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Preliminary communication

ORGANOCOBALT CLUSTER COMPLEXES

XIX*. NONACARBONYLTRICOBALTCARBON-SUBSTITUTED CARBONIUM IONS. FURTHER ^{13}C NMR DATA AND DISCUSSION

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Summary

By using either neat samples or very concentrated solutions in $CDCl_3$, the apical cluster carbon ^{13}C NMR resonances in some neutral $RCCo_3(CO)_9$ complexes have been observed in the region δ(C) 255-310 ppm. Apical cluster carbon atom resonances occur in the ^{13}C spectra of concentrated sulfuric acid solutions of $[(OC)_9Co_3CCRR']^+$ cations in the region δ(C) 255-286 ppm. Further discussion of the structure and bonding in these charged species is given.

We have reported and discussed the significance of the carbon-13 FT NMR spectra of $(OC)_9Co_3C$ cluster-substituted carbonium ions in a previous paper of this series. We noted that in these species, $[(OC)_9Co_3CCHR]^+$, signals due to all carbon atoms except the carbon atom in the Co_3C cluster were observed [2]. In theory, the signal due to the cluster carbon atom should be a 22 line pattern which, furthermore, would be broadened by the nuclear quadrupole moment of cobalt. Also, the generally limited solubility of the $RCCo_3(CO)_9$ complexes in organic solvents would add to these difficulties. In addition, the apical carbon atom might have too short a relaxation time to permit observation of its signal in solution. Further work, however, has defined conditions under which the cluster carbon atom resonances may be observed.

In our previous work, the ^{13}C NMR spectra were measured in solution (the neutral complexes in $CDCl_3$, the cationic complexes in concentrated sulfuric acid) at usual ^{13}C NMR concentrations (~ 0.25-0.5 *M*). Under these conditions, in the case of the neutral complexes, no signal due to the apical carbon atom could be seen. We have found that the apical cluster carbon atom signal may be observed

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*For part XVIII see ref. 1.

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best, as a broad multiplet ca. 40-50 Hz in width, in the region δ(C) 255-315 ppm downfield from tetramethylsilane when the ^{13}C NMR spectra of neat samples of the neutral compounds as oils or liquids are measured. When a small amount of $CDCl_3$ was added, the signal intensity decreased and with further dilution to ~ 1*M* the signal disappeared into the background noise.

A few of the alkylidynetricobalt nonacarbonyl complexes which we had prepared previously had melting points sufficiently low and/or solubilities in $CDCl_3$ sufficiently high for our purposes, and we prepared others containing long chain alkyl substituents on the α-carbon atom which were oils or low melting solids with good solubility.

The results obtained for the neutral $RCCo_3(CO)_9$ complexes are given in Table 1. These ^{13}C chemical shifts are far downfield from those of most carbon atoms in organic and organometallic compounds except for those of alkyl-substituted carbonium ions [3], some transition metal—carbene complexes (e.g., $(OC)_5CrC^{\star}(OMe)Ph$, δ(C*) 351.4 ppm [4]; $(OC)_5WC^{\star}(OEt)C{\equiv}CPh$, δ(C*) 286.1 ppm [5]) and —carbyne complexes (e.g., $CH_3C^{\star}{\equiv}W(CO)_4Cl$, δ(C*) 288.8 ppm [6]; $PhC{\equiv}C{-}C^{\star}{\equiv}W(CO)_4Br$, δ(C*) 230.6 ppm [5]). (The $RCCo_3(CO)_9$ complexes can, in principle, be regarded as adducts of a carbyne intermediate and the $Co_3(CO)_9$ unit, i.e., as triply-bridged carbyne complexes, as we have suggested before [7]. Indeed, the transfer of the carbyne ligand from $CH_3C{\equiv}Cr(CO)_4Br$ to cobalt in a reaction with dicobalt octacarbonyl to form the $CH_3CCo_3(CO)_9$ cluster has been reported recently [8]).

With the apical carbon chemical shifts in the neutral complexes now known, further investigation revealed also the apical carbon atom resonances in the ^{13}C NMR spectra of the cluster-substituted carbonium ions in concentrated sulfuric acid (Table 2). In only one case do we have comparative data for a cluster-substituted alcohol and the carbonium ion derived from it. In this example, the apical carbon atom becomes more shielded on going from the alcohol to the charged species, but the Δδ(C) (upfield) is relatively small, – 32.8 ppm. On the basis of this and the previous data [2], we conclude that the positive charge in these "carbonium" ions resides in large part on the cobalt atom. This would explain why these cations are such deactivated carbon-electrophiles. (For instance, they will alkylate *N,N*-dimethylaniline but not anisole [9]).

TABLE 1

^{13}C NMR SPECTRA OF SOME $RCCo_3(CO)_9$ COMPLEXES. APICAL CARBON ATOM RESONANCES [a]

R in $RCCo_3(CO)_9$	M.p. (°C)	δ(C) apical C atom, (ppm)	NMR sample
n-C_5H_{11}	72.5-75	305.6	$CDCl_3$ solution
n-$C_{10}H_{21}$	30-31	306.4	$CDCl_3$ solution
n-$C_9H_{19}CH(OH)$	46.5-47.5	306.0	$CDCl_3$ solution
$Me_3Si(H)C{=}CH$	53-54	283.0	$CDCl_3$ solution
n-$C_6H_{13}C(O)$	oil	276.3	neat sample
n-$C_9H_{19}C(O)$	oil	276.2	neat sample
$C_2H_5OC(O)$	45-46	258.4	neat sample
n-$C_{10}H_{21}OC(O)$	oil	257.6	$CDCl_3$ solution

[a] Positive values indicate decreased shielding relative to tetramethylsilane. ^{13}C 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 ± 0.2 ppm.

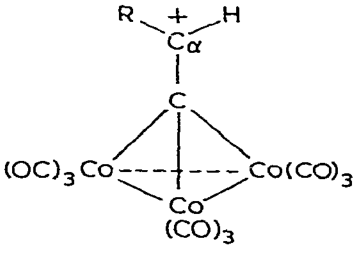
TABLE 2

^{13}C-NMR SPECTRA OF $(OC)_9Co_3C$-SUBSTITUTED CARBONIUM IONS. APICAL CARBON ATOM RESONANCES (In concentrated H_2SO_4) [a]

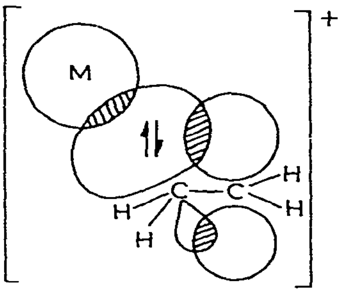
Carbonium ion	δ(C) apical C atom (ppm)
$[(OC)_9Co_3CCH_2]^+$	286.2
$[(OC)_9Co_3CCHCH_3]^+$	273.5
$[(OC)_9Co_3CC(CH_3)_2]^+$	257.8
$[(OC)_9Co_3CCHC_6H_5]^+$	267.0
$[(OC)_9Co_3CCHC_9H_{19}\text{-n}]^+$	273.2

[a] Cation spectra are referenced to external tetramethylsilane through the ^{19}F lock signal.

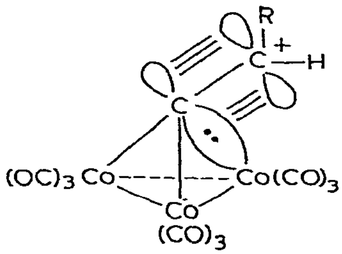
It is not yet clear how the charge delocalization implied by the NMR data occurs. In our initial report concerning these cationic complexes [9], we suggested that electron density could be supplied to the electron deficient α carbon atom by means of σ—π conjugation [10, 11], and for the sake of simplicity drew these cations in the carbonium ion form, I. Strictly speaking, "σ—π conjugation" is a vertical process in which the σ bond is delocalized without changing its bond length or angle [10]. The C—C—Co bond angle in $CH_3CCo_3(CO)_9$ is 131° [12], and this may be too large for effective conjugation of the type shown in its general form in II. Thus there may be some movement of the α carbon atom in I to reduce the C—C—Co bond angle so as to permit more effective lateral overlap, for which we may write III. Taken to its extreme, the picture shown in III, with such



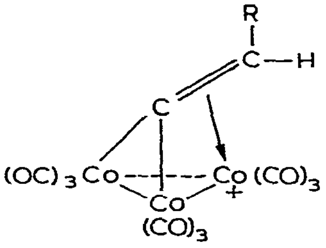
(I)



(II)

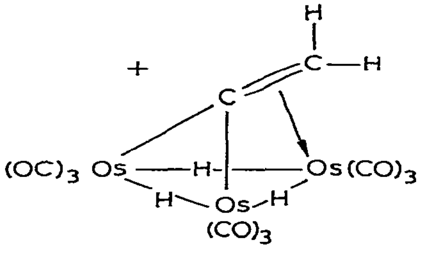


(III)



(IV)

nuclear movement, would lead to an olefin—metal cation π interaction, IV*. Proton NMR data obtained at – 10 °C indicated that such an interaction occurs in the related trihydridotriosmium nonacarbonyl-substituted cation, V [13] (however, at room temperature V is fluxional). If these cobalt cluster-stabilized carbonium ions are indeed cationic olefin complexes as depicted in IV, then one would expect to observe spin—spin coupling involving the *exo*-cluster carbon atom and the cobalt nucleus, $J(^{59}Co—^{13}C_\alpha)$, giving rise to an eight-line pattern for the C_α resonance. Although this is not seen, it may be significant that the α-carbon atom signals in the ^{13}C NMR spectra of all $[(OC)_9Co_3CCRR']^+$ ions are broader than those of the carbon atoms of alkyl substituents on the α-carbon atom. Thus the line width at half height for the C_α signal of $[(OC)_9Co_3CC_9H_{19}]^+$


(V)

was 25 Hz, as compared to the 5-12 Hz $W_{1/2}$ of the carbon atom signals of the C_9 chain. While this suggests that IV must be given serious consideration, no unambiguous experimental evidence is as yet available to distinguish between species with the apical substituent canted (III, IV) vs. I as the structure of our charged species. Upon the availability of suitable crystals of one of our carbonium ion salts, one may hope that X-ray crystallography will provide this information for the solid state structure, although the problem of its solution structure will remain.

We note that structure I remains a viable candidate for the $[(OC)_9Co_3CCHR]^+$ cations, as does the analogous symmetrical structure for the related acylium ion, $[(OC)_9Co_3CC{=}O]^+$ [14]. In the latter, the three cobalt-carbon framework orbitals of the cluster possess C_{3v} symmetry and transform as $a_1 + e$. The two π antibonding orbitals of the acylium CO are of e symmetry and appropriate for interaction with one of the filled e framework orbitals. This would provide a means whereby electron density would be transferred from the cluster to the electron-deficient CO group α to the CCo_3 cluster. A similar argument holds for the carbonium ions, in which electron density could be transferred to a vacant p orbital of e symmetry on electron-deficient α carbon atom.

It is clear that at the present time the question of the structure and bonding of the highly stabilized $[(OC)_9Co_3CCRR']^+$ cations remains unresolved.

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*This is the counterpart of the "bridging" transition state, in contrast to that stabilized by σ—π conjugation, a vertical process [10, 11]. It should be noted that both III and IV would be expected tobe fluxional species.

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References

11 D. Seyferth, M O. Nestle and A.T. Wehman, J. Amer. Chem. Soc., 97 (1975) in press.
2 D. Seyferth, G.H. Williams and D.D. Traficante, J. Amer. Chem. Soc , 96 (1974) 604.
3 J.B. Stothers Carbon-13 NMR Spectroscopy, Academic Press, New York, 1972, p. 217-238.
4 C.G. Kreiter and V. Formaček, Angew. Chem., 84 (1972) 155.
5 F.H. Kohler, H J. Kalder and E.O. Fischer, J. Organometal. Chem., 85 (1975) C19.
6 E.O. Fischer, G. Kreis, C.G. Kreiter, J. Müller, G. Huttner and H. Lorenz, Angew. Chem., 85 (1973) 618.
7 D. Seyferth, J.E. Hallgren, R.J. Spohn, A.T. Wehman and G H. Williams, XXIIIrd Intern. Congr. Pure and Appl. Chem., Special Lectures Pres. Boston, USA, 26-30 July 1971, Vol. 6, Butterworths, London, 1971, p. 133.
8 E.O. Fischer and A. Däweritz, Angew. Chem , 87 (1975) 360.
9 D. Seyferth, G.H. Williams and J E. Hallgren, J. Amer. Chem. Soc., 95 (1973) 266.
10 T.G. Traylor, W. Hanstein, H.J. Berwin, N.A. Clinton and R.S. Brown, J. Amer. Chem. Soc., 93 (1971) 5715.
11 T.G. Traylor, H J. Berwin, J. Jerkunica and M.L. Hall, Pure Appl. Chem., 30 (1972) 599.
12 P.W. Sutton and L.F. Dahl, J. Amer. Chem. Soc., 89 (1967) 261.
13 A.J. Deeming, S. Hasso, M. Underhill, A.J. Canty, B.F.G. Johnson, W.G. Jackson, J. Lewis and T.W. Matheson, J. Chem. Soc., Chem. Commun., (1974) 807.
14 D. Seyferth, J E. Hallgren and C.S. Eschbach, J. Amer. Chem. Soc., 96 (1974) 1730.