spectra. Four-coordinate Ni corphinoids are known to crystallize in a highly ruffled conformation as illustrated by the nickel octaethyl pyrrocorphinate structure.[14,43] Thus, in analogy with the Ni(OEP) case, the Raman spectrum of the crystal is that of a ruffled corphinoid, while the solution spectrum is that of a more planar Ni corphinoid. The core size is expected to be smaller for the ruffled structure than for the planar one. Hence, core contraction occurs and the large decrease in Ni corphinoid marker line frequencies for the crystalline form (1347 → 1334 cm^{-1} and 1641 → 1632 cm^{-1}) likely results from ruffling of the macrocycle and not from expansion of the core.

Recently, Waditschatka et al., using proton NMR spectroscopy, showed that Ni *ccccc*-octaethyl-pyrrocorphinate exchanges between two enantiomorphically ruffled conformers.[44-46] The exchange rate was found to be $2.9 \times 10^4\ s^{-1}$ at 25 °C. If in the present case exchange between two distinguishable ruffled forms is occurring, inversion of the ruffled forms of the Ni corphinoid must occur on a subnanosecond time scale because the faster Raman measurement shows no clear evidence of the presence of two forms—at least not forms similar to the crystalline form, which we believe takes on a ruffled structure. Another possibility, however, is that any ruffled forms existing in solution have nearly identical Raman spectra that are distinct from the ruffled species occurring in the polycrystalline solid.

Very recently we have completed an extensive Raman investigation of free and salt-extracted forms of F_{430} and of methylreductase.[47,48] Ruffling appears to play a role in the spectra of F_{430} in aqueous solution as the spectrum of the ruffled, 4-coordinate form is different from that of the 4-coordinate model, this in spite of the fact that the 6-coordinate forms of F_{430} and the model **2** are almost identical. Model **2** is sterically hindered at the periphery in a manner different from the two isomers of F_{430} and appears not to ruffle as easily as either the pyrrocorphinate or free F_{430}.

Conclusions

It has been shown that excellent quality resonance Raman spectra of Ni corphinoids, related to cofactor F_{430} of the methylreductase system, can be obtained. In fact, the Raman spectra of the Ni corphinoid complexes are strikingly similar to the reported spectrum of F_{430}. The high-frequency Raman lines of the Ni corphinoid vary in a manner analogous to the core-size marker lines of metalloporphyrins. In particular, the analogous structural marker lines identified for the Ni corphinoid provide a means by which the number and type of axial ligand(s) can be determined. The Ni corphinoid Raman lines, therefore, provide a useful structural probe of Ni corphinoids such as F_{430} in various environments including a site in a protein.[47,48]

Acknowledgment. I thank A. Eschenmoser, A. Pfaltz, and A. Fässler for providing the Ni corphinoids for the Raman studies and A. Eschenmoser for a useful communication on the interpretation of the data. I also thank A. K. Shiemke, R. A. Scott, and L. A. Andersson for helpful discussions.

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Temperature and Solvent Dependence of Scalar Coupling Constants in Salts of *trans*-$HFe(CO)_3PR_3^-$

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Abstract: Salts of $[trans\text{-}HFe(CO)_3PR_3]^-$ (PR_3 = $P(OMe)_3$, $P(OEt)_3$, PPh_3, and PEt_3) are observed to give variable NMR parameters depending on temperature and solvent. Of all the NMR parameters, the changes in phosphorus to hydride coupling constants are most dramatic. For example, [bis(triphenylphosphine)iminium$^+$][$HFe(CO)_3P(OEt)_3^-$] showed a 20-Hz change and sign inversion in J_{PH} in tetrahydrofuran over a temperature range of +50 to −70 °C. Both variable-temperature infrared spectroscopy and molecular orbital calculations have been conducted to explore the cause of such extraordinary behavior. The infrared data best fit a mechanism of changing H–Fe–CO angle enforced by a solvent stabilization of an internal dipole moment in the anion. Unlike the above compounds, anionic metal hydrides with phosphorus donor ligands positioned cis to the hydride ligand showed little dependence of temperature and solvent on scalar coupling constants.

The preparation and reactivity of salts of *trans*-$HFe(CO)_3PR_3^-$ (PR_3 = PMe_3, PEt_3, PPh_2Me, PPh_3, $P(OEt)_3$, $P(OMe)_3$) have recently been reported.[1] An X-ray crystal structure determination of a typical hydride, $[Et_4N]^+[HFe(CO)_3PPh_3]^-$ (**1**), showed the anion to be of pseudo-trigonal-bipyramidal (TBP) geometry (C_{3v} symmetry) with the three CO ligands bent out of the equatorial plane and toward the (unlocated) hydride ligand by 9.5 (3)°. The ν(CO) IR spectral data for **1** and analogous hydrides listed above were, in both solution and in the solid state, consistent with the molecular structure observed for **1**, i.e., of trans geometry. In only one derivative has a different geometrical isomer been observed: the hydride of PPN^+ *cis*-$HFe(CO)_3P(OPh)_3^-$ (**2**) is axial and the $P(OPh)_3$ ligand is equatorial in a pseudo-TBP structure.[2]

The signal for the hydride resonance for all hydride derivatives was about −9 (±0.5) ppm upfield from tetramethylsilane, and showed only a small dependence on P-donor ligand, solvent,

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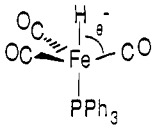

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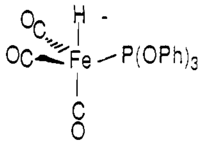

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counterion, or temperature.[1] Interestingly, the phosphorus–hydrogen coupling constants of *trans*-$HFe(CO)_3PR_3^-$ were highly dependent on temperature, systematically varying in the case of PPN^+ *trans*-$HFe(CO)_3P(OMe)_3^-$ in acetone from a room-temperature value of $|J_{PH}| = 15$ Hz to 0.0 Hz at −30 °C to $|J_{PH}| = 8.4$ Hz at −70 °C. In contrast, PPN^+ *cis*-$HFe(CO)_3P(OPh)_3^-$ had a very large J_{PH} (54 Hz) which was invariant to temperature.

Certainly trigonal-bipyramidal molecules and ions are well known for dynamic NMR behavior, which is usually due to rapid intramolecular site exchange within the NMR time scale. A temperature- and solvent-dependent equilibrium of two geometric isomers with extremely different J_{PH} values and a fast rate of exchange was first considered to be responsible for the variable J_{PH} in **1** and other trans derivatives. Yagupsky and Wilkinson have convincingly shown such behavior with $HIr(CO)_2(PR_3)_2$ (PR_3 = PPh_3, $P(C_6H_4F)_3$, and $PEtPh_2$) complexes.[3] Although these complexes displayed a single structure in the solid state, IR and NMR spectra indicated the presence of two isomeric pentacoordinate species in solution. The two species had J_{PH} values of opposite sign, and the equilibrium position (and observed J_{PH}) could be altered by changing the temperature or solvent. Although such an explanation for the NMR spectroscopic changes appeared eminently reasonable for the *trans*-$HFe(CO)_3PR_3^-$ complexes, as presented below our attempts to simultaneously fit both temperature-dependent NMR and temperature-dependent infrared parameters were inconsistent with this model.

Below, various models to explain the variable J_{PH} are explored. Since two- and three-bond coupling constants are known to depend on bond-angle changes,[4,5] we have considered the possibility that J_{PH} is dependent on subtle angle changes in the Fe coordination sphere. We propose that there is good evidence for solvent-stabilized bond-angle changes resulting from changes in solvent dielectric constant. Such dielectric constant changes may be achieved either by a change in solvent (THF vs. CH_3CN, for example) or by effects of temperature.

Experimental Section

A. Materials and Sample Preparations. An argon atmosphere glovebox and standard Schlenk techniques were used in all reactions and sample preparations. Deuterated solvents were obtained from Aldrich Chemical Co. and degassed prior to use. All solvents were stored over activated 3A molecular sieves and used as purchased except d_8-THF which was dried over Na^0/benzophenone and vacuum distilled prior to use. Bis(triphenylphosphine)iminium (PPN^+) and Et_4N^+ salts of $HFe(CO)_3PR_3^-$ were prepared as previously reported.[1,2] The sodium salt of *trans*-$HFe(CO)_3P(OMe)_3^-$ was prepared by in situ ion exchange, using 5 equiv of $Na^+BPh_4^-$ and PPN^+ *trans*-$HFe(CO)_3P(OMe)_3^-$.

Preparation of $PPN^+HFe(CO)_{3-x}(^{13}CO)_xP(OCD_3)_3^-$. The $P(OCD_3)_3$ ligand was prepared by treating PCl_3 with CD_3OD in the presence of an amine base. A typical reaction made use of a 250-mL Schlenk flask to which ~120 mL of Et_2O and 2.45 mL of PCl_3 (28 mmol) were added using strict O_2 exclusion techniques. In a separate flask, 11.9 mL of NEt_3(85 mmol), 3.10 g of CD_3OD (86 mmol), and 15 mL of Et_2O were mixed and degassed. The CD_3OD solution was then cannulated *slowly* onto the PCl_3 while keeping the reaction flask in dry ice–acetone. After approximately 20 min, the Et_2O and $P(OCD_3)_3$ product were vacuum transferred from the large white $DNEt_3^+Cl^-$ precipitate. The ether was then removed from $P(OCD_3)_3$ by simple distillation.

$Fe(CO)_4P(OCD_3)_3$ was prepared using the method described earlier for $Fe(CO)_4P(OCH_3)_3$,[6] replacing $P(OCH_3)_3$ by $P(OCD_3)_3$. Once this material was obtained it was enriched with ^{13}CO using photolysis as described by Darensbourg et al.[7] In order to prevent secondary coupling in the NMR, care was taken to minimize the amount of multi-^{13}CO-substituted compounds. Therefore, the reaction was monitored by IR and terminated when the relative enrichment reached ca. 45% all ^{12}CO, 40% monosubstituted ^{13}CO, and 15% disubstituted ^{13}CO. This prevented 100% monosubstitution, i.e., $Fe(CO)_3(^{13}CO)P(OCD_3)_3$. Upon isolation of these products, the corresponding hydride was prepared using the methanolic KOH/PPNCl procedure reported earlier.[1]

B. Instrumentation and Spectroscopic Methods. All nuclear magnetic resonance spectra were performed on a Varian XL 200 spectrometer. Proton and carbon NMR spectra were referenced to the deuterated solvent used. ^{31}P NMR spectra were referenced externally to H_3PO_4. The temperatures reported are ±1 °C. Spin-tickling experiments to determine relative coupling constant signs were attempted on PPN^+-$HFe(CO)_2(^{13}CO)P(OCD_3)_3^-$ at 22 °C in THF. The carbon-13 spectrum was of the AMX type and only the relative signs of J_{PH} to J_{PC} could be obtained. This was done by observing the ^{13}C signal while spin-tickling (irradiating with very low decoupling powers) successively the respective individual ^1H transitions. Attempts to determine the relative signs of J_{HC} to J_{PC} by observing ^{31}P and spin-tickling the ^1H transitions were not successful because of severe broadening of the ^{31}P line by J_{PD}.

The dependence of J_{PH} on concentration of hydride was determined by monitoring three different concentrations of $PPN^+HFe(CO)_3P(OMe)_3^-$ in CD_3CN at 22 °C. The concentrations of 0.11, 0.075, and 0.037 M were used and all spectra showed J_{PH} to be 4.21 (± 0.03) Hz (δ −9.35 (± 0.02) ppm).

Routine infrared spectra were obtained on IBM FTIR Models 32 or 85, using either 0.1-mm NaCl or 0.1-mm CaF_2 sealed cells. Variable-temperature IR data required a special cell (VLT-2) made by London Research and Industrial Instruments and purchased from Beckman Instruments. It made use of a 0.1-mm CaF_2 sealed IR cell attached to a stainless steel cold finger. Rheostat heaters fitted on either side of the cell regulated the cell temperature. The cell fit into an outer jacket which had its own windows, also fitted with adjustable heaters to avoid water condensation at low temperatures. Typically the IR cell was loaded in a drybox and the outer jacket sealed around the cell via an O-ring and four bolts. Once sealed an additional 25–50 mL of argon was injected into the outer jacket via an opening with a septum as seal to compensate for the reduced gas pressure at low temperatures. By way of a second opening sealed with a septum a thermocouple was introduced and attached to the IR cell for accurate temperature measurements (±1 °C). Dry ice–acetone was used to reach temperatures of −70 °C. Multiscans (>150) were typically collected.

C. Calculations. Fenske–Hall MO calculations[8] were performed on the model compound, $HFe(CO)_3PH_3^-$, using a VAX 11/780 computer. The internal P–Fe–CO angles used were 90, 95, 100, and 105°. Estimated bond distances were maintained at 1.55, 1.72, 1.17, 2.19, and 1.42 Å, for Fe–H, Fe–C, C–O, Fe–P, and P–H, respectively.

Assuming the contact term for nuclear spin–spin couplings predominates, two approaches to calculating coupling constants were attempted. The first approach was that derived by McConnell:[9]

$$K_{AB} = (64\pi^2/9)\beta^2(^3\Delta E)^{-1}(s_A|\delta(r_A)|s_A)(s_B|\delta(r_B)|s_B)P^2{}_{s_As_B} \qquad (1)$$

Here $(^3\Delta E)^{-1}$ is the mean exitation energy and $P^2{}_{s_As_B}$ is the s_A–s_B bond order. According to this method, K_{AB} is always positive; therefore, the Pople and Santry method,[10] which does not have this restriction, was also applied:

$$K_{AB} = (64\pi^2/9)\beta^2(s_A|\delta(r_A)|s_A)(s_B|\delta(r_B)|s_B)\Pi_{s_As_B} \qquad (2)$$

The mutual polarizability term, Π, for orbitals s_A and s_B can be written as

$$\Pi_{s_As_B} = 4\sum_i^{\text{occ}}\sum_j^{\text{unocc}}(\epsilon_i - \epsilon_j)^{-1}C_{is_A}C_{is_B}C_{js_A}C_{js_B} \qquad (3)$$

In this method K_{AB} can have either sign even though correlation between electrons of opposite spin is absent in this description. As expected the sign of the coupling constants sometimes differed in the two approaches, but the trends on changing θ were the same; i.e., both showed either an increase or decrease for a specific coupling constant. While a sign inversion in J_{PH} was not observed in the Pople and Santry method, the general trend of increasing positive J_{PH} with increasing θ was taken to be significant.

Based on ν(CO) infrared intensity ratios, angle calculations were carried out using a procedure described in the literature.[11] The areas

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Table I. Variable-Temperature NMR Spectral Data for $Cat^+HFe(CO)_3PR_3$-Complexes[a]

compound	solvent	temp, °C	ϵ^b	δ(Fe–H)	$J_{PH}{}^c$	$J_{PC}{}^c$	$J_{HC}{}^c$
$PPN^+HFe(CO)_4^-$	THF	+50	6.73				11.5
		0.0	8.24				11.8
		−70	11.59				12.0
$PPN^+HFe(CO)_3P(OMe)_3^-$	THF	+50	6.73	−9.26	14.85		
		+26	7.39	−9.20	11.92	10.9	13.6
		−20	9.01	−9.07	5.06	13.9	
		−60	10.98	−8.93	0.00		
		−70	11.59	*−8.91*	*1.77*	17.4	14.7
$PPN^+HFe(CO)_3P(OMe)_3^-$	acetone	+24	20.9	−9.12	8.79	12.0	13.87
		+10	22.7	−9.09	6.78		
		0	23.9	−9.06	4.93		
		−10	25.1	−9.04	3.31		
		−20	26.4	−9.00	1.31		14.29
		−30	27.6	−8.97	0.00		
		−40	28.9	−8.94	2.39		
		−50	30.1	−8.91	4.39		
		−60	31.4	−8.87	6.40		
		−70	32.6	−8.83	8.41	19.5	15.03
$PPN^+HFe(CO)_3P(OMe)_3^-$	CD_3CN	+50	31.1	−9.36	7.79		
		+26	35.8	−9.32	3.69		
		−20	44.8	−9.22	3.57		
		−40	48.7	−9.18	7.18		
$PPN^+HFe(CO)_3P(OMe)_3^-$	Me_2SO	+56		−9.44	8.27		
		+36		−9.42	5.36		
		+26	46.6	−9.40	3.80		
		+20		−9.39	0.00		
$Na^+HFe(CO)_3P(OMe)_3^-$	THF	+50	6.73	−9.37	13.69		
		+26	7.39	−9.28	11.17		
		−20	9.01	−9.15	6.61		
		−60	10.98	−9.00	0.00		
$Et_4N^+HFe(CO)_3P(OMe)_3^-$	THF	+26	7.39	−9.33	8.99		
		−20	9.01	−9.24	3.37		
		−60	10.98	−9.11	0.00		
$PPN^+HFe(CO)_3P(OEt)_3^-$	THF	+50	6.73	−9.16	8.55		
		+26	7.39	−9.09	4.52		
		−20	9.01	−8.94	0.00		
		−40	9.91	−8.87	5.54		
		−70	11.59	−8.75	11.62		
$PPN^+HFe(CO)_3PPh_3^-$	THF	+50	6.73	*−9.34*	*13.15*	7.9	14.1
		+29	7.31	−9.28	10.92	8.9	14.5
		0.0	8.24	−9.22	8.00	10.7	14.7
		−30	9.44	−9.13	4.75	12.3	14.8
		−70	11.59	9.00	0.00	15.1	15.1
$Et_4N^+HFe(CO)_3PPh_3^-$	CD_3CN	+50	31.1	−9.26	6.16		
		+26	35.8	−9.27	2.39		
	THF	amb	7.4	−9.12	11.98		
	acetone	amb	20.8	−9.02	6.4		
$Et_4N^+HFe(CO)_3PEt_3^-$	THF	+50	6.73	−9.37	4.93		
		+26	7.39	−9.33	3.24		
		−60	10.98	−9.18	0.00		
PPN^+ *cis*-$HFe(CO)_3P(OPh)_3^-$	THF	+26	7.39	−9.89	54.80		
		0.0	8.24	−9.91	54.32		
		−40	9.91	−9.96	56.49		
		−80	12.27	−10.02	57.98		
PPN^+ *cis*-$HFe(CO)_3P(OPh)_3^-$	acetone	0.0	23.9	−9.80	50.04		
		−40	28.9	−9.82	48.82		
		−80	33.8	−9.86	48.69		
PPN^+ *cis*-$HFe(CO)_3P(OPh)_3^-$	CD_3CN	amb	36.0	−9.88	41.55	1.6	11.08

[a] All anions are of the trans configuration except where noted. Italicized values represent calculated data obtained from a least-squares fit from the remainder of data points. Amb refers to ambient temperatures. [b] References: THF,[12] CH_3CN,[13] acetone.[14] [c] Absolute value of two-bond couplings in hertz, J_{PH} = phosphine/-ite to hydride, J_{PC} = phosphine/-ite to carbonyl carbon, J_{HC} = hydride to carbonyl carbon.

of the E and A_1 bands were determined by cutting and weighing three copies of each respective band on a Mettler balance accurate to ± 0.0001 g. The E band required deconvolution from a small overlap of the ν(MH) band. The angle θ (∠H–Fe–CO) was calculated using the expression $I_{A_1}/I_E = (\cos\theta + \rho)^2/\sin^2\theta$, where ρ is an electronic migration parameter and was taken to be zero in this study.

Results

A compilation of results from the variable-temperature NMR experiments is presented in Table I. An example of the behavior of the hydride resonance of PPN^+ *trans*-$HFe(CO)_3P(OMe)_3^-$ (**3**) upon changing temperature is shown in Figure 1. The resonances remain sharp at all temperatures and indicate that there is no line broadening due to solvent viscosity. The sharp lines at low temperatures also indicate that either no averaging process is occurring or an exceptionally low-energy barrier for averaging exists.

The largest separation of the hydride doublet signals for *trans*-$HFe(CO)_3PR_3^-$ was observed to be on the order of 15 Hz.

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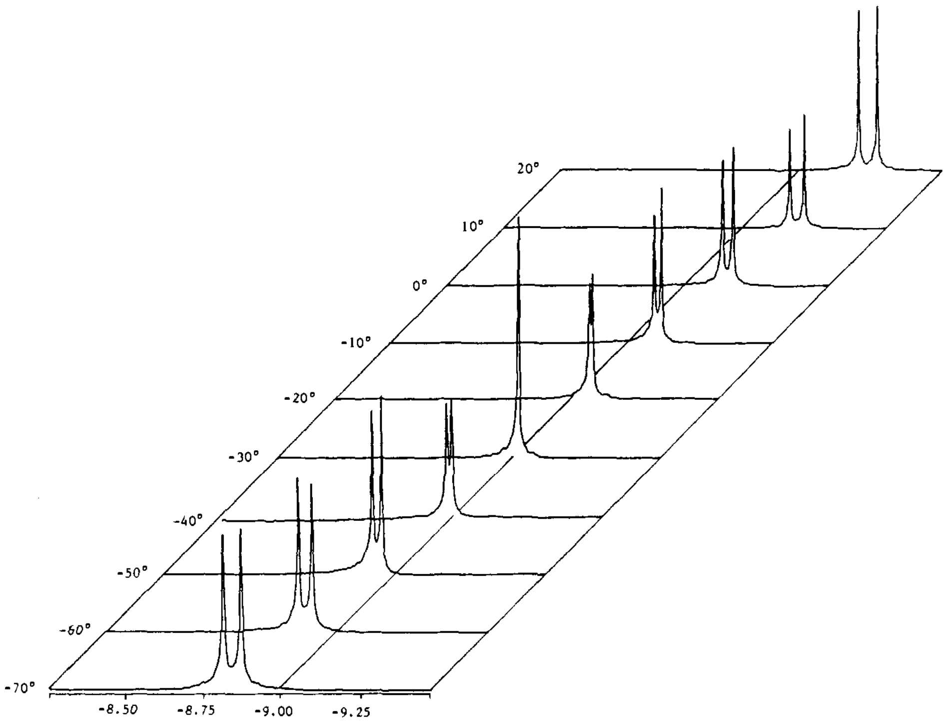

Figure 1. Variable-temperature profile of the ^{1}H NMR of PPN$^+$HFe(CO)$_3$P(OMe)$_3$$^-$ in acetone-d_6.

The few studies of purportedly TBP complexes containing a P-donor ligand and hydride trans to each other have reported J_{PH} coupling constants ranging from 5 to 50 Hz.[15] In order to substantiate that the observed spectra reflected a change in J_{P-H} values and not two variable hydride resonances, analogous ^{31}P NMR spectra of **3** were measured in THF as a function of temperature. Upon selective decoupling of the P(OCH$_3$)$_3$ protons, a doublet, centered at 214 ppm, J_{PH} = 9.0 Hz, was observed at 25 °C. This P − 31 doublet displayed the same behavior as the hydride doublet with lowering of temperature, i.e., $|J_{PH}| \rightarrow 0$ Hz.

The variable-temperature C-13 NMR of **3** in THF revealed a doublet of doublets, for the carbonyl carbons, centered at 223 ppm, at all temperatures measured. A doublet resulted upon broad-band proton decoupling of the C-13 spectrum. These results indicated the following: (1) the CO groups are equivalent, and (2) both the hydride and phosphorus atoms remain coordinated at all temperatures measured. Both J_{PC} and J_{HC} were shown to increase in absolute magnitude at lower temperatures; however, J_{HC} changed less dramatically. It should be mentioned that addition of ^{13}CO to solutions of PPN$^+$HFe(CO)$_3$P(OMe)$_3$$^-$ gave no PPN$^+$HFe(CO)$_4$$^-$ or any signs of ^{13}CO incorporation after 16 h.[1] Ligand lability is hence not problematical.

Table I also lists data obtained for several phosphine/-ite derivatives of *trans*-HFe(CO)$_3$PR$_3$$^-$ which show a similar J_{PH} dependence on temperature; i.e., on reduction of temperature J_{PH} decreased in absolute magnitude. Only in the case of P(OMe)$_3$ and P(OEt)$_3$ derivatives were we able to observe the reappearance of the doublet as lower and lower temperatures were achieved. Such behavior, exemplified in Figure 1, indicates either a coupling constant sign change ($+J \rightarrow 0 \rightarrow -J$ or $-J \rightarrow 0 \rightarrow +J$) with change in temperature, or the coupling constant returns to its original sign after passing through zero ($+J \rightarrow 0 \rightarrow +J$ or $-J \rightarrow 0 \rightarrow -J$). The latter possibility is reminiscent of a Karplus curve obtained by calculating the vicinal proton coupling constants while varying the dihedral angle in ethanic compounds.[5] A representative plot of J_{PH} (with one side taken arbitrarily as negative) vs. temperature is shown in Figure 2. Such plots have all yielded straight lines with $r > 0.99$. (Because accuracy of the point J_{PH} = 0 was limited by the digital resolution of the spectrometer, it was excluded in the linear regression analysis). This linear behavior is taken as good evidence of a coupling constant sign change since Karplus behavior should show at least some small curvature.

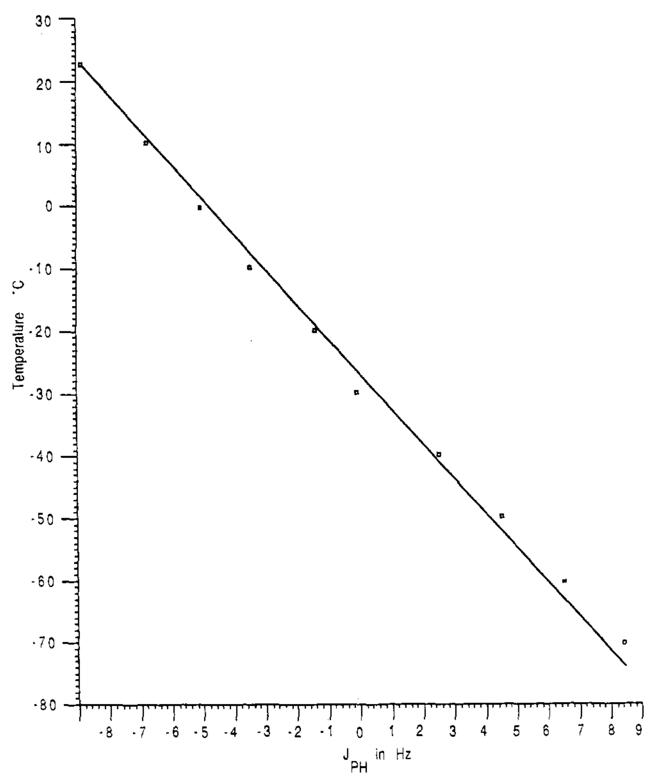

Figure 2. Dependence of J_{PH} on temperature (°C) for PPN$^+$HFe(CO)$_3$P(OMe)$_3$$^-$ in acetone-d_6. Signs of coupling constants were assigned as discussed in the text.

There is a small but regular downfield shift of δ(Fe–H) as the temperature is lowered (Table I). A direct relationship between chemical shift and J_{PH} is observed. Note also, Table I, that the coupling constants are not only temperature dependent but solvent dependent. For **3** the values of $|J_{PH}|$ vary from 11.92, 8.79, to 3.69 for THF, acetone, and acetonitrile solvents, respectively, at ca. 25 °C.

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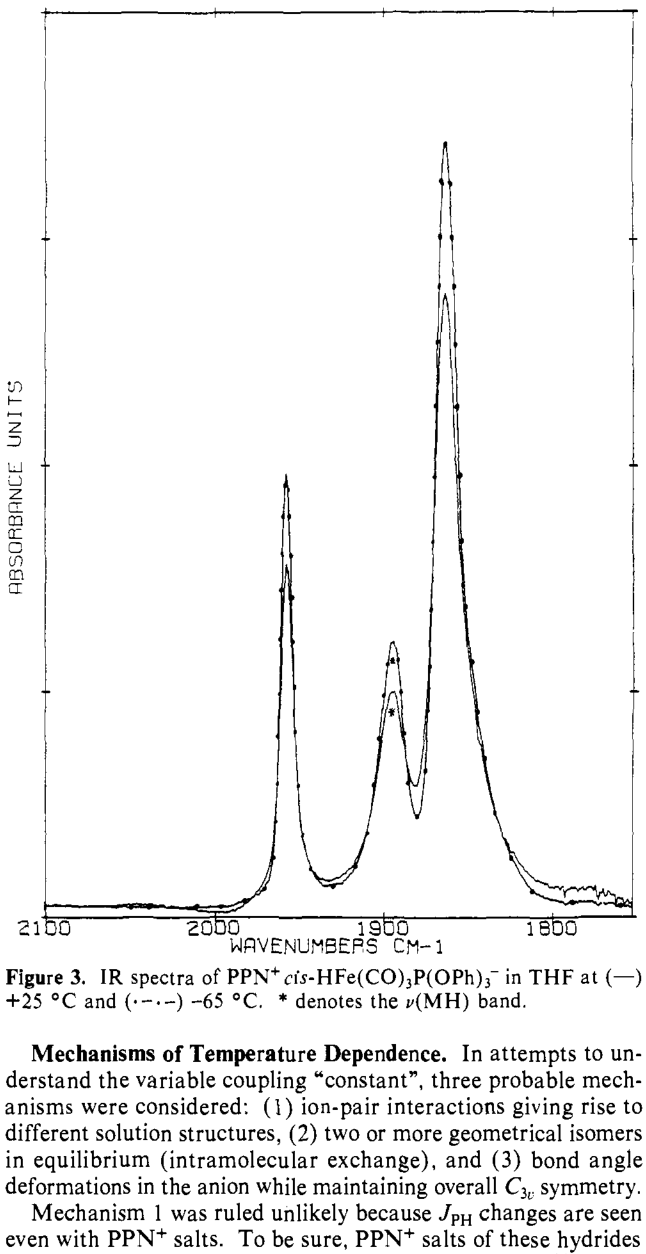

Figure 3. IR spectra of PPN$^+$*cis*-HFe(CO)$_3$P(OPh)$_3^-$ in THF at (—) +25 °C and (·–·–) -65 °C. * denotes the ν(MH) band.

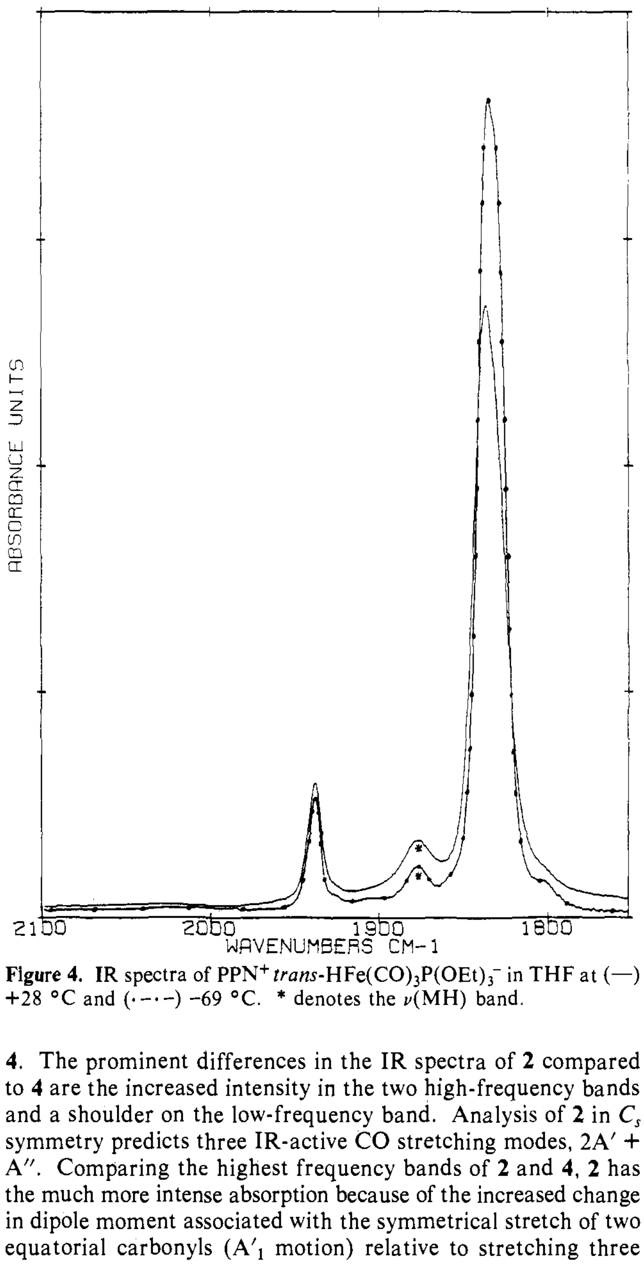

Figure 4. IR spectra of PPN$^+$*trans*-HFe(CO)$_3$P(OEt)$_3^-$ in THF at (—) +28 °C and (·–·–) -69 °C. * denotes the ν(MH) band.

Mechanisms of Temperature Dependence. In attempts to understand the variable coupling "constant", three probable mechanisms were considered: (1) ion-pair interactions giving rise to different solution structures, (2) two or more geometrical isomers in equilibrium (intramolecular exchange), and (3) bond angle deformations in the anion while maintaining overall C_{3v} symmetry.

Mechanism 1 was ruled unlikely because J_{PH} changes are seen even with PPN$^+$ salts. To be sure, PPN$^+$ salts of these hydrides exist in solution as ion pairs, particularly in THF solution.[16] There is, however, no specific contact interaction of the PPN$^+$ cation that perturbs the symmetry of the carbonylate, as determined by ν(CO) IR. Also, there was no dependence of J_{PH} on cat$^+$HFe(CO)$_3$PR$_3^-$ concentration. The fact that the Na$^+$ counterion has little effect on J_{PH} and δ(Fe–H) is mildly surprising and must reflect a *rapid* averaging site interchange since Na$^+$ is known to exist in solution as a solvent-separated ion pair and two other contact ion pairs with these anions.[1] Other studies of anionic hydrides have also shown minimal counterion effects on J_{PH}.[17]

To probe the possibilities of mechanisms 2 and 3 above, a solution structural technique faster than NMR was required. Variable-temperature infrared spectroscopy was carried out. The ν(CO) IR spectra for PPN$^+$*cis*-HFe(CO)$_3$P(OPh)$_3^-$ (**2**) and PPN$^+$*trans*-HFe(CO)$_3$P(OEt)$_3^-$ (**4**) in THF are shown in Figures 3 and 4, respectively. Figure 4 is representative of all *trans*-HFe(CO)$_3$PR$_3^-$ complexes, consisting of a weak high-frequency band (symmetric A$_1$ stretch), a very weak intermediate frequency (metal–hydrogen stretch), and a strong low-frequency band (asymmetric E stretch). Figure 3, however, is different in band ratios and reflects the difference in configuration between **2** and **4**. The prominent differences in the IR spectra of **2** compared to **4** are the increased intensity in the two high-frequency bands and a shoulder on the low-frequency band. Analysis of **2** in C_s symmetry predicts three IR-active CO stretching modes, 2A′ + A″. Comparing the highest frequency bands of **2** and **4**, **2** has the much more intense absorption because of the increased change in dipole moment associated with the symmetrical stretch of two equatorial carbonyls (A′$_1$ motion) relative to stretching three equatorial carbonyls (A$_1$ motion) in **4**. The middle band in both Figures 3 and 4 has been confirmed by H/D exchange to represent the metal–hydride stretch.[1,2] For **2** this band is of much stronger intensity because of strong coupling to the *trans*-CO stretch (A′$_2$ band, exhibited in Figure 3 as a low-frequency shoulder on the most intense A″ band). In the *trans*-HFe(CO)$_3$PR$_3^-$ analogues, there is no *trans*-CO to couple with, and as a result the ν(MH) has a weak absorption.

The J_{PH} in PPN$^+$ *cis*-HFe(CO)$_3$P(OPh)$_3^-$ was observed to be virtually invariant with temperature. Over these same temperatures the IR absorption bands in Figure 3 are typical; i.e., there is an overall enhancement of absolute intensity at low temperatures. If correction is made for the general intensity enhancement in the low-temperature spectrum, the -65 and +25 °C spectra are superimposable. The solution structure of **2** has also been confirmed to be the same as that observed in the solid state by obtaining an identical IR spectrum in KBr.[2] This indicates that **2** exists in solution as *one* species unperturbed from its cis configuration at all temperatures and thus gives only one J_{PH} value.

In contrast to **2**, the *trans*-HFe(CO)$_3$PR$_3^-$ complexes clearly show ν(CO) band ratio changes with temperature. Figure 4 shows the variable-temperature IR of PPN$^+$*trans*-HFe(CO)$_3$P(OEt)$_3^-$ (**4**) in THF. Upon cooling from +28 to -69 °C, there is an increase in the E-band intensity while the A$_1$ band remains the same or even decreases slightly in intensity. Similar observations

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Table II. Angle θ and J_{PH}[a] Data for $PPN^+HFe(CO)_3PR_3^-$

compound	solvent	temp (°C)	ϵ	I_E/I_{A_1}	θ (deg)	J_{PH} (Hz)
$PPN^+HFe(CO)_3P(OMe)_3^-$	THF	+50	6.73	7.681	70.16	-14.94
	CH_3CN	+50	31.1	8.663	71.24	-7.75
	THF	+25	7.42	8.881	71.45	-11.52
	acetone	+25	20.8	10.010	72.46	-9.47
	THF	-60	10.98	10.330	72.72	0.13
	acetone	+21	21.3	10.951	73.19	-8.73
	CH_3CN	+25	36.0	12.082	73.95	-3.64
	CH_3CN	-40	48.7	14.714	75.39	+7.05
	acetone	-68	32.4	16.985	76.36	+7.76
$PPN^+HFe(CO)_3P(OEt)_3^-$	THF	+28	7.33	9.233	71.78	-4.98
	THF	+28	7.33	9.132	71.69	-4.98
	THF	-64	11.22	12.920	74.45	+10.16
	THF	-69	11.53	14.185	75.13	+10.98
$PPN^+HFe(CO)_3PPh_3^-$	THF	+28	7.33	5.480	66.87	-10.85
	THF	+02	8.17	5.950	67.71	-8.13
	THF	-21	9.05	6.167	68.07	-5.72
	THF	-64	11.22	7.636	70.10	-1.23

[a] The values for J_{PH} were obtained from least-squares analysis of the data in Table I and have been assigned a sign as discussed in text.

were made on all *trans*-$HFe(CO)_3PR_3^-$ anions at all temperatures studied.

The most obvious clue offered by the spectra in Figure 4 is the maintenance of the two ν(CO) band pattern. There clearly are no new peaks or shoulders to indicate a second isomer at any temperature. The only way an equilibrating second species in solution (mechanism 2) could be envisioned is if both species possessed degenerate spectra with different band ratios. That is, at room temperature both species would be populated but at very low temperatures the thermodynamic trans isomer would predominate. This scenario is highly unlikely for the following reasons. First, IR is very sensitive to geometric and electronic changes in a substrate; therefore, a second isomer of identical IR is improbable. For example, in $HIr(CO)_2(PR_3)_2$ where a second isomer was suspected to be responsible for a variable J_{PH}, a second set of bands significantly displaced from the first was observable by solution IR.[3] Also, we have observed that simple differences in the spectra of cis and trans forms of $HFe(CO)_3PR_3^-$ include a 7-cm^{-1} difference in separation between high- and low-frequency bands and 9 cm^{-1} between ν(MH) and the low-frequency absorption. Next, in the dubious case that a truly degenerate species did exist, it would be expected from concentration levels necessary to enforce such coupling constant changes[18] that the band ratios would have been perturbed in a more dramatic way. Deuteration of these trans hydrides has revealed no significant shifts in ν(CO) band positions. Any other isomer in solution containing a CO group trans to the hydride should have given a dramatic ν(CO) shift[17] as is observed for *cis*-$HFe(CO)_3P(OPh)_3^-$.[2] Lastly, IR and NMR indicate that *cis*-$HFe(CO)_3P(OPh)_3^-$ does not permute to a second isomer in solution nor can it be forced to even at 160 °C.[2] This is suprising but it provides evidence that the pentacoordinate trans analogues are probably just as rigid. Any pseudorotation of *trans*-$HFe(CO)_3PR_3^-$ would initially necessitate H^- and PR_3 to be positioned in the equatorial plane. Such an intermediate should provide a substantial energy barrier to interconversion.[19]

Hence the a priori assumption that mechanism 2 was responsible for the variable NMR behavior yielded little evidence to support its existence. Therefore, mechanism 3, which takes account of angle deformations while maintaining overall C_{3v} symmetry, was considered. The ratio of intensities of the A_1 and E ν(CO) bands is sensitive to the H–Fe–CO_{eq} bond angle θ, structure **1**, as expressed in the equation:[11]

$$I_{A_1}/I_E = (\cos\theta + \rho)^2/\sin^2\theta \qquad (4)$$

The ρ parameter in eq 4 represents a transverse dipole moment change in the Fe–PR_3 bond which results from migration of π-electron density along the threefold molecular axis during the symmetrical stretching motion of the equatorial carbonyls. This leads to a small enhancement of the A_1 intensity. The value for ρ was calculated for $HFe(CO)_3PPh_3^-$ (**1**) using the A_1/E band ratio in THF at 26 °C from IR and θ taken from the solid-state structure. The value calculated for ρ (0.25) is only slightly larger than that calculated earlier for $Fe(CO)_4PPh_3$ (ρ = 0.18).[7] The values of θ listed in Table II were calculated assuming $\rho = 0$, and hence are not accurate in an absolute sense. Since ρ is independent of temperature, the difference in angle ($\Delta\theta$) over a temperature range may be calculated with confidence. Thus temperature/θ profiles of representative hydrides have been studied and the angle θ was observed to increase uniformly with a decrease in temperature. That is, **the anion becomes a more regular trigonal bipyramid as the temperature is decreased.** Furthermore, a plot of θ vs. J_{P-H} at respective temperatures for a particular solvent gives a remarkably straight line ($r > 0.98$). Approximately the same angle change, $\Delta\theta$, yields the same ΔJ_{PH} in different anions, i.e., ca. 4 Hz per degree θ.

The above data thus indicate that the changes in J_{PH} of *trans*-$HFe(CO)_3PR_3^-$ result not from an averaging of geometrical isomers, mechanism 2 above, but rather from an average angle change reflecting a breathing or umbrella motion of the anion, i.e., mechanism 3. The change in angle, and resultant orbital communication of nuclear spin polarization, was confirmed to be iron based, and *not* a change in angle at the phosphorus donor ligand by virtue of the linear dependence of J_{HC} on J_{PH} or J_{PC} and no observable change in $^3J_{PH}$ of the $P(OMe)_3$ ligand.

Solvent Dielectric Constant Effect. The dependence of the dielectric constant, ϵ, of a liquid on temperature is well known. Wyman and co-workers have shown that a simple expression (eq 5) holds for a large class of polar solvents.[20] Hence the question

$$(\epsilon + 1)T \propto \text{constant} \qquad (5)$$

arose as to whether the observed θ angle change and resultant changes in J_{PH} and infrared band intensities might be ultimately due to a change in solvent dielectric constant with temperature.

The dielectric constant of THF has been measured over the range of -75 to 25 °C.[12] Table II lists E/A_1 intensity ratio data, derived θ values, and ϵ at various T. A plot of J_{PH} vs. ϵ at respective temperatures is also found to be linear.

With the above success we compared IR (angle θ) and NMR spectral data of PPN^+ **3** in the solvents THF, acetonitrile, and acetone. These data are also given in Table II. The evidence is clear: **solvents of larger dielectric constants, whether achieved by a lowering of temperature or a change in molecular makeup, give rise to larger θ and smaller values of $|J_{PH}|$.** It should be noted that

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(18) If a cis to trans isomerization is responsible for the variable J_{PH}, the amount of cis form necessary to give the high-temperature J_{PH} was calculated to be ca. 30%. This calculation assumed the magnitude of a cis phosphorus to hydrogen coupling constant is ≈55 Hz, as found for **2**.

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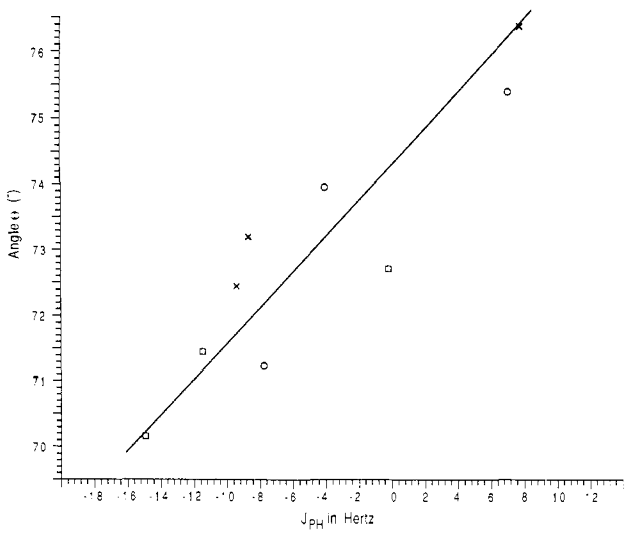


Figure 5. Angle θ taken from IR data vs. J_{PH} for $PPN^+HFe(CO)_3P(OMe)_3^-$ in THF (□), acetone (×), and acetonitrile (○).

the dielectric constant works well in describing the coupling constant changes as long as it is used within a specific solvent over a temperature range or in comparison of different solvents at a particular temperature. The analysis fails when incorporating the dielectric constants for all temperatures and solvents measured combined. A different solvent polarity factor might work better in such an analysis.

To further affirm that θ is the preeminent factor determining the value of J_{PH}, θ values measured in three different solvents are plotted vs. J_{PH} in Figure 5. Regardless of temperature or dielectric constant (those terms are factored out in the plot), a linear dependence is observed ($r = 0.91$). The data provide strong evidence that a solvation effect gives rise to the deformation of anion structure.

The conclusion that the metal carbonyl anion is solvated enough to enforce a molecular structure/electronic change is unusual. All previous solvent effects of ion-paired organometallics have been rationalized on the donor properties of the solvent.[16] That is, we have assumed that a *donor* interaction of aprotic, polar solvents with cations is the primary force in the separation of organometallic ion pairs, dissolution of salts, etc. Nevertheless, a review of earlier work finds evidence for anion solvation in THF solution. For example, conductivity studies of $PPN^+HFe(CO)_4^-$ in THF found the ion mobility of $HFe(CO)_4^-$ to be lower than expected.[21] In addition, the *insolubility* of **3** in 2,5-dimethyltetrahydrofuran, when it is freely soluble in THF, suggests a possible role for the more positive hydrogens of THF.

Fenske–Hall Molecular Orbital Calculations. Fenske–Hall calculations have been carried out on the representative anion, $HFe(CO)_3PH_3^-$, to determine if changes in the angle θ would cause a change in the coupling constants and in what direction, i.e., positive to negative or vice versa. Nuclear spin–spin couplings are based upon three types of electron-coupled interactions between the electrons and nuclei of the molecule concerned.[22] These are (1) a Fermi contact interaction between the electron and nuclear spins, (2) a magnetic dipolar interaction between the electron nuclear spins, and (3) an orbital interaction between the magnetic field produced by the orbital motion of the electrons and the nuclear magnetic dipole. The Fermi contact term usually is the predominant term especially when one of the nuclei is a proton. The dipole–dipole and spin–orbit contributions for couplings involving hydrogen are usually less than 7%.[4] The contact term describes J_{AB} as directly proportional to the s orbital density overlap and inversely proportional to the average excitation energy, ΔE. While neither the McConnell[9] nor the Pople and Santry[10] method showed an inversion of sign for J_{PH} while varying the angle θ from 75 to 90°, simply obtaining the correct slope of the change in J_{PH} was sufficient to determine the absolute sign. Both approaches to the calculation of coupling constants provided the following information on increasing angle θ from 75°: (1) J_{PH} became more positive (more s orbital overlap density), (2) J_{PC} became more negative, and (3) J_{HC} became more positive. Recalling that an inversion of sign is observed with J_{PH}, the first piece of information from the calculations indicates that at low angles of θ J_{PH} must be negative and at high angles J_{PH} must be positive. J_{PC} and J_{HC} both empirically increase in absolute magnitude on lowering temperature (increasing angle θ); therefore, to incorporate the theory J_{PC} must be negative in sign and J_{HC} positive.

Table III. Mulliken Atomic Charges from Fenske–Hall Calculations for $HFe(CO)_3PH_3^-$

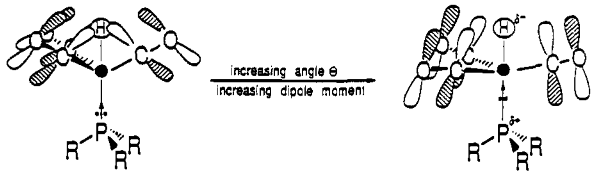
	Mulliken atomic charges					
θ^a (deg)	Fe	C	O	P	$H_p{}^b$	H^c
90	−0.201	−0.038	−0.233	+0.624	−0.109	−0.282
85	−0.220	−0.030	−0.233	+0.577	−0.105	−0.251
80	−0.248	−0.023	−0.237	+0.545	−0.102	−0.210
75	−0.285	−0.014	−0.244	+0.523	−0.101	−0.160
75→90	+0.084	−0.024	+0.011	+0.101	−0.008	−0.122

[a] Internal H–Fe–CO_{eq} angle. [b] H_p denotes the hydrogen atoms of PH_3. [c] H denotes the hydride ligand.

To test at least in part these sign conventions for the coupling constants, relative sign determinations were attempted via spin-tickle experiments. Compound **3** was enriched with ^{13}CO and, while observing the carbonyl carbon, the proton resonances were alternately irradiated at low power. From this experiment it was determined that at 26 °C both J_{PC} and J_{PH} were of the same sign. This is in agreement with the Fenske–Hall calculations which concluded that both J_{PH} and J_{PC} should be negative in the high-temperature limit. Attempts to determine the relative sign of J_{HC} were not possible owing to added coupling of the ligand protons (or deuterons) to phosphorus.

The calculations on $HFe(CO)_3PH_3^-$ also showed that on increasing angle θ the hydride ligand becomes more negative (−0.160 to −0.282) while phosphorus becomes more positive (+0.523 to +0.624), Table III. This change means that the dipole moment in the anion increases on bending the CO groups away from the hydride. This would explain why a more polar solvent would induce the largest angle θ and the more positive J_{PH} for these hydrides.

It is interesting that the smallest changes in J_{PH} are observed for *trans*-$HFe(CO)_3PR_3^-$ anions containing trialkylphosphine donor ligands. For example, in THF **3** has a ΔJ_{PH} of a 14.85 Hz over a 110 °C temperature range while $Et_4N^+HFe(CO)_3PEt_3^-$ (**5**) has a ΔJ_{PH} of only 4.93 Hz over the same temperature range. This result can be rationalized from the molecular orbital calculations. The smaller the angle θ, the more overlap there is of the hydride 1s orbital and the π^* orbital of the carbonyls. This so-called "direct donation"[23] of H^- electron density into the empty π^* orbital of the carbonyl ligand ultimately makes CO a poorer π acceptor from Fe and a better σ donor, with the result that the PR_3 ligand becomes less effective as a σ donor. An increase of θ weakens the H(1s)···CO(π^*) interaction, allows H^- to retain more electron density, allows CO to accept more electron density from Fe, and permits PR_3 to donate more negative charge, thus rendering the P more positive. This is the origin of the enhanced



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$H^-\cdots Fe\cdots P^+$ dipole moment at larger θ.

For anions containing the better donor ligands, such as *trans*-HFe(CO)$_3$PEt$_3^-$, the P–Fe–H system is more electron rich, and the H···CO interaction is expected to be stronger at small θ as compared to the analogous *trans*-HFe(CO)$_3$P(OMe)$_3^-$. Therefore, more extreme conditions of solvent polarity would be required to generate the angle change, charge separation, and diminution of this interaction for **5** as compared to **3**.

This "direct donation" also appears to be a salient feature of why J_{PH} becomes more positive as θ is increased. The calculations showed that the most prominent molecular orbital responsible for the increase in s overlap density of P and H was the σ(Fe–H) molecular orbital. At low angles (75°) the carbonyl interaction with hydride stabilizes this molecular orbital and the H 1s contribution is only 48%. At high angles (85°) this orbital rises in energy slightly and, more importantly, H 1s retains more electron density and now contributes 60% to this molecular orbital. Interestingly, the percent character of Fe 4s and P 3s also increases in this molecular orbital with increasing angle but in a lesser amount.

We have also examined other classes of anionic transition metal hydride complexes to see if similar behavior could be found. Both PPN$^+$ and Na$^+$ salts of the six-coordinate anion, *cis*-HW(CO)$_4$P(OMe)$_3^-$, in THF displayed *no* change in the J_{PH} value of ca. 31 Hz from +50 to −60 °C. The PPN$^+$ salt also had no significant changes in the hydride chemical shift (−4.3 ppm) with temperature while the Na$^+$ salt showed a 0.6-ppm downfield shift at −60° (−4.8 ppm) relative to the +50 °C value (−5.4 ppm). This shift might be attributed to the disruption of the $Na^+\cdots H—W$ interaction[24] at lower temperature by the increased dielectric constant of the solvent. As mentioned earlier, the recently isolated *cis*-HFe(CO)$_3$P(OPh)$_3^-$ (**2**) anion also showed no significant change in J_{PH} over the temperature range +26 to −80 °C. Consistent with this observation ν(CO) IR displayed no structural change in the anion.

Comments and Conclusions

We feel the evidence is convincing that an angular deformation gives rise to changes in J_{PH} for the anions *trans*-HFe(CO)$_3$PR$_3^-$. Simple motion of the carbonyl groups away from the hydride ligand substantially increases the dipole moment in the anion. The angle changes are mediated by the solvent's ability to stabilize the increased internal dipole moment in the anion. Possibly the reason that the *trans*-HFe(CO)$_3$PR$_3^-$ hydrides give changes in J_{PH} also accounts for the fact that cis hydrides such as *cis*-HFe(CO)$_3$P(OPh)$_3^-$ and *cis*-HW(CO)$_4$P(OMe)$_3^-$ do not. Simple angle deformations in the cis complexes would not be expected to yield significant changes in dipole moment.

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High-Field NMR Determination of Magnetic Susceptibility Tensors and Angular Correlation Factors of Halomethanes

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Abstract: Quadrupolar splittings in the high-resolution deuteron spectra of deuterated haloforms ($CX_3{}^2H$, X = Cl, Br, I) and methylene halides ($CX_2{}^1H^2H$) have been measured at 14.35 T (93.5 MHz) and used to determine the anisotropy or asymmetry of their molecular magnetic susceptibility tensors. By combination with the known isotropic susceptibilities, the principal susceptibility tensors have been deduced and decomposed into bond susceptibility tensors. Neither the average susceptibilities nor the principal susceptibility tensor elements of the complete halomethane series follow Pascal's additivity rules. The phenomenon is tentatively attributed to a variable paramagnetic contribution perpendicular to the C–X bond. Angular correlation Kirkwood g_2 factors have been determined for $CHCl_3$ and $CHBr_3$ and are compared with available literature data.

It was first demonstrated in 1978 by Lohman and MacLean[1] that high-field high-resolution NMR provides a simple tool to determine magnetic susceptibility anisotropies ($\Delta\chi$) and asymmetries ($\delta\chi$). The basis of the method is that molecules with anisotropic magnetic susceptibilities placed in the strong magnetic field of the spectrometer are subject to orienting torques. In the liquid this orientation is opposed by thermal motions and collisions, but at sufficiently high fields (>10 T for diamagnetic compounds) a net significant alignment results. This induced alignment is manifested in the NMR spectrum in the form of anisotropic nuclear interactions,[1-4] such as direct dipolar or electric quadrupole couplings. The effects which are proportional to the square of the magnetic induction B may be used to investigate magnetic properties and geometries of molecules[1-4] as well as for the determination of nuclear constants (e.g., quadrupole coupling constants).[5]

In this paper electric quadrupole splittings in monodeuterated haloforms and methylene halides have been used to investigate their magnetic susceptibilities. This investigation came about in a serendipitous way. Deuteriochloroform is commonly used as a solvent and heteronuclear lock signal source in high-resolution proton NMR spectroscopy. Difficulties with achieving a satisfactory and stable lock with this solvent at 600 MHz eventually

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