$\nu(O_2)$ of these complexes is observed around 890 cm^{-1}, confirming the presence of a coordinated peroxo group in the complexes. The coordinated OH gave a broad band around 3200 cm^{-1}. The molar conductivities of these complexes in aqueous solution are 392 and 380 Ω^{-1} cm^2 mol^{-1} respectively for the EDTA and the HEDTA complexes. In the solid state the complexes are diamagnetic at room temperature. Detailed solution EPR studies of the complexes are in progress. There seems to be a spin pairing of the two unpaired spins on ruthenium(IV) by an antiferromagnetic interaction. In basic solution the complex $[(Ru(EDTA))_2(OH)(O_2)]^{3-}$ is reversible with respect to oxygen uptake on heating. The solutions on losing O_2 give electronic spectra similar to those of Ru^{III}–EDTA complexes. The coordinated dioxygen in this complex cannot however be removed by purging N_2 or argon through the solution.

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Registry No. $[(RuEDTA)_2(OH)(O_2)](Et_4N)_3$, 80738-13-2; $[(RuHEDTA)_2(OH)(O_2)](Et_4N)_3$, 80764-28-9.

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Calculation of the ^{13}C NMR Paramagnetic Shielding in Tricarbonylcyclodienyliron(1+) Cations

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The generally unsatisfactory nature of the theory of ^{13}C NMR shifts in organometallic systems is well documented.[1,2] In a previous paper,[2] it was shown that calculations of the ^{13}C NMR paramagnetic shielding constants of the isoelectronic series tricarbonyl(η-benzene)chromium, tricarbonyl(η-cyclopentadienyl)manganese, tricarbonyl(η-cyclobutadiene)iron, tricarbonyl(η-allyl)cobalt, and tricarbonyl(η-ethylene)nickel using the self-consistent charge and configuration molecular orbital method[2] and the Pople–Karplus equation[3] correlated the observed downfield shifts of the carbonyl ligands and the upfield shifts of the ring carbon atoms in terms of the paramagnetic shielding constant σ^p, without recourse to considering variations in the diamagnetic term σ^d. Changes in the calculated values of σ^p within the above series involved changes in the three terms ΔE, $\langle r^{-3}\rangle_{2p}$, and $\sum Q_{AB}$ of the Pople–Karplus equation

$$\sigma^p = -\frac{K}{\Delta E}\langle r^{-3}\rangle_{2p}\sum Q_{AB}$$

where K is a constant, ΔE is the average excitation energy, $\langle r^{-3}\rangle_{2p}$ is the expectation value of the inverse cubed radius of the 2p orbital, and Q_{AB} involves bond-order/density matrix terms.[3] Our calculations showed clearly that variations in all three terms occur, and so purely qualitative discussions based on the above equation are not likely to be very successful.

Even since publication of our paper, there have been further

Table I. ^{13}C Shielding in $[BFe(CO)_3]^+$, CO, and $(C_6H_7)^+$

	carbonyl ^{13}C shielding			ring ^{13}C shielding							^{13}C shielding in free ligand			
					C_6H_7			C_7H_9				$(C_6H_7)^+$		
	C_5H_5	C_6H_7	C_7H_9	C_5H_5	C_3	$C_{2/4}$	$C_{1/5}$	C_3	$C_{2/4}$	$C_{1/5}$	CO	C_3	$C_{2/4}$	$C_{1/5}$
ΣQ_{AB}	1.176	1.175	1.169	1.419	1.422	1.427	1.360	1.427	1.413	1.374	1.333	1.433	1.525	1.438
$\langle r^{-3}\rangle_{2p}$	1.338	1.336	1.335	1.303	1.303	1.304	1.299	1.303	1.303	1.292	1.320	1.337	1.322	1.337
$(\Delta E)^{-1}$	0.349	0.420	0.539	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.245	0.2	0.2	0.2
σ^p	−530.1	−635.5	−812.1	−57.0	−357.8	−359.3	−341.1	−359.0	−356.3	−343.0	−416.2	−369.9	−389.3	−371.2
δ(exptl)	−202.7[a]	−208.12[b]	−207.89[b]	−90.9[a]	−89.0[b]	−101.35[b]	−63.74[b]	−99.43[b]	−102.60[b]	−92.58[b]	−181.3[c]	−180.7[d]	−138.7[d]	−180.7[d]

[a] Reference 13. [b] Reference 7. [c] Reference 14. [d] Estimated value from ref 15.

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illustrations of the limitations of the qualitative approach. For example, a recent discussion[4] of ^{13}C shifts in the series $CpFe(CO)LC(O)R$ ($L = CO, PR_3, P(OR)_3, CH_3NC$; $R = CH_3$, p-$C_6H_4OCH_3$) assumed that variations in ΔE were important in constrast to treatments in earlier studies[5] of similar systems in which ΔE was taken as constant. Similarly, a discussion[6] of the ^{13}C shifts in chalcocarbonyl complexes, e.g., $C_6H_6Cr(CO)_2CX$ ($X = O, S, Se$), again considers the ΔE term dominant but accounts for different correlations between ^{13}C shifts and the vibrational force constant k_{CO} (with varying X) in the series by the suggestion that the size of the carbon 2p atomic orbital could increase as the extent of the metal–CO back-bonding increases, thereby opposing the ΔE factor.

In this note we report calculations of ^{13}C shifts for the closely related tricarbonylcyclodienyliron(1+) cations $[BFe(CO)_3]^+$, $B = C_5H_5, C_6H_7, C_7H_9$, which provide a more stringent test of the above theoretical approach than the previous series since in the six- and seven-membered ring complexes there is considerable variation of ^{13}C shift within the ring carbon atoms that has previously been interpreted in terms of electron density.[7]

Method

The self-consistent charge and configuration molecular orbital method SCCCMO($\sigma + \pi$) was identical with that employed previously.[2] Experimental geometry was used for $[C_5H_5Fe(CO)_3]^+$,[8] and the structure for $[C_6H_7Fe(CO)_3]^+$ was taken from the analogous manganese compound.[9] The geometry of hexacarbonyl(*trans*-azulene)dimanganese[10] was modified to give a structure for the seven-membered ring cation. The same Fe–C(ring) distance of 2.1 Å[8] was used throughout. $\sum Q_{AB}$ values were calculated with use of the method of Pople and Karplus while the $\langle r^{-3}\rangle_{2p}$ values ($\zeta^3/3$ where ζ = orbital exponent) were calculated by modifying the neutral-atom exponent to allow for the charges on the carbon atoms. SCCCMO($\sigma + \pi$) calculations were also performed on the free carbon monoxide and the free cyclohexadienyl cation. For the CO the experimental geometry was used,[11] and the geometry of $(C_6H_7)^+$ was based on the experimental geometry of $[C_6(CH_3)_7]^+$.[12]

The values of ΔE for the free carbon monoxide ligand and for the carbonyls in $[BFe(CO)_3]^+$ were taken from energy-level differences as was done previously.[2] ΔE for the ring was 5.0 eV in $[BFe(CO)_3]^+$ and in the free ligand B. This constant value is reasonably close to the constant value (6.0 eV) in the previous work,[2] and thus consistency is ensured.

Results and Discussion

The calculated values of σ^p in the series $[BFe(CO)_3]^+$, $B = C_5H_5, C_6H_7$, or C_7H_9, are given in Table I together with the calculated $\sum Q_{AB}$, $\langle r^{-3}\rangle_{2p}$ and $(\Delta E)^{-1}$ values. Experimental values of δ are also listed. The corresponding values for the free CO and $(C_6H_7)^+$ ligands are included also. Comparison of the calculated values of σ^p for the above series and the free CO ligand again shows calculated *downfield* shifts in the ^{13}C carbonyl spectra of these complexes although the observed shifts show very little variation within the $[BFe(CO)_3]^+$ series; however, $[C_5H_5Fe(CO)_3]^+$ has both the predicted and the calculated least downfield shift. Again as in the previous calculations,[2] the calculated shielding constant involves variations in all three terms of the Pople–Karplus equation, reinforcing our previous conclusion that "qualitative discussions of ^{13}C shifts are not likely to be successful because of the necessity of taking into account all three terms in the Pople–Karplus formula".[2]

It is most gratifying that the SCCCMO theory applied to the Pople–Karplus equation again predicts an *upfield* shift of the complexed ring carbon atoms relative to free $(C_6H_7)^+$ and that the variation of these shifts with the ring carbon atom position agrees with the observed pattern. For example, in $[C_6H_7Fe(CO)_3]^+$, the order of both the calculated paramagnetic shielding (σ^p) and δ(experimental) is

$$C_{2/4} < C_3 < C_{1/5}$$

and for $[C_7H_9Fe(CO)_3]^+$ the order is

$$C_3 \approx C_{2/4} < C_{1/5}$$

These results for the $[BFe(CO)_3]^+$ series provide further evidence in support of our theoretical approach[2] and give us added confidence in the basic assumptions that in a series of closely related molecules both the diamagnetic shielding σ^d and the circulation on distant atoms σ' can be considered effectively constant.

Registry No. $[C_5H_5Fe(CO)_3]^+$, 32660-74-5; $[C_6H_7Fe(CO)_3]^+$, 49654-90-2; $[C_7H_9Fe(CO)_3]^+$, 46238-85-1; CO, 630-08-0; $(C_6H_7)^+$, 26812-57-7.

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