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Spectroscopic Behavior of $[(\pi\text{-}C_5H_5)_2Fe_2(CO)_3P(OCH_3)_3]$ and Related Compounds on Protonation of the Metal–Metal Bond[1]

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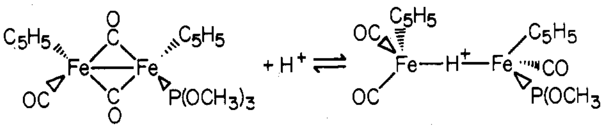
It has been known[2] for some years that a number of cyclopentadienylmetal carbonyl compounds containing metal–metal bonds can abstract a proton from strong acids to form species containing metal–hydrogen bonds. Early in our investigation of some of these reactions it was concluded that hydrogen-bridged M–H–M linkages, where M is a metal with other ligands attached, are formed. In particular, we were able to prepare a stable salt of the cation **2**.



(1)

1 **2**

During our work, a report was published[3] in which the same conclusion regarding the structure of $[CpFe(CO)_2]_2H^+$ (Cp = π-C_5H_5) was reached. Here we report nmr, ir, and electronic absorption spectra of **1** and **2** and related complexes. The relative basicities of **1**, $[CpFe(CO)_2]_2$, and $[CpRu(CO)_2]_2$ have been determined.

Experimental Section

General Data. All reactions and all handling of compounds were done under an atmosphere of nitrogen. The compounds $[CpM(CO)_2]_2$ (M = Fe, Ru), **1**, and the tetraphenylborate salt of **2** could be handled briefly in the air with no apparent harm but were stored under nitrogen in the dark at −20°. Solvents were generally deoxygenated by nitrogen purging or by several freeze–thaw cycles on a vacuum line. Where water could not be tolerated, benzene was distilled from sodium–benzophenone and acetone for spectra was distilled from P_4O_{10} or from Linde 4A molecular sieves *in vacuo*. Melting points were determined with open capillary tubes and are uncorrected. Infrared spectra were recorded on a Perkin-Elmer 225 spectrometer. Electronic spectra were obtained using Cary 17 and Cary 14 spectrophotometers. Nmr spectra were obtained with a Varian A-60A instrument.

Table I. ^{1}H Nmr Spectra[a]

Compd	$\tau(H)^b$	$\tau(C_5H_5)$	$\tau(CH_3)$
$[CpFe(CO)_2]_2$		5.11	
$\{[CpFe(CO)_2]_2H\}\{HSO_4\}$	36.3	4.66	
$[CpRu(CO)_2]_2$		4.67	
$\{[CpRu(CO)_2]_2H\}\{HSO_4\}$	29.1	4.18	
$Cp_2Fe_2(CO)_3P(OCH_3)_3$		5.33, 5.47^d	6.50^e
$\{Cp_2Fe_2(CO)_3P(OCH_3)_3H\}\{HSO_4\}$	36.3^c	4.79, 5.05^d	6.18^f

[a] All spectra are for acetic acid solutions. Protonated species were formed by adding 98% H_2SO_4 to these solutions. Chemical shifts are given in ppm. [b] Hydride of protonated species. [c] $J(^{31}P\text{–}^1H) = 44$ Hz. [d] The high-field cyclopentadienyl group is coupled to ^{31}P and, hence, bound to the iron which is bound to phosphorus. $J(^{31}P\text{–}H) = 1.5$ Hz. [e] $J(^{31}P\text{–}^1H) = 11$ Hz. [f] $J(^{31}P\text{–}^1H) = 11.5$ Hz.

$\{(Cp)_2(CO)_3Fe_2[P(OCH_3)_3]H\}\{B(C_6H_5)_4\}$. A red solution of 0.25 g of **1**[4] in 7 ml of acetic acid (deoxygenated by nitrogen purging) was treated with 0.70 ml of 98% H_2SO_4. The H_2SO_4 need not be degassed for this preparation. The resulting green solution was added to a well-stirred solution of 0.28 g $NaB(C_6H_5)_4$ in 14 ml deoxygenated water. The green powder was filtered in the air, washed with water, and dried. The product can be crystallized from 6 ml hot acetone–4.5 ml ether by slowing cooling to −20°; yield 74%; mp 154–159° dec. *Anal.* Calcd for $C_{40}H_{40}O_6Fe_2PB$: C, 62.38; H, 5.23; Fe, 14.50; B, 1.40. Found: C, 62.83; H, 5.14; Fe, 16.11; B, 1.30.

$[CpRu(CO)_2]_2$. This was prepared by the method of Blackmore, *et al.*,[5] using $[Ru(CO)_3Cl_2]_2$ prepared by the method of Cleare and Griffith.[6] The only way we found to obtain pure material from the pyrophoric benzene extract was tedious sublimation of aliquots at 160° (10 μ). The brown-orange sublimate was fractionally resublimed, first at 60° (10 μ) to remove yellow Cp_2Ru and then at 160° (10 μ) to produce light orange product. Even purer material can be obtained after a second fractional sublimation; yield 0.17 g, 3%; mp 175–176°.

***cis*- and *trans*-$[CpFe(CO)_2]_2$.**[7] The trans isomer was most easily obtained by crystallizing a sample of commercial material from hot ethanol. Crystallizing a sample in ethyl acetate at 0° again produces the trans isomer. By cooling this mother liquor to −78°, the cis isomer is obtained. Comparison of the KBr pellet ir spectra to those of Bryan, *et al.*,[7] showed that the trans compound was formed uncontaminated by the cis form but that the cis form was sometimes contaminated with the trans. Repeated preparations gave enough pure cis isomer for our studies.

Results and Discussion

^{1}H Nmr Spectra. When a solution of $[CpFe(CO)_2]_2$ in acetic acid is treated with a large excess of 98% H_2SO_4 (H_2SO_4:$[CpFe(CO)_2]_2 > 100$), the very dark red-purple solution becomes green and a signal appears in the metal hydride region at τ 36.3 ppm. The very high-field absorption immediately suggests that the hydride is in a bridging position.[8,9] Nmr spectra are summarized in Table I. In all compounds studied, protonation deshields the cyclopentadienyl groups, consistent with the introduction of positive charge. Of particular note, *both* cyclopentadienyl groups of each compound are shifted downfield, indicating a static terminal hydride structure to be very unlikely. The coupling of the bridging hydride and ^{31}P in **2** (44 Hz) is similar in magnitude to that found between bridging phosphorus and terminal hydrogen.[9d]

It was possible to make a quantitative estimate of the base strength of $[CpFe(CO)_2]_2$ in acetic acid solution. Addition of successive aliquots of 4.10 *M* H_2SO_4 in acetic acid to a solution of $[CpFe(CO)_2]_2$ caused the cyclopentadienyl signal at 5.11 ppm to decrease in intensity as the corresponding signal at 4.66 ppm of protonated product grew. These data were fitted to the equilibrium in eq 2. The product was taken as

$$[CpFe(CO)_2]_2 + H_2SO_4 \overset{K_2}{\rightleftharpoons} \{[CpFe(CO)_2]_2H^+\}\{HSO_4^-\} \tag{2}$$

$$K_2 = \frac{[\{[CpFe(CO)_2]_2H^+\}\{HSO_4^-\}]}{[[CpFe(CO)_2]_2][H_2SO_4]}$$

an ion pair because of the low dielectric constant of acetic acid.[10] The apparent equilibrium constant increases with increasing H_2SO_4 concentration, and we estimate that the value of K_2 at zero sulfuric acid concentration is $10^{-0.8}$ l. mol^{-1}.[11]

Table II. Electronic Spectra[a]

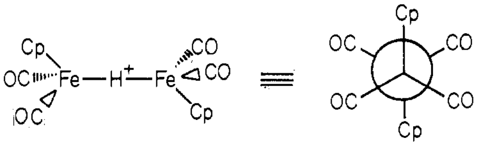
Compd		Band I	Band II	Band III	Band IV
trans-$[CpFe(CO)_2]_2$[b]	~15 sh	19.0	~24 sh	29.4	~37 sh
cis-$[CpFe(CO)_2]_2$[b]		19	~24 sh	28.6	~37 sh
$[CpFe(CO)_2]_2$[c]		19.6 (401)	~24.4 sh (1300)	29.3 (2010)	
$[CpFe(CO)_2]_2$[d]	~17.5 sh (270)	~19.8 sh (432)	~24 sh (1400)	29.0 (8240)	
$\{[CpFe(CO)_2]_2H\}\{HSO_4\}$[d,e]		19.6 (835), ~21 sh (880)			
$Cp_2Fe_2(CO)_3P(OCH_3)_3$[f]		17.9 (520)	Unresolved	29.2 (4150)	
$Cp_2Fe_2(CO)_3P(OCH_3)_3$[b]		18.2	~24 sh	28.4	
$\{Cp_2Fe_2(CO)_3P(OCH_3)_3H\}\{HSO_4\}$[b]		16.4, ~19.5 sh	23.3, 24.4	29.1	
$[CpRu(CO)_2]_2$[c]		~23 sh (600)	30.3 (6300)	37.6 (8800)	

[a] Energies in kK. ϵ values in parentheses. sh = shoulder. [b] KBr pellet, 80°K. [c] Acetic acid solution, 300°K. [d] Acetone solution, 300°K. [e] Prepared by treating 9 ml of acetone soluton of $[CpFe(CO)_2]_2$ with 1 ml of 98% H_2SO_4 at 0°. [f] Acetonitrile solution, 300°K.

Similar titrations of $[CpRu(CO)_2]_2$ and **1** were performed. Within experimental error, all of the added H_2SO_4 was consumed by base until 1 equiv had been used up, which places a lower limit on the equilibrium constants of $\sim 10^2$ l. mol^{-1} for both $[CpRu(CO)_2]_2$ and **1**. In agreement with our nmr results, we have been able to estimate basicities in acetic acid solution by a potentiometric method[11] and find values of $pK_B = 7.5 \pm 0.3$ and 5.9 ± 0.3 for $[CpFe(CO)_2]_2$ and **1**, respectively.

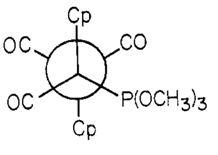
The rate of proton exchange between **1** and **2** is not known. It is of interest to note, however, that in contrast to mixtures of $[CpRu(CO)_2]$ and $[CpRu(CO)_2]H^+$ and mixtures of $[CpFe(CO)_2]_2$ and $[CpFe(CO_2)_2]_2H^+$, which show sharp (~1 Hz wide) cyclopentadienyl peaks, a mixture of **1** and **2** shows broad (~5 Hz) lines for both the C_5H_5 and CH_3 protons.

Infrared Spectra.[12] Symon and Waddington[3] studied the infrared spectrum of the protonated species $[CpFe(CO)_2]_2H^+$ in strong-acid media. They found just two strong bands near 2040 and 2010 cm^{-1} in the carbonyl stretching region. This suggests the rotamer **3** as the main species in these media. It also establishes that the carbonyl bridge structure of $[CpFe(CO)_2]_2$ is broken upon protonation.



3

We examined the infrared spectra of the phosphine-substituted species **1** and **2** and also found the CO bridges to be lost upon protonation. The protonated species, **2**, can be precipitated as the tetraphenylborate or hexafluorophosphate salts. The tetraphenylborate salt shows just three bands in the carbonyl region (2035, 1984, and 1955 cm^{-1}; KBr pellet), whereas the hexafluorophosphate derivative has five bands (2065, 2050, 2023, 1991, and 1969 cm^{-1}). These results suggest that at least two rotamers are present in the hexafluorophosphate salt. A sample of the tetraphenylborate salt stored at 4° for 5 months gave an infrared spectrum with bands at 2057, 2032, 2011, 1981, and 1951 cm^{-1}, as well as weak bands at 1765 and 1730 cm^{-1}. Presumably, a slow solid-state isomerization to produce a mixture of rotamers occurs, as well as some decomposition to bridged **1**. The two most likely rotamers of **2** present in these solids are **4** and **5**.



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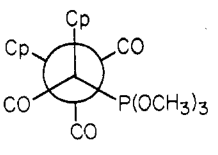

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Electronic Spectra. Previous work has identified intense, low-energy absorptions of the compounds $M_2(CO)_{10}$ (M = Mn, Tc, Re)[13,14] and $W_2(CO)_{10}^{2-}$ [15] as $d\sigma(M_2) \rightarrow d\sigma^*(M_2)$ transitions. Such a transition is lacking in the hydrido-bridged species $HW_2(CO)_{10}^-$.[15] The compounds in the present study exhibit several low-energy electronic absorption bands (Table II). Of interest is the observation that the lowest energy band of **1** splits into two components on protonation (Figure 1). Bands II and III of **1** are also modified significantly in the spectrum of **2**, and a dramatic color change from dark red-purple to green accompanies the **1** → **2** transformation. Previous oxidation studies[16] of $[CpFe(CO)_2]_2$ and related compounds have strongly indicated that the most easily ionized electrons are localized in the metal–metal bond. If this is the case, one might also expect that the lowest energy electronic transitions would originate in a metal–metal bonding orbital. Changes in the spectrum of **1** on protonation support this notion, and in particular the behavior of band III suggests that it could represent a $d\sigma(Fe_2) \rightarrow d\sigma^*(Fe_2)$ transition. In view of the complexity of these systems, however, detailed electronic spectral interpretations cannot be made with any confidence.

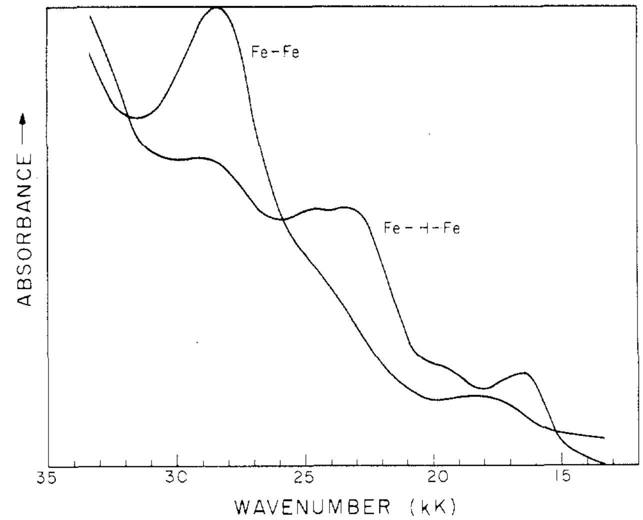

Figure 1. Liquid nitrogen temperature electronic spectra of KBr pellets of **1** (Fe–Fe) and the tetraphenylborate salt of **2** (Fe–H–Fe). At room temperature the band near 24 kK of **2** is not split into two components. The two bands of **2** at 16.4 and 19.5 kK are similar in appearance at room temperature.

Registry No. *trans*-$[CpFe(CO)_2]_2$, 32757-46-3; *cis*-$[CpFe(CO)_2]_2$, 33221-55-5; $\{[CpFe(CO)_2]_2H\}\{HSO_4\}$, 54062-95-2; $[CpRu(CO)_2]_2$, 12132-87-5; $\{[CpRu(CO)_2]_2H\}\{HSO_4\}$, 54062-97-4; $Cp_2Fe_2(CO)_3P(OCH_3)_3$, 54141-86-5; $\{(Cp)_2(CO)_3Fe_2[P(OCH_3)_3]H\}\{HSO_4\}$, 54062-99-6; $\{(Cp)_2(CO)_3Fe_2[P(OCH_3)_3]H\}\{BPh_4\}$, 54063-00-2; $\{(Cp)_2(CO)_3Fe_2[P(OCH_3)_3]H\}\{PF_6\}$, 54063-01-3.

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Synthesis and Spectral Properties of Metal Carbonyl Derivatives of the Tetrabasic, Nonchelating Phosphatriazaadamantane Ligand

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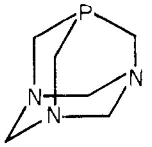
Although the inorganic chemistry of tetraazaadamantane ($N_4(CH_2)_6$, also known as hexamine or urotropin) has commanded a good deal of attention with respect to its reactions with main group or transition metal salts,[2] spectral properties of derivatives thus formed are in general not available. Similarly, low-valent organometallic complexes such as η^5-$C_5H_5Mo(CO)_2[N_4(CH_2)_6]$[3] or $Mo(CO)_5[N_4(CH_2)_6]$[4] have been prepared but not extensively studied. The recent synthesis[5] of phosphatriazaadamantane, PTA, prompted an investigation into the complexing properties of this novel tetrabasic, nonchelating ligand. In view of the fact that metal carbonyl moieties are known to bond to both N and P donor ligands, derivatives of the formulas $M(CO)_5PTA$ (M = Cr, Mo, W) and $Fe(CO)_4PTA$ as well as the N-methylated $[M(CO)_5PN_2(CH_2)_6NCH_3]^+I^-$ were prepared. For comparison, ir and nmr spectral data were also measured for the tetraazaadamantane complex $Mo(CO)_5[N_4(CH_2)_6]$.



PTA

Experimental Section

Materials. Phosphatriazaadamantane and tetraazaadamantane were prepared as described in the literature.[5,6] Bis(2-methoxyethyl) ether (diglyme), purified by reflux over and distillation from sodium under N_2, was used as solvent for the thermal reactions. Other solvents and chemicals were reagent grade and used without further purification.

Procedure. Stoichiometric amounts (6.37 mmol) of PTA and $M(CO)_6$ or $Fe(CO)_5$ were allowed to react in 15–20 ml of diglyme and refluxed under N_2 for 2–3 hr. Upon removal of solvent *in vacuo* a yellow to white residue was obtained, was washed with water, and was recrystallized from boiling hexane. Any excess $M(CO)_6$ was removed by sublimation at 1 mm and 40–50°. $Cr(CO)_5PTA$ was found to sublime slowly, over a period of days, at 90°. *Anal.* (Galbraith Laboratories) Calcd for $Cr(CO)_5[PN_3(CH_2)_6]$: C, 37.83; H, 3.46. Found: C, 37.67; H, 3.45. Calcd for $Mo(CO)_5[PN_3(CH_2)_6]$: C, 33.60; H, 3.08; mol wt 393. Found: C, 33.85; H, 3.11; mol wt 410. Calcd for $W(CO)_5[PN_3(CH_2)_6]$ C, 27.46; H, 2.51. Found: C, 27.24; H, 2.64. Calcd for $Fe(CO)_4[PN_3(CH_2)_6]$: C, 36.95; H, 3.72. Found: C, 37.23; H, 3.53. In all cases yields were approximately 50%.

Pentacarbonyl(tetraazaadamantane)molybdenum was obtained by allowing $Mo(CO)_6$ and $N_4(CH_2)_6$ to react in refluxing methylcyclohexane. A yellow crystalline precipitate was obtained on cooling, was washed with water, and was recrystallized from hexane.

Alternatively the $M(CO)_5L$ (L = PTA, $N_4(CH_2)_6$) complexes could be prepared by treating L with $M(CO)_5THF$, produced photochemically[7] in THF.

Infrared spectra were obtained on a Perkin-Elmer 521 spectrophotometer, calibrated in the CO stretching region with CO and H_2O vapor. A Jeolco MH-100 was used to obtain the proton nmr resonances; ^{31}P resonances were measured on a Jeolco C-60 HL spectrometer, equipped with a 24-MHz radiofrequency unit.

Results and Discussion

Air-stable crystalline solids result from reaction of PTA and excess $M(CO)_6$ (M = Cr, Mo, W) or $Fe(CO)_5$ in refluxing dry diglyme. Alternatively the group VI derivatives could be prepared by the photochemical synthesis of $M(CO)_5THF$ complex and subsequent thermal (25°) reaction with PTA *in situ.* Products obtained by this method are identical with those obtained by the thermal rupture of an M–CO bond; yields were also similar.

Spectral properties of the complexes are found in Table I. The infrared spectra for $M(CO)_5PTA$ complexes measured in the CO stretching frequency region show a pattern typical of monosubstituted octahedral metal carbonyl complexes, with frequencies very similar to those of phosphine-substituted complexes, the definitive feature being the position of the $A_1^{(1)}$ band with respect to the E band. $LM(CO)_5$ complexes in which L is a phosphorus donor generally exhibit ν_{CO} spectra in which the $A_1^{(1)}$ bands are higher in energy from the E mode, whereas if L is a nitrogen donor, the $A_1^{(1)}$ band is lower in energy from the E.[8] The latter is the case for $Mo(CO)_5$-$N_4(CH_2)_6$. The ν_{CO} ir spectrum observed for $Fe(CO)_4PTA$ is typical of axially substituted trigonal-bipyramidal iron carbonyl complexes.[9] C–K force constant values[10] for the PTA complexes are similar to those calculated for analogous carbonyl complexes containing phosphorus donor ligands[8] or, in the case of $MO(CO)_5[N_4(CH_2)_6]$, nitrogen donor ligands.[11]

The ^1H nmr data also suggest PTA to be phosphorus-bound to its metal carbonyl derivatives. Uncomplexed PTA in acetone exhibits two resonances, integrating 1:1, at δ 4.50 and 3.97 ppm. The latter resonance is split by 10 Hz and is assigned to the P–CH_2–N protons. The methylene protons adjacent to P in the metal carbonyl PTA complexes show both a resonance shift downfield from noncomplexed PTA as well as