

Preliminary communication

Coordination synthesis on metal centers

VI*. Reaction of tris(2-methoxyphenyl)chromium(III) with 2-butyne

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(Received March 31st, 1971)

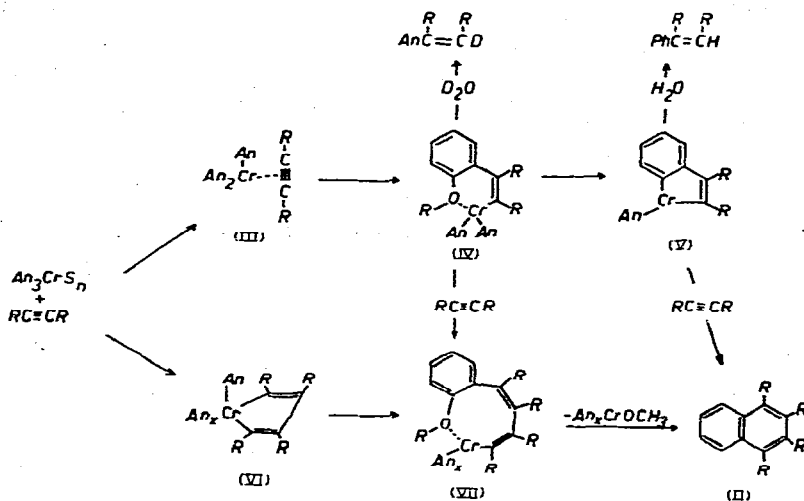
Solvated, crystalline tris(2-methoxyphenyl)chromium(III) and 2-butyne interact, either neat, or in tetrahydrofuran solution to give (in 40% yield), the insoluble bis(2-methoxyphenyl)chromium(II) (identified by conversion to the known bipyridyl (Bipy) complex $[(o\text{-CH}_3\text{OC}_6\text{H}_4)_2\text{Cr}(\text{Bipy})_2] \text{I}^2$). Hydrolysis of the reaction mixture gave, as major products, anisole, 2,2'-bianisyl, *cis*-2-(2-methoxyphenyl)-2-butene (I), a crystalline 2,3-bis(2-methoxyphenyl)-2-butene, m.p. 86–88°, 1,2,3,4-tetramethylnaphthalene (II) and hexamethylbenzene. Treatment of the reaction mixture with D₂O gave anisole and mono-deuterioanisole (isotopic composition D₀ 30%, D₁ 70%) and (2-CH₃OC₆H₄)C(CH₃)=C(CH₃)(D) (Ia) (isotopic composition D₀ 3%, D₁ 97%). The other compounds were not enriched in deuterium.

The formation of the deuterio-species (Ia) can be interpreted in terms of the rearrangement of an organochromium-acetylene complex (III) to a σ -bonded vinylchromium species³ (IV),

The tetramethylnaphthalene (II) is the only major product lacking the methoxyl group originally present in the *o*-anisyl groups bonded to chromium. It is therefore highly improbable that (II) is formed via the chromocycle (V)⁴ (Scheme I), since methoxyl extrusion at this stage should result in the presence of isolable quantities of 2-phenyl-2-butene in the hydrolysis products^{4,5}. A plausible route to (II) would involve the cyclisation, with concomitant extrusion of a CrOCH₃ residue, of an *o*-anisylbutadienylchromium species (VII). The latter can, in turn, be formed either by the interaction of the vinylchromium species (IV) with a second molecule of 2-butyne, or, by the transfer of an aryl group within an organochromium-bis(acetylene) complex (Scheme 1 (VI))⁵. The present evidence does not permit distinction between these mechanisms; however experiments are underway to determine whether the vinylchromium species (IV) is an intermediate in the formation of the tetramethylnaphthalene.

*For Part V see ref. 1.

**Whitesides and Ehmann have proposed that, in the reaction of Ph₃Cr(THF)₃ with 2-butyne, the chromocycle (V) is the precursor of 1,2,3,4-tetramethylnaphthalene⁴. Their results show that the lifetime of (V) is such as to permit the isolation of 2-phenyl-2-butene from the hydrolysis products.



Scheme I. (An = 2-methoxyphenyl and R = CH₃).

ACKNOWLEDGEMENT

We wish to thank Dr. W.E. Koerner and his associates, Monsanto Co., Research Center, St. Louis, Mo., U.S.A. for the mass-spectroscopic analysis.

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J. Organometal. Chem., 29 (1971) C31-C32