ArP{=}PAr{\cdot}W(CO)_5$	± 478[f]	105		
$Et_3P{=}P(CO_2Et){\cdot}W(CO)_5$	± 361.3	106		
cis- and *trans*-diphosphetes	$\pm(44$ and $63)$	107	2.218 and 2.202	127
phosphole tetramer	-362[f,m]	129	2.191 and 2.198	128

[a] Abbreviations used: Me = CH_3; Et = CH_2CH_3; *t*-Bu = $C(CH_3)_3$; Ph = C_6H_5; Mes = 2,4,6-trimethylphenyl; Mes* = 2,4,6-tri-*tert*-butylphenyl; Ar = 2,4,6-$(CF_3)_3C_6H_2$. [b] Values are for the two diastereomers of MePhP−PPhMe. [c] $Ph_2P{-}PPh_2$ in the solid state, sign relative to R_{eff}. [d] $F_2P{-}PF_2$ at −1 °C in 5 mol % $CFCl_3$. See reference for data obtained at other temperatures. [e] Solution data, $[Ph_3P{-}PPh_2][GaCl_4]$ dissolved in CH_2Cl_2. [f] Solid-state data. [g] Solution data, solvent not specified. [h] Solution data, $Me_3P{-}PF_5$ dissolved in CH_3CN at 37 °C. [i] Solution data, $Me_2HP{-}PF_5$ dissolved in CH_2Cl_2 at −10 °C. [j] Solid-state data. [k] M = Cr. [l] Solution data, $ArP{=}PAr{\cdot}Mo(CO)_5$ dissolved in $CDCl_3$. [m] The sign of $^{1}J(^{31}P,^{31}P)_{iso}$ is relative to R_{eff}, which is assumed to be positive.

(Mes* = 2,4,6-tri-*tert*-butyl phenyl) at one extreme, $^{1}J(^{31}P,^{31}P)_{iso} = -620$ Hz,[14] and $[FO_2P{-}PO_2F]^{2-}$ at the other, $^{1}J(^{31}P,^{31}P)_{iso} = +766$ Hz.[15] Of particular note is the large magnitude of $^{1}J(^{31}P,^{31}P)_{iso}$ for $[Mes^{*}N{\equiv}P{-}PPh_3]^{+}$, −405 Hz,[16] even though the P,P bond is unusually long, 2.625 Å,[17] compared to the typical P,P single bond, 2.20 Å.[18,19] Clearly, no simple relationship exists between $^{1}J(^{31}P,^{31}P)_{iso}$ and P,P bond length.

Reports of reliable measurements of **J**-tensors are very limited.[20] The anisotropy of **J**, ΔJ, is difficult to measure accurately due to its inherent association with the dipolar coupling constant, R_{DD} (vide infra); as a result, very few reliable experimental $\Delta J(^{31}P,^{31}P)$ values are known. A large value of ΔJ, +800 Hz, for the one-bond $^{31}P,^{31}P$ **J**-tensor for $Ag_4[O_3P{-}PO_3]$ has been reported,[21] while upper bounds of +450 Hz and +460 Hz have been set for ΔJ in tetramethyl- and tetraethyldiphosphine disulfide (TMPS and TEPS), respectively.[22,23] Similarly, a recent solid-state ^{31}P NMR study of the pentaphenylphosphinophosphonium cation, $[Ph_3P{-}PPh_2]^{+}$, indicated that $^{1}J(^{31}P,^{31}P)_{iso} = -323$ Hz and $\Delta J < 300$ Hz.[24]

The objectives of the present study are to provide the absolute sign of $^{1}J(^{31}P,^{31}P)_{iso}$ in cases where it is unknown experimentally, to investigate the significance of ΔJ, and to establish a preliminary basis for understanding the $^{1}\mathbf{J}(^{31}P,^{31}P)$-tensor in terms of molecular structure. Both nonrelativistic and relativistic zeroth-order regular approximation density functional theory (ZORA DFT) calculations of $^{1}\mathbf{J}(^{31}P,^{31}P)$ are presented for a number of molecules (Figure 1). The values of $^{1}J(^{31}P,^{31}P)_{iso}$ for these systems are representative of the range of $^{1}J(^{31}P,^{31}P)_{iso}$ values which has been observed experimentally (Table 1) and thus are ideal candidates for a computational investigation of $^{1}\mathbf{J}(^{31}P,^{31}P)$. Furthermore, the phosphorus nuclei exist in several different formal oxidation states and participate in a variety of bonding arrangements, thereby allowing potential trends in $^{1}J(^{31}P,^{31}P)_{iso}$ and $\Delta J(^{31}P,^{31}P)$, as well as in the mechanisms which contribute to $^{1}J(^{31}P,^{31}P)_{iso}$, to be identified.

2. Background and Theory

Ramsey[25−27] first described the theory of indirect nuclear spin−spin coupling in 1953 using second-order perturbation theory in terms of three mechanisms, which together account for the interaction of the coupled nuclei with the electronic network of the molecule. These mechanisms are generally denoted as the spin−orbit (SO), Fermi contact (FC), and spin−dipolar (SD) mechanisms and have been described in numerous review articles and textbooks (see ref 20 for a recent review). For any given spin−spin coupling tensor, all three of these mechanisms may be important, and in general, none may a priori be considered negligible;[28] however, in the early literature, it was common practice to assume the FC mechanism was the most important contributor to J_{iso}. The FC mechanism accounts for the interaction between a nuclear spin and an electron spin which has a finite probability of being at the nucleus (i.e., s electrons); this term is purely isotropic and, hence, does not

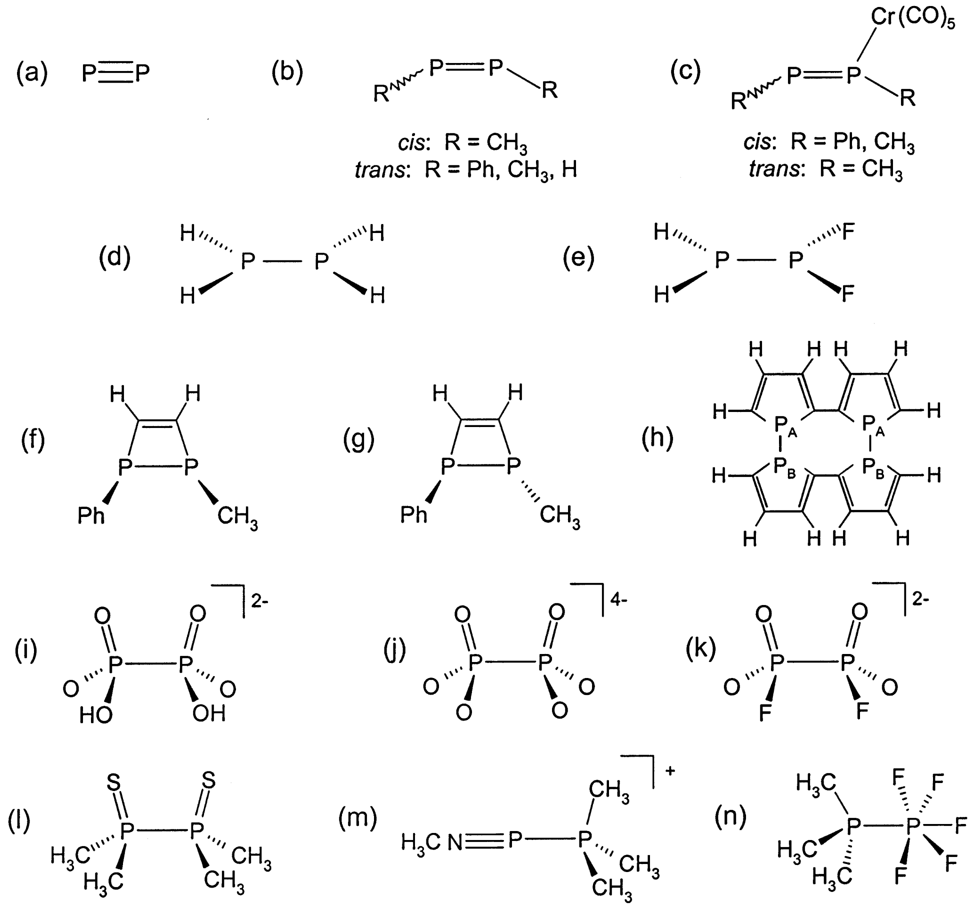

Figure 1. Molecules investigated in this study: (a) diphosphorus, (b) *cis*- and *trans*-diphosphene, (c) *cis*- and *trans*-η^1-diphosphene chromium pentacarbonyl, (d) biphosphine, (e) phosphinodifluorophosphine, (f) *cis*- and (g) *trans*-1,2-dihydro-1-methyl-2-phenyl-3,4-bis(*tert*-butyl)-1,2-diphosphete, (h) a phosphole tetramer, (i) dihydrogen hypophosphate, (j) hypodiphosphate, (k) difluorohypophosphate, (l) tetramethyldiphosphine disulfide, (m) trimethylphosphine phosphadiazonium cation, (n) trimethylpentafluorophosphine.

contribute to ΔJ. The SO mechanism describes the interaction between the nuclear magnetic moment and the orbital magnetic moment arising from the motion of the electrons and can be further divided into diamagnetic SO (DSO) and paramagnetic SO (PSO) contributions; the DSO mechanism depends on the ground electronic state and the PSO mechanism involves allowed excitations between the ground and singlet excited states. The PSO mechanism has been shown to contribute significantly to both J_{iso} and ΔJ in the presence of formal multiple bonds.[6,29] The third mechanism, SD, is the interaction between the nuclear magnetic moment and the magnetic field arising from the spin of the electrons not located at the nucleus. There also exists a purely anisotropic SD × FC cross term, which contributes largely to ΔJ but does not contribute to J_{iso}.

In 1977, Pyykkö[30] extended Ramsey's nonrelativistic theory to include relativistic effects; other relativistic theories have since been presented.[31,32]

The **J**-tensor may be characterized by J_{iso}, ΔJ, and asymmetry parameter, η[29,33,34]

$$J_{iso} = (J_{11} + J_{22} + J_{33})/3 \tag{1}$$

$$\Delta J = J_{33} - \frac{J_{11} + J_{22}}{2} \tag{2}$$

$$\eta = \frac{J_{22} - J_{11}}{J_{33} - J_{iso}} \tag{3}$$

where the principal components, J_{11}, J_{22}, and J_{33}, are ordered according to $|J_{33} - J_{iso}| \geq |J_{11} - J_{iso}| \geq |J_{22} - J_{iso}|$. Often, it is convenient to express $\mathbf{J}(N,N')$ in terms of a *reduced* coupling tensor, $\mathbf{K}(N,N')$, which is independent of the magnetogyric ratios, γ_N and $\gamma_{N'}$ of the two coupled nuclei, N and N'

$$\mathbf{K}(N,N') = 4\pi^2\mathbf{J}(N,N')/h\gamma_N\gamma_{N'} \tag{4}$$

K is expressed in SI units of kg m^{-2} s^{-2} A^{-2} (equivalently, N A^{-2} m^{-3} or T^2 J^{-1}).

The anisotropy of **J**, ΔJ, contributes to the *effective* dipolar coupling constant

$$R_{eff} = R_{DD} - \frac{\Delta J}{3} \tag{5}$$

where the dipolar coupling constant, R_{DD}, is given by

$$R_{DD} = \frac{\mu_0}{4\pi}\left(\frac{\hbar}{2\pi}\right)\gamma_N\gamma_{N'}\langle r_{NN'}{}^{-3}\rangle \tag{6}$$

In the above equation, μ_0 is the vacuum permeability constant, $4\pi \times 10^{-7}$ H m^{-1}, and $\langle r_{NN'}{}^{-3}\rangle$ is the motionally averaged value of the inverse cube of the distance between the two coupled nuclei. This dependence on internuclear distance makes the measurement of R_{eff} an attractive means of determining the bond length if the structure is not known.[33,35,36] However, the

TABLE 2: Structural Data for the Molecules Investigated in This Study[a,83]

molecule	structure source	ref
P≡P	electronic spectroscopy; r(PP) = 1.8934 Å	84
cis-MeP═PMe	idealized structure using r(PP) = 2.034 Å, r(CH) = 1.08 Å, ∠PPC = 120.0°, ∠CPPC = 0.0°, ∠HCP = 109.5°	
trans-HP═PH	optimized using RHF/6-311G(3df,3pd)	
trans-*R*P═PR, R = Me, Ph	based on the structure of Mes*P═PMes* from an X-ray diffraction study; Mes* groups were replaced by Ph or CH_3 with $r(C_{aryl}H)$ = 1.08 Å, $r(C_{Me}H)$ = 1.08 Å, $\angle HC_{Me}P$ = 109.5°	86
cis-(η^1-RP═PR)$Cr(CO)_5$, R = Me, Ph	based on the structure of *cis*-(Mes*P═PMes)$Cr(CO)_5$ from an X-ray diffraction study; Mes* and Mes groups were replaced by *R*═Me, Ph with $r(C_{Me}H)$ = 1.08 Å, $\angle HC_{Me}P$ = 109.5° and $r(C_{aryl}H)$ = 1.08 Å, $\angle HC_{aryl}C$ = 120.0°	88
trans-(η^1-Me_3P═PMe_3)$Cr(CO)_5$	based on the structure of $[PCH(SiMe_3)_2]_2Cr(CO)_5$ from an X-ray diffraction study; $SiMe_3$ groups were replaced by H with $r(C_{Me}H)$ = 1.08 Å, $\angle HC_{Me}P$ = 109.5°	145
cis- and *trans*-diphosphetes	based on the structures of *cis*- and *trans*-diphosphetes from an X-ray diffraction study; *tert*-butyl groups were replaced by H with r(CH) = 1.08 Å	127
phosphole tetramer	based on the structure of the phosphole tetramer from an X-ray diffraction study; Ph and Me groups were replaced by H with $r(C_{aryl}H)$ = 1.08 Å, $\angle HC_{aryl}C$ = 120.0°	128
H_2P-PH_2	microwave spectroscopy	131
H_2P-PF_2	microwave spectroscopy	118
$M_2[HO_3P-PO_3H]$	X-ray diffraction data	
	M = Na	120
	M = NH_4	121
$[O_3P-PO_3]^{4-}$	idealized structure using r(PP) = 2.329 Å, r(PO) = 1.544 Å, ∠OPO = 110.7°, ∠OPP = 108.2°	
$[FO_2P-PO_2F]^{2-}$	optimized using RHF/6-311G**	
$[MeN\equiv P-PMe_3]^+$	based on the structure of $[Mes^*N\equiv P-PPh_3][SO_3CF_3]$ from an X-ray diffraction study; Mes* and Ph groups were replaced by CH_3 with $r(C_{Me}H)$ = 1.08 Å and $\angle HC_{Me}P$ = 109.44°	17
$Me_2(S)P-P(S)Me_2$	X-ray diffraction data	22
Me_3P-PF_5	optimized using RHF/6-311G**	

[a] Me = CH_3; Ph = C_6H_5; Mes = 2,4,6-trimethylphenyl; Mes* = 2,4,6-tri-*tert*-butylphenyl.

reliability of any NMR-based bond-length determination depends critically on knowing the significance of the contribution of ΔJ to R_{eff}.

There are a number of experimental approaches for determining ΔJ, discussed in detail in the literature.[20,36] Briefly, ΔJ may be measured via R_{eff} for solid samples[24,37−40] or samples dissolved in liquid crystalline media using NMR spectroscopy.[41−45] For small molecules, precise values of R_{eff} may be obtained from hyperfine coupling constants measured in molecular beam or high-resolution microwave spectroscopy experiments.[46−48] The anisotropy of **J** is exceedingly difficult to quantify experimentally due mainly to uncertainties in the motional averaging corrections for R_{DD}, especially if the difference between R_{eff} and R_{DD} is small (i.e., ≤10%).

Another approach to investigate **J**-tensors is via modern computational techniques. However, the reliable and accurate calculation of **J**-tensors presents a major theoretical challenge.[20,49−51] Only recently have reliable and computationally feasible methods for calculating **J**-tensors become available. Two different approaches have had success: an ab initio multiconfigurational self-consistent field approach and DFT. The application of these methods to the calculation of **J**-tensors as well as nuclear magnetic shielding tensors has been reviewed.[20,49−54] To obtain near-quantitative agreement with experiment, the use of large basis sets that describe the electron density in the vicinity of the coupled nuclei particularly well is essential.[50,54−57] In addition, electron correlation, vibrational averaging,[58,59] solvent effects,[60] and, in the case of systems containing "heavy" nuclei, relativistic effects remain important issues in the calculation of **J**-tensors.

In this study, we focus on the ZORA DFT approach because of its versatility and applicability to relatively large systems, as opposed to ab initio methods, which are currently limited to small molecules containing relatively light atoms. Also, the recent successes of DFT calculations of **J**-tensors are particularly encouraging.[24,54,60−68] For example, in the case of $[Ph_3P-PPh_2]^+$, where $^1J(^{31}P,^{31}P)_{iso} = -323$ Hz, DFT results on a model compound, $[Me_3P-PMe_2]^+$, yield $^1J(^{31}P,^{31}P)_{iso} = -427$ Hz, in qualitative agreement with experiment.[24]

3. Computation Details and Methods

3.1. Atomic Coordinates. The molecular structures used to generate the nuclear coordinates for our **J**-tensor calculations are described in Table 2. In some cases, structures were modified by replacing bulky ligands with less computationally demanding substituents. Where X-ray diffraction data are unavailable, computationally optimized structures, obtained from calculations using Gaussian 98,[69] or idealized models were employed in the **J** calculation.

3.2. $^1\mathbf{J}(^{31}\mathbf{P},^{31}\mathbf{P})$ Calculations. DFT calculations of $^1\mathbf{J}(^{31}P,^{31}P)$ were performed using the CPL module[55,64,65,70] of the Amsterdam density functional (ADF) program.[71,72] The Vosko−Wilk−Nusair (VWN) local density approximation,[73] with the Becke[74]−Perdew[75] generalized gradient approximations (GGA), was used for the exchange-correlation functional. Relativistic calculations included spin−orbit and/or scalar corrections and were carried out using the ZORA formalism.[76−79] In some cases, because the ZORA DFT method overestimates the contribution from the PSO mechanism, ΔJ is dominated by the PSO term.[65] The FC, SD, PSO, and DSO mechanisms were included in all **J** calculations; a description of these mechanisms, as implemented in the ZORA formalism, has been previously presented.[64]

The basis sets available with the ADF program consist of Slater-type functions. The TZP basis set is of triple-ζ quality with one set of polarization functions while the TZ2P basis set has two sets of polarization functions. For relativistic calculations, the TZ2P basis set, optimized for ZORA calculations, was consistently used on the phosphorus nuclei. In the case of the chromium pentacarbonyl diphosphene complexes, the TZ2P basis set was used for phosphorus while TZP basis sets were used for all remaining atoms.

3.3. Conformational Energy Barrier Calculations. Calculations of energy barriers for H_2P-PH_2 and H_2P-PF_2 were carried out using Gaussian 98[69] at the restricted Hartree−Fock (RHF) level employing Dunning's correlation-consistent cc-pVTZ basis sets[80] on all nuclei.

3.4. Computers. All calculations were carried out using either an IBM RS/6000 workstation, a Linux-based PC with an AMD Athlon microprocessor, or a Linux-based cluster with dual AMD 1800+ Athlon processor nodes.

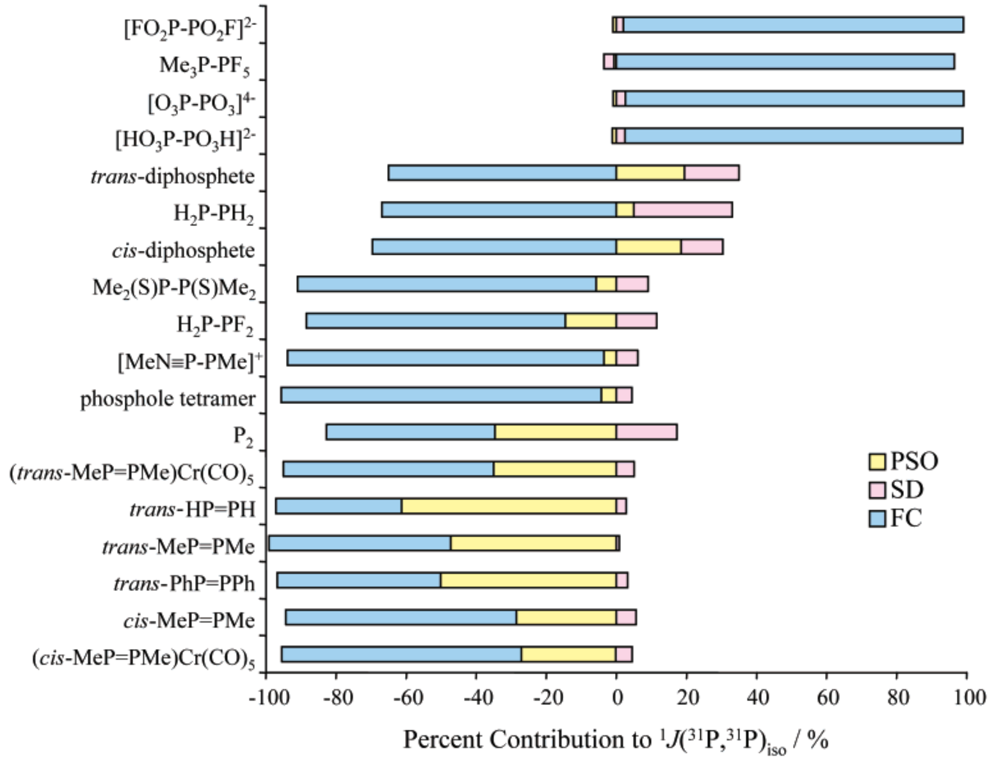

Figure 2. Contributions of the FC, PSO, and SD mechanisms to the nonrelativistic calculated values of ${}^1J({}^{31}P,{}^{31}P)_{iso}$. The DSO contribution is negligible compared to contributions from the other coupling mechanisms and has not been included here. Results for H_2P-PH_2 and H_2P-PF_2 are for the conformation where $\varphi = 180°$; see insets of Figure 3 and 5 for definition of φ. The structure assumed for $[HO_3P-PO_3H]^{2-}$ is that given in ref 121. In all cases, the magnitude of the contribution from the FC mechanism exceeds that from the SD mechanism.

4. Results and Discussion

Calculated indirect ${}^{31}P,{}^{31}P$ spin−spin coupling tensors for each of the molecules (see Figure 1) will be presented and compared with available experimental data. A discussion of the general trends observed for ${}^1\mathbf{J}({}^{31}P,{}^{31}P)$ and factors affecting ${}^1J({}^{31}P,{}^{31}P)_{iso}$ for the above systems will follow. The importance of relativistic effects on ${}^1\mathbf{J}({}^{31}P,{}^{31}P)$ was investigated by carrying out relativistic spin−orbit and/or scalar ZORA DFT calculations on most of the molecules in this study. Relativistic corrections were less than 10% and do not warrant further discussion. This is not surprising, given that phosphorus is a relatively light nucleus ($Z = 15$) and, in most cases examined, phosphorus is not bonded to a heavy atom.

4.1. Model Systems. *(a) P≡P.* The simplest molecule on which to perform a ${}^1\mathbf{J}({}^{31}P,{}^{31}P)$ calculation is diphosphorus. Although ${}^1J({}^{31}P,{}^{31}P)_{iso}$ cannot be determined easily by NMR experiments for this molecule, due to the magnetic equivalence of the nuclei, one can compare the *reduced* coupling constant, ${}^1K(P,P)_{iso}$ (see eq 4), to other diatomic molecules, such as dinitrogen, for which experimental[81] and theoretical[55,82,83] values of ${}^1J({}^{15}N,{}^{14}N)_{iso}$ are known. Our ZORA DFT result for N_2,[83] employing $r_e(N,N) = 1.09769$ Å,[84] yielded ${}^1K(N,N)_{iso} = +17 \times 10^{19}$ kg m^{-2} s^{-2} A^{-2}; however, further calculations of ${}^1K(N,N)_{iso}$ for N_2 indicate that ${}^1K(N,N)_{iso}$ is highly sensitive to bond-length variation, in agreement with a report in the literature,[82c] and that ${}^1K(N,N)/10^{19}$ kg m^{-2} s^{-2} A^{-2} $= -908.12r(N,N) + 1015.8$, resulting in a change in the sign of ${}^1K(N,N)_{iso}$ at $r(N,N) \simeq 1.119$ Å. The experimental value of ${}^1K(N,N)_{iso}$ is $(\pm)20 \pm 7 \times 10^{19}$ kg m^{-2} s^{-2} A^{-2} (calculated from ${}^1J({}^{15}N,{}^{14}N)_{iso} = (\pm)1.8 \pm 0.7$ Hz);[81] the absolute sign of ${}^1J({}^{15}N,{}^{14}N)_{iso}$ cannot be conclusively determined from our calculations, given the strong dependence of ${}^1K(N,N)_{iso}$ on $r(N,N)$. Our nonrelativistic DFT calculations for P_2 yield values of ${}^1J({}^{31}P,{}^{31}P)_{iso} = -497.8$ Hz and ${}^1K(P,P)_{iso} = -252 \times 10^{19}$ kg m^{-2} s^{-2} A^{-2}. The negative sign of ${}^1K(P,P)_{iso}$ for P_2 arises due to the large negative contributions from the FC and PSO mechanisms, shown in Figure 2, indicating the importance of the relative signs of the various mechanisms to ${}^1J({}^{31}P,{}^{31}P)_{iso}$.[28] For multiply bonded P,P systems, the phosphorus 3p orbitals play a dominant role in P,P bonding and the s character tends to concentrate in the lone electron pairs on phosphorus.[3,6] As a result, the noncontact terms, which are controlled by orbitals of higher orbital angular momentum (i.e., orbitals other than s orbitals), make significant contributions to ${}^1K(P,P)_{iso}$.[3,6] The magnitude of ${}^1K(P,P)_{iso}$ for P_2 compared to ${}^1K(N,N)_{iso}$ for N_2 increases due to the increase in atomic number. The dependence of ${}^1K_{iso}$ on atomic number is a well-known trend which can be explained, to a first approximation, in terms of the s electron density at the nucleus for ground-state atoms, $|\psi_{ns}(0)|^2$, and the atomic averages of the distance between the nucleus and the valence p electrons, $\langle r^{-3}\rangle_{np}$, both of which are known to increase with atomic number down a group and across a row in the Periodic Table.[6] For example, in a theoretical investigation of ${}^1\mathbf{K}$ for a series of interhalogen diatomic molecules, the magnitudes of ${}^1K_{iso}$ and ΔK were shown to depend linearly on the product of the atomic numbers of the coupled nuclei.[54]

A large, positive value of ΔJ, 2287 Hz, was obtained for P_2, which is an order of magnitude larger than ${}^1J({}^{31}P,{}^{31}P)_{iso}$. However, the ZORA DFT method has been known to overestimate ΔJ in cases where the PSO term is large,[65] as found here for P_2. The largest and smallest principal components of ${}^1\mathbf{J}({}^{31}P,{}^{31}P)$ lie perpendicular and parallel to the P,P bond axis, respectively; this orientation is consistent with that obtained by Bryce et al. in a study of ${}^1\mathbf{K}$ for a series of diatomic halides.[54]

(b) RP═PR′ (R = H, CH_3, Ph). While the only experimental evidence for the existence of diphosphene, HP═PH, is as a

TABLE 3: Calculated[a] and Experimental Values of ^{1}J(^{31}P,^{31}P) for Substituted Diphosphenes and Diphosphene Chromium Pentacarbonyl Complexes

	method	contributions to J_{iso}/Hz[b] PSO	SD[c]	FC	total J_{iso}/Hz	ΔJ/Hz
		Free Ligand				
trans-HP═PH	nonrel	−418	21	−245	−642	−1105
	scalar rel	−417	−219[d]		−637	−1097
	SOS-CI[e]	−498	22	−76	−552	
cis-CH_3P═PCH_3	nonrel	−254	50	−587	−791	−988
trans-CH_3P═PCH_3	nonrel	−403	29	−345	−719	−1162
trans-PhP═PPh	nonrel	−401	26	−381	−756	−1147
	scalar rel	−401	−346[d]		−747	−1139
trans-RP═PR’	exp				±(519−670)	
		$Cr(CO)_5$ Complex[f]				
(*cis*-CH_3P═PCH_3)$Cr(CO)_5$	nonrel	−239	42	−607	−804	−917
(*cis*-PhP═PPh)$Cr(CO)_5$	nonrel	−231	44	−646	−833	−890
	scalar rel	−231	−587[d]		−818	−888
	spin−orbit rel	−231	−586[d]		−817	−880
(*cis*-Mes*P═PMes)$Cr(CO)_5$	exp[g]				±603	
(*trans*-CH_3P═PCH_3)$Cr(CO)_5$	nonrel	−265	−38	−454	−681	−940
(*trans*-Mes*P═PMes)$Cr(CO)_5$	exp[g]				±518	

[a] By use of DFT and employing ZORA TZ2P basis sets on all atoms, unless otherwise indicated. [b] The DSO contribution for all systems is less than 1 Hz. [c] Includes contributions from both the SD and the (FC−SD) cross term. [d] SD and FC contributions cannot be separated in this formalism. [e] From ref 104. [f] Basis set TZ2P was used for phosphorus atoms and TZP for all remaining atoms. [g] Solution ^{31}P NMR data; ref 88.

product of the thermal decomposition of H_2P-PH_2,[85] many substituted diphosphenes have been isolated, the first being *trans*-Mes*P═PMes*.[86] The synthesis of asymmetrically substituted diphosphenes has subsequently been reported.[87] Several *cis*-diphosphenes are known, although in each case, the P═P moiety serves as a ligand bonded to a metal center (vide infra). Theoretical investigations of the P,P double bond have been carried out, with diphosphene used as a model compound.[88−97] Reviews of this chemistry have been published.[98,99]

Before presenting our calculated results of $^1\mathbf{J}(^{31}P,^{31}P)$ for diphosphenes, it is instructive to review previous work on related systems. The first ^{31}P NMR spectra for *trans*-Mes*P═PMes* in the solid state were reported by Zilm et al.[100] The two phosphorus nuclei have the same isotropic chemical shift (CS) and apparent coincident CS tensor orientations, suggesting an A_2 spin system for the phosphorus spin pair. As a result of the assumed magnetic equivalence of the two phosphorus nuclei, $^1J(^{31}P,^{31}P)_{iso}$ was not determined. A reinvestigation and close examination of the spinning sideband fine structure of this system by McDowell et al.[101] revealed that, while the phosphorus nuclei have the same isotropic chemical shifts, their CS tensor orientations are not exactly coincident, thereby allowing the measurement of $^1J(^{31}P,^{31}P)_{iso}$. This study represents the first measurement of $^1J(^{31}P,^{31}P)_{iso}$ for a coupled spin pair with identical isotropic shifts.[101] The intrinsic anisotropic CS and dipolar interactions, which lead to recoupling of the *J* interaction, ultimately allow for the determination of the magnitude of $^1J(^{31}P,^{31}P)_{iso}$.[101] Values of $^1J(^{31}P,^{31}P)_{iso}$ were obtained from a 2D *J*-resolved NMR experiment, $^1J(^{31}P,^{31}P)_{iso} = \pm 580 \pm 20$ Hz,[101] and using average Hamiltonian theory (in conjunction with ^{31}P NMR data), $^1J(^{31}P,^{31}P)_{iso} = \pm 577 \pm 15$ Hz.[101] More recently, a number of asymmetrically substituted diphosphenes have been investigated using ^{31}P NMR spectroscopy.[102,103] The values of $^1J(^{31}P,^{31}P)_{iso}$ in substituted diphosphenes range from ±510 to ±670 Hz. Although the absolute sign of $^1J(^{31}P,^{31}P)_{iso}$ is not known for these systems, results from early ab initio calculations, for example, the sum-over-states configuration interaction (SOS-CI) method,[2,104] suggest that $^1J(^{31}P,^{31}P)_{iso}$ is negative as a consequence of a large negative contribution from the PSO mechanism. The FC contribution is negative and of comparable magnitude to that from the PSO mechanism (Figure 2).

Table 3 summarizes our calculated results for $^1\mathbf{J}(^{31}P,^{31}P)$ in several diphosphenes, literature results for HP═PH,[104] and experimental values for substituted diphosphenes. These results strongly support the contention that $^1J(^{31}P,^{31}P)_{iso}$ is negative in these compounds and consistently predict that ΔJ is large in magnitude (i.e., on the order of 10^3 Hz). The DFT results for diphosphenes from this work are in excellent agreement with the experimental range of $^1J(^{31}P,^{31}P)_{iso}$ values for diphosphenes, predicting a value of $^1J(^{31}P,^{31}P)_{iso}$ that is in the upper range of experimental results.

Contributions to $^1J(^{31}P,^{31}P)_{iso}$ from each coupling mechanism are listed in Table 3 and depicted in Figure 2. The PSO mechanism dominates for HP═PH (65% contribution), making a large negative contribution to $^1J(^{31}P,^{31}P)_{iso}$, which is consistent with predictions from the literature;[104] however, the FC contribution is also significant. For PhP═PPh, the PSO and FC mechanisms make approximately equal contributions to $^1J(^{31}P,^{31}P)_{iso}$ (53 and 50% contribution, respectively). Again, these results illustrate the importance of the noncontact terms, particularly the PSO mechanism, in systems containing formal P,P double bonds.

The only experimental report of $^1J(^{31}P,^{31}P)_{iso}$ for *cis*-diphosphenes is for complexes of the type (*cis*-η^1-Mes*P═PMes)M$(CO)_5$, where one phosphorus nucleus is coordinated to a metal center (M = Cr, Mo, W).[88] Values of $^1J(^{31}P,^{31}P)_{iso}$ have also been reported for the analogous trans metal complexes, (*trans*-η^1-Mes*P═PMes)M$(CO)_5$ (M = Cr, Mo, W).[88] Here, the terms cis and trans describe the relative orientation of the substituents bonded to the phosphorus nuclei. Comparison of experimental $^1J(^{31}P,^{31}P)_{iso}$ values for the cis and trans isomers of (η^1-Mes*P═PMes)M$(CO)_5$ indicates that $^1J(^{31}P,^{31}P)_{iso}$ is consistently larger in magnitude for the cis isomer by 85, 67, and 48 Hz for the Cr, Mo, and W metal complexes, respectively (see Table 1 for $^1J(^{31}P,^{31}P)_{iso}$ values). Values of $^1J(^{31}P,^{31}P)_{iso}$ (Table 1) have also been reported for ArP═PAr·M$(CO)_5$ (Ar = 2,4,6-$(CF_3)_3C_6H_2$; M = Mo, W), where the diphosphene ligand is coordinated in an η^1 fashion to the M$(CO)_5$ moiety via the lone electron pair on one of the phosphorus atoms.[105] Other examples of phosphorus-containing ligands coordinated to a metal center are complexes of the type: R_3P═PR′·M$(CO)_5$ (M = Mo, W).[106] The Mo complex exhibits definite zwitterionic behavior with a P,P bond (2.156

Å) that is closer in length to a single P,P bond (2.24 Å) than that of a double P,P bond[86] (2.03 Å). For a variety of alkyl and aryl R,R′ groups, values of $^{1}J(^{31}P,^{31}P)_{iso}$ range from ±361 to ±444 Hz. Last, values of $^{1}J(^{31}P,^{31}P)_{iso}$, determined from a ^{31}P NMR study in solution, have been reported for both *cis*- and *trans*-diphosphetes, where the phosphorus nuclei are directly bonded in a four-membered ring (see Figure 1).[107]

To examine the effects of coordination on the sign and magnitude of $^{1}J(^{31}P,^{31}P)_{iso}$ and ΔJ for various isomers, calculations were carried out on both *cis*- and *trans*-η^1-$CH_3P{=}PCH_3$, as well as $CH_3P{=}PCH_3$ bound to a metal center, (*cis*- and *trans*-η^1-$CH_3P{=}PCH_3$)$Cr(CO)_5$. Further calculations of $^{1}\mathbf{J}(^{31}P,^{31}P)$ were performed on the more computationally demanding molecule, (*cis*-η^1-$PhP{=}PPh$)$Cr(CO)_5$, to verify the adequacy of our simplified dimethyl model as well as to investigate the importance of relativistic effects in a system containing a transition metal. Results for $^{1}J(^{31}P,^{31}P)_{iso}$ and ΔJ, as well as the contributions of the various mechanisms to $^{1}J(^{31}P,^{31}P)_{iso}$, for the diphosphene chromium complexes and free ligands are summarized in Table 3. Qualitative agreement between our calculations and experimental results is met, even for the Cr pentacarbonyl complexes. Although the calculations slightly overestimate the magnitude of $^{1}J(^{31}P,^{31}P)_{iso}$, they correctly predict that $^{1}J(^{31}P,^{31}P)_{iso}$ for the free diphosphene ligand is slightly larger in magnitude for the cis isomer than that for the trans isomer, in agreement with experimental reports.[6] For both isomers, the PSO and FC mechanisms make significant contributions to $^{1}J(^{31}P,^{31}P)_{iso}$; in fact, together these mechanisms make up 94% of $^{1}J(^{31}P,^{31}P)_{iso}$ for *cis*-$CH_3P{=}PCH_3$ and 99% for *trans*-$CH_3P{=}PCH_3$. The calculations also predict that ΔJ is larger for *trans*-$CH_3P{=}PCH_3$ compared to that for *cis*-$CH_3P{=}PCH_3$, due to a larger contribution from the PSO mechanism.

Results obtained for the diphosphene chromium pentacarbonyl complexes are compared with those determined experimentally for (*cis*- and *trans*-η^1-Mes*P=PMes)$Cr(CO)_5$ (Table 3).[88] Again, the calculations slightly overestimate $^{1}J(^{31}P,^{31}P)_{iso}$ for the *cis*- and *trans*-diphosphene $Cr(CO)_5$ complexes compared to values determined experimentally; however, they correctly predict that $^{1}J(^{31}P,^{31}P)_{iso}$ is larger in magnitude for (*cis*-η^1-$CH_3P{=}PCH_3$)$Cr(CO)_5$ compared with that for (*trans*-η^1-$CH_3P{=}PCH_3$)$Cr(CO)_5$. Further, the results consistently indicate that the sign of $^{1}J(^{31}P,^{31}P)_{iso}$, which has not been determined experimentally, is negative for diphosphene in both the free ligand and the Cr complexes. In the diphosphene cases investigated herein, the FC term is the dominant mechanism for $^{1}J(^{31}P,^{31}P)_{iso}$; however, the PSO mechanism is also important. Note that the calculations suggest that $^{1}J(^{31}P,^{31}P)_{iso}$ and ΔJ are on the same order of magnitude for each of the *cis*- and *trans*-diphosphenes, as well as for their $Cr(CO)_5$ analogues. Differences between $^{1}\mathbf{J}(^{31}P,^{31}P)$ results for (*cis*-η^1-$PhP{=}PPh$)$Cr(CO)_5$ compared to the simplified model, (*cis*-η^1-$CH_3P{=}PCH_3$)$Cr(CO)_5$, are slight (Table 3). In addition, inclusion of relativistic effects is not important in determining $^{1}\mathbf{J}(^{31}P,^{31}P)$, even with a first-row transition metal coordinated to a phosphorus atom.

(c) $H_2P{-}PH_2$. Considerable experimental and theoretical attention has been given to $^{1}J(^{31}P,^{31}P)_{iso}$ in biphosphines $R_2P{-}PR'_2$, due to the marked dependence of $^{1}J(^{31}P,^{31}P)$ on molecular conformation.[2,6,108−114] The conformation is described by a dihedral angle, φ, between the bisectors of the two H−P−H angles (see inset of Figure 3 for definition of φ). Indirect experimental evidence that $^{1}J(^{31}P,^{31}P)_{iso}$ is dependent on conformation was first reported in 1970 in a variable-temperature NMR study of $F_2P{-}PF_2$[108] and later for PhMeP−PMePh[109] and related systems.[6,110] The general trend for biphosphines appears to be as follows: a large negative $^{1}J(^{31}P,^{31}P)_{iso}$ value is observed for the conformation when $\varphi \simeq 0°$ while $^{1}J(^{31}P,^{31}P)_{iso}$ is small and positive for $\varphi \simeq 180°$.[2] Since biphosphines are not fixed in a particular conformation, observations of $^{1}J(^{31}P,^{31}P)_{iso}$ represent conformationally averaged values.

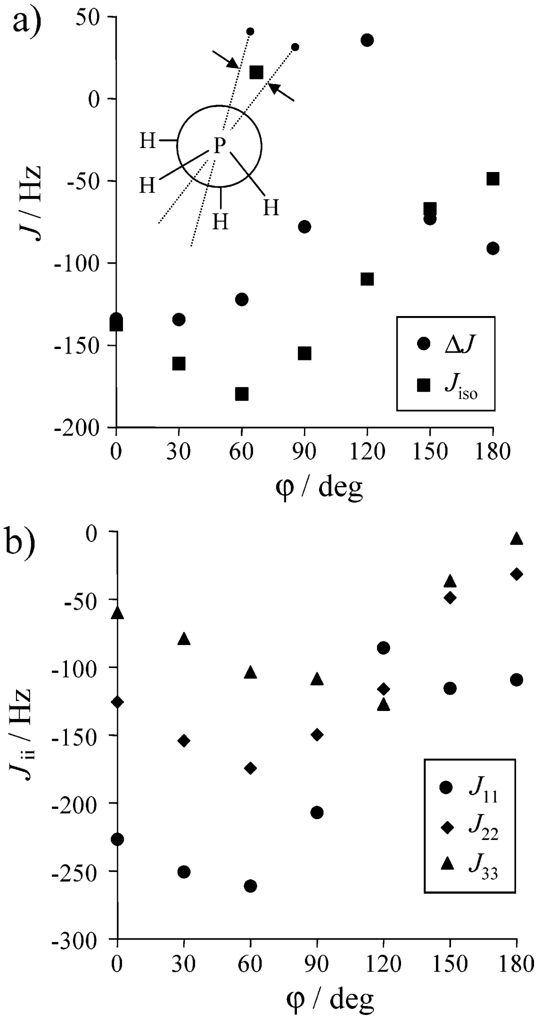

Figure 3. Dependence of (a) $^{1}J(^{31}P,^{31}P)_{iso}$ and $\Delta J(^{31}P,^{31}P)$ and (b) the principal components of $^{1}\mathbf{J}(^{31}P,^{31}P)$, J_{11}, J_{22}, J_{33}, on the dihedral angle, φ, for $H_2P{-}PH_2$ using nonrelativistic DFT.

Table 4 summarizes our $^{1}\mathbf{J}(^{31}P,^{31}P)$ results for $H_2P{-}PH_2$, including contributions of the various coupling mechanisms to $^{1}J(^{31}P,^{31}P)_{iso}$. The FC mechanism dominates $^{1}J(^{31}P,^{31}P)_{iso}$, making a substantial negative contribution to $^{1}J(^{31}P,^{31}P)_{iso}$, in agreement with previous theoretical studies.[110,112,113] Considerable variation in the magnitude of the FC contribution is observed upon rotation of φ, decreasing significantly from 0° (−235 Hz) to 180° (−96 Hz). The SD mechanism is positive and sizable for all conformations and remains at a value relatively independent of the dihedral angle, while the PSO term is positive and varies considerably with dihedral angle.

The data for $^{1}J(^{31}P,^{31}P)_{iso}$ and ΔJ, as well as the principal components of $^{1}\mathbf{J}(^{31}P,^{31}P)$, are plotted as a function of φ in Figure 3. The experimental value of $^{1}J(^{31}P,^{31}P)_{iso}$ for liquid $H_2P{-}PH_2$ is −108.0 ± 0.2 Hz at room temperature.[115] To estimate the calculated value of $^{1}J(^{31}P,^{31}P)_{iso}$ at room temperature (298 K), an average over all conformations, weighted according to the Boltzmann distribution, must be determined. The energy for rotation of a PH_2 group about the P−P bond in $H_2P{-}PH_2$ is plotted in Figure 4. Our calculations (RHF/cc-pVTZ) indicate

TABLE 4: Experimental and Calculated Values of $^{1}J(^{31}P,^{31}P)$ for $H_2P{-}PH_2$

	contributions to J_{iso}/Hz[a]				
	PSO	SD[b]	FC	total J_{iso}/Hz	ΔJ/Hz
experimental[c]				−108.0 ± 0.2	
calculated[d]					
$\varphi = 0°$	49	48	−235	−137	−134
$\varphi = 30°$	32	44	−238	−161	−134
$\varphi = 60°$	11	40	−230	−180	−122
$\varphi = 90°$	8	39	−202	−155	−78
$\varphi = 120°$	11	40	−161	−110	36
$\varphi = 150°$	9	41	−117	−67	−73
$\varphi = 180°$	7	41	−96	−49	−91
average[e]				−96	
calculated[f]					
$\varphi = 0°$	50	−176		−125	−130

[a] DSO contribution is 0.06 Hz for all values of φ. [b] Includes contributions from both the SD and the (FC−SD) cross term. [c] From ref 115. [d] Nonrelativistic DFT results using TZ2P basis sets. [e] Weighted over all conformations at 298 K according to the Boltzmann distribution; see text. [f] Spin−orbit relativistic ZORA DFT results using TZ2P basis sets; SD and FC contributions cannot be separated in this formalism.

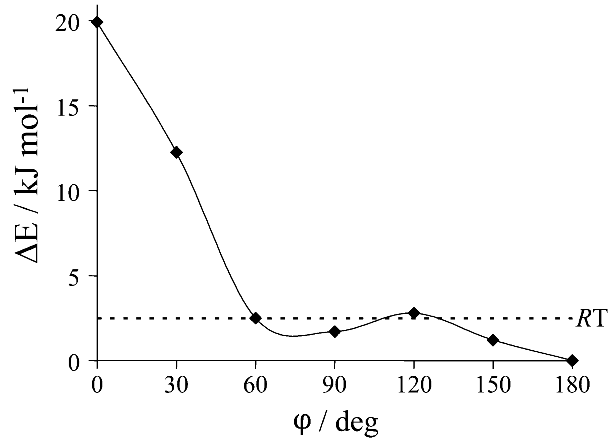

Figure 4. Energy barrier to internal rotation for $H_2P{-}PH_2$ calculated at the RHF level of theory using cc-pVTZ basis sets. All energies are with respect to that at $\varphi = 180°$, and the dashed line represents the product of the gas constant and 298.15 K, $RT = 2.4790$ kJ mol^{-1}.

that the lowest energy is obtained for $\varphi = 180°$ and that the energy profile is relatively flat for rotation about the P,P bond between $\varphi = 60$ and 180°; these conclusions are in qualitative agreement with a theoretical report in the literature.[116] The weighted, calculated average for $^{1}J(^{31}P,^{31}P)_{iso}$, −96 Hz, agrees well with the experimental value, −108.0 Hz.[115]

The anisotropy of $^{1}\mathbf{J}(^{31}P,^{31}P)$ for $H_2P{-}PH_2$ is comparable in magnitude to $^{1}J(^{31}P,^{31}P)_{iso}$ for all orientations considered; however, the dependence of ΔJ on dihedral angle is not smooth, as is evident in Figure 3. The anomalous behavior of ΔJ at $\varphi = 120°$ arises from the definition of ΔJ (eq 2) and the need to order the principal components relative to $^{1}J(^{31}P,^{31}P)_{iso}$. The distinct decrease in J_{33} and increase in J_{11} is responsible for the sudden, dramatic increase in ΔJ at $\varphi = 120°$.

(d) $H_2P{-}PF_2$. The experimental value of $^{1}J(^{31}P,^{31}P)_{iso}$ for liquid phosphinodifluorophosphine, $H_2P{-}PF_2$, measured at 233 K is ±211 Hz.[117] Experimentally, the conformation with $\varphi = 180°$ is the most stable.[118] Results from DFT calculations of $^{1}\mathbf{J}(^{31}P,^{31}P)$ as a function of dihedral angle are given in Table 5 and plotted in Figure 5. The calculated contributions of the various mechanisms to $^{1}J(^{31}P,^{31}P)_{iso}$ indicate that, while the FC mechanism is largest in magnitude, the PSO and SD contributions are also significant. However, since the SD and PSO contributions are of similar magnitude but opposite sign, to a large extent, they cancel.

TABLE 5: Experimental and Calculated $^{1}J(^{31}P,^{31}P)$ Tensors for $H_2P{-}PF_2$

	contributions to J_{iso}/Hz[a]				
	PSO	SD[b]	FC	total J_{iso}/Hz	ΔJ/Hz
experimental[c]				±211	
calculated[d]					
$\varphi = 0°$	−44	36	−175	−183	217
$\varphi = 30°$	−49	35	−189	−203	218
$\varphi = 60°$	−59	32	−217	−243	212
$\varphi = 90°$	−60	32	−239	−267	177
$\varphi = 120°$	−50	34	−242	−258	−126
$\varphi = 150°$	−44	36	−228	−236	91
$\varphi = 180°$	−44	36	−219	−227	79
average[e]				−231	

[a] The DSO contribution is 0.2 Hz for all values of φ. [b] Includes contributions from both the SD and the (FC−SD) cross term. [c] From ref 117. [d] Nonrelativistic DFT results using TZ2P basis sets. [e] Weighted over all conformations at 233 K according to the Boltzmann distribution; see text.

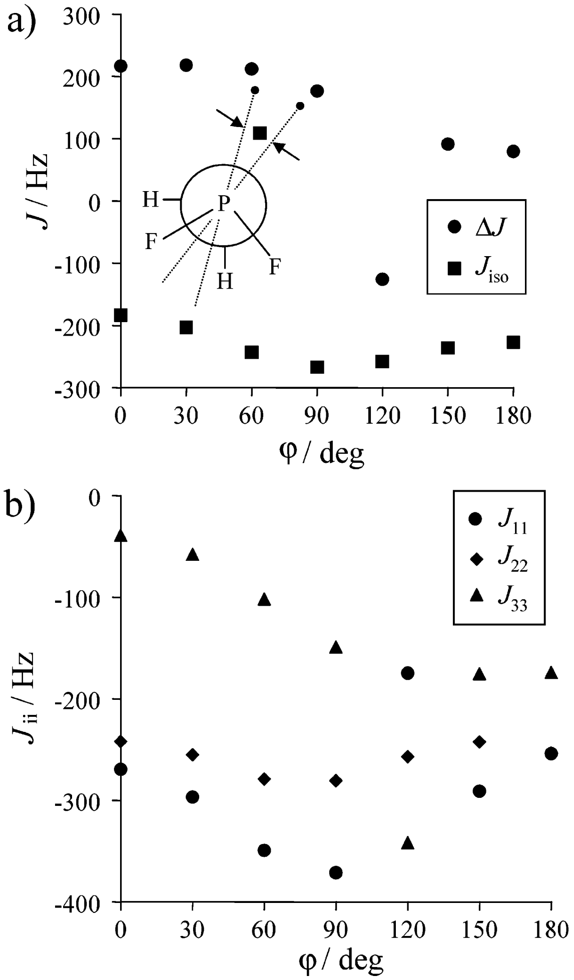

Figure 5. Dependence of (a) $^{1}J(^{31}P,^{31}P)_{iso}$ and $\Delta J(^{31}P,^{31}P)$ and (b) the principal components of $^{1}\mathbf{J}(^{31}P,^{31}P)$, J_{11}, J_{22}, J_{33}, on the dihedral angle, φ, for $H_2P{-}PF_2$ using nonrelativistic DFT.

Analogous to $H_2P{-}PH_2$, $^{1}J(^{31}P,^{31}P)_{iso}$ must be weighted according to the Boltzmann distribution at 233 K over all the conformations when comparing the calculated value of $^{1}J(^{31}P,^{31}P)_{iso}$ with the experimental value. The rotational energy as a function of φ (see Figure 6) indicates that $\varphi = 180°$ is significantly more stable than any other rotamer, in agreement with experiment.[118] The weighted average of $^{1}J(^{31}P,^{31}P)_{iso}$ over

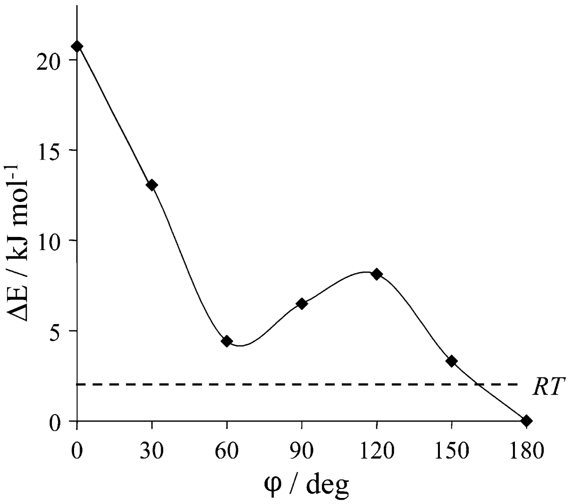

Figure 6. Energy barrier to internal rotation for $H_2P{-}PF_2$ calculated at the RHF level of theory using cc-pVTZ basis sets on all atoms. All energies are with respect to that at $\varphi = 180°$; the dashed line represents the product of the gas constant and temperature ($T = 233$ K), $RT = 1.9385$ kJ mol^{-1}.

all conformations, −231 Hz, is in good agreement with the magnitude of the experimental value, ±211 Hz,[117] and indicates that the sign of this coupling constant is negative.

The behavior of ΔJ for $H_2P{-}PF_2$ is similar to that for $H_2P{-}PH_2$ with an anomalous datum point at $\varphi = 120°$, arising from the definition of ΔJ (eq 2) and the need to order the principal components relative to $^1J(^{31}P,^{31}P)_{iso}$. The distinct increase in J_{11} and decrease in J_{33} is responsible for the discontinuity in ΔJ at $\varphi = 120°$. The magnitudes of $^1J(^{31}P,^{31}P)_{iso}$ and ΔJ are comparable for $H_2P{-}PF_2$.

In contrast to both $H_2P{-}PH_2$ and $H_2P{-}PF_2$, a recent theoretical investigation of $^1J(^{31}P,^{31}P)_{iso}$ using DFT for the model compound, $[H_3P{-}PH_2]^+$, indicates that $^1J(^{31}P,^{31}P)_{iso}$ and ΔJ vary only slightly, by approximately ±15 Hz, upon changing the dihedral angle.[24] The weighted, calculated value of $^1J(^{31}P,^{31}P)_{iso}$ for $[H_3P{-}PH_2]^+$, −341 Hz, is in qualitative agreement with that determined experimentally for $[Ph_3P{-}PPh_2]^+$, −323 Hz. The FC term is the dominant contributor to $^1J(^{31}P,^{31}P)_{iso}$ for $[H_3P{-}PH_2]^+$, $H_2P{-}PH_2$, and $H_2P{-}PF_2$.

(e) $[HO_3P{-}PO_3H]^{2-}$. The diphosphate family is an interesting series of compounds on which to perform $^1\mathbf{J}(^{31}P,^{31}P)$ calculations particularly because of the large reported value of ΔJ for $Ag_4[O_3P{-}PO_3]$, +800 ± 80 Hz.[21] Since the magnitude of ΔJ is substantial, it is desirable to test the performance of the **J** calculations for these systems. The experimental value of $^1J(^{31}P,^{31}P)_{iso}$ for $Ag_4[O_3P{-}PO_3]$ is estimated to be 500 Hz.[21] The magnitude and sign of $^1J(^{31}P,^{31}P)_{iso}$ have also been determined for the related system, sodium diphosphite, $[HO_2P{-}PO_3]^{3-}$, dissolved in D_2O, +465.5 ± 1.0 Hz.[119]

Several structures have been reported for $M_2[HO_3P{-}PO_3H]$, (M = Na, NH_4, H_3O).[120−122] We carried out $^1\mathbf{J}(^{31}P,^{31}P)$ calculations on the $[HO_3P{-}PO_3H]^{2-}$ framework of the disodium[120] and diammonium[121] hypophosphate complexes and also on an idealized model for $[O_3P{-}PO_3]^{4-}$ (see Table 2 for structure details). Our $^1\mathbf{J}(^{31}P,^{31}P)$ results for $[O_3P{-}PO_3]^{4-}$ and $[HO_3P{-}PO_3H]^{2-}$ are compared to experimental results for the related systems, $Ag_4[O_3P{-}PO_3]$ and $[HO_2P{-}PO_3]^{3-}$, in Table 6. The calculations correctly predict that the signs of $^1J(^{31}P,^{31}P)_{iso}$ and ΔJ are positive in these systems. Agreement between the magnitudes of experimental and calculated values is good for $^1J(^{31}P,^{31}P)_{iso}$ but poor for ΔJ; in both cases, the magnitudes are underestimated by the calculations. With regard to ΔJ, an accurate determination of the error is difficult to obtain experimentally; hence, the error in ΔJ is probably significantly larger than the quoted value, 800 ± 80 Hz.[21] Any experimental determination of ΔJ requires knowledge of R_{DD} and therefore r_{PP} (see eqs 5 and 6); however, any motion of the P,P bond vector in the solid state will decrease R_{DD} from what one calculates assuming a rigid, stationary P,P bond. Therefore, neglect of vibrational and librational averaging in our model may also explain discrepancies between calculated and experimental values for ΔJ.

TABLE 6: Calculated ^{1}J(^{31}P,^{31}P) Tensors for $[HO_3P{-}PO_3H]^{2-}$ and $[O_3P{-}PO_3]^{4-}$ Compared to the Experimental Results for $Ag_4[O_3P{-}PO_3]$ and $[HO_2P{-}PO_3]^{3-}$

	J_{iso}/Hz	ΔJ/Hz
Experimental		
$Ag_4[O_3P{-}PO_3]^a$	±500	+800 ± 80
$[HO_2P{-}PO_3]^{3-}$	465[119]	
Calculated^b		
$[O_3P{-}PO_3]^{4-c}$	+408	+386
$[NH_4]_2[(HO)O_2P{-}PO_2(OH)]^d$	+399	+394
$[NH_4]_2[(HO)O_2P{-}PO_2(OH)]^e$	+347	+376

[a] Experimental value from ref 21. [b] Nonrelativistic DFT calculations employing the TZ2P basis set. [c] Idealized structure; see Table 2. [d] Calculated using the structure for $[NH_4]_2[HO_3P{-}PO_3H]$; from ref 121. [e] Calculated using the structure for $Na_2[HO_3P{-}PO_3H]$; from ref 120.

Inspection of the mechanisms for $^1J(^{31}P,^{31}P)_{iso}$ (Figure 2) indicates that contributions from the noncontact terms, SD and PSO, are negligible compared to the FC mechanism. This is expected for $[HO_2P{-}PO_3]^{3-}$ based on the dominant P,P σ bonding in this molecule.[28,123] Also, a large contribution to $^1J(^{31}P,^{31}P)_{iso}$ from the FC mechanism has been observed in cases where the substituents on phosphorus have large electronegativities. The use of phosphorus 3s electrons in phosphorus−substituent bonds is reduced when the substituents have high electronegativities, thereby increasing the s character of the P,P bond and resulting in a larger contribution from the FC mechanism to $J(^{31}P,^{31}P)_{iso}$.[119]

(f) $[FO_2P{-}PO_2F]^{2-}$. The largest positive experimental value for $^1J(^{31}P,^{31}P)_{iso}$ is that reported for potassium difluorodiphosphate, $K_2[FO_2P{-}PO_2F]$, +766 Hz;[15] a comparable value was observed for the related compound, $Na_3[FO_2P{-}PO_3]$, $^1J(^{31}P,^{31}P)_{iso} = +650$ Hz.[15] Both measurements were carried out in neutral aqueous solutions. The ZORA DFT $^1\mathbf{J}(^{31}P,^{31}P)$ calculations indicate that the sign of $^1J(^{31}P,^{31}P)_{iso}$ is positive, +421 Hz; however, the magnitude is underestimated compared to the experimental value, +766 Hz. The largest contribution to $^1J(^{31}P,^{31}P)_{iso}$ is from the FC mechanism, +416 Hz, which again may be qualitatively rationalized in terms of the increased s character of the P,P bond due to the reduced participation of phosphorus 3s electrons in the P,F and P,O bonds. The magnitudes of ΔJ, +385.3 Hz, and $^1J(^{31}P,^{31}P)_{iso}$, +421 Hz, are comparable. Disagreement between experimental and calculated results for $^1J(^{31}P,^{31}P)_{iso}$ may be due to the use of a structure which does not accurately represent $[FO_2P{-}PO_2F]^{2-}$ in aqueous solution; recall that the structure used was computationally optimized since an experimental geometry for $[FO_2P{-}PO_2F]^{2-}$ is unavailable in the literature (see Table 2). In addition, our calculation of $^1\mathbf{J}(^{31}P,^{31}P)$ is carried out on an isolated ion, neglecting the effects of solvent and hydrogen bonding, which likely play important roles in the determination of $^1\mathbf{J}(^{31}P,^{31}P)$ for this anion.

(g) $Me_3P{-}PF_5$. The experimental value of $^1J(^{31}P,^{31}P)_{iso}$ for $Me_3P{-}PF_5$, measured in liquid acetonitrile at 37 °C, is +715 Hz,[123] which is comparable to the largest positive value of

$^1J(^{31}P,^{31}P)_{iso}$ observed for $K_2[FO_2P-PO_2F]$.[15] The calculated value of $^1J(^{31}P,^{31}P)_{iso}$, +414 Hz, is underestimated compared to the experimental value, but the positive sign of $^1J(^{31}P,^{31}P)_{iso}$ is correctly reproduced. The FC mechanism dominates $^1J(^{31}P,^{31}P)_{iso}$ and the noncontact terms are negligible (Figure 2) due to the absence of P,P π bonds in this molecule.[28,123] The calculated value of ΔJ is +425 Hz, comparable to $^1J(^{31}P,^{31}P)_{iso}$. Again, the use of an optimized geometry and neglect of solvent effects in our calculation of $^1\mathbf{J}(^{31}P,^{31}P)$ may, in part, be responsible for the unsatisfactory agreement with experiment.

(h) $[MeN{\equiv}P-PMe_3]^+$. The trimethylphosphine phosphadiazonium cation, $[MeN{\equiv}P-PMe_3]^+$, is a model for the cationic complex, $[Mes^*N{\equiv}P-PPh_3][SO_3CF_3]$, for which a large negative value of $^1J(^{31}P,^{31}P)_{iso}$, −405 Hz,[16] is observed in the solid state, despite an unusually long P,P bond, 2.625 Å.[17] The difference between R_{DD} and R_{eff} is slight, indicating that ΔJ is small (eq 5). The calculated value of $^1J(^{31}P,^{31}P)_{iso}$, −170 Hz, for $[MeN{\equiv}P-PMe_3]^+$ is significantly smaller than the experimental value for $[Mes^*N{\equiv}P-PPh_3][SO_3CF_3]$, likely due to the use of an oversimplified model in the calculation. The largest contribution to $^1J(^{31}P,^{31}P)_{iso}$ comes from the FC term, −175 Hz (Figure 2). The calculated value of ΔJ, +178 Hz, is similar in magnitude to $^1J(^{31}P,^{31}P)_{iso}$.

(i) $Me_2(S)P-P(S)Me_2$. Tetramethyldiphosphine disulfide (TMPS), $Me_2(S)P-P(S)Me_2$, and a similar compound, tetraethyldiphosphine disulfide (TEPS), $Et_2(S)P-P(S)Et_2$, have been investigated by ^{31}P NMR of single crystals as well as of powdered crystalline samples.[22,23] In both cases, $^1J(^{31}P,^{31}P)_{iso}$ is small: −18.7 Hz for TMPS[124,125] and +30 Hz for TEPS.[126] The solid-state ^{31}P NMR experiments indicate that the upper limits of ΔJ are approximately 450 and 460 Hz, respectively, for TMPS and TEPS.[22,23] Our $^1\mathbf{J}(^{31}P,^{31}P)$ calculation for TMPS yields a value of −158 Hz for $^1J(^{31}P,^{31}P)_{iso}$, an order of magnitude larger compared with experiment, and +276 Hz for ΔJ. Clearly, agreement with experimental results is not achieved in this case.

(j) Diphosphetes. Diphosphetes are an interesting class of compounds where the phosphorus nuclei participate in a four-membered heterocyclic environment (see Figure 1). The X-ray crystal structures[127] of *cis*- and *trans*-diphosphete indicate that the P,P and C,C bond lengths are within the range of similar acyclic compounds, suggesting that the phosphorus lone electron pairs are localized in these diphosphetes.[107] Solution and solid-state ^{31}P NMR studies have been carried out on both the *cis*- and *trans*-diphosphetes.[107] Although $^1J(^{31}P,^{31}P)_{iso}$ was too small to be detected in the ^{31}P NMR spectra acquired in the solid state, $^1J(^{31}P,^{31}P)_{iso}$ values were determined for the cis and trans isomers in solution: ±44 and ±63 Hz,[107] respectively.

The ZORA DFT calculations of $^1J(^{31}P,^{31}P)_{iso}$ for both *cis*- and *trans*-diphosphete agree well with the values determined using solution ^{31}P NMR spectroscopy (see Table 7). The relative magnitudes of $^1J(^{31}P,^{31}P)_{iso}$ for the cis and trans isomers are correct with $^1J(^{31}P,^{31}P)_{iso}$ being larger for *cis*-diphosphete than that for the trans isomer. Also, the calculations predict that the sign of $^1J(^{31}P,^{31}P)_{iso}$ is negative for both isomers. Calculated values of ΔJ for the cis and trans isomers were found to be −209 and −174 Hz, respectively. Since ΔJ manifests itself in an NMR spectrum as $\Delta J/3$, this gives −70 and −60 Hz for *cis*- and *trans*-diphosphete, respectively. In the experimental study of the diphosphetes,[107] ΔJ was assumed to be negligible and $R_{eff} \simeq R_{DD} = 1.8$ kHz for both isomers. Hence, since $\Delta J/3 \ll R_{DD}$, neglect of ΔJ in the analysis of the ^{31}P NMR spectra is reasonable in this case.[107]

TABLE 7: Experimental and Calculated Values of $^1J(^{31}P,^{31}P)_{iso}$ for the Molecules Containing P,P Bonds Considered in This Study

molecule	$^1J(^{31}P,^{31}P)_{iso}$/Hz experimental	calculated[a]
(cis-η^1-PhP═PPh)Cr(CO)$_5$[b]	±603[c]	−833
(cis-η^1-CH$_3$P═PCH$_3$)Cr(CO)$_5$[b]	±603[c]	−804
cis-CH$_3$P═PCH$_3$		−791
trans-PhP═PPh	−580	−756
trans-CH$_3$P═PCH$_3$		−718
(*trans*-η^1-PhP═PPh)Cr(CO)$_5$[b]	±518[d]	−681
trans-HP═PH	−590	−642
P_2		−498
phosphole tetramer	−362	−411
H_2P-PF_2	−211	−231[e]
$[MeN{\equiv}P-PMe_3]^+$	−405	−170
TMPS	−19	−158
cis-diphosphete	±63	−123
H_2P-PH_2	−108	−96[f]
trans-diphosphete	±44	−63
$[HO_3P-PO_3H]^{2-}$	+500	+399[g]
$[O_3P-PO_3]^{4-}$	+500	+408
Me_3P-PF_5	+717	+414
$[FO_2P-PO_2F]^{2-}$	+766	+421

[a] Results from nonrelativistic DFT calculations using TZ2P basis sets, unless otherwise indicated. [b] Nonrelativistic DFT results using the TZ2P basis set on phosphorus and TZP on all other atoms. [c] $^1J(^{31}P,^{31}P)_{iso}$ determined for (cis-$^1\eta$-Mes*P═PMes)Cr(CO)$_5$. [d] $^1J(^{31}P,^{31}P)_{iso}$ determined for $[PCH(SiMe_3)_2]_2Cr(CO)_5$. [e] Weighted over all conformations at 233 K according to the Boltzmann distribution; see text. [f] Weighted over all conformations at 298 K according to the Boltzmann distribution; see text. [g] Structure from ref 121.

Figure 2 indicates that each of the PSO, SD, and FC mechanisms make significant contributions to $^1J(^{31}P,^{31}P)_{iso}$, although the FC mechanism dominates. Compared to other molecules containing P,P single bonds, the diphosphetes have an unexpectedly large contribution from the PSO mechanism. A large contribution from the PSO mechanism is typical of molecules containing formal P,P double-bonds, thus hinting that there may indeed be some double-bond character in the diphosphetes.

(k) Phosphole tetramer. The phosphole tetramer was first synthesized in 1982, and the X-ray crystal structure[128] was subsequently reported. A solid-state ^{31}P NMR investigation was carried out,[129] revealing that the four phosphorus atoms consist of two magnetically equivalent spin pairs and may be treated as an AB spin system (see Figure 1). The phosphorus CS tensors were characterized using various solid-state NMR techniques and high-level ab initio calculations. In addition, the magnitude and relative signs of the indirect and direct $^{31}P,^{31}P$ nuclear spin interactions were determined, $^1J(^{31}P,^{31}P)_{iso} = -362$ Hz and $R_{DD} = +1{,}800$ Hz, respectively. In the analysis of the ^{31}P NMR spectra, the difference between R_{DD} and R_{eff} was found to be small, 73 ± 50 Hz, and was attributed to either vibrational averaging or the small value of ΔJ.

The ZORA DFT calculations of $^1\mathbf{J}(^{31}P,^{31}P)$ for the phosphole tetramer are in excellent agreement with experiment. The negative sign of $^1J(^{31}P,^{31}P)_{iso}$ is reproduced, and there is less than a 15% difference between the calculated, −411 Hz, and experimental, −362 Hz, values of $^1J(^{31}P,^{31}P)_{iso}$ (see Table 7). The anisotropy of $\mathbf{J}$ is relatively small in magnitude, +178 Hz, indicating that the difference between R_{DD} and R_{eff} may indeed be attributed to ΔJ. From our calculation, $\Delta J/3 \approx 60$ Hz, which agrees well with the value observed experimentally, $R_{DD} - R_{eff} = 73$ Hz.

Examination of the mechanisms for $^1J(^{31}P,^{31}P)_{iso}$ for the phosphole tetramer indicates that the FC mechanism is the chief

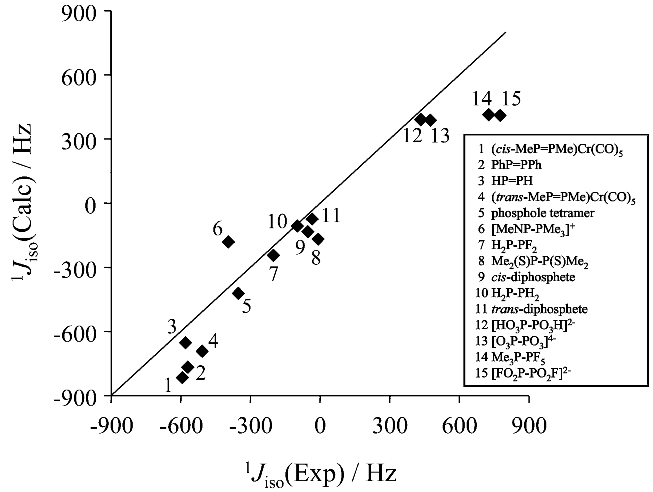

Figure 7. Experimental vs nonrelativistic calculated $^{1}J(^{31}P,^{31}P)_{iso}$ values for the phosphorus-containing molecules considered in this study; the diagonal line indicates perfect agreement between calculated and experimental results. The correlation coefficient, R^2, is 0.86.

contributor (Figure 2). The PSO and SD mechanisms make contributions of equal magnitude but opposite sign, resulting in a net cancellation.

4.2. Trends in ^{1}J(^{31}P,^{31}P). The calculated and experimental values of $^{1}J(^{31}P,^{31}P)_{iso}$ for the molecules considered in this study are summarized in Table 7 and plotted in Figure 7. The diagonal line with slope = 1 in Figure 7 indicates perfect agreement between calculated and experimental $^{1}J(^{31}P,^{31}P)_{iso}$ values; any deviation from this line indicates a discrepancy between experimental and calculated $^{1}J(^{31}P,^{31}P)_{iso}$ values. In cases where the sign of $^{1}J(^{31}P,^{31}P)_{iso}$ is unknown experimentally, the sign of the calculated value is assumed to be correct. Given the success of the theoretical approach at correctly calculating the sign of $^{1}J(^{31}P,^{31}P)_{iso}$ when known experimentally, this is a reasonable assumption.

Figure 7 illustrates the qualitative agreement between calculated and experimental values of $^{1}J(^{31}P,^{31}P)_{iso}$. The range of observed values is reproduced, with the largest disagreement for large, positive values of $^{1}J(^{31}P,^{31}P)_{iso}$. In these cases, the calculations consistently underestimate the magnitude of $^{1}J(^{31}P,^{31}P)_{iso}$. For molecules where $^{1}J(^{31}P,^{31}P)_{iso}$ is found to be large and negative, the calculated results overestimate the magnitude of $^{1}J(^{31}P,^{31}P)_{iso}$. This discrepancy may be due to the fact that a more accurate description of the nuclear region is required for these FC-dominated $^{1}J(^{31}P,^{31}P)_{iso}$ values. Also note that, for all the model systems considered herein, excluding the diphosphenes, the value of ΔJ is on the same order of magnitude as $^{1}J(^{31}P,^{31}P)_{iso}$. For systems containing formal multiple P,P bonds, ΔJ is typically on the order of 1000 Hz. Although $\Delta J/3$ is relatively small compared to the ^{31}P,^{31}P dipolar coupling, ~2000 Hz, in these systems, the experimentalist should be aware that R_{eff} may differ from R_{DD} by as much as 15%. Last, examination of the contributions of the individual mechanisms to $^{1}J(^{31}P,^{31}P)_{iso}$ indicates that although the FC mechanism is the principal contributor in most cases, the PSO contribution is also significant, even dominant, where formal multiple P,P bonds exist.[28] This is intuitive from the physical description of the $^{1}J(^{31}P,^{31}P)_{iso}$ mechanisms. The FC mechanism dominates $^{1}J(^{31}P,^{31}P)_{iso}$ for systems where σ bonding is prevalent, while the "noncontact" mechanisms are important for P,P π bonding systems. Our calculations support this rationale, as evidenced by Figure 2.

4.3. Factors Affecting $^{1}J(^{31}P,^{31}P)_{iso}$. In the spirit of earlier studies,[2] we discuss variations in $^{1}J(^{31}P,^{31}P)_{iso}$ in terms of formal oxidation state of phosphorus atoms, electronegativity of substituents bonded to phosphorus, stereospecific arrangement of ligands, and phosphorus coordination number. As well, we comment on the role that vibrational averaging and solvent effects might have in comparing calculated and experimentally observed $^{1}J(^{31}P,^{31}P)_{iso}$ values.

(a) Phosphorus oxidation state: Experimental observations have led to the conclusion that negative values for $^{1}J(^{31}P,^{31}P)_{iso}$ are typically observed for P(III),P(III) or P(III),P(V) spin pairs, whereas positive, or small negative, values of $^{1}J(^{31}P,^{31}P)_{iso}$ are observed for P(V),P(V) spin pairs.[2,6] These observations are reproduced by our theoretical results. Compounds 12, 13, and 15 represent systems where both phosphorus nuclei are in the +5 oxidation state and large positive $^{1}J(^{31}P,^{31}P)_{iso}$ values are observed for these systems both computationally and experimentally. Compound 14 is a P(IV)$^+$,P(VI)$^-$ system; hence, on the basis of the formal oxidation state of phosphorus, a positive, or small negative, value is anticipated for $^{1}J(^{31}P,^{31}P)_{iso}$, as given by our calculations. Likewise, compounds 1−11, with the exception of 8, represent systems where both phosphorus nuclei are in the +3 oxidation state and a range of negative $^{1}J(^{31}P,^{31}P)_{iso}$ values is observed. Compound 8, TMPS, has an experimental value of $^{1}J(^{31}P,^{31}P)_{iso}$ of −18.7 Hz, a small, negative value characteristic of a P(V),P(V) system; our calculated value, −157.5 Hz, significantly overestimates the magnitude of $^{1}J(^{31}P,^{31}P)_{iso}$.

(b) Electronegativity: The electronegativity, χ, of substituents directly bonded to phosphorus also plays a role in determining $^{1}J(^{31}P,^{31}P)_{iso}$.[2,3,6,130] An increase in χ results in an increase in the magnitude of $^{1}J(^{31}P,^{31}P)_{iso}$.[2,3,6,130] In fact, a linear relationship was found for $^{1}J(^{31}P,^{31}P)_{iso}$ vs χ for directly bonded phosphorus nuclei.[130c] A specific example of the dependence of $^{1}J(^{31}P,^{31}P)_{iso}$ on χ was observed for $[Ph_3P{-}PPh_2]^+$ and $[Ph_2(Cl)P{-}PPh_2]^+$ where $^{1}J(^{31}P,^{31}P)_{iso}$ was found to increase from 323 to 406 Hz[141] upon replacing one phenyl group with a chlorine atom. This experimental trend has been explained[3] in terms of the s character of the P,P bond, which increases with an increase in χ and is evident in our data when the results for compounds $H_2P{-}PH_2$ and $H_2P{-}PF_2$, as well as $[HO_3P{-}PO_3H]^{2-}$ and $[FO_2P{-}PO_2F]^{2-}$, are considered (see Table 7). In both cases, replacing hydrogen with a more electronegative element, i.e., fluorine, results in an increase in $^{1}J(^{31}P,^{31}P)_{iso}$. Furthermore, Figure 2 indicates that there is an increased contribution from the FC mechanism for the fluorine-substituted systems, supporting the simple argument of an increase in s character of the P,P bond.

(c) Stereoisomers of ligands (cis vs trans): The use of $^{1}J(^{31}P,^{31}P)_{iso}$ values to distinguish between various isomers is common practice in inorganic and organometallic chemistry given that larger $^{1}J(^{31}P,^{31}P)_{iso}$ values are generally observed for cis isomers compared to the analogous trans isomers. In this report, three examples reproduce this trend, MeP=PMe, (η^1-MeP=PMe)Cr(CO)$_5$, and the diphosphetes. In each case, $^{1}J(^{31}P,^{31}P)_{iso}$ is greater for the cis isomer compared to the trans isomer due to a greater contribution from the FC mechanism for the cis isomer (Figure 2). Overall, the results agree qualitatively with experiment.

(d) Coordination number: $^{1}J(^{31}P,^{31}P)_{iso}$ values are often used as diagnostic tools for confirming coordination of a phosphorus-containing ligand to a metal.[2] The general observation is a reduction in the magnitude of $^{1}J(^{31}P,^{31}P)_{iso}$ in the free ligand upon coordination; however, exceptions do occur when atoms with high electronegativities are involved.[2,6] We investigated $^1J(^{31}P,^{31}P)_{iso}$ for the diphosphene ligand in its free form as well as coordinated to a metal center, i.e., (η^1-MeP=PMe)Cr(CO)$_5$. For the trans isomer, $^1J(^{31}P,^{31}P)_{iso}$ decreased in magnitude from −718 to −681 Hz upon coordination to Cr, while, for the cis isomer, $^1J(^{31}P,^{31}P)_{iso}$ increased slightly in magnitude from −791 Hz to −804 Hz upon coordination. Although our $^1J(^{31}P,^{31}P)_{iso}$ results for the cis isomer do not follow experimental observations upon coordination, they are still satisfactory in that they qualitatively reproduce experimental $^1J(^{31}P,^{31}P)_{iso}$ values for these computationally challenging transition metal-containing systems.

(e) Molecular structure and environment: The structure employed in the calculation is a critical factor in obtaining reliable results for $^1\mathbf{J}(^{31}P,^{31}P)$. However, an ideal representation of the true experimental system is often difficult or impossible to obtain due to lack of structural data, the inability to replicate the actual environment of the molecule of interest, or simply because the computational demand of replicating the system of interest is too high. Since experimental structures are often unknown, idealized models or computationally optimized structures must be employed in the calculation of $^1\mathbf{J}(^{31}P,^{31}P)$. However, if the structure is an inadequate representation of the true system, unavoidable discrepancies between calculated and experimental $^1\mathbf{J}(^{31}P,^{31}P)$ will result. In addition, all $^1\mathbf{J}(^{31}P,^{31}P)$ calculations are carried out on rigid, isolated molecules and do not account for the effects of solvent and/or hydrogen bonding. Given that most experimentally determined $^1J(^{31}P,^{31}P)_{iso}$ values are measured using ^{31}P NMR spectroscopy in solution, the presence of solvent molecules and hydrogen bonding may be important in the determination of $^1J(^{31}P,^{31}P)_{iso}$ for certain systems.[60] For example, in systems containing coordinatively unsaturated P,P bonds, the electron lone pairs on phosphorus will interact with Lewis acid solvents or nearby hydrogen atoms; as a result, the total $^1J(^{31}P,^{31}P)_{iso}$ will change due to the modified roles of the FC, PSO, SD, and DSO mechanisms. Last, effects of motional averaging on **J**-tensors are known to be important,[58,59] especially for small molecules; however, vibrational and librational averaging are not accounted for in our calculations.

5. Conclusions

In this study, a comprehensive survey of calculated $^1J(^{31}P,^{31}P)_{iso}$ values is presented using ZORA DFT. Qualitative agreement is achieved between experimental and calculated $^1J(^{31}P,^{31}P)_{iso}$ values for a series of molecules where the phosphorus atoms participate in a variety of bonding environments. The calculations are certainly sufficiently reliable that one can use the computations to predict the sign of $^1J(^{31}P,^{31}P)_{iso}$. Our results are encouraging because many of the systems investigated herein are computationally challenging due to the presence of transition-metal nuclei, multiple bonds and/or electron lone pairs on phosphorus, or simply the size of the molecule. Inspection of the mechanisms which contribute to $^1J(^{31}P,^{31}P)_{iso}$ indicates that while the FC term is usually the dominant mechanism, the PSO term is of equal or greater importance for molecules containing formal multiple P,P bonds. In most cases, the SD mechanism makes a non-negligible contribution to $^1J(^{31}P,^{31}P)_{iso}$, whereas in all cases, the DSO mechanism is negligible and contributes <1% to $^1J(^{31}P,^{31}P)_{iso}$. Finally, for systems containing formal multiple P,P bonds, ΔJ may make significant contributions to measured values of R_{eff}; thus, experimental attempts to equate R_{eff} with R_{DD} may be incorrect. Given the success of ZORA DFT calculations in reproducing observed $^1J(^{31}P,^{31}P)_{iso}$ values, we recommend this approach as a tool for estimating ΔJ.

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