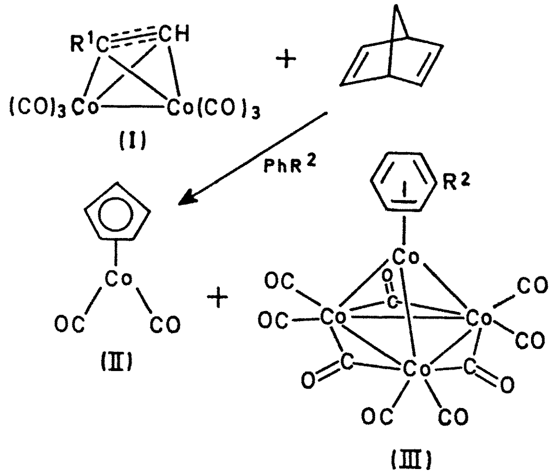
A Cobalt Induced Cleavage Reaction and a New Series of Arenecobalt Carbonyl Complexes

By I. U. KHAND, G. R. KNOX, P. L. PAUSON,* and W. E. WATTS

(Department of Pure and Applied Chemistry, University of Strathclyde, Glasgow, C.1)

Summary Reaction of bicyclo[2,2,1]hepta-2,5-diene with alkynedicobalt hexacarbonyls in inert solvents gives dicarbonylcyclopentadienylcobalt, but in aromatic hydrocarbons arene-nonacarbonyltetracobalt complexes are formed.

WE have treated the complexes ($R^1C \equiv CH)Co_2(CO)_6$, (I), ($R^1$ = H or Ph), with an excess of norbornadiene in different solvents. When the reaction was conducted in dimethoxyethane or in iso-octane, the major product, obtained in high yield (based on Co), was dicarbonylcyclopentadienylcobalt (II). This must result from scission (reverse Diels–Alder reaction) of part of the norbornadiene to acetylene and cyclopentadiene. From the known rate data for this reaction[1] it is clear that no significant scission would occur under the conditions we used and we conclude that this reaction must be initiated by complexes (I) or their decomposition products. Other cobalt complexes reacted similarly; *e.g.* $PhCCo_3(CO)_9$ yielded a norbornadiene complex $PhCCo_3(CO)_7C_7H_8$ which could function as an intermediate in the Diels–Alder scission, and on prolonged reaction gave a trinuclear cyclopentadienylcobalt complex.



When the solvent was an aromatic hydrocarbon, PhR^2 (R^2 = H or Me), the major cobalt-containing products were shown by analysis and mass and n.m.r. spectra to have constitutions $(PhR^2)Co_4(CO)_9$. We formulate these as having structure (III) in view of the appearance of strong bridging as well as terminal carbonyl peaks in the i.r. Analogous complexes have been obtained from xylene, mesitylene, and anisole. The structure (III) is derived from that[2] of $Co_4(CO)_{12}$ by simple replacement of 3 apical CO groups by the arene and we find that simple warming of arenes with this carbonyl, $Co_4(CO)_{12}$ or with dicobaltoctacarbonyl which readily decomposes to $Co_4(CO)_{12}$,[3] yields the same complexes, *e.g.* $C_6H_3Me_3Co_4(CO)_9$.

In addition to the above products, the reaction of norbornadiene with complexes (I) yields hydrocarbon and ketonic products derived from norbornadiene, acetylene, and carbon monoxide.

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