Anionic Acetylenic Complexes of Group VI Metal Carbonyls

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Summary Anionic complexes containing an acetylene group σ-bonded to a Group VI transition metal, $M(CO)_5-C{\equiv}CR^-$, were prepared from $M(CO)_6$ and $RC{\equiv}C^-$, where M is Cr, Mo, or W, and R is Ph or Me.

A LARGE number of anionic complexes of the type $M(CO)_5X^-$ have been prepared[1] by photolysis of a Group VI metal carbonyl and an anionic base such as halide ion or pseudohalide ion. We report the synthesis of a series of compounds where the substituent is a substituted acetylide ion. Derivatives of all three Group VI metals have been prepared where X is phenylacetylene or methylacetylene.

The alkyl and aryl derivatives were prepared by irradiating the metal hexacarbonyls in the presence of the acetylide anions. The complex anions were isolated as the bistriphenylphosphineiminium[2] (hereafter abbreviated as ppn$^+$) salts. The products were obtained as yellow crystalline solids in yields of 20—50%. The salts behave as 1:1 electrolytes in nitromethane.

The i.r. spectrum of each complex taken in methylene chloride solution, shows a pattern of bands in the carbonyl stretching region (1700—2200 cm.$^{-1}$) consistent with C_{4v} symmetry: *e.g.*, $ppnW(CO)_5C{\equiv}CPh$, $\nu_{C\equiv C} = 2080$ vw; $\nu_{CO} = 2043$w, 1908s, and 1851m. Three bands are assigned to carbonyl stretches and one band to the acetylenic stretching frequency. Only minor differences were noted in the position of these bands in all of the complexes. No evidence for the presence of acetylenic hydrogen was observed in the i.r. spectra.

A comparison of the carbonyl stretching frequencies observed for the acetylide complexes with those observed for the cyanide complexes, $M(CO)_5CN^-$, indicate that the π acceptor strength of the acetylide ligand is qualitatively comparable with the cyanide ion. A similar comparison with the complexes $M(CO)_5PPh_3$ suggests that the metal–carbon bond in the acetylide group is stronger than the metal–phosphorus bond. Thus it would be expected that triphenylphosphine would not displace the acetylide group.

The assignment of the acetylenic stretching frequency to bands in the region of 2080 cm.$^{-1}$ strongly supports the absence of any π-bonded acetylenic groups such as are found in[3] $(PhC{\equiv}CPh)_3$ WCO, and compare closely with the known σ-bonded derivative[4] π-$C_5H_5Mo(CO)_3C{\equiv}CPh$. Thus it is concluded that unlike the halide or pseudohalide complexes $M(CO)_5L^-$ (where L = Br, I, CN, or SCN) which form bridged dimers $M_2(CO)_{10}L^-$ no dinuclear species are obtained.

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