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# FLUOROCARBON-ALKYNE COMPLEXES OF TRANSITION METALS

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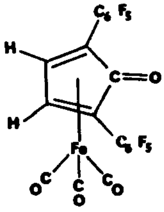
In a recent publication (1) we reported our investigations of the reactions of 3,3,3-trifluoropropyne, $CF_3C\equiv CH$, with pentacarbonyliron and octacarbonyldicobalt. We now report the results of the reactions of the new unsymmetrical fluorocarbon alkyne pentafluorophenylacetylene (2), $C_6F_5C\equiv CH$, with carbonyl compounds of iron and cobalt. Some new reactions of octacarbonyldicobalt with other alkynes are also discussed.

Pentafluorophenylacetylene reacts with pentacarbonyliron at 120°C over 18 hours to give a pale yellow solid, $(C_6F_5C_2H)_2Fe(CO)_4$, and small amounts of fluorocarbon by-products which have not been fully characterized. The spectroscopic properties of the organoiron complex (Table 1) indicate that it is bis-2,5-(pentafluorophenyl)cyclopentadienonetricarbonyliron (I). Thus, the $^1H$ n.m.r. spectrum shows a single resonance at τ 3.38, and, as has been demonstrated (1) for the related complex bis-2,5-(trifluoromethyl)cyclopentadienonetricarbonyliron, this can best be correlated with a structure in which the

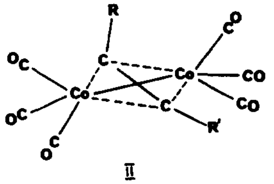


I

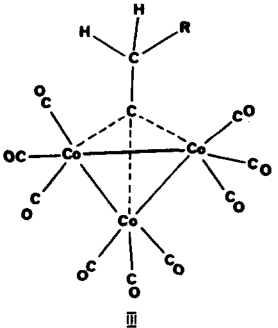
protons are attached to carbon atoms $C_3$ and $C_4$ in the cyclopentadienone ring (3). As in the similar reaction between 3,3,3-trifluoropropyne and pentacarbonyliron (1), only one of the three possible structural isomers is formed.

Investigations of the reactions of pentafluorophenylacetylene with $Fe_2(CO)_9$ and $Fe_3(CO)_{12}$ at 80°C show that in addition to the complex I, unstable red oils and an unstable yellow crystalline solid are obtained. These compounds have not yet been fully characterized.

The reactions of pentafluorophenylacetylene with octacarbonyldicobalt at 60°C for 20 hours gives an alkyne complex, $Co_2(CO)_6C_6F_5C_2H$, as a dark red crystalline solid. The infrared and n.m.r. data for this complex (Table 1) is very similar to that of many other alkyne-cobalt complexes of similar formula (4) and which are known to contain a bridging alkyne unit (5), so that the complex can be formulated as II ($R = C_6F_5$, $R' = H$). When octacarbonyldicobalt and an excess of pentafluorophenylacetylene react at 85°C for 60 hours, an additional organo-cobalt complex, $Co_3(CO)_9CCH_2C_6F_5$ is formed. This complex is isolated as a dark red crystalline solid. The infrared and $^1H$ and $^{19}F$ n.m.r. spectra of this complex (Table 1) are consistent with structure III ($R = C_6F_5$) (6).



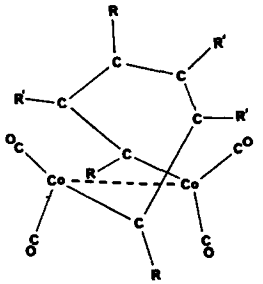
II



III

There are no reports of the isolation of the similar complex (III; $R = C_6H_5$), from the direct reaction of octacarbonyldicobalt and phenylacetylene. However, Stone and co-workers (7) have recently reported such a direct synthesis of the complex $Co_3(CO)_9CCH_2CF_3$ (III; $R = CF_3$) from octacarbonyldicobalt and 3,3,3-trifluoropropyne. We have now been able to confirm that $Co_3(CO)_9CCH_2CF_3$ is formed, albeit in very low yield, from the reaction of 3,3,3-trifluoropropyne and octacarbonyldicobalt at 85°C for 20 hours. We have also isolated the known complex $Co_3(CO)_9CCH_3$ (III; R = H) (8), by direct reaction of acetylene and octacarbonyldicobalt at 80°C for 60 hours. Previously, this compound had been obtained by acid attack on $Co_2(CO)_6C_2H_2$ (II; R, R' = H) (9) and by dehalogenation of $CH_3CCl_3$ with octacarbonyldicobalt (6).

Whereas the reaction of octacarbonyldicobalt and a large excess of hexafluorobut-2-yne at 110°C gives only the complex $Co_2(CO)_6CF_3C_2CF_3$ (II; R, R' = $CF_3$) (10), we have previously shown (1) that a different complex (IV; R = $CF_3$, R' = H) is formed from octacarbonyldicobalt and 3,3,3-trifluoropropyne under identical reaction conditions. We have now re-investigated the reaction of octacarbonyldicobalt and hexafluorobut-2-yne at higher temperatures. From the reaction at 155°C for 45 hours, we have isolated the purple crystalline solid $Co_2(CO)_4(CF_3C_2CF_3)_3$, and a small amount of hexakis(trifluoromethyl)benzene. There is a marked similarity in both the infrared spectra and the $^{19}F$ n.m.r. chemical shift data for this purple complex (Table 1) and the complex IV (R = $CF_3$, R' = H) reported previously (1). We therefore suggest that $Co_2(CO)_4(CF_3C_2CF_3)_3$ has the structure IV (R, R' = $CF_3$) which is similar to the known structure of the related complex $Co_2(CO)_4(Bu^tC_2H)_2(HC_2H)$ (11). The formation of hexakis(trifluoromethyl)benzene in the reaction is presumably a result of thermal cleavage of the organo-cobalt bonds and is a common feature of such reactions (12).



IV

Analogous complexes of acetylene and pentafluorophenylacetylene could not be prepared.

TABLE 1

Spectroscopic Data for the New Organo-Transition Metal Complexes

| | I.R. (carbonyl region) | N.M.R.* |
|---|---|---|
| $(C_6F_5C_2H)_2Fe(CO)_4$ | 2083(s), 2032(s), 2020(sh)<br>1660(s), 1647(s) | $^1H$; τ 3.38<br>$^{19}F$; 130 (doublet), 149 (triplet), 155 (multiplet) |
| $Co_2(CO)_6C_6F_5C_2H$<br>II; R = $C_6F_5$, R' = H | 2098(s), 2061(vs), 2040(vs), 2031(vs) | $^1H$; τ 3.55<br>$^{19}F$; 138 (doublet), 155 (triplet), 162 (multiplet) |
| $Co_3(CO)_9CCH_2C_6F_5$<br>III; R = $C_6F_5$ | 2099(m), 2051(vs), 2038(vs), 2020(m) | $^1H$; τ 5.03<br>$^{19}F$; 144 (doublet), 156 (triplet), 162 (multiplet) |
| $Co_3(CO)_9CCH_2CF_3$<br>III; R = $CF_3$ | 2107(m), 2060(vs), 2042(s), 2027(m) | $^1H$; τ 5.59 (quartet)<br>$^{19}F$; 66 (triplet) |
| $Co_3(CO)_9CCH_3$<br>III; R = H | 2100(m), 2050(vs), 2037(s), 2012(m) | $^1H$; τ 6.31 (singlet) |
| $Co_2(CO)_4(CF_3C_2CF_3)_3$<br>IV; R, R' = $CF_3$ | 2117(m), 2093(s), 2079(m), 2074(sh), 2038(w) | $^{19}F$; 53.2 (quartet), 56.5 (multiplet), 60.4 (doublet) |

* $^{19}F$ ppm referred to $CFCl_3$ as internal standard.

Analytical data for the complexes prepared is given in Table 2.

TABLE 2

Some Physical Data for the New Organo-Transition Metal Complexes

| | m.p. | | C | H | F |
|---|---|---|---|---|---|
| $(C_6F_5C_2H)_2Fe(CO)_4$ | decomp. 250°C | Calc. | 43.5 | 0.4 | 34.4 |
| | | Found | 44.0 | 1.0 | 34.8 |
| $Co_2(CO)_6C_6F_5C_2H$ | 51-52°C | Calc. | 35.2 | 0.2 | 19.9 |
| II; R = $C_6F_5$, R' = H | | Found | 35.5 | 0.9 | 19.1 |
| $Co_3(CO)_9CCH_2C_6F_5$ | 88-89.5°C | Calc. | 32.8 | 0.3 | 15.3 |
| III; R = $C_6F_5$ | | Found | 33.4 | 1.0 | 15.1 |
| $Co_2(CO)_4(CF_3C_2CF_3)_3$ | sublimes without | Calc. | 26.8 | | 47.8 |
| IV; R, R' = $CF_3$ | melting | Found | 26.2 | | 47.4 |

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