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(μ_2-Dihaloacetylene)-hexacarbonyldicobalt (*Co–Co*) Compounds and Their Reaction with Cobalt Carbonyls[a]

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(μ_2-Acetylene)-hexacarbonyldicobalt (*Co–Co*) compounds (I) give a wide variety of reactions of the coordinated C_2 moiety [2], while reactions of the substituents of the acetylene were reported in only a few cases [3]. Haloacetylenic derivatives can be hoped to be reactive starting materials for such studies.

We prepared and characterized some dihaloacetylenic derivatives can be hoped to be reactive starting materials for such studies.

We prepared and characterized some dihaloacetylene (I) derivatives and studied their reaction with $Co_2(CO)_8$ or $[Co(CO)_4]^-$. The results of this study will be reported here.

Results and Discussion

Dihaloacetylenic (I) derivatives were prepared in n-hexane solution by the reaction of $Co_2(CO)_8$ with the corresponding acetylene. Dichloro* and dibromoacetylene* were transferred into the reaction vessel by a deoxygenated Ar or N_2 stream from the reaction mixture in which they were prepared (using the hypohalogenite method [4] for all X_2C_2, X = Cl, Br, I derivatives). I_2C_2 was isolated in pure form, carefully dried and reacted as such . The reaction of X_2C_2 compounds was clean at room temperature and good yields (50–70%) of $(\mu_2\text{-}X_2C_2)Co_2(CO)_6$ derivatives were obtained.

The structure of the complexes was investigated by IR spectroscopy (Table I). Four fundamental bands were observed in the ν(C–O) range, instead of five [5, 6] which could be expected on the basis of the selection rules of the C_{2v} point group. Because of the unusual high intensity and somewhat broader

TABLE I. Infrared ν(C–O) Spectra and Analytical Data of $(X_2C_2)Co_2(CO)_5L$ (L = CO, ER_3) Compounds.

Ligands		ν(C–O) Bands[a] (cm^{-1}) and Assignment[b]						Analyses					
X	L	$\nu_1(a_1)$	$\nu_4(b_1)$	$\nu_2(a_1) + \nu_6(b_2)$	$\nu_5(b_1)$	$\nu(^{31}C\text{–}O)$		Co%		P%		MW[f]	
						Ax.	Equ.	Calc.	Found	Calc.	Found	Calc.	Found
Cl	CO	2108.6(m)	2074.6(s)	2050.1(vs)	2039 (sh, w)	2007 (vw)	2000 (vw)	–	–[c]	–	–	–	–
Br	CO	2107.0(m)	2074.2(s)	2049.5(vs)	2039.2(sh, w)	2006 (vw)	1998 (vw)	–	–[c]	–	–	–	–
I	CO	2102.9(m)	2071.5(s)	2047.1(vs)	2035.8(sh, w)	2004.6(vw)	1998.3(vw)	20.9	20.5	45.0[e]	43.9[e]	563.7	555
I	Pbu_3^n	2074.8(s),	2029.6(vs),	2021.2(s),	2012.7(sh, w),	1985.3(m)		–	–	–	–	–	–
I	PPh_3	2075.4(s),	2033.8(vs),	2022.5(s),	2015.1(sh, w),	1987.3(m)		14.8	14.3	3.9	4.1	798.0	760
I	$AsEt_3$	2076.3(s),	2029.9(vs)	2024.6(s),	2012.5(sh, w),	1985.1(m)		16.9	16.4	10.8[d]	9.9[d]	697.8	685
I	$SbEt_3$	2076.6(s),	2031.1(vs),	2023.9(s),	2013.5(sh, w)	1986.1(m)		–	–	–	–	–	–

[a] Spectra were taken in n-hexane solution with simultaneous calibration (DCl). [b] Assignment according to refs. 4–6. [c] These compounds were identified by the analogy of the IR spectra. [d] As%. [e] I%. [f] Osmometric, in benzene.

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**Dihaloacetylenes should be handled with the greatest care because of danger of explosion, which can take place also spontaneously even in solutions!*

form of the third band (in order of appearance), we suppose that this band contains both the $\nu_2(a_1)$ and $\nu_6(b_2)$ absorptions in one band envelope. This assignment is also supported by the large separation of the isotopic satellites, as observed in the case of some diiron hexacarbonyl derivatives [5]. We interprete both effects as a novel example of the deformation [6, 7] of MOs of the metal carbonyl skeleton caused by the strong electronic effect of the substituents of an organic ligand – in this case without reduction of the symmetry.

Because of the somewhat anomalous behaviour of the ν(C–O) spectra the structure of the complexes was confirmed also by preparation of some mono-ER_3 (E = P, As, Sb) derivatives. The infrared data of these complexes (Table I) showed good agreement with those of the monosubstitued tertiary phosphine derivatives of other $(\mu_2\text{-}B)_2Co_2(CO)_6$ compounds (B = C, P, As [8, 9]).

In preparative experiments we found always – together with the $(X_2C_2)Co_2(CO)_6$ compounds – the unexpected formation of $[Co_3(CO)_9C]_2$ [10, 11]. We performed therefore a further systematic investigation on this finding.

The formation of the hexanuclear species was found to be favored by increasing the starting Co_2/C_2I_2 ratio. Thus when the former ratio was 0.5, 1.0, 2.0 and 3.0 the ratio of the products $(C_2I_2)Co_2(CO)_6/[Co_3(CO)_9C]_2$ changed from 130 to 46, 4.9 and 0.07 respectively without significant change in the yield (70 ± 10%) of the neutral Co carbonyls. (the quantitative experiments were evaluated using the IR spectra. The values were determined earlier [12]). These observations suggested that the hexanuclear complex is formed from the $(C_2X_2)Co_2(CO)_6$ compounds in a reaction with excess $Co_2(CO)_8$.

This supposition was proved also preparatively. $(I_2C_2)Co_2(CO)_6$ was reacted with $Co_2(CO)_8$ (1:2 molar ratio, n-hexane, 25 °C, 3 h) and with $NaCo(CO)_4$ (1:2 molar ratio, THF, 30 °C, 2 h). $[Co_3(CO)_9C]_2$ was obtained with good yields (65 and 45% resp.) in both cases. Thus the derivatives seem to be true intermediates in the above described formation of $[Co_3(CO)_9C]_2$.*

The reaction leading to $[Co_3(CO)_9C]_2$ probably involes carbyne [14] intermediates in agreement with the recent findings of Fischer and Däweritz [15] who were able to synthesize $Co_3(CO)_9CMe$ from $Br(CO)_4CrCMe$ and $Co_2(CO)_8$. Both reactions can be interpreted as preparative proofs of the partial sp^2 or sp character [10, 16] of the apical carbon in the $Co_3(CO)_9CY$ series.

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*It should be noted that the reactions reported here represent the second [13] good-yield synthetic route to prepare $[Co_3(CO)_9C]_2$.