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Preliminary communication

ISOLATION, CHARACTERIZATION, AND STABILITY OF α-[(ETHYNYL)DICOBALT HEXACARBONYL] CARBONIUM IONS

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Summary

Stable carbonium ion salts of the type $[(HC{\equiv}CC^+R^1R^2)Co_2(CO)_6]Z^-$ ($R^1 = R^2 = CH_3$, $Z = SbF_6$; $R^1 = R^2 = C_6H_5$, $Z = SbF_6$; $R^1 = CH_3$, $R^2 = H$, $Z = BF_4$; $R^1 = R^2 = H$, $Z = BF_4$) were isolated upon treatment of the corresponding alcohol complexes with $HF\cdot SbF_5$ or $HBF_4\cdot Et_2O$ at —45°C. Extensive charge delocalization onto the $Co_2(CO)_6$ moiety of the cations was evidenced in the IR by an increase in ν(CO) and in the proton NMR spectra which exhibited very small downfield shifts relative to the alcohol precursors ($\Delta\delta$). The pK_{R^+} values for the cations were essentially the same regardless of other substituents at the carbonium ion center and were approximately equal to that of the triphenylmethyl cation.

The tremendously enhanced stability of carbonium ions adjacent to organotransition metal moieties has been demonstrated in a number of systems and interest continues regarding the magnitude and origin of this stabilization [1]. In an earlier report [2] we provided preliminary evidence for the stabilization of α-carbonium ion centers by the (ethynyl)dicobalt hexacarbonyl group from the facile acid-catalyzed dehydration of propargylic alcohol complexes (e.g. Ia ($R^1 = R^2 = CH_3$) → IIa) and from the protonation of Ia in trifluoro acetic acid to generate cation IIIa ($R^1 = R^2 = CH_3$). Seyferth and coworkers have also reported the facile Friedel—Crafts acylation of (diphenylacetylene)dicobalt hexacarbonyl and have studied extensively the related $(CO)_9Co_3CCRR^+$ system [4—6]. These systems are of particular interest since they possess unique structural features which may affect the extent and mechanism of charge delocalization.

We now report that ions IIIa ($R^1 = R^2 = CH_3$), IIIb ($R^1 = R^2 = C_6H_5$), IIIc ($R^1 = CH_3$; $R^2 = H$), and IIId ($R^1 = R^2 = H$) can be isolated as stable SbF_6^- or BF_4^- salts by treatment of propionic anhydride solutions of alcohols Ia—Id with an excess of $HF\cdot SbF_5$ (for Ia, Ib) or $HBF_4\cdot Et_2O$ (for Ic, Id) at —40°C. Addition of anhydrous ether and filtration at —40°C under

TABLE 1

^{1}H NMR SPECTRA OF $[\mathrm{H^aC{\equiv}CC(OH)R^1R^2}]\mathrm{Co_2(CO)_6}$ AND $[(\mathrm{H^aC{\equiv}CC^+R^1R^2})\mathrm{Co_2(CO)_6}]\mathrm{Z^-}$ [a]

		Alcohol δ (ppm)	Cation δ (ppm)	Δδ (ppm)
$R^1 = R^2 = CH_3$	R^1	1.5	2.2	−0.7
	H^a	6.2	7.6	−1.4
$R^1 = R^2 = C_6H_5$	R^1	7.4	7.6	−0.2
	H^a	6.7	8.2	−1.5
$R^1 = CH_3$; $R^2 = H$	R^1	1.5	2.2 (d, J 6 Hz)	−0.7
	R^2	5.0	6.6 (dq, ^1J 6 Hz; ^2J 2 Hz)	−1.6
	H^a	6.2	7.7 (d, J 2 Hz)	−1.5
$R^1 = R^2 = H$	R^1	4.7	5.3—5.5 (m) [b]	−0.7
	H^a	6.2	7.9 (d, J 2 Hz)	−1.7

[a] Spectra (90 MHz) of both alcohols and cations were obtained in SO_2 at −20°C and referenced to external TMS. [b] Appeared as two lines centered at 5.3 ppm and three lines centered at 5.5 ppm separated by 13 Hz at both 60 and 90 MHz.

nitrogen afforded the products as dark red or red-black solids in good yield (IIIa, 78%; IIIb, 64%; IIIc, 81%; IIId, 78%)*. Hydrolysis in the solid state by atmospheric moisture required several hours but was rapid in solution (ether/5% aqueous bicarbonate), regenerating the original alcohols almost quantitatively.

The IR spectra of IIIa—IIId in CH_2Cl_2 indicate significant charge delocalization onto the cobalt carbonyl moiety. The carbonyl absorptions of the alcohols which appear at 2025, 2050 and 2090 cm^{-1} (CH_2Cl_2) are shifted to 2085, 2105 and 2130 cm^{-1} (CH_2Cl_2) in the cations ($\Delta\nu$ ca. + 40—60 cm^{-1}). This shift indicates increased C—O bonding as would be expected from decreased d(Co) → π^*(CO) donation in the electron-deficient cations.

The ^{1}H NMR spectra of the salts proved very informative. Table 1 summarizes the spectra of ions IIIa—IIId and the precursor alcohols. The most striking feature of the NMR data is the very small downfield shifts of proton resonances in going from alcohols to carbonium ions (Δδ). These shifts are much less than in the uncomplexed propargyl systems [7] (e.g. $CH_3C{\equiv}CC(CH_3)_2OH \rightarrow CH_3C{\equiv}CC^+(CH_3)_2$, Δδ −2.3) but are comparable to those in some other metal-stabilized ions (e.g. $C_5H_5FeC_5H_4C^+HCH_3$, Δδ = −0.8 [8]; $(CO)_9Co_3CC^+HCH_3$, Δδ −0.6 [5]; $(CO)_3CrMeC_6H_4C^+HCH_3$, Δδ −1.0 [9]). While ^{1}H chemical shifts do not provide a reliable quantitative measure of charge density, the data presented here strongly suggest extensive charge dispersal in these cations.

The orientation of the carbonyl *p*-orbital (assuming sp^2 hybridization) relative to the cobalt atoms is pertinent to the mode of delocalization in the cations. In addition to the three static orientations presented in Fig. 1, dynamic structures involving interconversion between these by rocking or rotation might also be considered. While we cannot at this time conclude unequivocally

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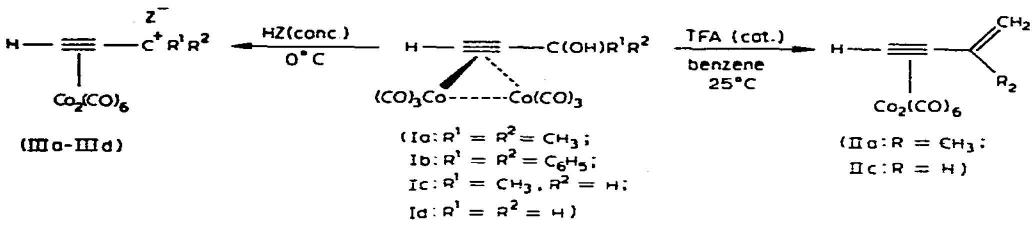
*Elemental analyses were obtained for IIIb and IIIc. Found: C, 34.7; H, 1.7; F, 15.7%. IIIb calcd.: C, 35.3; H, 1.6; F, 16.0. Found: C, 27.5; H, 1.3. IIIc calcd. C, 28.2; H, 1.2%.



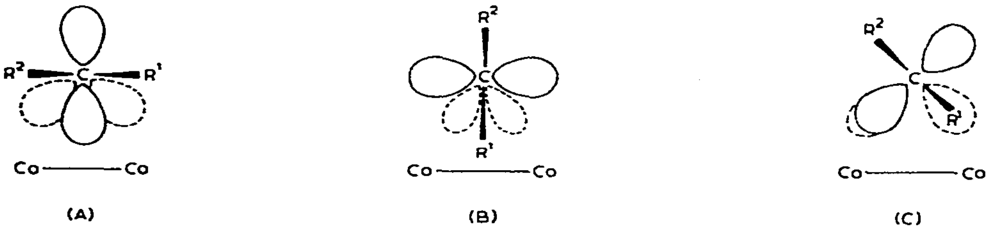


Fig. 1. Possible orientations of cations as viewed down the alkyne axis. Dotted lines represent Co → π^*(alkyne) orbitals.

which of the possibilities is operative, we make the following observations. The methyl resonance of IIIa appears as a single peak in CD_2Cl_2 (−70°C, +30°C), SO_2 (−20°C), and CF_3CO_2H (0°C)*. While this is consistent with static structure A, equivalence due to rotational time averaging or accidental degeneracy cannot be ruled out. The spectrum of the propargyl complex, on the other hand, is not that expected for either AB_2 or ABC spin systems. At present we have no definitive interpretations for the observed spectrum and firmer conclusions regarding the structures of these cations await ^{13}C NMR studies and other experiments in progress.

The p*K*'s for ionization of alcohols Ia, Ib and Id in aqueous sulfuric acid were determined spectrophotometrically** and are presented in Table 2 together with those of a few reference compounds. The pK_{R^+} values for the

TABLE 2

pK_{R^+} VALUES FOR SOME STABLE CARBONIUM IONS

Carbonium ion	pK_{R^+}
IIIa	−7.2
IIIb	−7.4
IIId	−6.8
α-Ferrocenylmethyl	−1.5 [8]
Triphenylmethyl	−6.6 [10]
α-[(Benzene)chromium tricarbonyl]methyl	−11.8 [9]

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*The chemical shift of the methyl resonance of IIIa in CD_2Cl_2 (not in SO_2) was temperature- and concentration-dependent but remained a singlet throughout. This may be due to ion-pairing.

**Values for pK_{R^+} were obtained by the method of Deno and coworkers [10]. Absorbance was monitored at 380 nm for Ia, 400 nm for Ib, and 500 nm for Id.

cobalt-complexed cations are seen to be essentially the same regardless of other substituents at the carbonium ion center and were approximately equal to that of the triphenylmethyl cation. An adjacent (ethynyl)dicobalt hexacarbonyl group thus stabilizes a carbonium ion to a considerably greater extent than does the (benzene)chromium tricarbonyl group but less than the ferrocenyl moiety.

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