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CONSTRAINED PHOSPHITE ESTER COMPLEXES OF η-CYCLOPENTADIENYLIRON DICARBONYL HALIDES

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Summary

The synthesis of complexes of the type η-$C_5H_5Fe(CO)LX$, where X = Cl, Br or I and L = $P(OCH_2)_3CR$ (R = CH_3, C_2H_5 or C_3H_7), is reported. Near- and far-infrared, proton magnetic resonance, and conductimetric measurements were taken, which characterized the complexes as non-conducting covalent species in solution. All PMR spectra showed a sharp doublet η-cyclopentadienyl signal ($J(PH) \sim 1.0$ Hz) and a sharp doublet resonance for the ligand OCH_2 protons ($J(POCH) \sim 5.0$ Hz), suggesting a structure in solution similar to that of other neutral η-cyclopentadienyliron carbonyl complexes. The expected two δ(FeCO) modes and one ν(FeCO) mode were identified in the far-infrared spectra. The single strong ν(CO) band observed in the near-infrared spectra indicated that the complexes are single conformers of the covalent compounds η-$C_5H_5Fe(CO)LX$. The order in the position of the ν(CO) varied with the halogen group as expected (Cl > Br > I) from electronegativity considerations. The position of the ν(CO) in these complexes compared with that for analogous complexes where the ligand was an alkyl or aryl phosphine or phosphite suggested that bicyclic $P(OCH_2)_3CR$ ligands are better π-acceptors than phosphines or other phosphites.

Introduction

Because numerous reports [1-10] in the literature have indicated that the reaction of a ligand with η-$C_5H_5Fe(CO)_2X$ compounds may yield either the covalent substitution product, η-$C_5H_5Fe(CO)LX$, or ionic addition products, or both, it was of interest to us to investigate the nature of the reaction between η-$C_5H_5Fe(CO)_2X$ compounds and the bicyclic phosphite esters $P(OCH_2)_3CR$ (R = CH_3, C_2H_5, or C_3H_7) and to characterize the products.

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Treichel et al. [1], prepared several covalent and ionic derivatives of η-C_5H_5-$Fe(CO)_2X$ compounds using various ligands and observed a remarkable consistency in the position of the η-cyclopentadienyl PMR signals of the ionic compounds. The position of the η-cyclopentadienyl resonances of these compounds in relation to that of $[\eta\text{-}C_5H_5Fe(CO)_3]^+$ was reflective of higher electron density on the ring, while the CO stretching frequencies indicated different degrees of π-backbonding to the CO ligand [1]. Thus, it was of particular interest to examine the η-cyclopentadienyl ring proton resonance in the PMR spectra of our complexes in view of Treichel's observations [1], and by obtaining both near- and far-infrared spectra, it was hoped that structural features of the complexes could be substantially elucidated.

Experimental

Chemicals

η-$C_5H_5Fe(CO)_2Cl$ and η-$C_5H_5Fe(CO)_2I$ were prepared according to the procedure of Piper et al. [11]. η-$C_5H_5Fe(CO)_2Br$ was synthesized according to the method of Hallam et al. [12]. The dimer $[\eta\text{-}C_5H_5Fe(CO)_2]_2$, necessary for preparing these compounds, was purchased from Alfa Inorganics, Inc., and was used as received. $P(OCH_2)_3CCH_3$ was prepared according to Verkade et al. [13], $P(OCH_2)_3CC_2H_5$ was synthesized by the method of Wadsworth and Emmons [14], and Hendricker's method [15] was employed for the preparation of $P(OCH_2)_3CC_3H_7$. WARNING: THE BICYCLIC PHOSPHITES USED IN THIS STUDY HAVE BEEN SHOWN TO EXHIBIT UNUSUALLY HIGH TOXICITY WHEN INJECTED INTRAPERITONEALLY IN MICE [16]. Therefore, it is mandatory that proper care in the handling of these materials or their complexes be exercised.

Spectral measurements

The infrared spectra in the region of 4000 to 600 cm^{-1} were obtained with a Perkin—Elmer Model 621 double-beam grating spectrophotometer. Spectra were recorded for chloroform, acetone, and acetonitrile solutions contained in a 0.2-0.3 mm sodium chloride cell; all spectra were recorded versus air in the reference beam. Far-infrared spectra in the region 800 to 200 cm^{-1} were obtained for Nujol mulls supported between polyethylene windows, using a Perkin—Elmer Model 621 double beam grating spectrophotometer; these spectra were also recorded versus air in the reference beam. Spectra were calibrated with polystyrene film.

The proton magnetic resonance spectra of all complexes were obtained using a Varian Associates Model A-60 spectrometer. Spectra were recorded for approximately 15 to 20% deuterochloroform solutions at normal probe temperature; tetramethylsilane was employed as an internal reference for all spectra.

Analytical methods

Carbon and hydrogen contents were ascertained by combustion using an F and M Carbon-Hydrogen-Nitrogen Analyzer, Model 185.

Conductivity measurements

Conductivities were determined for 10^{-3} molar acetone solutions using an Industrial Instruments RC16B2 conductivity bridge and a Sargent Model S-29885 conductivity cell with a cell constant of 0.679138 cm^{-1}. All conductivities were measured at a temperature of 25.0°C.

General apparatus

A Hanovia 200-watt, Model 654A-10, ultraviolet light (maximum intensity in a range from 3130 to 5780 Å) was used for all photochemical preparations. The light source was placed parallel to the quartz reaction tube (24 cm in height with an inside diameter of 2.5 cm and a 24/40 ground glass joint at the top) at a distance of approximately six cm.

The chromatography column used to purify the complexes was 10 cm in height with an inside diameter of one cm. Woelhm neutral alumina was loaded on the column from a chloroform slurry until a column approximately four cm high was obtained.

Preparation of phosphite ester complexes

One general method was employed to prepare all the η-$C_5H_5Fe(CO)LX$ (X = Cl, Br, or I; L = phosphite ester) complexes. A mixture of the appropriate phosphite ester and η-$C_5H_5Fe(CO)_2X$ compound in 30 ml cyclohexane was placed in a quartz tube under a flush of nitrogen. The solution was magnetically stirred and was irradiated with ultraviolet light for one and one-half hours. Upon completion of the reaction, the solid crude brown product (n-pentane was added at this point in the cases of the ethyl- and propyl-phosphite derivatives to insure complete precipitation) was collected on the suction filter and then dissolved in several ml of chloroform. The chloroform solution was then passed through a small column of Woelhm neutral alumina, and the eluate was reduced in volume by vacuum evaporation. One or two ml of carbon tetrachloride were added, and then n-pentane was slowly added, in portions while continuously swirling the contents of the flask, until the point of precipitation or near-precipitation was reached (in some cases, it was necessary to reduce the volume of the contents by vacuum evaporation in order to induce crystallization). Finally, the product was collected on the suction filter, washed with n-pentane, and was dried and stored under vacuum. Preparative data for each of the complexes are summarized in Table 1, along with results for the carbon-hydrogen analyses and conductance measurements.

Results and discussion

The monocarbonyl derivatives with the formulation η-$C_5H_5Fe(CO)LX$, where X = Cl, Br, or I and L = $P(OCH_2)_3CR$ (R = CH_3, C_2H_5, or C_3H_7), are brown solids which undergo slight decomposition in air upon standing for weeks or longer. The iodo complexes are dark brown in color, while the chloro and bromo derivatives are an intermediate shade of brown. All of the complexes are insoluble in cyclohexane, n-pentane, and other common hydrocarbons at room temperature, but they are soluble in chloroform, acetone, and acetonitrile at room temperature. On a qualitative basis, the solubilities of the complexes vary as $I > Br > Cl$ and $C_3H_7 > C_2H_5 > CH_3$.

TABLE 1

PREPARATIVE, ANALYTICAL, AND CONDUCTIVITY DATA FOR η-$C_5H_5Fe(CO)LX$ COMPLEXES

Compound	Preparative		Analytical Found (Calcd.)(%)		Conductivity	
	g(mmol) η-$C_5H_5Fe(CO)_2X$	g(mmol) $P(OCH_2)_3CR$	C	H	Conc. $M \times 10^{-3}$	Λ(cm^2 mho mol$^{-1\,a}$)
η-$C_5H_5Fe(CO)[P(OCH_2)_3CCH_3]Cl$	0.20(0.94)	0.14(0.95)	39.44 (39.74)	3.98 (4.24)	1.104	9.47
η-$C_5H_5Fe(CO)[P(OCH_2)_3CC_2H_5]Cl$	0.20(0.94)	0.15(0.93)	41.40 (41.59)	4.64 (4.65)	0.924	4.35
η-$C_5H_5Fe(CO)[P(OCH_2)_3CC_3H_7]Cl$	0.15(0.71)	0.12(0.68)	43.12 (43.31)	4.86 (5.03)	0.799	10.12
η-$C_5H_5Fe(CO)[P(OCH_2)_3CCH_3]Br$	0.20(0.78)	0.11(0.74)	35.29 (35.05)	3.77 (3.74)	1.136	4.34
η-$C_5H_5Fe(CO)[P(OCH_2)_3CC_2H_5]Br$	0.20(0.78)	0.13(0.80)	36.87 (36.86)	4.30 (4.13)	1.105	3.50
η-$C_5H_5Fe(CO)[P(OCH_2)_3CC_3H_7]Br$	0.20(0.78)	0.14(0.80)	38.66 (38.55)	4.21 (4.48)	1.018	5.34
η-$C_5H_5Fe(CO)[P(OCH_2)_3CCH_3]I$	0.20(0.66)	0.10(0.68)	31.37 (31.16)	3.43 (3.33)	0.972	6.85
η-$C_5H_5Fe(CO)[P(OCH_2)_3CC_2H_5]I$	0.20(0.66)	0.11(0.68)	32.75 (32.91)	3.65 (3.68)	0.786	5.64
η-$C_5H_5Fe(CO)[P(OCH_2)_3CC_3H_7]I$	0.20(0.66)	0.12(0.68)	34.34 (34.55)	3.94 (4.01)	0.885	6.33

[a] All conductances measured in acetone solution at 25.0°C. Value for the 1:1 electrolyte tetrabutylammonium bromide: 135.05 cm^2 mol^{-1} in acetone.

The infrared spectra of all the complexes (Table 2), recorded for chloroform, acetone, and acetonitrile solutions in the ν(CO) region, exhibit only a single strong ν(CO). All literature reports have so far demonstrated that ionic compounds such as $[\eta$-$C_5H_5Fe(CO)_2L]^+X^-$ show two strong bands in the ν(CO) region while the covalent complexes η-$C_5H_5Fe(CO)LX$ exhibit only one strong band. Some covalent complexes have shown two ν(CO) bands which are the result of the presence of two conformers in solution [17,18]. Thus, the appearance of only a single strong band in the infrared spectra of the complexes (Table 2) is substantial evidence that they are indeed single conformers of the covalent substitution products, η-$C_5H_5Fe(CO)LX$. The conductances (Table 1) of the complexes, measured in acetone solution at 25.0°C, conclusively show that the formulation of the compounds as the covalent species in solution is correct. This conclusion is in accord with the observation that most reactions of tertiary alkyl (or aryl) phosphites with η-$C_5H_5Fe(CO)_2X$ compounds lead to the formation of products resulting from CO replacement only [19].

Several other inferences may be drawn from the infrared data for these complexes. First, it should be noted that the ν(CO) for all complexes is lower than for the respective starting dicarbonyl halide, which is to be expected when replacement of a CO group by a poorer π-accepting phosphite ligand occurs. Secondly, the order in the position of the ν(CO) varies with the halogen group as expected (Cl > Br > I) from electronegativity considerations. Thirdly, the similarity of the ν(CO) position for all three phosphites indicates that the alkyl

TABLE 2

CARBONYL STRETCHING FREQUENCIES FOR η-$C_5H_5Fe(CO)_2X$ AND η-$C_5H_5Fe(CO)LX$ COMPOUNDS

Compound	ν(CO) (cm^{-1})[a]		
	Chloroform	Acetone	Acetonitrile
η-$C_5H_5Fe(CO)_2Cl$	2062 2017	2057 2008	2062 2004
η-$C_5H_5Fe(CO)[P(OCH_2)_3CCH_3]Cl$	1994	1982	1981
η-$C_5H_5Fe(CO)[P(OCH_2)_3CC_2H_5]Cl$	1994	1982	1981
η-$C_5H_5Fe(CO)[P(OCH_2)_3CC_3H_7]Cl$	1992	1982	1981
η-$C_5H_5Fe(CO)_2Br$	2059 2008	2053 2004	2053 1996
η-$C_5H_5Fe(CO)[P(OCH_2)_3CCH_3]Br$	1989	1981	1980
η-$C_5H_5Fe(CO)[P(OCH_2)_3CC_2H_5]Br$	1989	1981	1980
η-$C_5H_5Fe(CO)[P(OCH_2)_3CC_3H_7]Br$	1989	1981	1980
η-$C_5H_5Fe(CO)_2I$	2050 2008	2050 2000	2044 2000
η-$C_5H_5Fe(CO)[P(OCH_2)_3CCH_3]I$	1984	1976	1975
η-$C_5H_5Fe(CO)[P(OCH_2)_3CC_2H_5]I$	1982	1976	1975
η-$C_5H_5Fe(CO)[P(OCH_2)_3CC_3H_7]I$	1984	1976	1975

[a] Intensity of all bands strong.

"tail" group does not affect the coordination properties of the bridgehead phosphorus. Finally, the ν(CO) band in these complexes appears at higher frequency than for analogous compounds [1,2,17,18] where the ligand is an alkyl or aryl phosphine or phosphite, implying that the bicyclic phosphites are better π-acceptors than the phosphines or other phosphites.

The appearance of the ν(CO) for a given complex at nearly identical values for acetone and acetonitrile solutions but at much higher values for chloroform solutions occurs as a result of solvent—solute interactions. Assuming that solvent molecules interact with a CO group, the ν(CO) should decrease as the interaction (solvent polarity) increases [19] as is observed. It is also apparent that halogen—solvent interaction is much less important for these complexes than CO—solvent interaction because halogen—solvent interaction would be greatest in the more polar solvent and would lead to an increase in the CO stretching frequencies [19].

Finally, the appearance of only one band in the ν(CO) region of the infrared spectra is evidence of the absence of conformational isomerism because splitting of the observed CO mode into two bands would have occurred if conformational effects were operative [19]. This is in agreement with the observations of Brown et al. [18], who prepared complexes of the type η-$CH_3C_5H_4Fe(CO)LX$ and noted that those where L was $P(OCH_2)_3CCH_3$ (a ligand where rotation of the P—O—C groups is impossible) exhibited no isomerism.

The low-frequency spectral data for the η-$C_5H_5Fe(CO)LX$ complexes are recorded in Table 3. It is expected that two δ(FeCO) modes and one ν(FeCO) mode will appear in the range 340 to 680 cm^{-1} [21]. The identification of the three observed bands in the 526 to 580 cm^{-1} region as δ(FeCO) and ν(FeCO) modes is quite reasonable in view of the following considerations: (1) The spectrum of $P(OCH_2)_3CCH_3$ has been found to simplify, upon complexation, to basically five bands, none of which occurs in the region ~520 to ~650 cm^{-1} [21]; (2) the spectra of the corresponding ethyl- and propyl-phosphite esters each ex-

TABLE 3

LOW FREQUENCY INFRARED DATA FOR η-$C_5H_5Fe(CO)LX$ COMPLEXES[a]

Compound	ν(Fe—CO) and δ(FeCO)			Ligand bands	Other bands
η-$C_5H_5Fe(CO)[P(OCH_2)_3CCH_3]Cl$	564s(sh)	557s	526s	652s, 498vw, 460w, 415w, 273w	372vs[b], 365s(sh)[b] 299vs[c]
η-$C_5H_5Fe(CO)[P(OCH_2)_3CC_2H_5]Cl$	565w(sh)	554s	534s	646s, 524m(sh), 491vvw, 459vvw, 410-418w(br)	382w[b], 365w[b] 289-294w(br)[c]
η-$C_5H_5Fe(CO)[P(OCH_2)_3CC_3H_7]Cl$	575m	552m	527w	638m(sh), 490vvw, 459m, 411vvw	376vvw[b], 362vvw[b], 292-295w(br)[c]
η-$C_5H_5Fe(CO)[P(OCH_2)_3CCH_3]Br$	563vs	554vs	532vs	651vs, 493w, 458w, 413m, 269m	594w[d], 367s[b], 221w[c]
η-$C_5H_5Fe(CO)[P(OCH_2)_3CC_2H_5]Br$	565w(sh)	553m	536s	650vs, 640vs, 492w, 459w, 414w(sh), 322w, 270-276w(br)	381w[b], 364m[b]
η-$C_5H_5Fe(CO)[P(OCH_2)_3CC_3H_7]Br$	580s	556s	531s	419w	376w[b], 366w(sh)[b]
η-$C_5H_5Fe(CO)[P(OCH_2)_3CCH_3]I$	568w	554m	537m	655s, 516w(sh), 409vw, 267vw	592vw(sh)[d], 364vw[b]
η-$C_5H_5Fe(CO)[P(OCH_2)_3CC_2H_5]I$	565m	550s	536s	643s, 421w, 320vw, 269-276vw(br)	384w[b], 362w[b],
η-$C_5H_5Fe(CO)[P(OCH_2)_3CC_3H_7]I$	579m	554m	535m	491-493vvw(br), 416-419m(br), 261vvw	375m[b]

[a] Spectra recorded between 800 and 200 cm^{-1} for Nujol mulls between polyethylene plates. [b] "Ring-Tilt" and iron—ring stretching vibration. [c] ν(Fe—X). [d] ν_{14}' [C—C bend (⊥)].

hibit only one band in the 520 to 580 cm^{-1} region when uncomplexed and would be expected to behave in a manner similar to that of $P(OCH_2)_3CCH_3$; (3) bands due to ring tilt, iron—ring stretching, and iron—halogen stretching vibrations are expected to be found at frequencies less than 370 cm^{-1} [20]; (4) in metal carbonyl complexes containing phosphorus-donor ligands, ν(MP) and δ(CMP) modes usually appear at frequencies lower than 200 cm^{-1} [21]; and (5) spectra of the related η-$C_5H_5Fe(CO)LX$ complexes where L = $P(n\text{-}C_4H_9)_3$ were found to contain three bands in the region 530 to 580 cm^{-1} attributable to δ(FeCO) and ν(FeCO) modes [20].

It is tempting to assign the lower-frequency band to the single expected ν(FeCO) vibration, but an unequivocal assignment cannot be made because coupling of δ(FeCO) and ν(FeCO) modes would be expected [21,23]. Nevertheless, it is quite likely that the two higher-frequency bands are δ(FeCO) modes and the lower-frequency band is predominantly a ν(FeCO) mode in view of the fact that δ(FeCO) modes in η-$C_5H_5Fe(CO)_2X$ compounds (X = Cl, Br, or I) have been assigned at frequencies above 530 cm^{-1} [20,23-25].

Both ν(CO) and ν(MCO) vibrations are affected by changes in the amount of π-bonding between the metal and the CO group [23], and it has been suggested [26,27] that a lowering of the C—O bond order and of ν(CO) will be accompanied by a concomitant increase in the M—C bond order and in ν(MCO). In these complexes, ν(FeCO) is found at considerably higher values than are the corresponding frequencies in the unsubstituted η-$C_5H_5Fe(CO)_2X$ compounds [20, 23-25]. As a result of the mixing of bending and stretching modes, the frequencies of both δ(FeCO) and ν(FeCO) modes should increase upon complexation [24], and when the frequencies in Table 3 are compared with those assigned for η-$C_5H_5Fe(CO)_2X$ compounds [20, 23-25], it is clear that such an increase has occurred.

Ligand bands in the complexes were identified by comparison with spectra obtained for the uncomplexed and complexed ligands [28]. The small frequency shifts occurring upon complexation are expected because the local symmetry of a constrained system like a phosphite ligand should not undergo appreciable alteration. Metal—halogen stretching frequencies are dependent upon the oxidation state of the metal [29], and because no change in oxidation state would be expected upon substitution of a natural phosphite ligand for a neutral CO group, it is not surprising that the values of ν(FeX) (Table 3) vary little from the ν(FeX) values that have been recorded for η-$C_5H_5Fe(CO)_2X$ compounds [20,25]. The identification and tentative assignment of ν_{14}' in two of the complexes was made on the basis of a similar assignment by Parker [20] for some related complexes. Bands listed in Table 3 that appear in the 375 to 385 cm^{-1} region may be "ring-tilt" vibrations (if Manning's assignments [25] for η-$C_5H_5Fe(CO)_2X$ compounds are followed), but assignment of any vibrations in the vicinity of 410 cm^{-1} is impossible because of the presence of ligand absorptions. Bands observed in the narrow region 362 to 367 cm^{-1} most likely result from iron—ring vibrations, although such vibrations are ordinarily observed at slightly lower frequencies that are in the range 348 to 358 cm^{-1} [20,24].

TABLE 4

PMR DATA FOR η-$C_5H_5Fe(CO)_2X$, η-$C_5H_5Fe(CO)LX$ AND $P(OCH_2)_3CR$ COMPOUNDS[a]

Compound	(η-C_5H_5)[b]	J(PH)	(—OCH_2—)[c]	J(POCH)	H_γ[d]	H_β[d]	H_α[d]
$P(OCH_2)_3CCH_3$			3.93	1.8	0.72		
$P(OCH_2)_3CC_2H_5$			3.96	1.6	0.80	0.89	
$P(OCH_2)_3CC_3H_7$			3.94	1.9	0.88	0.96	1.10
η-$C_5H_5Fe(CO)_2Cl$	5.07						
η-$C_5H_5Fe(CO)[P(OCH_2)_3CCH_3]Cl$	4.75	0.8	4.34	5.0	0.87		
η-$C_5H_5Fe(CO)[P(OCH_2)_3CC_2H_5]Cl$	4.74	1.0	4.36	5.0	0.90	1.00	
η-$C_5H_5Fe(CO)[P(OCH_2)_3CC_3H_7]Cl$	4.75	1.0	4.38	5.1	0.94	1.00	1.20
η-$C_5H_5Fe(CO)_2Br$	5.07						
η-$C_5H_5Fe(CO)[P(OCH_2)_3CCH_3]Br$	4.76	1.0	4.34	5.0	0.85		
η-$C_5H_5Fe(CO)[P(OCH_2)_3CC_2H_5]Br$	4.76	1.0	4.35	5.0	0.88	1.00	
η-$C_5H_5Fe(CO)[P(OCH_2)_3CC_3H_7]Br$	4.76	0.9	4.37	4.8	0.93	1.01	1.20
η-$C_5H_5Fe(CO)_2I$	5.07						
η-$C_5H_5Fe(CO)[P(OCH_2)_3CCH_3]I$	4.78	1.0	4.36	5.0	0.87		
η-$C_5H_5Fe(CO)[P(OCH_2)_3CC_2H_5]I$	4.78	1.0	4.34	5.0	0.87	0.96	
η-$C_5H_5Fe(CO)[P(OCH_2)_3CC_3H_7]I$	4.78	1.0	4.34	5.0	0.93	1.03	1.18

[a] Chemical shifts (δ) in ppm downfield with respect to tetramethylsilane as internal standard. $P(OCH_2)_3CR$ compounds measured in chloroform; all others measured in deuterochloroform. Coupling constant values in Hz. [b] Sharp singlet for η-$C_5H_5Fe(CO)_2X$ compounds; sharp doublet for phosphite ester complexes. [c] Sharp doublet. [d] R group ("tail") protons labeled —$CH_\alpha CH_\beta CH_\gamma$.

The PMR spectra (Table 4) of all complexes exhibit a sharp doublet for the η-cyclopentadienyl protons which arises from spin—spin coupling with the ligand phosphorus atom. The chemical shift of the η-cyclopentadienyl signal for the complexes is upfield relative to that for the corresponding unsubstituted η-$C_5H_5Fe(CO)_2X$ compounds. The increased shielding of the ring protons upon replacement of a CO group by a phosphite is consistent with the observation from the infrared spectra that the ν(CO) is decreased upon substitution. Both trends indicate that more electron density has been placed on the metal atom upon substitution. In other words, the η-cyclopentadienyl ring is not as good a σ-donor in the monocarbonyl complexes as in the dicarbonyl starting materials.

The constancy in chemical shift position of the ring protons (a phenomenon observed by Treichel et al. [1], for some ionic complexes) is not surprising in view of the fact that the alkyl "tail" of the phosphite ester has no effect upon the coordination properties of the bridgehead phosphorus atom. King and Pannell have also noticed a consistent position of the η-cyclopentadienyl resonance of some η-cyclopentadienyl iron carbonyl complexes having phosphorus ligands of different π-accepting abilities, and they have invoked "saturation of the ring" to account for the consistency [30].

The coupling constant values, J(PH), were small in magnitude (1 Hz) and were similar to, or just slightly less than, J(PH) values for other iron complexes of the same type [1,30] but were less than the J(PH) values for related η-C_5H_5-$Mo(CO)_2LX$ complexes [31]. The similarity in values for our iron complexes suggests that the geometry of all the complexes is identical.

The —OCH_2— protons of the phosphite ligands are deshielded in all complexes with respect to the signal for the corresponding uncomplexed ligand by approximately 0.4 ppm. The chemical shift position of the —OCH_2— protons is essentially the same for all the complexes, indicating that the three phosphite ligands are equally efficient σ-donors or π-acceptors.

The J(POCH) values are nearly identical for all complexes, which is again reflective of identical geometry among the complexes. The J(POCH) values increase upon coordination of the ligand to the metal atom. This increase is similar to that observed for other metal carbonyl complexes involving these phosphites [31,32].

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