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METHYLIDINETRICOBALT NONACARBONYL COMPOUNDS

III*. EVIDENCE FOR Co—CO(ORGANIC) INTERACTION IN $Co_3(CO)_9CCH{=}CRCOOR'$ (R = H, ALKYL, Ph; R' = H, Me) DERIVATIVES

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Summary

IR evidence was found for interaction between two cobalt atoms of the cluster and the carboxylic or ester carbonyl in $Co_3(CO)_9CCH{=}CRCOOR'$ (R = H, alkyl, Ph; R' = H, Me) compounds. The results afford independent proof for assignment of the ν(C—O) bands of $Co_3(CO)_9CY$ complexes according to the selection rules of the C_{3v} point group.

Introduction

In course of a study [2] of the stereochemistry of carbonylation of terminal acetylenes [3] we prepared IIa and IIb according to reaction 1 as suggested by Albanesi and Gavezzotti [4, 5]. A remarkable broadening and/or splitting of the doubly degenerate [6] C—O bands was observed in the IR spectra of these compounds.

This observation was of interest since, except for the broadening of the $\nu_4(e)$ band in the spectrum of $Co_3(CO)_9CCH_2Ph$ [7], the asymmetry of the Y group seemed not to affect the shape of the ν(C—O) spectrum [9] of these trigonal clusters, even in the case of such rather asymmetric Y groups as α-naphthyl or diversely substituted phenyl groups [8]**.

We describe below some further studies along the same lines.

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[*] For Part II see ref. 1.

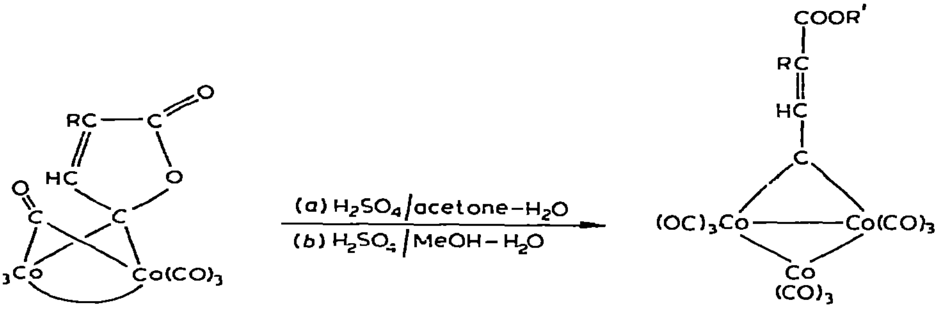
[**] Assignment in [8] seem to be in error, cf. [6].

TABLE 1

IR DATA FOR $Co_3(CO)_9CCH{=}CRCOOR'$ COMPOUNDS IN THE ν(C—O) REGION (solvent: n-hexane, calibration: simultaneous with DCl)[a]

No.	R	R'	$\nu_1(a_1)$	$\nu_4(e)$	$\nu_2(a_2)$	$\nu_6(e)$	$\nu_5(e)$	$\nu_3(a_2)$	ν(C=O) (organic)
IIa	H	H	2102.7 m	2054.1 vs(br)	2039.8 s	2016.5 m	[b]	[b]	[b]
IIc	Me	H	2103.0 m	2054.0 vs(br)	2040.1 s	2020.0 m(br)	2013 w(sh)	2002 vw	1720 w
IIe	n-Pr	H	2102.5 m	2055.8 s(sh) 2052.7 vs	2038.1 s	2022.1 m 2016.8 m	2010 vw(sh)	2002.3 w	1740 w
IIg	Ph	H	2103.1 m	2055.3 vs(br) (plato)	2039.7 s	2023.4 m 2018.5 m	2011 vw(sh)	2003.2 w	[b]
IIb	H	Me	2103.1 m	2056 (sh) 2053.3 vs	2039.5 s	2023.4 w 2018.9 w	2012 vw(sh)	2001 w	1740 w
IId	Me	Me	2102.7 m	2056.1 s 2052.3 vs	2038.8 s	2023.0 m 2017.9 m	2010 vw(sh)	2001.9 w	1745 w
IIf	n-Pr	Me	2103.3 m	2053 vs(br)	2039.7 s	2023.4 w 2018.9 w	2010 vw(sh)	2001 w	1780 w
IIh	Ph	Me	2102.8 m	2056.8 s 2052.4 vs	2039.3 s	2023.0 m 2017.8 m	2010 vw(sh)	2002.5 w	1740 w

[a] See ref. 13. [b] Could not be observed because of low solubility of the compound.



(I) (II) (1)

R′ = H for route *a*, R′ = Me for route *b*.
IIa R = R′ = H; b, R = H, R′ = Me; c, R = Me, R′ = H; d, R = R′ = Me; e, R = n-Pr, R′ = H; f, R = n-Pr, R′ = Me; g, R = Ph, R′ = H; h, R = Ph, R′ = Me.

Results and discussion

We extended reaction 1 to further starting compounds I and obtained compounds IIc-h with moderate yields (cf. Experimental, Table 2). The structures of the starting derivatives I were known from previous studies [2]. The new compounds were identified by analyses (Table 2), and the steric configuration of the organic part was studied by ^{1}H NMR spectroscopy (see Experimental, Table 3). As expected, the substituents around the C=C double bond retain the relative positions which they occupied in the lactone complexes: the configuration is most probably *Z* for all the complexes II.

The ν(C—O) IR spectra (Table 1 and Fig. 1) of the compounds are similar to those of IIa and IIb but sometimes with even more pronounced characteristic features. These characteristics can be summarized as follows:

(i). A clear splitting of the $\nu_4(e)$* and $\nu_6(e)$ bands is observed in almost all cases.

(ii). The components of ν_4 and ν_6 are not of exactly equal intensity in the spectra. In the case of ν_4 the component at lower wave numbers is always somewhat more intense, and this can be explained by overlapping with ν_2. In the case of ν_6, the component at lower wave numbers is usually the more intense. Overlapping with ν_2 would act in the opposite direction, but this intensity difference can be readily explained if it is attributed to the presence of the almost completely hidden ν_6 band or, more probably, the bands derived from this degenerate vibration.

(iii). In all but one case the appearance of a new [with respect to the general shape of the spectra of $Co_3(CO)_9Y$ compounds] band is observed at about 2000 cm^{-1}. This band can be attributed to the $\nu_3(a_2)$ vibration which according to the selection rules of the C_{3v} point group is IR inactive. This assignment is in accordance with the expected position [6] of the ν_3 band.

(iv). The shape and width of the non-degenerate a_1 bands ν_1 and ν_2 remain unaltered with respect to those of other $Co_3(CO)_9CY$ compounds [6, 9].

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* The bands are denoted according to the C_{3v} assignment [6].

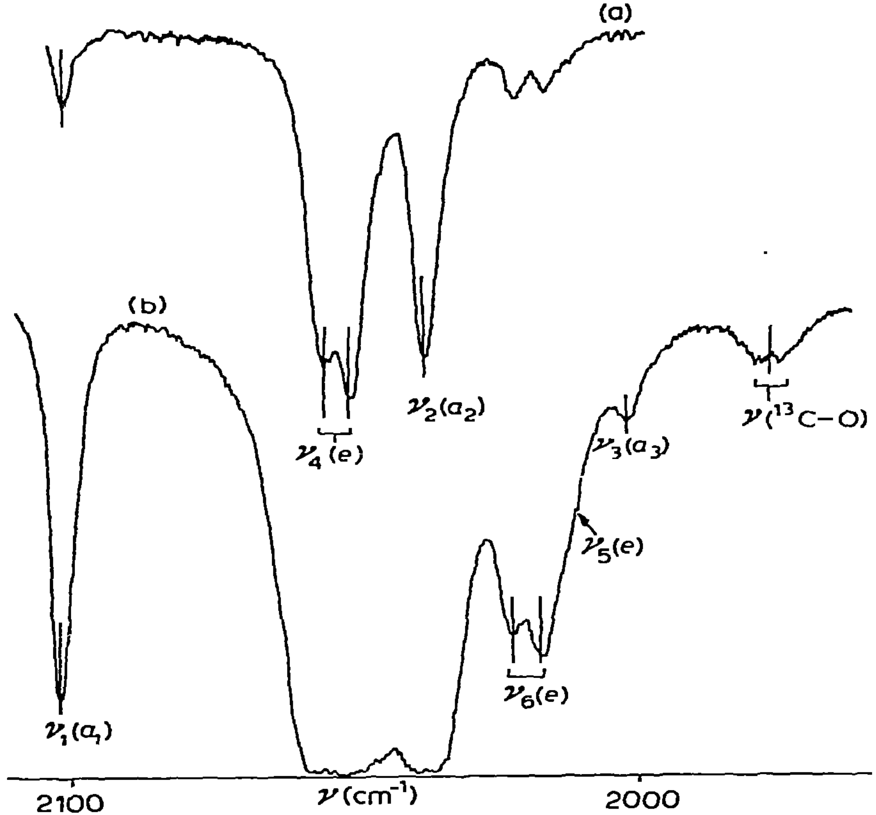

Fig. 1. IR spectrum of $Co_3(CO)_9CCH{=}C(n\text{-}Pr)COOH$ in the terminal (CO) range, at (a) lower and (b) higher concentration. (Solvent: n-hexane.)

These features of the spectra suggest a considerable decrease in the symmetry of the $Co_3(CO)_9C$ skelton. For two reasons, this can hardly be caused by an electronic effect of the substituent through the apical carbon:

(a). The electronic effect of Y should be symmetric on the $Co_3(CO)_9C$ part of the molecule since it acts at the apical carbon which is on the C_3 axis of the molecule.

(b). The possibility that the electronic effect of the substituent operates through partially filled *p*-orbitals* of the apical carbon in a manner which destroys the threefold symmetry of the electronic system of the $Co_3(CO)_9$ moiety must be ruled out because no indication of band splitting was found for compounds with Y substituents having comparable electronic effects (e.g. Y = C_2F_5 [1], Ph, or COOR [10]) to those in the present series.

A possible explanation would be that since the unsaturated acid or ester substituents are in fixed positions (because of conjugation) there would be an asymmetric "size effect" on the vibrating molecule. This can be ruled out for the following reasons:

(a). Comparison of the size of the substituents with that of α-naphthyl group [8], for example, shows that even heavier substituents do not cause any detectable band splitting.

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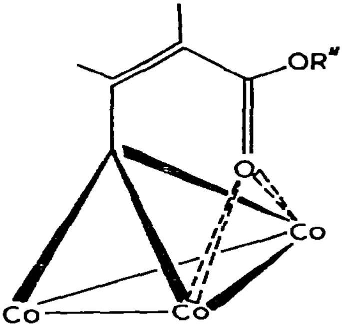
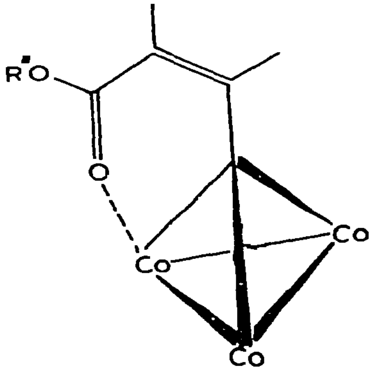
* As a consequence of the partial sp^2 and/or sp character [9] of this carbon atom.

(b). Recently it was shown [11] that even a much more marked size asymmetry in the substituents of $Co_2(CO)_6(HC{\equiv}CH)$ compounds does not affect the formal C_{2v} symmetry of the $Co_2(CO)_6$ moiety while a strong asymmetry in the electron distribution does.

It thus has to be assumed that the band splitting is caused by electronic effects, but that these do not act by transmission through the π and/or σ bond system of the molecule, i.e. through the apical carbon but by electronic (coordinative) interaction between the carbonyl-oxygen of the COOR′ group and one or two of the cobalt atoms as in the representations (A) and (B). Both of these structures are of C_s symmetry allowing 9 ($\Gamma = 5a' + 4a''$) IR active vibrations, which is the number of bands we believe to be implicated in the spectra (8 of these can actually be observed). X-ray data of several $Co_3(CO)_9CY$ compounds [9, 12] suggest form (B) to be more probable because of the steric effect of the "equatorial" carbonyls in (A).



(A)



(B)

The *e*-splitting effect as well as the appearance of ν_3 was more pronounced in the ester derivatives. We attribute this to H-bonding between the two carboxylic oxygen atoms, which would counteract the coordinative interaction between the Co atom(s) and the "organic" carbonyl group. The "organic" (C—O) bands were not informative on this point. Their position is rather high for α,β-unsaturated acids or esters, but it cannot be decided whether this is a consequence of conjugation with the cluster [9] or of electron density changes caused by the suggested coordinative effect.

The above results also support the assignment [6] of the ν(C—O) bands according to the selection rules of the C_{3v} point group. The assignment of 5 bands can directly be confirmed, ν_1 and ν_2 because of their unaltered shape, ν_4 and ν_6 because of their observed splitting, and ν_3 because of its appearance in the expected range. This evidence together with the results which served as the basis for the earlier [6] assignment seems to be fairly conclusive.

Experimental

Measurements were made with the following instruments: Carl Zeiss UR-20 (IR), Varian T60 (^{1}H NMR), Dampfdruckosmometer (Knauer) (mol. wt.).

TABLE 2

ANALYTICAL AND OTHER DATA FOR THE $Co_3(CO)_9CCH{=}CRCOOR'$ COMPOUNDS PREPARED

No.	R	R'	Mol. wt.[a] Found (calcd.)	Co % Found (calcd.)	Yield[b] (%)
IIa	H	H	523 (515.00)	34.8 (34.16)	13
IIc[c]	Me	H	538 (526.98)	34.1 (33.55)	24
IIe[c]	n-Pr	H	567 (557.08)	30.8 (31.75)	13
IIg[c]	Ph	H	611 (591.09)	30.0 (29.88)	36
IIb	H	Me	549 (529.03)	34.1 (33.42)	23
IId[c]	Me	Me	553 (541.98)	32.9 (32.62)	38
IIf[c]	n-Pr	Me	586 (568.08)	32.0 (31.12)	16
IIh[c]	Ph	Me	624 (605.12)	29.6 (29.10)	13

[a] Osmometric in benzene. [b] Calculated with respect to the apical carbon. [c] New compound.

TABLE 3

^1H NMR DATA FOR SOME $Co_3(CO)_9CCH(a){=}CRCOOR'(b)$ COMPOUNDS
(solvent: CCl_4 internal standard TMS)

No.	R	R'	Spectra and assignment (δ in ppm, J in Hz)
IIe	n-Pr	H	δ_1 1.06, d, $J = 6$, 3H, (γ-Me in n-Pr) δ_2 1.73, m (4 visible components), 2H, (β-CH_2 in n-Pr) δ_3 2.8, m (ill-resolved), 2H, (α-CH_2 in n-Pr) δ_4 4.1, m (7 visible components), 1H, (a) δ_5 11.82, s, (disappears upon addition of D_2O), 1H, (b)
IIb	H	Me	δ_1 2.83, q, $J_1 = J_2 = 8$, 1H, (a) δ_2 3.76, s, 3H, (b) δ_3 4.09, q, $J_1 = 8$, $J_2 = 6$, 1H, R = H[a]
IId	Me	Me	δ_1 1.42, d, $J = 4$, 3H, R = Me δ_2 3.72, s, 3H (b) δ_3 4.36, q, $J_1 = 9$, $J_2 = 5$, (a)
IIh	Ph	Me	δ_1 3.73, s, 3H, (b) δ_2 4.76, q, $J_1 = 18$, $J_2 = 10$, 1H, (a) δ_3 7.32, m, 5H, R = Ph

[a] Interaction between R = H and (a) protons proved by spin—spin decoupling technique.

Starting compounds I were prepared as described earlier [2, 3]. Compounds II were prepared on 1-10 mmole scale by a method essentially the same as that suggested by Albanesi and Gavezzotti [4, 5]. The products were isolated by cooling the reaction mixture overnight and subsequently purified by 2 or 3 recrystallizations from n-hexane. Compounds IIa-d were further purified by sublimation at 60-70°/1-2 torr.

Analytical results and yields are listed in Table 2. The organic moiety of the products II was characterized also by ^1H NMR spectroscopy and the characteristic data and assignments are shown in Table 3. The data are in full agreement with the suggested nature and arrangement of the organic groups. The quadruplet form of the (a) protons supports the *Z* configuration around the C=C double bond [14]. The coupling constants show somewhat higher values than expected for similar fully organic systems [15] but the *J* values (see e.g. IIb) are significantly lower than those observed for the most closely similar system [16] having a *trans* configuration. We attribute the high values of the coupling constants to conjugation with the $Co_3(CO)_9C$ moiety.

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