Reactions of Azobenzene–Cobalt Carbonyl Complexes with $C_2(CF_3)_2$: Structure of $PhN{:}NC_6H_4C(CF_3){:}C(CF_3)COCo(CO)_2$ and a New Quinolone Synthesis

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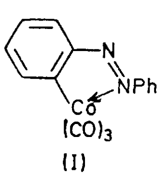
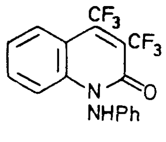
Summary *N*-Anilinoquinolones are formed from phenylazophenyl-2*C*,*N*′-cobalt complexes and hexafluorobut-2-yne; the structure of a *trihapto*-acryloylcobalt complex, obtained from the same reaction, is also reported.

Several years ago, Japanese workers showed[1] that azobenzenes (azbH) can be carbonylated to form indazolones and dioxoquinazolines in the presence of $Co_2(CO)_8$. Later, Heck[2] showed that carbonylation of a presumed intermediate, $(azb)Co(CO)_3$ (I), in methanol, afforded instead 2-methoxycarbonylhydrazobenzene.



(I)



(II)

We now report that the reaction between (I) and hexafluorobut-2-yne affords a mixture of an organic compound (II), and an organocobalt derivative (III). Generally, longer reaction times favour the formation of (II); thus the relative yields of (II) and (III) are 30 and 60% (12 h) and 65 and 25% (18 h). The organic compound (II) was identified as the *N*-anilinoquinolone shown, and is a paleyellow solid, m.p. 210—211° [M 372·068; other peaks at m/e 92 ($C_6H_5NH^+$) and 355 ($P-OH^+$); ν(CO), 1660; ν(NH), 3283 cm^{-1}].

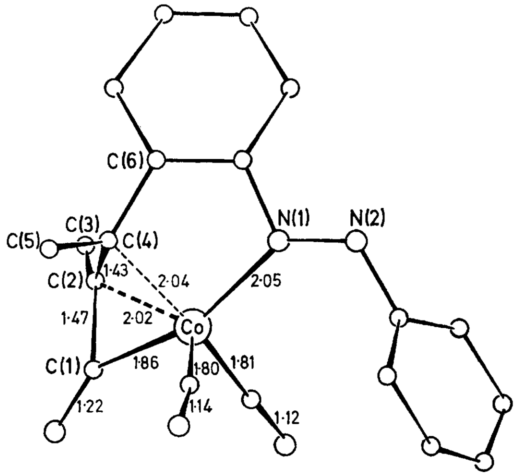


FIGURE. *Molecular structure of complex* (III) [*Fluorine atoms omitted from* C(3) *and* C(5)].

The organo-cobalt derivative (III) is an extremely volatile red-brown solid, m.p. 115—117°, showing two strong ν(CO) bands at 2075 and 2033 cm^{-1}. In addition a third band of medium intensity occurs at 1849 cm^{-1}. The mass spectrum is not informative, showing ions up to m/e ~870, apparently arising from thermal decomposition. A crystal structure revealed the novel molecular arrangement shown in the Figure.

Crystal data: $C_{19}H_9CoF_6N_2O_3$, $M = 486$; red monoclinic crystals; $a = 10·35$, $b = 14·12$, $c = 13·50$ Å, $\beta = 102·9°$; $D_m = 1·65$, $D_c = 1·67$ g cm^{-3} for $Z = 4$.

A total of 687 visually estimated non-zero independent reflections (Mo-K_α radiation) was refined by standard heavy-atom procedures to a current conventional R value of 8·8%.

The molecule is formed by insertion of one acetylene and one CO molecule into the cobalt–carbon bond of (I); concomitant rearrangement results in bonding from the nitrogen *adjacent* to the metallated ring, rather than from N(2). The resulting system can be described as a *trihapto*-acryloyl-cobalt system; alternatively, the metal can be considered to be π-bonded to C(2) and C(4), (mean Co–C, 2·0 Å) and σ-bonded to C(1) [Co–C(1), 1·86 Å]. There is no significant difference between the C–C bond lengths within the acryloyl system. The Co–N(1) bond length is 2·05(2) Å, and other dimensions within the azobenzene group are in good agreement with those found in *trans*-azobenzene.[3]

An unstable *trihapto*-acryloyl-cobalt complex shows an acyl ν(CO) band as high as 1840 cm^{-1}, the high frequency being attributed to ring strain.[4] In the present case, the dihedral angle between the planes defined by atoms C(1)–C(2)–C(3)–C(4) and C(2)–C(4)–C(5)–C(6) is 43°, and indicates the considerable distortion of the olefin skeleton in complex (III).

The reaction leading to (II) and (III) has also been found to occur with substituted azobenzenes, and in all cases, both compounds corresponding to (II) and (III) were obtained. This reaction represents a new route to substituted 2-quinolones, a type of compound of which few examples have been described previously.

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