

Activation of Alkynes by Transition Metals

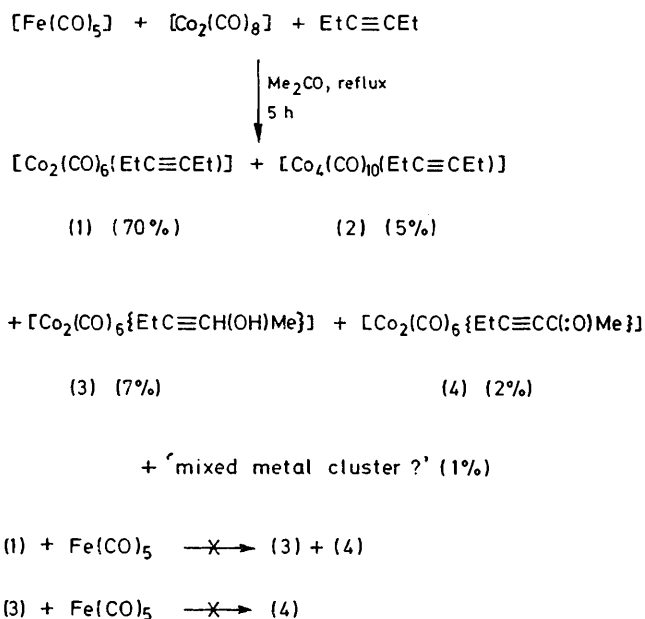
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Summary Activation of alkynes leading to oxygen incorporation α to the triple bond is observed when $[\text{Fe}(\text{CO})_5]$, $[\text{Co}_2(\text{CO})_8]$, and an internal alkyne are heated

in refluxing acetone; evidence for the possible formation of a mixed acetylenic iron-cobalt cluster has also been obtained.

SOME of the many studies of transition metal cluster compounds are currently focused on mixed metal clusters. So far few reports have dealt with acetylenic mixed metal clusters,¹ whereas the chemistry of acetylenic homo-metal clusters is well developed.² In the case of mixed iron and cobalt species an attempted preparation of mixed clusters from $[\text{Co}_2(\text{CO})_8(\text{PhC}\equiv\text{CPh})]$ and $[\text{Fe}(\text{CO})_5]$ failed;³ $[\text{FeCo}_3(\text{CO})_{10}(\text{PhC}\equiv\text{CPh})]^-$ and $[\text{FeCo}_2(\text{CO})_8(\text{PhC}\equiv\text{CPh})]$ have been reported but not fully characterized from various reactions of $[\text{HFeCo}_3(\text{CO})_{12}]$.⁴ With the aim of obtaining acetylenic mixed metal clusters of iron and cobalt we have examined the reaction of a mixture of $[\text{Fe}(\text{CO})_5]$ and $[\text{Co}_2(\text{CO})_8]$ with alkynes. However, the most significant result was not the formation of mixed metal clusters, but the activation of the alkynes.



SCHEME

$[\text{Fe}(\text{CO})_5]$, $[\text{Co}_2(\text{CO})_8]$, and hex-3-yne were heated in refluxing acetone for 5 h under N_2 ; several organometallic complexes were obtained (Scheme) which were characterized by elemental analysis, and mass, i.r., and ^1H and ^{13}C n.m.r. spectroscopy. Elution of the reaction products on a

silica column with light petroleum-chloroform gave five bands. Analytical data showed that two of the components were the acetylenic carbonyl cobalt derivatives (1)⁵ and (2),⁵ in which the alkyne maintained its identity. Two other components have the same Co_2C_2 tetrahedral core structure as (1), but oxygen has been incorporated into the alkyne. They were characterized as the complexes (3) and (4): (3), red-brown oil, mass spectrum: m/e 384 (M^+), followed by loss of 6 CO; i.r.: ν_{max} (CCl_4) 3623m (OH), and 2093m, 2053vs, 2030vs, 2012s, and 2010m(sh) (all C=O) cm^{-1} ; ^1H n.m.r.: δ (CDCl_3) 5.02 (q, CH), 2.83 (q, CH_2), 2.72 (s, OH), 1.46 (d, CHMe), and 1.25 (t, CH_2Me); ^{13}C n.m.r.: δ (CDCl_3) 200.4 (CoCO), 102.2 and 100.7 ($\equiv\text{C}$), 68.1 (CH), 26.1 (CH_2), 24.4 (CHCH_3), and 15.0 p.p.m. (CH_2CH_3); (4), red-brown oil, mass spectrum: m/e 382 (M^+), followed by loss of 6 CO + intense peaks expected for fragmentation of the ketone ligand; i.r.: ν_{max} (CCl_4) 2100m, 2063vs, 2038vs 2034s(sh) 2015m(sh) and 1665ms (all C=O) cm^{-1} ; ^1H n.m.r.: δ (CDCl_3) 2.91 (q, CH_2), 2.41 (s, COMe), and 1.32 (t, Me); ^{13}C n.m.r.: δ (CDCl_3) 200.6 (CO), 198.9 (CoCO), 102.6 and 87.2 ($\equiv\text{C}$), 30.2 (COCH_3), 26.3 (CH_2), and 15.0 p.p.m. (CH_2CH_3). Complexes (3) and (4) were not obtained from the reaction of $[\text{Fe}(\text{CO})_5]$ and (1) under the same conditions; (1) was recovered largely unchanged, and some (2) was formed. Similarly, heating (3) in refluxing acetone in the presence of $[\text{Fe}(\text{CO})_5]$ does not give the ketone derivative (4). These results show that complexes (3) and (4) are not formed from further reaction of (1) with $[\text{Fe}(\text{CO})_5]$, and that (4) is not formed by reaction of (3) with $[\text{Fe}(\text{CO})_5]$. The fifth component was obtained as a dark brown powder, and a crystalline sample could not be obtained for characterization. However, its mass spectrum indicated that it was possibly a mixed metal cluster of the type $[\text{FeCo}_2(\text{CO})_7(\text{EtC}\equiv\text{CEt})_2]$, analogous to the $[\text{Fe}_3(\text{CO})_8(\text{alkyne})_2]$ complex reported previously.⁶

Activation of one of the methylene groups α to the triple bond was also observed in the reaction of $[\text{Fe}(\text{CO})_5]$ and $[\text{Co}_2(\text{CO})_8]$ with oct-4-yne. Besides the homologues of (1) and (2), $[\text{Co}_2(\text{CO})_6(\text{Pr}^n\text{C}\equiv\text{CPr}^n)]$ and $[\text{Co}_4(\text{CO})_{10}(\text{Pr}^n\text{C}\equiv\text{CPr}^n)]$, the oxygenated alkyne derivative $[\text{Co}_2(\text{CO})_6\{\text{Pr}^n\text{C}\equiv\text{CCH}(\text{OH})\text{Et}\}]$ was obtained as a red-brown oil, mass spectrum: m/e 412 (M^+), followed by loss of 6 CO; i.r.: ν_{max} (CCl_4) 3625w (OH), and 2093m, 2053vs, 2032vs, 2021s, and 2008m(sh.) (all C=O) cm^{-1} ; ^1H n.m.r.: δ (CDCl_3) 4.58 (t, CH), 2.74 (t, CCH_2), 2.68 (s, OH), 1.69 (m, CH_2CH_2 and CHCH_2), and 1.09 and 1.04 (each t, Me).

(Received, 2nd April 1979; Com. 336.)

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