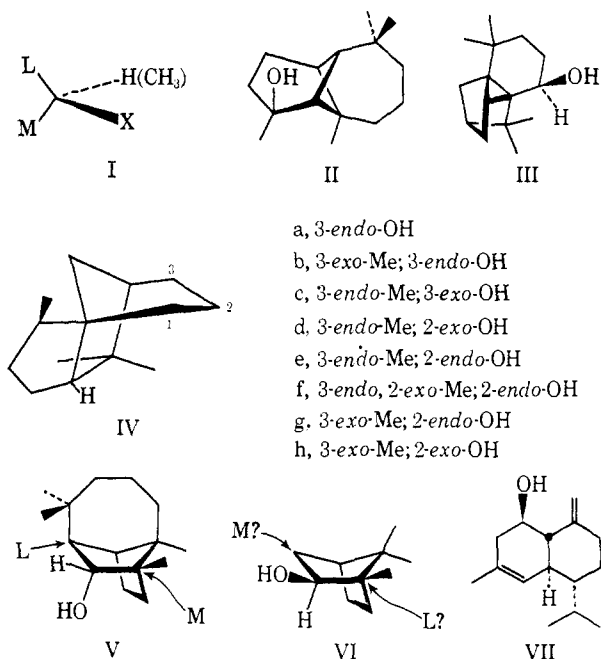


Figure 1. The induction of CD at ca. 525 nm on sequential addition of chiral donors to $\text{Eu}(\text{FOD})_3$. The solvent is CCl_4 , except in the case of longiborneol (CHCl_3). The different curves are not to scale. The insert shows an actual trace for the $\text{Eu}(\text{FOD})_3$ - α -phenethylamine system. Menthol and phenethylamine illustrate cases in which the 1:1 complex has a weaker CD effect of the same sign as the 2:1 complex. The opposite is observed in the case of longiborneol.

0.04–0.17 M in the limiting complex component. This generally implies the use of the less hindered, more soluble, FOD reagents. In addition the narrow lines (see Figure 1) can only be recorded accurately at slow sweeps (<2 nm/min). Second, additional CD bands are induced in this region; we take the largest one observed in the range 523.5–526.5 nm for this correlation. Third, detailed analysis of ψ induced *vs.* molar ratio plots (Figure 1) reveals the two stages of complexing⁹ and that in certain cases the 1:1 complex can have a CD effect in the opposite sense of the 2:1 complex (for example neoisothujanol in the figure or entries 14 and 28 from the table). It is thus possible for a strong CD effect of a relatively stable 1:1 complex to mask the opposing effect of the 2:1 complex at all molar ratio values studied. In such cases a complete curve analysis is required. Entries 12 and 22, apparent exceptions to the sign rule, likely deviate due to this effect. Fourth, the method should not be applied to polyfunctional compounds since donor groups that are locally symmetric can induce CD effects due to more distant asymmetric centers.

At present, of 32 chiral alcohols examined only two (entries 4 and 8) do not display CD effects large enough for a dependable assignment, 24 correlate based on the normal sequence rule, two (entries 12, 22) appear exceptional due to an unusually strong CD associated with the 1:1 complex. The four remaining examples, the borneols (V, VI), illustrate the need for consideration of steric requirements rather than the Cahn–Ingold–Prelog sequence rule. In the case of the sesquiterpenes we assume that the bulky *exo* substituent increases the steric requirement of the tertiary carbon making it “larger than” the quaternary center; thus the large

(9) The determination of sequential binding constants and stoichiometry by the nmr method still appears to be a difficult task with a complicated four-parameter analysis required for each set of proton shifts; see B. L. Shapiro and M. D. Johnston, Jr., *J. Amer. Chem. Soc.*, **94**, 8185 (1972). In contrast ψ_{induced} *vs.* ρ plots yield binding constants readily without computer curve fitting due to the expected large difference in $[\theta]$ for complexes of different stoichiometry: N. H. Andersen and A. Moore, to be submitted for publication.



CD effects observed correlate with the sign rule. For the terpenes we find no obvious steric basis for reversing the normal sequence rule; borneol and isoborneol stand as exceptions to the rule.¹⁰ The more limited data for amines suggest extension of the rule to the amino donor group.

With this method, shift reagent studies can now serve to define both relative and absolute configuration in natural product studies.

Acknowledgment. This work was partially supported by National Institutes of Health Grant GM-18143.

Supplementary Material Available. A listing of induced CD for $\text{Eu}(\text{FOD})_3$ -chiral ligand complexes will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D. C. 20036. Remit check or money order for \$3.00 for photocopy or \$2.00 for microfiche, referring to code number JACS-74-603.

(10) It is worth noting that borneol is the only exception to the MTPA ester correlation.^{6b}

(11) Alfred P. Sloan Foundation Fellow.

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Organocobalt Cluster Complexes. XIII. Nuclear Magnetic Resonance Spectroscopic Evidence Concerning the Stabilization of (Nonacarbonyltricobalt)carbon Substituted Carbonium Ions¹

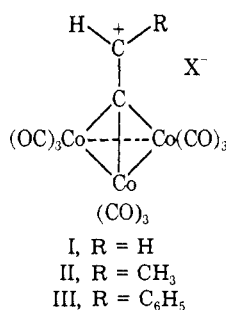
Sir:

We have reported recently² concerning the preparation, isolation and reactivity of the carbonium ion salts

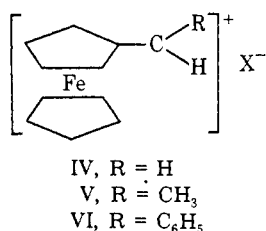
(1) Part XII: D. Seyferth, J. E. Hallgren, R. J. Spohn, G. H. Williams, M. O. Nestle, and P. L. K. Hung, *J. Organometal. Chem.*, in press.

(2) D. Seyferth, G. H. Williams, and J. E. Hallgren, *J. Amer. Chem. Soc.*, **95**, 266 (1973).

I, II, and III ($X = PF_6^-$). All three appeared to be un-



usually stable. We report here concerning the application of proton and carbon-13 nmr spectroscopy to the study of these carbonium ions. The results provide dramatic evidence for stabilization of these carbonium ions through charge delocalization into the CCo₃ cluster system. To provide a more quantitative picture, we have compared the ¹H and ¹³C nmr spectroscopic parameters of I, II, and III ($X = HSO_4^-$) with those of the corresponding ferrocenylmethyl carbonium ions, IV, V, and VI, whose extraordinary and amply



demonstrated stability has been the subject of much discussion and some controversy.³

Table I summarizes the proton chemical shifts for I, II, and III and for the alcohols from which these were derived by treatment with concentrated sulfuric acid or trifluoroacetic acid. In addition, [(OC)₉Co₃CCHCH₃]⁺PF₆⁻ was prepared as the pure solid² and the proton nmr spectrum of its freshly prepared solution in nitromethane was examined.

The hydrogens α to the CCo₃ cluster become less shielded on going from the alcohols to the carbonium ions, but the shifts are not at all large, compared to those observed in other less stabilized systems (e.g., Me₂CHOH \rightarrow Me₂C⁺H, $\Delta\delta = 8.5$ ppm⁴). A comparison of the chemical shifts of the protons bonded to the carbonyl carbon atoms in I, II, and III with those of the analogous carbonyl protons in IV, V, and VI^{3a,5} (R = H, 5.75 ppm; R = CH₃, 7.03 ppm; R = Ph, 7.92 ppm) shows striking similarities and this suggests a similar degree of stabilization for I, II, and III.

The carbon-13 nmr spectra of I, II, and III were more informative. Olah⁶ has used the chemical shifts of carbon resonances in ¹³C nmr spectra as a measure of the electron densities of the carbon atoms being studied, and thus a comparison of the carbonyl carbon resonances of I, II, and III with those of the alcohols

(3) Recent papers which provide references to earlier literature: (a) J. J. Dannenberg, M. K. Levenberg, and J. H. Richards, *Tetrahedron*, **29**, 1575 (1973); (b) S. Lupan, M. Kapon, M. Cais, and F. H. Herbstein, *Angew. Chem.*, **84**, 1104 (1972); (c) R. Gleiter, R. Seeger, H. Binder, E. Fluck, and M. Cais, *ibid.*, **84**, 1107 (1972).

(4) G. A. Olah, E. B. Baker, J. C. Evans, W. S. Tolgyesi, J. S. McIntyre, and I. J. Bastien, *J. Amer. Chem. Soc.*, **86**, 1360 (1964).

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Table I. Proton Nuclear Magnetic Resonance Spectra of (OC)₉Co₃CCH(R)OH and (OC)₉Co₃CCHR⁺X⁻ ^a

Alcohol, δ (ppm)	Cation, δ (solvent) (ppm)	$\Delta\delta$, ppm
(OC) ₉ Co ₃ CCH ₂ OH	(OC) ₉ Co ₃ CCH ₂ ⁺	
CH ₂ 5.21	5.8 (H ₂ SO ₄)	-0.6
	5.7 (CF ₃ CO ₂ H)	-0.5
(OC) ₉ Co ₃ CCH(CH ₃)OH	(OC) ₉ Co ₃ CCHCH ₃ ⁺	
CH 5.4	6.7 (H ₂ SO ₄)	-1.3
	6.9 (CF ₃ CO ₂ H)	-1.5
	6.9 (PF ₆ ⁻ salt in CH ₃ NO ₂)	-1.5
CH ₃ 1.8	2.4 (H ₂ SO ₄)	-0.6
	2.5 (CF ₃ CO ₂ H)	-0.7
	2.4 (PF ₆ ⁻ salt in CH ₃ NO ₂)	-0.6
(OC) ₉ Co ₃ CCH(C ₆ H ₅)OH	(OC) ₉ Co ₃ CCHC ₆ H ₅ ⁺	
CH 6.2	7.7 (H ₂ SO ₄)	-1.5
	8.2 (CF ₃ CO ₂ H)	-2.0
C ₆ H ₅ 7.4	7.2 (H ₂ SO ₄)	+0.2
	7.6 (CF ₃ CO ₂ H)	-0.2

^a Alcohol spectra were obtained in chloroform-*d* and are referenced to internal tetramethylsilane. Cation spectra are referenced to tetramethylsilane contained in a capillary inside the nmr tube. The methyl group signal for the methyl-substituted carbonium ions (in nitromethane, sulfuric acid, and trifluoroacetic acid) was a doublet ($J = 7$ Hz). The methyne proton for these same carbonium ions appears as a quartet ($J = 7$ Hz). For the phenyl-substituted and unsubstituted carbonium ions, the methyne proton and methylene proton signals (respectively) were singlets.

from which they were derived should give an indication of the degree of charge delocalization in these carbonium ions.

Table II shows the pertinent ¹³C nmr data for I, II,

Table II. Carbon-13 Nuclear Magnetic Resonance Spectra for (OC)₉Co₃CCH(R)OH and (OC)₉Co₃CCHR⁺HSO₄⁻ ^a

	Alcohol (ppm)	Cation (ppm)	Δ , ppm
	(OC) ₉ Co ₃ CCH ₂ OH	(OC) ₉ Co ₃ CCH ₂ ⁺ HSO ₄ ⁻	
Carbonyl carbon	77.6	91.1	-13.5
C≡O	200.6	192.7	+7.9
	(OC) ₉ Co ₃ CCH(CH ₃)OH	(OC) ₉ Co ₃ CCHCH ₃ ⁺ HSO ₄ ⁻	
Carbonyl carbon	82.5	119.9	-37.4
CH ₃	28.5	26.2	+2.3
C≡O	200.5	193.2	+7.2
	(OC) ₉ Co ₃ CCH(C ₆ H ₅)OH	(OC) ₉ Co ₃ CCH(C ₆ H ₅) ⁺ HSO ₄ ⁻	
Carbonyl carbon	88.8	124.5	-35.7
Ph-C ₁	146.2	135.4	+10.8
Ph-C ₂	128.8	129.9	-1.1
Ph-C ₃	126.8	129.3	-2.5
Ph-C ₄	128.6	132.6	-4.0
C≡O	200.0	192.4	+7.6

^a Alcohol spectra are referenced to internal tetramethylsilane. Cation spectra are referenced to external tetramethylsilane through the ¹⁹F lock signal. All cation spectra were obtained in concentrated sulfuric acid as solvent. All spectra were proton decoupled.

and III and their parent alcohols.⁷ Noteworthy is how small the changes in the carbonyl carbon chemical shifts are on going from the alcohol to the carbonium

(7) Positive values indicate decreased shielding relative to tetramethylsilane. Carbon-13 nmr spectra were obtained in the Fourier transform mode utilizing a Bruker HFX-90 spectrometer interfaced with a Digilab FTS-NMR-3 data system. Chemical shifts are accurate to ± 0.1 ppm.

Table III. Carbinyl Carbon ^{13}C Resonances in IV, V, and VI^{a,b}

R =	Alcohol (ppm)	Carbonium ion (ppm)	$\Delta\delta$, ppm
IV, H	60.6	86.8	-26.2
V, CH ₃	65.5	117.6	-52.1
VI, C ₆ H ₅	72.1	121.5	-49.4

^a From ref 12. ^b Alcohol spectra are referenced to internal TMS, cation spectra (in concentrated sulfuric acid) to external TMS through the ^{19}F lock signal.

ion, smaller even than the comparable changes, $\Delta\delta$, in the ferrocenylcarbinyl series (Table III). By way of comparison, $\Delta\delta$ for the carbinyl carbon atom when Me_2CHOH is converted to $\text{Me}_2\text{CH}^+[\text{SbF}_6]^-$ is 255.3 ppm.⁶ Upon examination of Tables II and III, we note that the chemical shifts of the carbinyl carbon atoms in both series of carbonium ions follow the normal order observed when substituents on a fully substituted carbon atom are varied from R=H (most shielded) to CH₃ to Ph (least shielded), rather than for substituents on an electron-deficient trivalent carbon atom, where the CH₃-substituted carbon atom is less shielded than the analogous Ph-substituted carbon atom.⁸ These results are a rather clear-cut indication that the carbinyl carbon atoms in I, II, and III are nearly fully bonded and only slightly electron deficient. The slight increase in shielding of the CH₃-carbon when II is formed from the alcohol and of the C-1 carbon of the phenyl group in III provides further confirmation of this.

The data in Table II suggest that the positive charge in I, II, and III has been delocalized to a large extent onto the cobalt atoms. The observed slight increase in shielding of the carbon atoms of the carbon monoxide ligands when the alcohols are converted to the carbonium ions speak in favor of this view. If the cobalt atoms are more electron deficient in the cations I, II, and III than in the corresponding alcohols, then the carbon monoxide ligands would be expected to be bonded more tightly in the cations. The consequent movement of the CO carbon atoms to a position closer to the cobalt atoms might be expected to result in increased shielding due to the diamagnetic anisotropic shielding effect of the cobalt atoms. Any change in chemical shift of the apical carbon atom of the CCO_3 cluster on going from the alcohol to the carbonium ion remains unknown since a signal due to this carbon atom was not observed in the ^{13}C nmr spectra of the alcohols and the carbonium ions. This is readily understandable; the line for this carbon atom would be broadened by the adjacent cobalt atoms (nuclear quadrupole broadening) and the three adjacent cobalt atoms would split this line into a 22-line pattern.⁹

On the basis of a comparison of the $\Delta\delta$ values in Tables II and III it is tempting to suggest that I, II, and III are somewhat more stabilized than IV, V, and VI. While this conclusion may not be valid, the $(\text{OC})_3\text{Co}_3\text{C}$ -substituted carbonium ions certainly appear to be at least as stabilized as the corresponding ferrocenylmethyl carbonium ions. While stabilization of π -complexed carbonium ions is a well-known phenomenon in transi-

tion metal-organic chemistry,¹⁰ stabilization of carbonium ions in σ -bonded organo transition metal structures is much less well documented.¹¹ In IV, V, and VI the ^{13}C nmr spectra suggest that the positive charge is delocalized onto all carbon atoms of both ligands and, in some part, onto the iron atom.¹² A different mechanism of charge delocalization must be operative in I, II, and III. All the observations discussed above are compatible with our previous proposal² that I, II, and III are stabilized to a high degree by σ - π conjugation, *i.e.*, lateral overlap between the vacant p orbital of the carbinyl carbon atom and the filled σ -bonding orbital involving the C-Co bond of the cluster.

Although much of the positive charge in I, II, and III appears to reside at the cobalt atoms, many nucleophiles attack these cations at the carbinyl carbon atoms.² It is significant, however, that I, II, and III are rather weak electrophilic reagents. This is indicated by the fact that they will undergo electrophilic aromatic substitution reactions with only highly nucleophilic aromatic substrates such as *N,N*-dimethylaniline and pyrrole. It is noteworthy also that triphenylphosphine, which might be expected to form stable phosphonium salts on reaction with I, II, or III at the carbinyl carbon atom, reacts with the hexafluorophosphate salts of these cations to give immediate decomposition with violent gas evolution. Presumably the site of attack is at cobalt rather than at the carbinyl carbon atom.

Acknowledgment. The authors are grateful to the National Science Foundation (NSF Grant GP 31429X) for generous support of this work.

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Synthesis of 1,4-Diketones by Reductive Coupling of α,α' -Dibromo Ketones

Sir:

1,4-Diketones are precursors of furans^{1a} and pyrroles^{1b} as well as thiophenes^{1c} in the widely applicable Paal-Knorr synthesis^{1d} and have also been used extensively as intermediates of natural products derived from cyclopentenones, especially jasmones, prostaglandins, and rethrolones.² During our work on allyl

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