

ACETYLENIC DERIVATIVES OF METAL CARBONYLS I. SUBSTITUTION REACTIONS OF $\text{Co}_2(\text{CO})_6\text{C}_2\text{RR}'$ COMPLEXES

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INTRODUCTION

Acetylenic complexes, obtained through the reaction of acetylene derivatives $\text{R}-\text{C}\equiv\text{C}-\text{R}'$ with metalcarbonyls, offer the opportunity of studying in detail the influence of R and R' groups upon the ease of formation of σ or π bonds through donation or acceptance of electrons and consequently their influence upon the stability of the complexes obtained.

If the R or R' group is an electron donor (as for example, an alkyl group) this group will tend to render the acetylene electrons π^* more easily available for the formation of a σ bond to the metal. On the other hand, when the group is an electronegative substituent (for example CF_3) the back-donation of electrons by the metal atom towards the antibonding π^* orbitals of the acetylene will be facilitated.

In this connection it is known, as observed by Chatt *et al.* that on account of the phenomenon of balance of the σ donor and π acceptor power of the acetylenes, these can displace each other more or less easily in Pt(II) complexes, according with higher or lower electronegativity of the R and R' groups.

In particular it was observed that on increase of the π acceptance power of the acetylenic derivatives leads to an increase of the stability of the complex and of the difficulty of the displacement by an acetylenic derivative, having a lower π acceptance character.

Consequently we thought it would be interesting to examine the behaviour of a series of complexes $\text{Co}_2(\text{CO})_6\text{C}_2\text{RR}'$, in which the substituents R and R' are chosen as to give a gradual variation of the σ and π bonding character of the acetylenic derivatives, in reactions, that involve the exchange of acetylenes:



The study of such a reaction and the determination of the equilibrium position is in fact a direct measure of the stability of these complexes in solution, depending on the nature of the substituents R, R', R'' and R'''. The compounds examined are listed in Table I.

References are given for compounds previously reported and these were prepared by the method described. The others are new compounds and their preparation and characterization are given in the Experimental section.

The results of this investigation are of interest because it will show if the acetylenes, which form the more stable monomeric metal complexes, also form the

more stable bridged metal complexes. Furthermore, in this study a larger number of acetylenes are examined than were used previously¹, in an attempt to gain a better understanding of the importance of the σ donor and π acceptor properties of the acetylenes for the formation of such metal complexes.

TABLE I
COMPOUNDS OF THE TYPE $\text{Co}_2(\text{CO})_6\text{C}_2\text{RR}'$ INVESTIGATED

R	R'	References
C_6H_5	C_6H_5	2
C_6H_5	H	2
H	H	2 ^a
CH_3	CH_3	2
CH_3	C_6H_5	This work
CH_3	H	This work
COOCH_3	COOCH_3	3
CF_3	CF_2	4
CH_2Cl	CH_2Cl	This work
$\text{CH}_2\text{N}(\text{C}_2\text{H}_5)_2$	$\text{CH}_2\text{N}(\text{C}_2\text{H}_5)_2$	This work
COOH	COOH	This work

^a The preparation of this complex was not reported in detail³ and was carried out like the preparation of $\text{Co}_2(\text{CO})_6\text{C}_2\text{HCH}_3$.

EXPERIMENTAL PART

(A) Preparation of dicobalt hexacarbonylacetylenes

$\text{Co}_2(\text{CO})_6\text{C}_2(\text{CH}_3)(\text{C}_6\text{H}_5)$. In a double-necked reaction flask with gas inlet and outlet, a solution of 8.7 g of dicobalt octacarbonyl (25.4 mmole) in petroleum ether (40–70°) was allowed to react with 3.4 g of 1-phenylpropyne (29 mmole) under an atmosphere of carbon monoxide. The reaction, which was accompanied by an initial evolution of carbon monoxide, was carried out at room temperature for approx. 24 h. Afterwards the solution was filtered under inert gas and purified by passing through a Kieselgel 0.2–0.5 column petroleum-ether 40–70° eluent. The solvent was evaporated *in vacuo* and 5.6 g of pure $\text{Co}_2(\text{CO})_6\text{C}_2(\text{CH}_3)(\text{C}_6\text{H}_5)$ was obtained (yield about 55%). The compound is a viscous red-brown oil soluble in common organic solvents. Its purity was checked by thin-layer chromatography (silica gel G, *n*-heptane). (Found: C, 44.50; H, 2.05; O, 23.77; mol. wt. cryoscop. in cyclohexane, 389. $\text{C}_{15}\text{H}_8\text{Co}_2\text{O}_6$ calcd.: C, 44.80; H, 2.01; O, 23.83%; mol.wt., 402.) The infra-red bands in the carbonyl region are as follows: 2091 (m), 2053.5 (s), 2028 (s), and 2011 (m) cm^{-1} (solvent *n*-heptane).

$\text{Co}_2(\text{CO})_6\text{C}_2(\text{CH}_2\text{Cl})_2$. Using a procedure similar to that which has been described above 9.5 g (28 mmole) of dicobalt octacarbonyl and 4.1 g (34 mmole) of 1,4-dichloro-2-butyne were reacted in a solution of petroleum ether (40–70°). At the end of the reaction (about 8 h at room temperature) a red precipitate was formed which was filtered and dissolved in petroleum ether. The solution was allowed to crystallize at –20°; the mother liquors were concentrated *in vacuo* and allowed to crystallize. The two crops of crystals were put together and recrystallized from

petroleum ether: 4.8 g (yield 42%) of $\text{Co}_2(\text{CO})_6\text{C}_2(\text{CH}_2\text{Cl})_2$ were obtained in the form of bright red crystals soluble in the common organic solvents. The purity of the compound was checked by paper chromatography (Whatman type 3 NM; n-heptane/ethyl ether 9:1). (Found: C, 29.09; H, 0.92; O, 23.40; mol. wt. cryoscop. in cyclohexane, 401. $\text{C}_{10}\text{H}_4\text{Cl}_2\text{Co}_2\text{O}_6$ calcd.: C, 29.37; H, 0.99; O, 23.48%; mol. wt., 409.) The compound decomposes at temperatures above 90° , without melting. The infrared bands in the carbonyl regions are as follows: 2102.5 (m), 2066.5 (s), 2045 (s), 2029.5 (m), and 2021 (m) cm^{-1} (solvent n-heptane).

$\text{Co}_2(\text{CO})_6\text{C}_2[\text{CH}_2\text{N}(\text{C}_2\text{H}_5)_2]_2$. To a solution of 10.0 g (30.4 mmole) of dicobalt octacarbonyl in petroleum ether ($40\text{--}70^\circ$) was added 6.9 g (35 mmole) of N,N'-tetraethyl-2-butyne-1,4-diamine at room temperature. After a period of 24 h the solution was filtered and purified through Kieselgur column (eluent petroleum ether). After removal of the solvent by vacuum evaporation, about 8.6 g of $\text{Co}_2(\text{CO})_6\text{C}_2[\text{CH}_2\text{N}(\text{C}_2\text{H}_5)_2]_2$ were obtained in the form of a dense brown liquid (yield 58.7%). Purity was checked by thin-layer chromatography (adsorbent silica gel G 30%, cellulose 70%; eluents ethyl ether and n-heptane). The compound is soluble in common organic solvents. (Found: C, 44.43; H, 5.82; N, 5.76; O, 19.89; mol. wt. cryoscop. in cyclohexane, 468. $\text{C}_{18}\text{H}_{24}\text{Co}_2\text{N}_2\text{O}_6$ calcd.: C, 44.83; H, 5.02; N, 5.81; O, 19.91%; mol. wt., 482.) The infrared bands in the carbonyl regions are as follows: 2088.5 (m), 2049.5 (s), 2027 (s) and 2017 (s) cm^{-1} (solvent n-heptane).

$\text{Co}_2(\text{CO})_6\text{C}_2\text{H}(\text{CH}_3)$. About 20 mmole of propyne were condensed by liquid air in thick-walled glass ampoule containing 4.9 g (14.3 mmole) of dicobalt octacarbonyl dissolved in petroleum ether ($40\text{--}70^\circ$). The ampoule was sealed and allowed to stand for a period of about 3 days at room temp. $\text{Co}_2(\text{CO})_6\text{C}_2\text{H}(\text{CH}_3)$ was obtained (yield 1.6 g, 35%) in the form of a dense red-brown oil soluble in organic solvents. The purity of the compound was checked by thin-layer chromatography (silica gel G, n-heptane). (Found: C, 33.1; H, 1.29; O, 29.26; mol. wt. cryoscop. in cyclohexane, 320. C, 33.16; H, 1.26; O, 29.45%; mol. wt., 326.) The infrared bands in the carbonyl region are as follows: 2094.5 (m), 2054.5 (s), 2030.5 (s), 2021 (s) and 2012 (m) cm^{-1} (solvent n-heptane).

$\text{Co}_2(\text{CO})_6\text{C}_2(\text{COOH})_2$. Acetylenedicarboxylic acid (4.56 g, 40 mmole) was added to 9.5 g (28 mmole) of dicobalt octacarbonyl in petroleum ether (carbon monoxide atmosphere). The suspension (the acid is practically insoluble in petroleum ether) was refluxed in a water bath at 50° for 4 days in continuous agitation. A red precipitate was obtained, filtered and washed with petroleum ether ($40\text{--}70^\circ$) in which it was found to be practically insoluble. Non-reacted dicobalt octacarbonyl and tetracobalt dodecacarbonyl were found in the solution. The precipitate was dried by suction and dissolved in ethyl ether. After crystallization at -20° , 7.28 g of $\text{Co}_2(\text{CO})_6\text{C}_2(\text{COOH})_2$ were obtained as orange microcrystalline powder (yield 65%). This was insoluble in apolar organic solvents, scarcely soluble in water and soluble in polar organic solvents. Paper chromatography (Whatman 3NM, 10% NH_3 in water) showed the compound to be pure. (Found: C, 29.97; H, 0.55; O, 40.31. $\text{C}_{10}\text{H}_2\text{Co}_2\text{O}_{10}$ calcd.: C, 30.02; H, 0.50; O, 40.00%.) The infrared absorption bands in the carbonyl regions are as follows: 2110 (m), 2077 (s) and 2049 (s) cm^{-1} (solvent ethyl ether). The infra-red spectra were obtained with a I.R.7 Model Beckmann spectrophotometer with double beam and NaCl optics. The gas chromatographic analyses were carried out with a Bf Model Fractovap apparatus (Carlo Erba).

(B) Displacement reactions

Description of the methods. Figure 1 shows the type of ampoule used in the experiments. The following technique was used. Ten ml of the compound solution in n-heptane was placed in the ampoule and CO bubbled from a side tube to saturate the solution and expel the air. The bubbling tube was then closed, the ampoule was evacuated after cooling with liquid air and then was filled with CO at a pressure slightly lower than the atmosphere. The acetylene derivative was introduced separately: in the case of gaseous derivatives (acetylene, propyne etc.), the ampoule

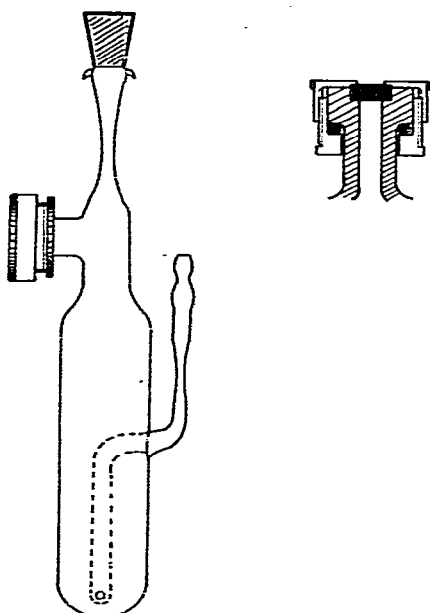


Fig. 1. (A) Ampoule used for displacement reactions. In the neck is the withdrawing system. (B) Cross section of the withdrawing system. The black zones represent silicon rubber septum and o-rings as used in gas chromatography; the dashed zones represent glass, the others metal.

was filled with the derivative instead of CO, in the case of liquid derivatives (phenylacetylene, 2-butyne, etc.) we preferred to use a microsyringe and introduce them via the rubber membrane after the ampoule had been sealed; solid derivatives such as diphenylacetylene, on the other hand, were dissolved in the initial solution together with the compound. The ampoule was sealed and then placed in a thermostat bath at the constant temperature; at intervals a microsyringe was used to take off standard volumes of solution (0.030 ml) via the rubber membrane. These were analysed by means of thin-layer chromatography. Depending on the reaction being examined, the following substrates were used in the chromatographical technique: silica gel G; Kieselgur G, alumina D 5, powdered cellulose D and suitable mixtures of these in various proportions; as developers: n-heptane, ethyl ether and mixtures of these were used. The acetylenecobalt carbonyl complexes examined are listed in Table 1.

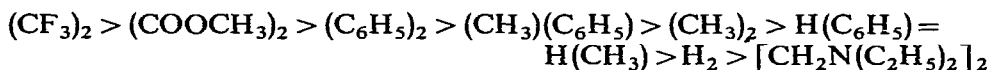
Displacement tests were carried out at different temperatures (25–40–50°). In all the experiments the complex/substituent concentration ratio was 1 : 1.3.

The compounds $\text{Co}_2(\text{CO})_6\text{C}_2(\text{CH}_3)_2$, $\text{Co}_2(\text{CO})_6\text{C}_2\text{HCH}_3$ and $\text{Co}_2(\text{CO})_6\text{C}_2\text{H}_2$

cannot be separated by thin-layer chromatography. Therefore it was necessary to modify the method and to carry out the reactions in ampoules of the type previously described⁵. The reaction gas was analysed by gas chromatography in the following conditions: 10 m column of 20% OS-702 on chromosorb P (column diameter 8 × 6 mm); column temperature 100°; evaporator temperature 140°; carrier gas He; gas flow rate 3 l/h.

RESULTS AND DISCUSSION

From the results of these experiments it was possible to show that the ligand displacement takes place in the following order.



This order means that each acetylene derivative in the compounds which we studied can replace the derivatives which follow it and be replaced by those which precede it.

Some pairs, such as $(\text{COOCH}_3)_2/(\text{C}_6\text{H}_5)_2$, $(\text{CH}_3)_2/\text{H}(\text{C}_6\text{H}_5)$, $\text{H}_2/[\text{CH}_2\text{N}(\text{C}_2\text{H}_5)_2]_2$ can give substitutions in both directions. In these cases the relative amounts of the acetylene complexes present at equilibrium were measured and the position of the acetylene in the series established accordingly. The positions in the series are explained by the fact that substitution in one direction is definitely favoured with respect to substitution in the other.

For the central part of the series the differences in the substitution reactions of the different acetylene derivatives are very small. This may be due to the mesomeric factors which are superposed on the inductive effect derived from one of the groups.

The data obtained, however, confirm that the compounds examined show, in general, a stability gradually increasing with the increase in the electronegativity of the R and R' groups and consequently an energy lowering of the acetylene derivative antibonding π^* molecular orbitals.

This increased stabilisation is therefore linked with the weakening of a σ bond, formed by the π electrons of the acetylenic group, and with the strengthening of the π bond due to increased back-donation of the electrons from cobalt *d*-orbitals to the π^* orbitals of the acetylene derivative.

This result that dative bonding is more important in these compounds than is σ bonding is in accordance with the previous results^{1,6,7} and conclusions reached for the monomeric platinum acetylene compounds.

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SUMMARY

In this work the substitution reactions were studied, of one acetylenic deriv-

ative, by another, in the complexes $\text{Co}_2(\text{CO})_6\text{C}_2\text{RR}'$ in which R and R' = CF_3 , COOCH_3 , C_6H_5 , CH_2Cl , CH_3 , $\text{CH}_2\text{N}(\text{C}_2\text{H}_5)_2$ and H.

On the basis of such reactions, relative stabilities of the various acetylenic derivatives were determined and discussed in terms of the acceptor character of the different acetylenes. Also reported are the preparations and properties of some new compounds of this series.

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