

PROTONATED KETONES AS NMR MODELS FOR ORGANOTRANSITION METAL CATIONS

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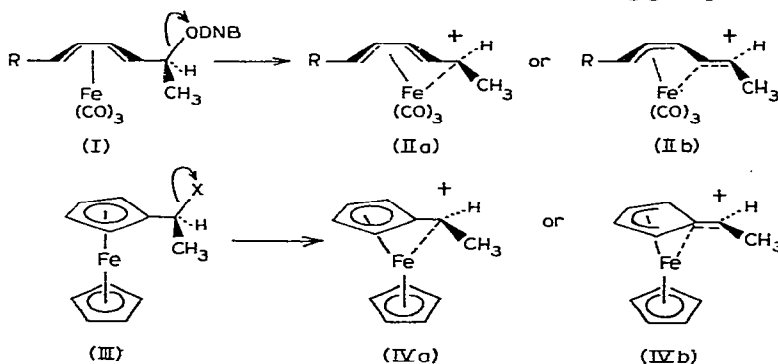
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SUMMARY

A study of ferrocenyl ketones in $\text{CDCl}_3/\text{SO}_2/\text{FSO}_3\text{H}$ solution at low temperature has shown that these protonated ketones are excellent NMR models for the corresponding ferrocenylcarbinyl cations. Comparison of the results of a similar study of tricarbonyl(*trans,trans*-dienone)iron complexes to the limited NMR data available for the corresponding tricarbonyl (*trans*- π -pentadienyl)iron cations suggests strongly that the protonated ketones are good models for the latter cations also. A qualitatively similar pattern of downfield NMR shifts as that observed on protonation of dienone- $\text{Fe}(\text{CO})_3$ complexes is caused by oxidation of dienol- $\text{Fe}(\text{CO})_3$ complexes to dienone- $\text{Fe}(\text{CO})_3$ complexes. These data are interpreted as favoring a conjugative mechanism for stabilization of ferrocenylcarbinyl and tricarbonyl (*trans*- π -pentadienyl)iron cations as opposed to one involving neighboring group participation by iron. Owing to exchange with free fluorosulfonic acid, NMR signals for hydrogens on carbonyl oxygen were not observed.

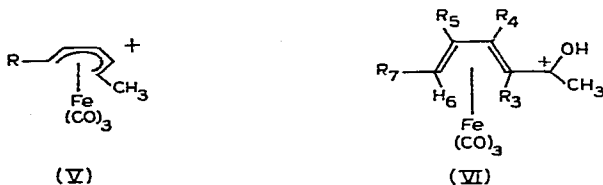
INTRODUCTION

Solvolysis studies in 80% aqueous acetone have demonstrated the existence of tricarbonyl(*trans*- π -pentadienyl)iron cations [(IIa) or (IIb)]^{1,2}. Their precursors, complexed dienyl esters (I), exhibit reactivity similar to that of ferrocenyl carbinyl esters. The solvolysis reactions proceed by departure of the leaving group *exo* to iron and with



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retention of configuration as is the case for ferrocenyl esters(III)¹⁻³. Two proposals to explain the role of iron in the ferrocenyl system have been advanced. These are participation of iron as a nucleophilic neighboring group with direct bonding between iron and the carbon atom at the reaction center [(IIa) and (IVa)]^{3,4*} and iron-carbon hyperconjugation [(IIb) and (IVb)]⁶. Both proposals are consistent with our solvolysis data for system (I)². Ferrocenyl carbinyl cations (IV) have been studied in conc. sulfuric acid solutions using NMR spectroscopy^{7**}. Attempts to prepare the *trans* cations (II) for direct NMR study lead to the more stable *cis* cations (V) instead^{8,9}. To avoid this isomerization problem, we have studied protonated tricarbonyl(*trans,trans*-dienone)iron complexes (VI) as models of the cations (II). The study of one compound

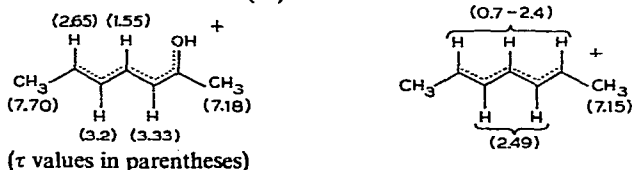


[(VI), R₇=CH₃] in H₂SO₄ has been reported^{2b}, and we now report the results of a more extensive study.

RESULTS AND DISCUSSION

Uncomplexed dienones

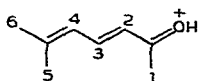
Olah and Calin have pointed out that protonated saturated ketones make poor NMR models for secondary carbonium ions owing to the small importance of the hydroxy carbonium ion resonance contributor¹⁰. Protonated ketones are good NMR models for relatively stable carbonium ions¹¹ and have been used in this way often¹². For example, protonated cyclohexadienones^{12h, 12i} and the analogs cyclohexadienyl carbonium ions¹³ exhibit similar NMR absorption. More closely related to our tricarbonyl(*trans*- π -pentadienyl)iron cations are their uncomplexed analogous, all-*trans*-pentadienyl carbonium ions. The data in Table 1 shows that protonated all-*trans*-dienones are excellent NMR models for the corresponding all-*trans*-pentadienyl carbonium ions in agreement with our earlier conclusion^{2b}. The downfield shifts of the vinyl hydrogens on protonation ($\Delta\tau$) especially show the same alternation along the chain as encountered in formation of pentadienyl carbonium ions by protonation of trienes¹⁴. Chemical shifts for protonated all-*trans*-3,5-heptadienone and all-*trans*-3,5-heptadien-2-yl cation¹⁴ are shown below for comparison. Since solvolysis results indicate that the Fe(CO)₃ complexed pentadienyl cations (II) are more stable than their uncomplexed analogs², the protonated complexed ketones (VI) may be good NMR models for cations (II).



* For a recent discussion which favors this mechanism see ref. 5.

** See ref. 6 for an alternative interpretation of these spectra.

TABLE 1

 AVERAGE $\Delta\tau$ VALUE FOR PROTONATION OF DIENONES AND DIENALS^{a-d}

 Substituent $\Delta\tau$ for substituent hydrogen(s) (ppm)

Substituent	Position of substituent					
	1	2	3	4	5	6
H	-0.1 ^e	0.60	1.19	0.5	1.15 ^f	
CH ₃	0.52		0.4 ^e	0.23 ^e		0.35
C ₆ H ₅						0.26 ^g

^a In 60% SO₂/40% CDCl₃ (v/v). ^b $\Delta\tau = \tau(\text{SO}_2/\text{CDCl}_3) - \tau(\text{SO}_2/\text{CDCl}_3/\text{FSO}_3\text{H})$, shifts relative to internal tetramethylsilane. ^c Compounds protonated were the all-*trans* isomers of 2,4-pentadienal; 3,5-heptadienone; 5-methyl-3,5-heptadienone; 6-phenyl-3,5-heptadienone; and 4-methyl-6-phenyl-3,5-heptadienone. ^d Signals for hydrogen on carbonyl oxygen are not observed owing to exchange broadening. ^e One determination only. ^f The shift falls to 0.65–0.70 ppm in the presence of a 6-phenyl substituent. ^g Determined from the centers of gravity of the phenyl multiplets.

TABLE 2

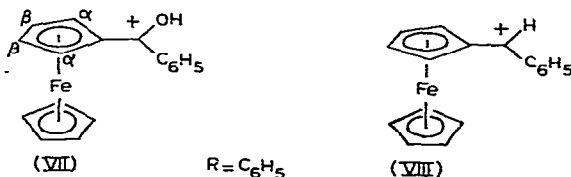
 NMR CHEMICAL SHIFTS (τ)^a FOR ACYL FERROCENES AND FERROCENYL CARBYNYL CATIONS

Compound	Unprotonated ^b				Protonated ^c			
	H _x	H _β	C ₅ H ₅	R	H _x , H _{x'}	H _β	C ₅ H ₅	R
(VII) R=H	5.20	5.20	5.65	0.34	5.38, 4.60	4.00, 3.70	5.1	0.70
(VII) R=CH ₃	5.22	5.38	5.72	7.60	4.95, 4.68	4.1	5.30	7.41
(VII) R=C ₆ H ₅	5.15	5.35	5.76	2.0–2.7	5.0, 4.3	4.0	5.45	1.9–2.6
(VIII) $\text{Fc}-\overset{+}{\text{C}}\text{H}-\text{C}_6\text{H}_5$ ^d					5.3, 4.7	3.9–3.7	5.2	2.1–2.4

^a Relative to internal tetramethylsilane; ppm. ^b In 40% CDCl₃/50% SO₂ (v/v) at -20°. ^c In 40% CDCl₃/60% SO₂ (v/v) with 1.0–1.5 eq FSO₃H at -70°. ^d Relative to internal tetramethylammonium chloride (τ 6.9 ppm) in conc. sulfuric acid, see ref. 28.

Acyl ferrocenes

Table 2 shows chemical shift data for acylferrocenes. The fact that the downfield shifts on protonation vary widely from one position to another and are generally larger for the acylated ring than the other as well as lack of any NMR signal above τ 10 ppm characteristic of metal protonation favors protonation at carbonyl oxygen in the presence of FSO₃H*. Ketone (VII), R=C₆H₅ in strong acid exhibits NMR absorption which is strikingly similar to the corresponding ferrocenyl carbonyl cation (VIII) (see



* No NMR signal for the proton on oxygen was observed owing to exchange. More acidic media which allow observation of this signal^{12a,12c} caused rapid decomposition of the organotransition metal compounds.

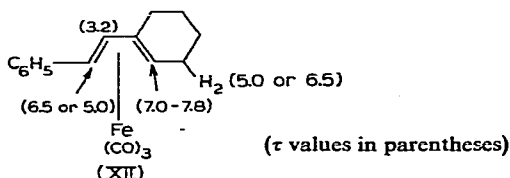
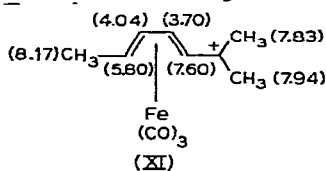
Table 2). The quantity $\Delta\nu = [\tau(\text{H}_{\alpha\text{av}}) - \tau(\text{H}_{\beta\text{av}})]$, which has been discussed by Cais *et al.*⁷ decreases in the protonated ketones in the same way it does in the ferrocenyl carbonyl cations themselves as the ability of group R to accommodate positive charge increases. We conclude that in the ferrocenylcarbonyl system protonated ketones are excellent NMR models for the corresponding cations (IV).

In agreement with this conclusion, Traylor and Ware⁶ have found that σ^+ for α -ferrocenyl (α -Fc) determined by comparing basicities of acetylferrocene and acetophenones in aq. H_2SO_4 ¹⁵ agrees with $\sigma_{\alpha\text{-Fc}}^+$ determined from solvolysis rates and from Foote-Schleyer correlation¹⁴ of carbonyl stretching frequencies. The latter correlation is expected to fail when neighboring group participation occurs¹⁶. Since conjugative (resonance) stabilization and neighboring group participation are competitive processes¹⁷, it is questionable whether participation could occur in protonated acylferrocenes in competition with the enormous conjugative stabilization expected from α -hydroxy. The σ_p^+ constants for $p\text{-OH}^*$, $p\text{-OCH}_3^*$ and $p\text{-Fc}$ are -0.92 ¹⁸, -0.778 ¹⁸ and -0.6 to -0.7 ⁶ respectively. Since proportionality between σ_p^+ and σ_z^+ values has been demonstrated for OCH_3 and Fc ⁶, we expect that $\alpha\text{-OH}$ will be a better electron donor (more negative σ^+) than $\alpha\text{-Fc}$. But if neighboring group participation and conjugative stabilization are strictly competitive, the participation by iron would not occur unless $\alpha\text{-Fc}$ were the better electron donor. NMR comparison of protonated acylferrocenes to ferrocenylcarbonyl cations suggests that the same type of electron donation from Fc is important in both. Thus, our results agree with Traylor's⁶ proposal that electron release from ferrocenyl groups in ferrocenylcarbonyl cations occurs by a conjugative mechanism, such as iron-carbon hyperconjugation (IVb).

Tricarbonyl(dienone)iron complexes

Table 3 lists NMR parameters for tricarbonyl (dienone)iron complexes both in the presence and in the absence of FSO_3H . The spectrum of tricarbonyl(3,5-heptadienone)iron [(VI), $\text{R}_3\text{-R}_5 = \text{H}$, $\text{R}_7 = \text{CH}_3$] in $\text{CDCl}_3/\text{SO}_2/\text{FSO}_3\text{H}$ was virtually identical to that in H_2SO_4 ^{2a} except that the signals were sharper. No signals above τ 10 ppm were observed. Use of SbF_5 or $\text{SbF}_5\text{-FSO}_3\text{H}$ as acid yielded identical spectra. Thus the ketone carbonyl oxygen is the site of protonation as it is in H_2SO_4 ^{2a}. The spectra did not change when the amount of FSO_3H was increased from 1.0 to 1.5 equivalents. We conclude, therefore, that protonation is complete when 1 eq. FSO_3H is present and that no significant diprotonation¹⁹ is occurring. The starting dienone complexes could be recovered by quenching the acidic solutions with excess sodium carbonate suspended in methylene chloride. Fig. 1 contains the downfield shifts produced by protonation ($\Delta\tau$ values) of the complexed dienones. Average $\Delta\tau$ values for hydrogen substituents are recorded in structure (X) (Fig. 1). They are characterized by a large shift for H_6 and a very small shift for H_3 and are similar to shifts in the ferrocenyl ketones in that the more remote hydrogen (H_6 or H_β) suffers the largest downfield shift on protonation.

* A referee has pointed out that order of σ_p^+ values for OH and OCH_3 is the reverse of that expected on the basis of relative inductive effects of H and CH_3 and that ionization potential measurements suggest that the gas phase order is the expected one. However, only substantiated values in solution are relevant to our discussion; and reactions in acidic solutions for which σ_p^+ for both OH and OCH_3 have been determined have always given significantly more negative values for OH, see ref. 18.



Since completion of this work, NMR data for two tricarbonyl(*trans*- π -pentadienyl)iron cations, (XI)^{9a} and (XII)^{9b} have become available. These data reveal the same strong deshielding of H₆ and unexpectedly high field signals for H₃ observed for protonated ketones. Thus, in this case also protonated ketones appear to be good NMR models for the corresponding cations. The assignment of H₂ in (XII), which is of obvious interest, needs confirmation by deuterium labeling before any weight may

TABLE 3

NMR SPECTRAL DATA FOR COMPLEXED DIENONES


 In 40% CDCl₃/60% SO₂ (v/v) at -20 to -30°.

Compound ^a	Chemical shifts, τ^b (signal multiplicity) ^c						Coupling constants (Hz) ^d
	1-CH ₃	R ₃	R ₄	R ₅	H ₆	R ₇	
(VIa) R ₇ =CH ₃	7.90 (s)	8.65 (d)	4.25 (q)	4.65 (q)	8.35 (m)	8.50(d)	$J_{34}=J_{56}=8$ $J_{45}=J_{67}=6$
(VIb) R ₃ =R ₅ =D, R ₇ =CH ₃	7.9 (s)		4.3 (s)		8.4 (b)	ca. 8.5	
(VIc) R ₅ =R ₇ =CH ₃	7.90 (s)	8.68 (d)	4.35 (d)	7.80 (s)	ca. 8.45 (m)	ca. 8.45	$J_{34}=8$
(VID) R ₄ =R ₇ =CH ₃	7.89 (s)	9.10 (s)	7.50 (s)	4.85 (d)	ca. 8.5 (m)	ca. 8.5	$J_{56}=7$
(IXa) R ₇ =CH ₃		8.35 (s)		4.55 (m)	8.45	8.45	
(VIe) R ₇ =C ₆ H ₅	7.80 (s)	8.25 (d)	3.95 (m)	4.05 (m)	7.35 (d)	2.60 (s)	$J_{34}=8, J_{56}=8-9$
(IXb) R ₇ =C ₆ H ₅		8.02 (s)		3.95 (d)	7.65 (s)	2.65 (s)	$J_{56}=9$

 In 40% CDCl₃/60% SO₂ (v/v) + 1-1.3 eq. FSO₃H at -50° to -60°.

Compound	Chemical shifts, τ^b (signal multiplicity) ^c						Coupling constants (Hz) ^d
	1-CH ₃	R ₃	R ₄	R ₅	H ₆	R ₇	
(VIa) R ₇ =CH ₃	7.85 (s)	8.55 (d)	3.60 (m)	4.20 (m)	6.95 (b)	8.25 (d)	$J_{34}=8, J_{67}=6$
(VIb) R ₃ =R ₅ =D, R ₇ =CH ₃	7.55 (s)		3.60 (b)		7.0 (b)	8.30 (d)	$J_{67}=6$
(VIc) R ₅ =R ₇ =CH ₃	7.07 (s)	8.55 (d)	3.65 (d)	7.55 (s)	7.1 (m, b)	8.30 (d)	$J_{34}=8, J_{67}=6$
(VID) R ₄ =R ₇ =CH ₃	7.60 (s)	9.02 (s)	7.39 (s)	4.30 (d)	7.1 (m, b)	8.30 (d)	$J_{56}=9, J_{67}=6$
(IXa) R ₇ =CH ₃				4.20 (d)		8.30 (d)	$J_{56}=10, J_{67}=5$
(VIe) R ₇ =C ₆ H ₅	7.43 (s)	8.17 (d)	3.4 (m)	3.4 (m)	6.20 (d)	2.50 (s)	$J_{34}=7, J_{56}=9$
(IXb) R ₇ =C ₆ H ₅		7.5-8.0 ^e		3.60 (d)	6.35 (d)	2.55 (s)	$J_{56}=9$

^a Only substituents other than hydrogen are listed. ^b Chemical shifts were measured relative to internal tetramethylsilane and are accurate to at least ± 0.03 ppm except where approximate values are indicated. ^c s=singlet, d=doublet, q=quartet, m=multiplet, b=broad. ^d From first order analysis where permissible, maximum error ± 1 Hz. ^e No separate signal for H₃ is discernible. The range assigned spans the upfield portion of the methylene envelope.

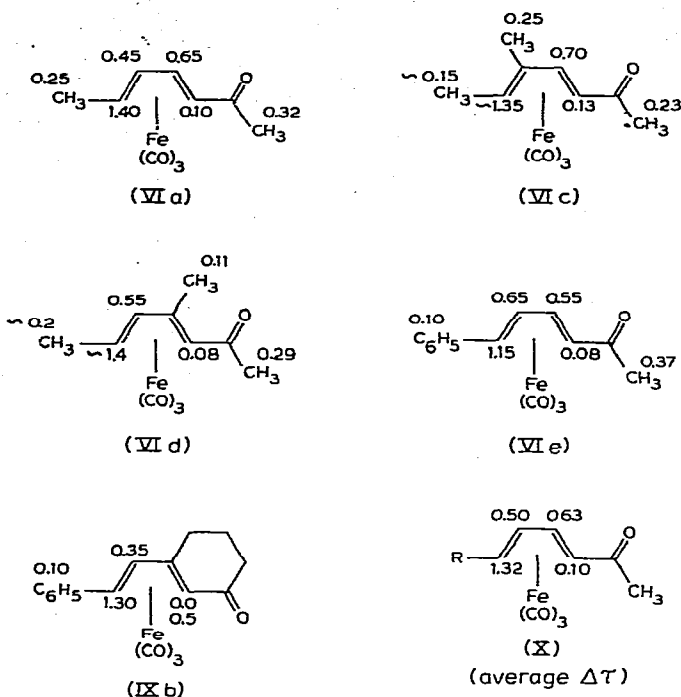
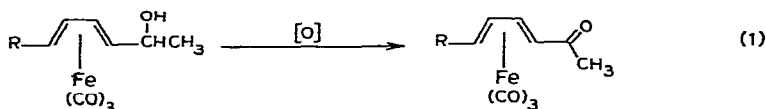


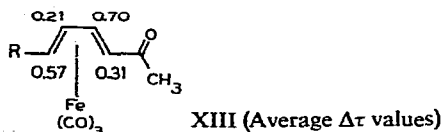
Fig. 1. $\Delta\tau$ Values for protonation of complexed dienones. $\Delta\tau = \tau(\text{CDCl}_3/\text{SO}_2) - \tau(\text{CDCl}_3/\text{SO}_2/\text{FSO}_3\text{H})$. Average $\Delta\tau$ values for diene hydrogens are given in structure (X).

be placed on its interpretation. As we have pointed out previously^{2a}, these data seem to be more in accord with structure (IIa) than with (IIb). However, since the $\text{Fe}(\text{CO})_3$ group can cause dramatic and as yet unpredictable shielding effects, the interpretation is not convincing.

As happens on protonation of the complexed dienones, increased electron demand at C_2 also occurs when complexed dienols are oxidized to ketones (reaction 1). The downfield NMR chemical shifts caused by this reaction ($\Delta\tau_{\text{ox}}$) are reasonably

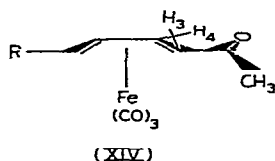


constant for a given hydrogen through a series of compounds*. Average values are listed with structure (XIII) below. Comparison of $\Delta\tau$ and $\Delta\tau_{\text{ox}}$ values requires correction for the long range anisotropic effects of the ketone carbonyl which operate in



* Compounds studied were (VIa), (VIc)-(VIe) and all-*trans*-sorbalddehyde- $\text{Fe}(\text{CO})_3$ and the corresponding ψ -*exo*²⁰ dienol complexes. NMR spectra were in CDCl_3 .

opposite directions in the two cases. The dienone complexes possess *s-cis* conformations (XIV)²⁰ in which H₃ and H₄ are deshielded by the ketone carbonyl^{21,*}. Proton-



ation of the carbonyl group will reduce its anisotropic effects^{12c} and reduce $\Delta\tau$ at positions 3 and 4. In contrast, a change from CHO to C=O at C₂ obviously causes strong carbonyl deshielding of H₃ and H₄ which augments their $\Delta\tau_{ox}$ values. We wish to compare only those shifts caused by change in electron donation to C₂. Thus $\Delta\tau$ values (see (X), fig. 1) for H₃ and H₄ must be modestly increased and $\Delta\tau_{ox}$ values (XIII) for H₃ and H₄ must be decreased considerably. The corrections will be larger at H₄ than at H₃^{21,**}. It can be seen that the effect of these corrections is to make the pattern of $\Delta\tau$ and $\Delta\tau_{ox}$ values very similar: H₃ small, H₄ and H₅ moderate, and H₆ large. The $\Delta\tau$ values are larger, as expected.

Clearly the $\Delta\tau_{ox}$ shifts are associated with conjugative electron release from the dienyl-Fe(CO)₃ group. This is so because classic neighboring group participation does not occur in ketones^{16,***}. In fact, unless the geometry of the dienone complexes is significantly different from that of Fe(CO)₃ complexes of other dienes, the iron-carbonyl carbon distance will be 3.0–3.2²⁰, too long for significant bonding. Since ketone protonation produces the same pattern of downfield shifts as oxidation, it is reasonable to assume that both sets of shifts arise owing to increased electron release to C₂ by the same conjugative mechanism. Furthermore, since solvolysis rates show that the α -(dienyl)Fe(CO)₃ group is a poorer electron donor than α -ferrocenyl, neighboring group participation by iron in competition with conjugative stabilization by α -OH is unlikely. Thus our data favor iron-carbon hyperconjugation (Iib) as the mechanism by which the α -(dienyl)Fe(CO)₃ group stabilizes cations.

CONCLUSION

The conclusion that the strikingly similar solvolysis reactions of complexed dienyl esters (I) and ferrocenylcarbinyl esters (III) proceed via cations which are stabilized by the same mechanism, iron-carbon hyperconjugation, is obviously appealing. Traylor *et al.*²⁴ have pointed out that hyperconjugation is a "vertical" process involving no relative movement of the metal cationic center. Charge transfer measurements have revealed that the dramatic cation stabilizing ability of groups R_nMCH₂⁻,

* Two current models for carbonyl anisotropy^{21a,21b} both predict deshielding of H₃ and H₄ but do not agree quantitatively.

** Our best estimates of the corrective increments based on Jackman and Sternhell's diagrams^{21b} are $\Delta\tau(H_3)$ 0.05, $\Delta\tau(H_4)$ 0.10; $\Delta\tau_{ox}(H_3)$ -0.15, $\Delta\tau_{ox}(H_4)$ -0.30 ppm.

*** Interactions do occur in special cases such as when a tertiary amine function is forced to approach a carbonyl closely. The ketone IR stretching frequency is lowered in such cases²². The carbonyl stretching frequencies of our dienone complexes, 1682 ± 3 cm⁻¹ in CCl₄, are significantly higher than those of ferrocenyl ketones⁶ in which the distance between iron and the carbonyl carbon is too large for bonding to occur²³.

where $M = \text{Si, Sn, Pb, and Hg}$, is at least mostly vertical in nature²⁴. Thus, present evidence suggests that stabilization of cationic centers by main group and transition metals formally in the β -position all stem from the same vertical conjugative process for which metal-carbon hyperconjugation is an attractive model.

EXPERIMENTAL

General

Infrared spectra were recorded as 100 mg/ml solutions in CCl_4 using a Beckman IR-10 spectrometer and were calibrated using the 1603 cm^{-1} band of polystyrene. Thin layer chromatography was performed on silica-gel layers with the use of iodine vapor as a visualization reagent. Elemental analyses were performed by the University of Massachusetts Research Services Microanalytical Laboratory under the direction of Mr. Charles Meade. Preparation of previously known compounds was accomplished as referenced: uncomplexed dienones²⁵, (VIa)²⁰, (VIId)²⁶, (VIe)²⁰, (IXb)²⁶. The ferrocenyl ketones were kindly supplied by Dr. Paul A. Roling, University of Massachusetts.

NMR spectra

Spectra were recorded on a Varian A-60 spectrometer equipped with a variable temperature accessory. Temperatures were calibrated using a methanol sample and are accurate to $\pm 3^\circ$. Tetramethylsilane was employed as an internal standard in all the work. Low temperature samples were prepared by dissolving 30–50 mg of a ketone in ca. 0.08 ml CDCl_3 (1% TMS) at room temperature followed by condensation of 0.12–0.15 ml of anhydrous SO_2 into the sample as it was cooled in a dry ice/acetone bath. The tube was sealed with a tight-fitting rubber cap. The NMR spectrum of this sample was recorded at -20° . After the sample had been recooled in the dry ice/acetone bath, FSO_3H (reagent grade) was added from a capillary dropper to give deep red solutions until excess acid could be detected by NMR at -50 to -60° . The NMR spectrum of this sample was then recorded. The cold solution was quenched by pouring it into a suspension of ca. 2 g NaHCO_3 in 20 ml of cold methylene chloride. The resulting yellow solution was washed with water, and the methylene chloride layer was dried (MgSO_4) and evaporated. The residue was dissolved in chloroform, filtered (Metricel-Alpha 8) and characterized as the starting dienone complex by IR, NMR and TLC.

Assignments of the NMR signals were made by analogy to previous NMR data for diene- $\text{Fe}(\text{CO})_3$ complexes^{1,20,26} and on the basis of specific substitution of methyls or deuterium for hydrogen at known positions on the diene.

Tricarbonyl(*trans,trans*-3,5-heptadienone-3,5- d_2)iron (VIb)

This compound was prepared in 13% yield by treating the deuterated dienone²⁵ with excess $\text{Fe}_2(\text{CO})_9$ in refluxing ether. The crude product was chromatographed on alumina and crystallized from Skelly Solve-B at -78° to give yellow crystals possessing physical properties identical to those reported for the perprotio compound²⁰.

Tricarbonyl(*trans,trans*-5-methyl-3,5-heptadienone)iron (VIc)

trans,trans-5-Methyl-3,5-heptadienone (1.9 g, 15.7 mmol) was heated at reflux

with 5.0 g of $\text{Fe}_2(\text{CO})_9$ (13.3 mmol) under nitrogen in diethyl ether for 17 h. After filtration, ether was removed on a rotary evaporator leaving an oil which was chromatographed on alumina. Elution with Skelly Solve-B removed unreacted dienone and elution with CH_2Cl_2 removed (VIc). Crystallization of the crude orange oil from 5 ml of Skelly Solve-B at -78° gave 1.19 g (30%) of a yellow solid: m.p. $61-64^\circ$; IR (CCl_4) 2050, 1990 ($\text{C}\equiv\text{O}$) and 1680 cm^{-1} ($\text{C}=\text{O}$). A 2,4-dinitrophenylhydrazone derivative was prepared and recrystallized 3 times from ethyl acetate to give dark red crystals: m.p. $198-200^\circ$. (Found: C, 49.95; H, 3.64; Fe, 12.5; N, 12.64; O, 25.20. $\text{C}_{17}\text{H}_{16}\text{FeN}_4\text{O}_7$ calcd.: C, 45.96; H, 3.68; Fe, 12.5; N, 12.61; O, 25.21%)

Tricarbonyl(trans-3-propenyl-2-cyclohexenone)iron (IXa)

trans-3-Propenyl-2-cyclohexenone^{2c} (1.2 g, 8.8 mmol) was heated at reflux with 7 g of $\text{Fe}_2(\text{CO})_9$ (19 mmol) under nitrogen in diethyl ether for 17 h. After filtration, ether was removed on a rotary evaporator leaving an oil which was purified by chromatography on alumina exactly as (VIc) (see above). Four recrystallizations from 10 ml portions of hexane gave (IXa) as 0.8 g (30% yield) of orange crystals: m.p. $86-87.2^\circ$; IR (CCl_4) 2050, 1980 ($\text{C}\equiv\text{O}$) and 1680 cm^{-1} ($\text{C}=\text{O}$). A 2,4-dinitrophenylhydrazone derivative prepared in the usual way²⁷ was separated into 2 components by preparative TLC. The uppermost band on crystallization from ethyl acetate gave red crystals: m.p. 191° (dec.); UV λ_{max} (CHCl_3) 397 nm (ϵ 41,500). (Found: C, 47.45; H, 3.63; Fe, 12.1; N, 12.80; O, 24.47. $\text{C}_{18}\text{H}_{16}\text{FeN}_4\text{O}_7$ calcd.: C, 47.37; H, 3.53; Fe, 12.24; N, 12.28; O, 24.58%)

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