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Carbonium ion stabilization by (η^5-cyclopentadienyl)dicarbonylnitrosylchromium; a ^{1}H and ^{13}C NMR study

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Abstract

The ^{1}H and ^{13}C NMR spectra of a series of (η^5-cyclopentadienyl)dicarbonylnitrosylchromium-substituted carbonium ions have been determined. These data suggest that the same mechanism is responsible for the stabilization of carbonium ions by (η^5-cyclopentadienyl)dicarbonylnitrosylchromium as is operational in the analogous ferrocene and cymantrene complexes.

Introduction

In the course of early investigations on the organic chemistry of ferrocene derivatives it was discovered that α-hydroxyferrocene and vinylferrocenes exhibit unusual reactivity [1–3]. This enhanced reactivity has been attributed to the unusual stability of α-ferrocenylcarbonium ions. The great stability of α-metallocenylcarbonium ions has also been demonstrated by the isolation of stable salts of many of these cations [4].

Carbonium ions adjacent to metallo-aromatic centers have been the subject of considerable study. The vast majority of these studies have been completed on ferrocene analogs [5,6], however, carbonium ions adjacent to ruthenocene [1,7], osmocene [1,7], cymantrene [6,8], (η^6-benzene)tricarbonylchromium [9] and (η^4-cyclobutadiene)tricarbonyliron [10] have also been investigated but to a lesser extent.

The ^{1}H and ^{13}C NMR spectra of metallocenylcarbonium ions of ferrocene, cymantrene, benzenechromium tricarbonyl and cyclobutadieneiron tricarbonyl have been studied, in an attempt to elucidate the mechanism of stabilization of cationic

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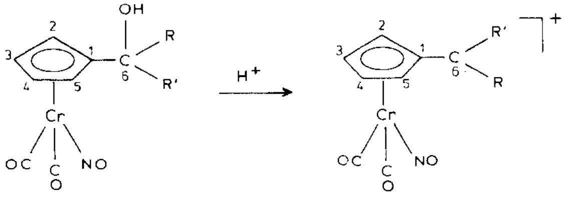
centers adjacent to metallo-aromatic systems [9–19]. We have previously reported that (η^5-cyclopentadienyl)dicarbonylnitrosylchromium is a strongly electron-donating group based upon the free radical polymerization of (η^5-vinylcyclopentadienyl) dicarbonylnitrosylchromium [20] and the acidity of (η^5-carboxycyclopentadienyl)dicarbonylnitrosylchromium [21]. We have also reported that alcohol and ketone groups adjacent to the cyclopentadienyl ring in (η^5-cyclopentadienyl)dicarbonylnitrosylchromium exhibit chemistry that is typical of highly stabilized carbonium ion intermediates in a manner analogous to that observed in ferrocene chemistry [21,22]. Recently England and Reeves [23] have reported the pK_{R^+} values of (η^5-cyclopentadienyl)dicarbonylnitrosylchromium-stabilized carbonium ions. We report here the ^1H and ^{13}C NMR spectra of (η^5-cyclopentadienyl)dicarbonylnitrosylchromium-stabilized carbonium ions.

Results and discussion

α-(η^5-Cyclopentadienyl)dicarbonylnitrosylchromium carbonium ions IB–VB were prepared by adding fluorosulfonic acid to cold solutions of the corresponding alcohols IA–VA in $CDCl_3$ under nitrogen in an NMR tube.

The ^1H NMR spectra of carbonium ions IB–VB are summarized in Table 1, along with $\Delta\delta$ values ($\Delta\delta = \delta(\text{ion}) - \delta(\text{alc})$ (ppm)). These resonances were assigned using the same technique as was previously described for the corresponding alcohols [21].



(A) (B)

I, R = H, R' = CH_3
II, R = H, R' = Ph
III, R = R' = CH_3
IV, R = CH_3, R' = Ph
V, R = R' = Ph

It is of interest to note that the proton NMR spectra of carbonium ions IB, IIB, and IVB, which were formed from the corresponding chiral alcohols, exhibit apparent diastereotopic ring protons, even though there is no longer a chiral center

Table 1

^1H NMR chemical shifts δ [a] ($\Delta\delta$) [b] of carbonium ions I–V in $FSO_3H/CDCl_3$

Ion	R	R'	C(2,5)	C(3,4)	$\overset{+}{C}H$	CH_3	Ph
IB	H	CH_3	5.35 (0.18) 4.69 (−0.40)	6.07 (1.19)	6.38 (1.75)	1.89 (−0.24)	
IIB	H	Ph	5.54 (0.25) 5.11 (0.50)	6.17 (1.21) 5.94 (0.98)	7.34 (1.85)		7.34 (−1.2)
IIIB	CH_3	CH_3	5.37 (0.23)	5.96 (1.16)		2.28 (0.89)	
IVB	CH_3	Ph	4.93 (−0.22) 5.40 (0.16)	5.93 (1.12)		2.27	7.21 (−0.07)
VB	Ph	Ph	5.34 (0.26)	5.97 (1.09)			7.22 (0.0)

[a] ppm from TMS in a capillary. [b] $\Delta\delta = \delta(\text{ion}) - \delta(\text{alc})$ (ppm).

Table 2

^{1}H NMR comparisons of α-ferrocenyl [a], α-cymantrenyl [b], and carbonium ions IB–VB [c]

R,	R′	Ferrocenyl [a]			Cymantrenyl [b]			IB–VB		
		H(2,5)	H(3,4)	H(6)	H(2,5)	H(3,4)	H(6)	H(2,5)	H(3,4)	H(6)
H	CH_3	4.49	6.21	7.12				5.35	6.07	6.38
		5.03	6.36					4.69		
H	Ph	4.77	6.24	8.09	5.45	6.12	7.4	5.11	6.17	7.34
		5.52	6.45		5.91			5.54	5.94	
CH_3	CH_3							5.37	5.96	
CH_3	Ph	4.76	6.24		5.74	6.34		4.93	5.93	
		5.18			6.16			5.40		
Ph	Ph				5.87	6.23		5.34	5.97	

[a] Ref. 13, 14. [b] 14. [c] This work.

in the molecule. Similar results have also been observed in analogous ferrocenyl [13,14] and cymantrenyl [14] carbonium ions. Hindered rotation about the C(1)–C(6) bond has been found in α-ferrocenyl and α-cymantrenyl carbonium ions [11–19], and the C(1)–C_{exo} bond in the analogous (η^4-cyclobutadiene)tricarbonyliron systems [10]. Similar hindered rotation in carbonium ions IB, IIB and IVB would induce chirality, and would thus account for the diastereotopic effects observed in their NMR spectra.

It is of interest to compare the proton NMR spectra of carbonium ions IB–VB with the analogously substituted ferrocene [13,14] and cymantrene [14] derivatives. The data in Table 2 indicate that the chemical shifts of the ring protons of carbonium ions IB–VB occur at lower field than the analogously substituted ferrocene derivatives, and at higher field than the analogously substituted cymantrenyl derivatives.

The carbon NMR spectra of alcohols IA–VA, are summarized in Table 3. The assignment of the carbon resonances of the cyclopentadienyl ring are based upon comparison of the ^{13}C–^1H coupled and decoupled NMR spectra, and on the basis that carbons C(2) and C(5) are expected to exhibit a greater diastereotopic effect than the more distant C(3) and C(4) carbons in alcohols IA, IIA, and IVA. Analogous assignments have been made unequivocally for 2,5-dideuteroferrocenyl alcohols [16]. The assignment of the other carbon resonances in these alcohols are based on a comparison of the ^{13}C–^1H coupled and decoupled spectra and on standard ^{13}C chemical shift data [24].

As is demonstrated in Table 3, the carbon NMR spectra of alcohols IIIA and VA in which R and R′ are the same, exhibit three cyclopentadienyl resonances. However, in alcohols IA, IIA, and IVA, which contain a chiral center, each cyclopentadienyl carbon produces a unique resonance, as both the C(2,5) and C(3,4) carbons exhibit diastereotopic behavior. These results are typical of similarly substituted cyclopentadienyl ring carbons in many other metallo-aromatic systems [11,14–16,19].

The carbon NMR spectra of carbonium ions IB–VB obtained in fluorosulfuric acid/$CDCl_3$ are summarized in Table 4, along with $\Delta\delta$ values ($\Delta\delta = \delta(\text{ion}) - \delta(\text{alc})$ (ppm)). These resonances were assigned using the same techniques as described for the corresponding alcohols (vide supra). Analogous assignments have been made unequivocally for 2,5-dideuteroferrocenyl carbonium ions [16].

Table 3

^{13}C NMR chemical shifts δ [a] of alcohols IA–VA in $CDCl_3$

Alcohol	R	R′	C(1)	C(3,4)	C(2,5)	COH	$(CO)_2$	C_{ipso}	C_o	C_m	C_p	CH_3
IA	H	CH_3	119.07	90.73	89.91	65.27	238.21					25.39
				90.04	89.77							
IIA	H	Ph	117.36	91.14	90.18	71.86	237.87	143.64	129.71	127.31	129.30	
				91.00	89.56							
IIIA	CH_3	CH_3	123.95	90.52	88.67	70.00	237.87					32.60
IVA	CH_3	Ph	122.92	92.03	89.29	73.30	237.53	147.62	128.96	125.66	128.00	32.05
				91.56	87.64							
VA	Ph	Ph	120.79	95.05	88.74	79.00	237.32	147.56	129.03	128.07	128.68	

[a] ppm from internal TMS.

Table 4

^{13}C NMR chemical shifts δ [a] ($\Delta\delta$) [b] of carbonium ions IB–VB in $FSO_3H/CDCl_3$

Ion	R	R′	C(1)	C(2)	C(5)	C(3)	C(4)	C^+	CO	C_{ipso}	C_o	C_m	C_p	CH_3
IB	H	CH_3	112.7	102.4	102.1	104.1	103.9	133.9	215.0					18.0
			(−6.4)	(11.7)	(12.1)	(14.2)	(14.1)	(68.6)	214.7					(−7.4)
									(−23.3)					
IIB	H	Ph	107.3	106.0	100.5	109.9	107.6	140.8	216.3	130.8	132.2	130.8	136.6	
			(−10.1)	(14.9)	(9.5)	(19.7)	(18.)	(68.9)	215.4	(−12.8)	(2.5)	(3.5)	(7.3)	
									(−22.0)					
IIIB	CH_3	CH_3	107.5	100.3		108.5		179.0	218.2					26.3
			(−16.4)	(9.8)		(19.8)		(109.)	(−19.7)					(−6.3)
IVB	CH_3	Ph	107.1	101.6	101.2	110.4	105.55	178.4	219.1	136.8	130.2	129.5	136.1	26.2
			(−15.8)	(9.6)	(9.7)	(21.1)	(17.9)	(105.1)	218.2	(−10.8)	(1.2)	(3.8)	(8.1)	(−5.8)
									(−18.9)					
VB	Ph	Ph	105.5	101.7		106.6		198.5	221.7	138.2	133.3	130.1	138.0	
			(−15.3)	(6.7)		(17.9)		(119.5)	(−15.6)	(−9.4)	(4.3)	(1.1)	(9.0)	

[a] ppm from TMS in a capillary. [b] $\Delta\delta = \delta(\text{ion}) - \delta(\text{alc})$ (ppm).

As is demonstrated by the data in Table 4, the carbon NMR spectra of carbonium ions IIIB and VB, in which R and R′ are the same, exhibit three cyclopentadienyl carbon resonances. However carbonium ions IB, IIB, and IVB, which were formed from the corresponding chiral alcohols exhibit five cyclopentadienyl carbon resonances, suggesting hindered rotation about the C(1)–C(6) bond in these ions, as previously described (vide supra). Similar diastereotopic effects have also been observed in the carbon NMR spectra of analogous ferrocenyl [11,16,19] and cymantrenyl [14] carbonium ions.

Carbon NMR spectroscopy allows the direct observation of the carbonium ion center as well as the carbons directly bonded to it, whereas the proton NMR spectroscopy is often limited to positions α or β to the cationic center. Solvent and anisotropy effects are significantly smaller than polarization effects on carbon NMR shifts. Therefore carbon NMR shifts have been found to be a good indication of π-electron density on carbon atoms of similar hybridization and substitution, whereas this is not necessarily true for proton NMR shifts [25,26]. Thus it is of interest to make a detailed comparison of the carbon NMR spectra of carbonium ions IB–VB with analogously substituted ferrocenyl and cymantrenyl carbonium ions. As is demonstrated by the data in Table 5, carbon NMR resonances due to the carbonium ion center, C(6), of carbonium ions IB–VB appear significantly downfield from those due to ferrocenyl carbonium ions of similar structure [14,16,19], and slightly upfield from those due to the analogous cymantrenyl carbonium ions [14,15]. From these data and the NMR theory of carbon chemical shifts [25,26], it follows that the π-electron density at the carbonium ion center decreases in the series ferrocenyl ≈ (η^5-cyclopentadienyl)dicarbonyltriphenylphosphinemanganese > (η^5-cyclopentadienyl)dicarbonylnitrosylchromium ≈ cymantrenyl > benzyl. The same general trend is seen in the pK_{R^+} values reported earlier [23].

In the carbon NMR spectra of ferrocenyl carbonium ions the signals due to the carbon atoms of the cyclopentadienyl ring appear downfield from the signals observed in the corresponding alcohols [14,16,19]. However, in the cymantrenyl carbonium ions described thus far [14,15] and in carbonium ions IB–VB described in this study, a downfield shift occurs only for the signals due to the carbons C(2)

Table 5

The values δ [a] and ($\Delta\delta$) [b] for the carbonium ion carbon in the ions of the AC^+RR' type

A	R = H, R′ = CH_3	R = H, R′ = Ph	R = R′ = CH_3	R = CH_3 R′ = C_2H_3	R = CH_3, R′ = Ph	R = R′ = Ph
Ferrocenyl [c]	119.5	121.5	158.6	160.6	158.6	
	(54.1)	(49.4)	(89.9)	(90.)	(86.7)	
IB–VB [d]	133.9	140.8	179.0		178.4	198.5
	(68.5)	(68.9)	(109.)		(105.1)	(119.5)
Cymantrenyl [e]		144.5		193.1	184.2	201.0
		(74.1)		(122.9)	(112.3)	(123.8)
Cymantrenyl [f] P(Ph)$_3$	115.8	121.2	155.6		157.0	168.8
	(51.2)	(50.0)	(86.4)		(84.5)	(91.1)
Phenyl [e]		199.7	253.4	260.0	228.3	210.9
		(123.5)	(180.3)	(187.0)	(157.8)	(131.5)

[a] ppm from TMS in a capillary. [b] $\Delta\delta = \delta(\text{ion}) - \delta(\text{alc})$ (ppm). [c] Ref. 11. [d] This work. [e] Ref. 14. [f] Ref. 15.

Table 6

The values of $\Delta\delta$ [a] for the C(1) carbon of the cyclopentadienyl ring in the A-radical of the carbenium ions of the AC$^+$ RR′ type

A	R = H, R′ = CH	R = H, R′ = Ph	R = R′ = CH$_3$	R = CH$_3$, R′ = C$_2$H$_5$	R = CH$_3$, R′ = Ph	R = R′ = Ph
Ferrocenyl [b]	12.5	7.1	1.2		−2.1	
IB–VB [c]	−6.4	−10.1	−16.4		−15.8	−15.3
Cymantrenyl [d]		−9.9		−16.3	−15.7	−14.7
Cymantrenyl [e] P(Ph)$_3$	−8.4	−11.4	−17.2		−16.2	−10.2
Phenyl [d]	−6.5	−10.5	−11.3		−6.4	−9.3

[a] $\Delta\delta = \delta(\text{ion}) - \delta(\text{alc})$ (ppm). [b] Ref. 11. [c] This work. [d] Ref. 14. [e] Ref. 15.

through C(5). An upfield shift occurs for the signal of the C(1) carbon, on going from the alcohol to the corresponding carbonium ion (Table 6).

It is of interest to compare the carbonyl region of the carbon NMR spectra of IB–VB and cymantrenyl carbonium ions as depicted in Table 7. Two important observations can be made from this data: first the metal carbonyl chemical shifts of I–V are much more sensitive to the change in going from an alcohol to the corresponding carbonium ion than are corresponding cymantrenyl carbonyl resonances. Second, IB–VB are the only reported metallo-aromatic carbonium systems to exhibit diastereotopic carbonyl resonances at ambient temperatures. The observed diastereotopic effect suggests hindered rotation about the cyclopentadienylchromium axis as well as about the C(1)–C(6) bond. The only other example of a diastereotopic effect of this kind is reported for (η^5-cyclopentadienyl)carbonyldiphosmanganese, in which the phosphorus NMR spectrum exhibits two phosphorus resonances.

The data presented in this paper clearly indicate hindered rotation about the C(1)–C(6) bond in IB–VB. It also suggests that the mode of stabilization operating in these carbonium ions is very similar in nature to that which occurs in the isoelectronic ferrocenyl and cymantrenyl carbonium ions.

Experimental

All operations were conducted under nitrogen. ^{1}H NMR spectra were recorded on a Varian A-60 (60 MHz) spectrometer and are referenced to TMS in a capillary

Table 7

The δ [a] and ($\Delta\delta$) [b] for the metal carbonyl carbon in the ions of the AC$^+$ RR′ type

A	R = H, R′ = CH$_3$	R = H, R′ = Ph	R = R′ = CH$_3$	R = CH$_3$, R′ = Ph	R = R′ = Ph
IB–VB [c]	215.0 214.7 (−23.3)	216.3 215.4 (−22.)	218.2 (−19.7)	219.1 218.2 (−18.9)	221.7 (−15.6)
Cymantrenyl [d]		214.2 (−9.7)		215.4 (−8.3)	217.1 (−7.3)
Cymantrenyl [e] P(Ph)$_3$	223.0 (−9.9)	222.7 (−10.0)	224.4 (−8.9)	223.5 (−9.3)	224.3 (−7.6)

[a] ppm from TMS in a capillary. [b] $\Delta\delta = \delta(\text{ion}) - \delta(\text{alc})$ (ppm). [c] This work. [d] Ref. 14. [e] Ref. 15.

tube suspended in the NMR tube. ^{13}C NMR spectra were recorded on a JEOL FX-100 (25.1 MHz) using a pulse width of 9 μs (74°) with a pulse delay of 1 s and proton decoupling. The spectra were referenced to TMS in a capillary tube suspended in the NMR tube. The (η^5-cyclopentadienyl)dicarbonylnitrosylchromium carbonyls used in this study were prepared by literature procedures [21].

Samples for ^1H NMR spectra were prepared by adding approximately 0.2 ml of fluorosulfonic acid to a degassed solution of alcohol (50–60 mg) in 0.2 ml of $CDCl_3$ in an NMR tube under nitrogen at −40°C. The sample was then allowed to warm to room temperature, and the proton NMR spectrum recorded at 34°C. The samples for ^{13}C NMR were prepared in a manner similar to that used above, however, 100–120 mg of alcohol was used to prepare the sample.

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