Journal of Organometallic Chemistry, 114 (1976) 213—217
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ELECTRONIC EFFECTS AND THE INFRARED SPECTRA OF μ_2-ALKYNEHEXACARBONYLDICOBALT COMPOUNDS *

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(Received January 23rd, 1976)

Summary

The influence of the electronic structure of R and R′ in species of general formula $(RC_2R')Co_2(CO)_6$ on their infrared spectra in the ν(C—O) region provides independent evidence for the assignment of the carbonyl stretching bands.

Introduction

There are still some discrepancies in the interpretation of the ν(C—O) spectra of the compounds $(\mu_2\text{-L})_2M_2(CO)_6$, where μ_2-L is a bridging ligand such as CO, P, As, S, SR, etc. and M = Co, Fe. The main matter in dispute is the question of whether the axial and equatorial CO ligands can be regarded as equivalent [3—5] or not [6—9]. Of course, the force-constant computation problem is easier in the former case but careful calculations have shown [10,11] that good agreement between the calculated and observed data can only be achieved if the axial and equatorial CO ligands are regarded as not equivalent.

Early force-constant calculations [10] led us to try to find independent evidence for the assignment which was the basis of these calculations. We have focused our attention mainly on compounds of general formula $(\mu_2\text{-alkyne})Co_2(CO)_6$, arguing that if the electronic effect of the μ_2-alkyne group were large enough, it should be reflected in differences in the spectroscopic behaviour of the various CO groups. In the present communication we outline the first results of this study.

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* The main results of this work were taken from a thesis [1] and presented at a Conference [2].

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Results and discussion

We have sought experimental evidence for the theoretical assignment of the ν(C—O) spectrum of the alkyne hexacarbonyl dicobalt complexes by attempting to observe the sixth $\nu(^{12}$C—O) band, $\nu_3(a_2)$, which is formally IR-inactive (under the C_{2v} selection rules).

A reduction in symmetry was expected, in view of the asymmetry of alkynes containing two substituents markedly different in electron donor-acceptor properties, corresponding to an effective symmetry lower than C_{2v} for the electronic system of the $C_2Co_2(CO)_6$ moiety. It should be noted that such an effect has implicitely been described [12] in connection with an explanation of the differences in the ν(C—O) spectra of $(RC_2R')Co_2(CO)_6$ ($R \neq R'$) compounds and of $Co_2(CO)_7(C_4O_2RR')$, "lactone" complexes. The experiments reported here were therefore aimed not only at providing further evidence on the assignment of the ν(C—O) spectra of $(RC_2R')Co_2(CO)_6$ complexes but also in attempting to find experimental verification of the (generalized) supposition that if the electronic asymmetry is sufficient at the two bridgehead carbon atoms the reduction below C_{2v} symmetry may be sufficient to be observable spectroscopically.

We prepared and investigated (in one case re-investigated) the $Co_2(CO)_6$-derivatives of a series of alkynes, previously reported by one of us [13], in which one substituent of the C_2 moiety was phenyl and the other a highly-fluorinated phenyl or biphenyl group. This was a fortunate choice for, the ν(C—O) spectra of these compounds (Fig. 1, Table 1) showed not only the appearance of the "sixth", $\nu_3(a_2)$ band *, but also three $\nu(^{13}$C—O) isotopic satellites in the 2000—1950 cm^{-1} region. The appearance of the sixth fundamental, as well as its position relative to the rest of the spectrum, agrees well with the results of earlier calculations [11].

The triplet form of the lower isotopic band system can be interpreted as follows. For those acetylenic complexes, the spectra of which obey the C_{2v} selection rules, generally only two ^{13}CO isotopic satellites can be observed in the 2000—1950 cm^{-1} range. One component (at higher wavenumbers) of these was assigned [10,11] to axial, the other to equatorial ^{13}CO substitution. In the present case it can reasonably be supposed that the triplet form of the lower isotopic band system is caused by the electronic asymmetry of the $C_2Co_2(CO)_6$ moiety if this gives rise to a difference between the two (according to C_s symmetry) sets of equatorial carbonyl groups in addition to that between axial and equatorial carbonyl groups.

The hypothesis that the triplet form of the lower isotopic band system is due to a marked difference in the electron density of two sets of equatorial carbonyls, which again is due to the difference in electron donor—acceptor properties of the two atoms in bridge positions, demands that the lower $\nu(^{13}$C—O) satellites of the $Co_2(CO)_7(C_4O_2RR')$ "lactone" complexes should also appear as a triplet. Probably because of the low solubility of these compounds, however, there has been no report of this [12,15—17]. A re-investigation of the spectrum

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* It should be noted that another team independently observed [14] this "sixth" band at other $(\mu_2\text{-}RC_2R')Co_2(CO)_6$ compounds containing R and R' substituents of markedly different electron donor-acceptor properties.

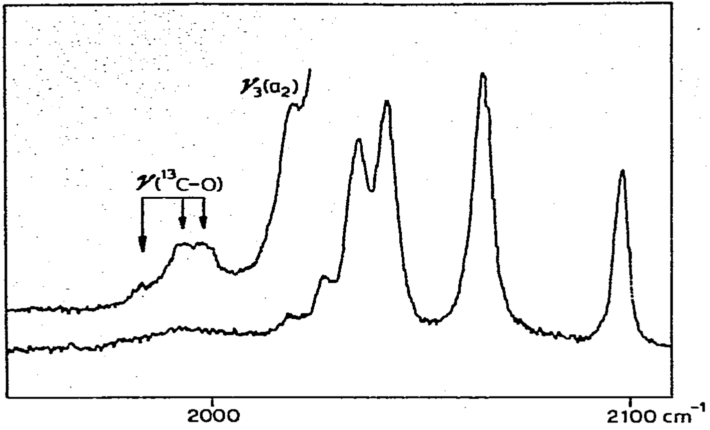
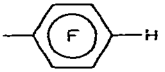
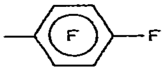
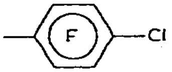
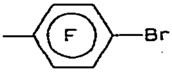
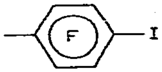
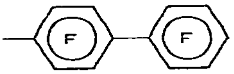


Fig. 1. The ν(C—O) spectrum of $(C_6F_5C_6F_4C_2H_5)Co_2(CO)_6$.

of the R = H, R′ = n-hexyl derivative [16] (which has a higher solubility than its homologues) furnished the spectrum shown Fig. 2, in which a well-separated isotopic triplet can clearly be seen.

TABLE 1

IR SPECTRA OF $(\mu_2\text{-}PhC_2X)Co_2(CO)_6$ COMPOUNDS

X	ν(C—O) bands (cm^{-1}) and assignment [a]						$\nu(^{13}C—O)$
	$\nu_1(a_1)$	$\nu_4(b_1)$	$\nu_6(b_2)$	$\nu_2(a_1)$	$\nu_5(b_1)$	$\nu_3(a_2)$	
	2098.0	2064.4	2041.0	2034.4	2026.4	2018.8	1994.7 (sh) 1992.2 1982.4 (sh)
	2098.2	2064.3	2041.7	2034.7	2026.5	2019.4	1998.2 (sh) 1991.3 1982 (sh)
	2098.2	2064.5	2042.0	2035.2	2027.0	2020.0	1996.0 (sh) 1992.8 1983.4 (sh)
	2098.5	2065.1	2042.4	2035.4	2027.4	2020.0	1995.5 (sh) 1992.4 1984.4 (sh)
	2098.4	2064.9	2042.2	2035.3	2027.4	2019.0	1994.7 1991.7 1982.5 (sh)
	2099.0	2065.8	2042.8	2036.1	2028.0	2020.8	1998.6 (sh) 1994.5 1984.4 (sh)

[a] Assignment according to C_{2v} formal symmetry, based on [13] and the present work.

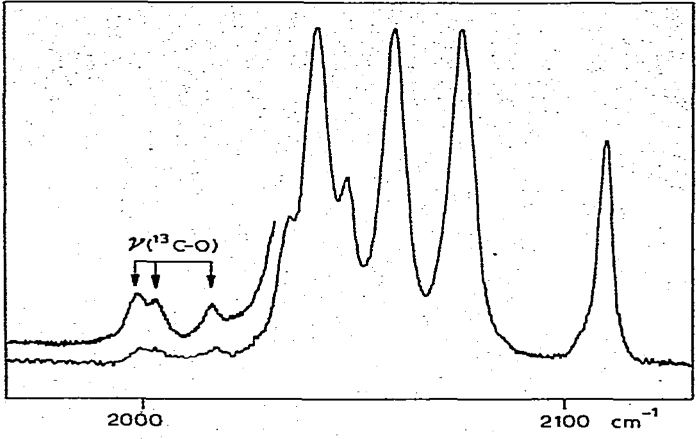


Fig. 2. The ν(C—O) spectrum of $Co_2(CO)_7(C_4O_2H.n\text{-}Hex)$.

Experimental

IR spectra were taken with a Carl Zeiss (Jena, G.D.R.) UR-20 instrument with a LiF prism. Absorption maxima were measured in n-hexane solution using simultaneous DCl calibration [18].

The alkyne complexes were generally prepared by the reaction of equimolar amounts of the acetylene and $Co_2(CO)_8$, according to published techniques [19, 20]. Because of the perfluoraryl groups, the compounds could be well crystallized. The products were recrystallized from n-pentane. The structures of two products were also deduced from analyses, others were assumed by analogy with preparative and IR spectra.

$(C_6F_5C_2Ph)Co_2(CO)_6$. Analysis: found: Co, 20.6, $C_{20}H_5Co_2F_5O_6$ calcd.: Co, 21.3%. Mol. wt.: found (osmometric, benzene) 570; calcd.: 554.0.

$(BrC_6F_5C_2Ph)Co_2(CO)_6$. Analysis: found: Co, 18.8. $C_{20}H_5BrCo_2F_4O_6$ calcd.: 19.2%. Mol. wt.: found (osmometric, benzene) 630; calcd.: 615.4.

Acknowledgement

The authors are indebted to Prof. L. Markó (Veszprém) and to Prof. G. Bor (Zürich) for stimulating discussions as well as to Prof. S.F.A. Kettle (Norwich), Dr. P.L. Staghellini (Torino) and Prof. G. Bor for communicating their results to us prior to publication. One of the authors (G.V.) acknowledges a fellowship from the Hungarian Ministry of Education.

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