

COORDINATION SYNTHESIS ON METAL CENTERS

VII*. REACTION OF TRIS(2-, 3-, AND 4-METHOXYPHENYL)CHROMIUM WITH 2-BUTYNE

R. P. A. SNEEDEN and H. H. ZEISS

Monsanto Research S.A., Eggbühlstrasse 36, CH 8050 Zürich (Switzerland)

(Received January 24th, 1972)

SUMMARY

All the major, and some of the minor, products formed by the interaction of tris(2-, 3-, and 4-methoxyphenyl)chromium and 2-butyne have been isolated and identified. In the reaction of tris(2-methoxyphenyl)chromium, a novel reaction (methoxyl extrusion), involving the formation of 1,2,3,4-tetramethylnaphthalene, has been detected. Deuterolytic studies in the same system have proved that *cis*-(2-CH₃-OC₆H₄)C(CH₃)=C(CH₃)Cr is formed during the reaction. The mechanism of the reaction of organochromium compounds with acetylenes is discussed in terms of these new results.

INTRODUCTION

In preliminary studies¹ it was found that tris(2-methoxyphenyl)chromium-(III)** [(2-An)₃Cr] reacted with 2-butyne to give, by methoxyl extrusion, 1,2,3,4-tetramethylnaphthalene. In view of the unusual nature of this reaction, the studies were extended to the isomeric tris(3- and 4-methoxyphenyl)chromium systems. The primary objective was to ascertain whether this methoxyl extrusion was indeed peculiar to the reaction of (2-An)₃Cr system with 2-butyne, or whether it involved an unusual ether cleavage in the final reaction product.

RESULTS AND DISCUSSION

The isomeric tri-2-, 3-, and 4-anisylchromium compounds were prepared in the usual manner² from the appropriate arylmagnesium halide and CrCl₃(THF)₃ in tetrahydrofuran. (2-An)₃Cr was extremely soluble in tetrahydrofuran, but could be isolated as garnet crystals by the appropriate manipulations. (3- and 4-An)₃Cr were obtained directly from the reaction mixtures as silky orange-red needles. All three

* For Part VI see ref. 1.

** Throughout the text anisyl (An) will be used in place of methoxyphenyl.

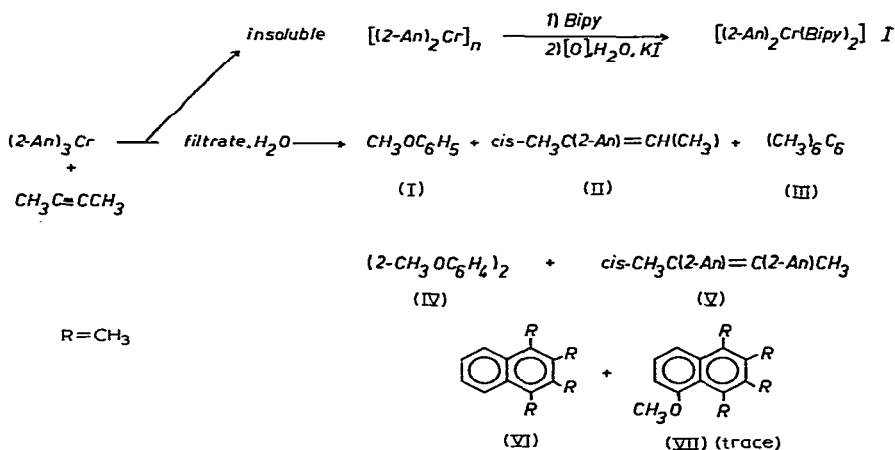
organochromium compounds reacted with HgCl_2 , in tetrahydrofuran, to give high yields of the appropriate anisylmercury chlorides. This proves that no isomerization, or loss of methoxyl had occurred during the formation of the σ -bonded organochromium species.

In three parallel experiments the isomeric $(\text{An})_3\text{Cr}$ compounds were allowed to react with 2-butyne, at 0 to 20°, for 1 to 2 weeks.

(a). $(2\text{-An})_3\text{Cr}$

Filtration of the final reaction mixture, under argon, gave a yellow solid, shown to be $(2\text{-An})_2\text{Cr}^{\text{II}}$ by conversion into the known di-2-anisylbis(2,2-bipyridine)-chromium(III) iodide³. Hydrolysis of the filtrate gave the products shown in Scheme 1. The major products were (I), the mono- and disubstituted butenes (II) and (V), hexamethylbenzene (III) and the methoxyl-free naphthalene (VI).

SCHEME 1

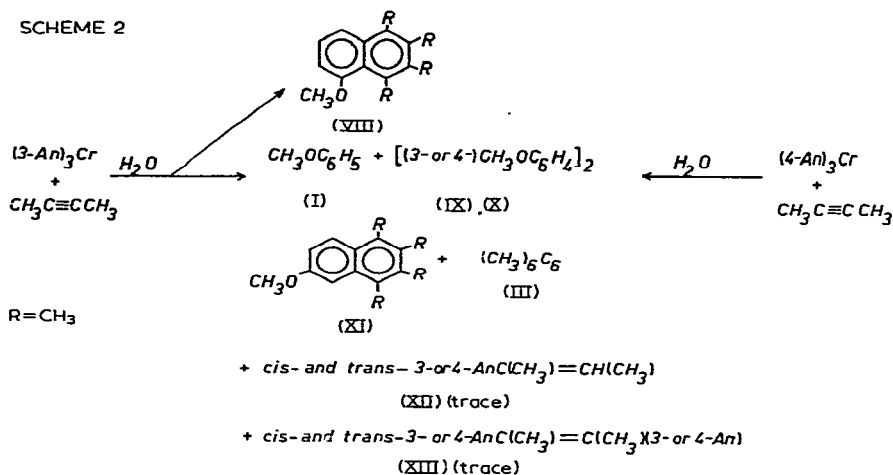


In a repeat experiment, deuterolysis of the total reaction mixture (after 1 week) gave *cis*-2-(2-anisyl)-3-deuterio-2-butene (97% D_1) and 2-deuterioanisole as the only major deuterium containing products.

(b). $(3\text{- and } 4\text{-An})_3\text{Cr}$

The final hydrolytic products from these reactions were similar, Scheme 2, the only difference being that $(3\text{-An})_3\text{Cr}$ gave both 5- and 6-methoxy-1,2,3,4-tetramethylnaphthalene [(VIII) and (XI)] whilst $(4\text{-An})_3\text{Cr}$ gave only 6-methoxy-1,2,3,4-tetramethylnaphthalene (XI). However, in contrast to the reaction with $(2\text{-An})_3\text{Cr}$, both the present reactions gave the *cis* and *trans* isomers of the mono- and dianisylbutenes [(XII) and (XIII) respectively]. Furthermore no methoxy-free compounds (e.g. 1,2,3,4-tetramethylnaphthalene) were detected amongst the reaction products. The methoxyl extrusion process is therefore particular to the *ortho*-anisyl-chromium compound.

SCHEME 2



Mechanism of the reaction of triorganochromium compounds with acetylene

The accumulated results from the reactions of a variety of organochromium compounds with a variety of acetylenes^{1,2,4-21} indicate that any mechanism for these reactions must account for the formation of three main groups of products:

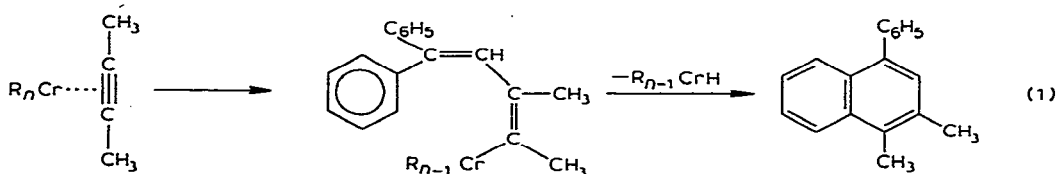
Group I, those derived from one, or two of the organic groups bonded to chromium (or a fragmentation product thereof) and one acetylenic unit, *e.g.* the mono- and disubstituted butenes, (II) and (V), Scheme 1.

Group II, those derived from one, or two of the organic groups bonded to chromium and two acetylenic units, *e.g.* the methoxytetramethylnaphthalenes (VIII) and (XI), Scheme 2, or 1,4-diphenylbutadiene [from $(\text{C}_6\text{H}_5)_3\text{Cr}$ and $\text{CH}\equiv\text{CH}^{11}$].

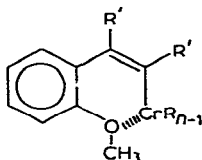
Group III, those derived from three acetylenic units with and without the organic groups bonded to chromium, *e.g.* $(\text{CH}_3)_6\text{C}_6$ or 1,6-diphenylhexatriene, [from $(\text{C}_6\text{H}_5)_3\text{Cr}$ and $\text{CH}\equiv\text{CH}^{11}$].

Group I

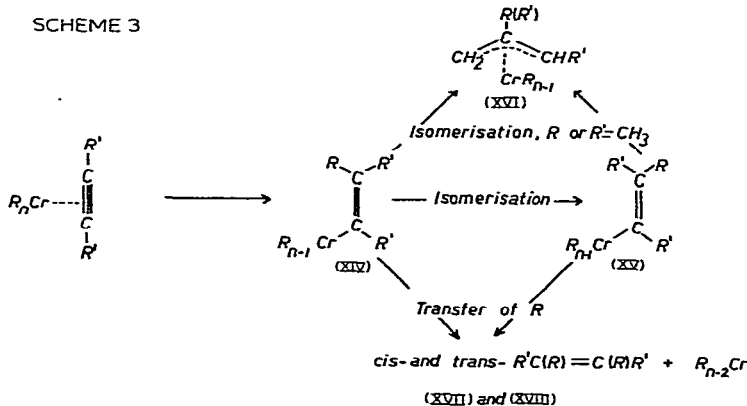
The formation of these compounds can be rationalized in terms of an isomerization within an organochromium-acetylene complex^{9,16}. In this process one of the organic groups (or a fragmentation product thereof^{10,16,19}) bonded to chromium is transferred to the complexed acetylene, giving a σ -bonded *cis*-vinylchromium species [(XIV), Scheme 3]. The isolation of isotopically pure *cis*-2-(2-anisyl)-3-deuterio-2-butene, in the present work can only be interpreted in terms of such an isomerization. Also, the formation of 1,2-dimethyl-4-phenylnaphthalene, from tris(α -phenylstyryl)-chromium and 2-butyne²⁰, can be interpreted in terms of an initial transfer of a styryl group to complexed acetylene followed by metal hydride elimination, eqn. (1), $\text{R}=(\text{C}_6\text{H}_5)_2\text{C}=\text{CH}$.



Trivinylchromium is known to be thermally unstable⁷, and arylvinylmetallic compounds are known to be configurationally unstable²². It is therefore to be expected that the *cis*-vinyl-chromium species should undergo fragmentation and isomerization reactions. In the present work, the fact that the 2-anisyl-chromium compound gives only *cis*-2-(2-anisyl)-2-butene can be ascribed to the stabilizing influence of the *ortho*-CH₃O group in the *cis*-vinyl-chromium species. In the absence



of any stabilizing influence (*e.g.* the 3- or 4-anisyl-, or methyl-¹⁰ chromium compounds) isomerization to the *trans*-vinyl-chromium compounds, (XV), Scheme 3, occurs.



When R or R' is a methyl group a second type of isomerization, involving a hydrogen shift, leads to a π -allylic chromium species [(XVI), Scheme 3]. Fragmentation of the three organochromium compounds (XIV), (XV) and (XVI) would lead to the corresponding monomeric ethylenes and dimeric butadienes (or transformation products thereof). In the reaction of (CH₃)₃Cr and C₆H₅C≡CC₆H₅ all three ethylenic products (*i.e.* *cis* and *trans*- α -methylstilbene and α -benzylstyrene) have been isolated⁹.

A third transformation possible in the vinylchromium compounds (XIV) and (XV) is the transfer of a second organic group to give the disubstituted butenes or stilbenes (XVII) and (XVIII) (R' = CH₃ or C₆H₅), Scheme 3. The results of the present work (*i.e.* the isolation of the 2,3-dianisyl-2-butenes, Schemes 1 and 2) together with those with the triphenyl- and tri-2-tolylchromium systems⁸ confirm the occurrence of this reaction.

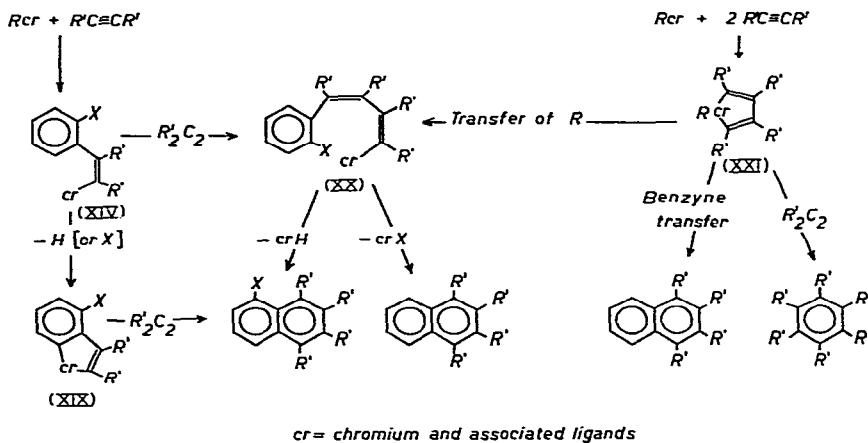
Group II/III.

The method of formation of products involving two or more acetylenic units (*e.g.* the substituted naphthalenes and hexasubstituted benzenes) remains a subject of controversy. The point of contention is the sequence in which the acetylenic units are united, and as a corollary, whether the substituted naphthalene and benzene

originate from a common intermediate. Three mechanisms have been proposed, Scheme 4.

Two of these mechanisms involve the interaction of the *cis*-vinylchromium intermediate¹ (XIV), or the derived chromocycle²⁰ (XIX) with a second molecule of acetylene, to give the naphthalene, either via the σ -bonded butadienyl-chromium complex (XX), Scheme 4, or directly. In these mechanisms the formation of the hexa-substituted benzene follows an independent path.

SCHEME 4

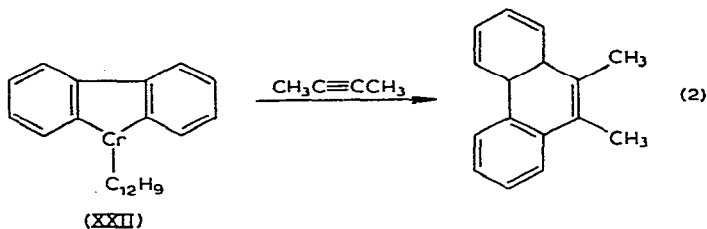


In view of the present results, however, it is improbable that the chromocycle (XIX) ($X = OCH_3$) is an intermediate in naphthalene formation, since the formation of 1,2,3,4-tetramethylnaphthalene [from $(2-An)_3Cr$ and 2-butyne] clearly involves the loss of OCH_3 . Were this to occur in the formation of the chromocycle [*i.e.* to give (XIX) ($X = H$)] then the corresponding phenylbutenes should be found amongst the products. The presence of neither *cis*- nor *trans*-phenyl-2-butene could be detected amongst the trace products.

In the third mechanism it is suggested¹⁷ that two acetylene units, complexed to a low-valent chromium species, interact to give the chromocycle* (XXI), Scheme 4. The latter can undergo a variety of transformations. Thus reaction with a third molecule of acetylene would give the hexasubstituted benzene. The transfer of an organic group, *per se*, would result in the σ -bonded butadienyl species (XX). Alternatively a fragmentation product of the organic group, bonded to chromium, can be transferred; thus when R is aryl, transfer of a benzyne unit would give the substituted naphthalene. The latter process could involve the loss of the *ortho*-substituent. The observation²⁰ that the dibenzochromole (XXII) reacts with 2-butyne to give 9,10-

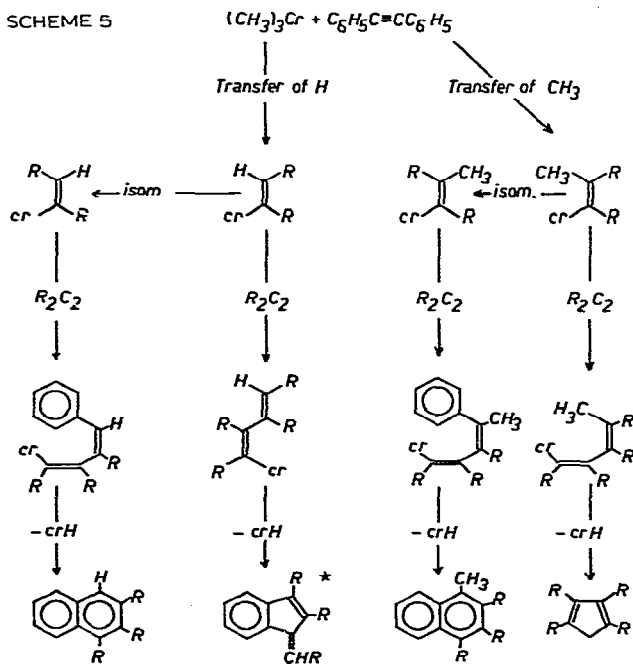
* This "chromocycle" has been variously formulated as complexed "cyclobutadiene", or a complexed butadiene diradical, or its valence tautomer [the metallocycle (XXI)]^{2,7,17}. The recent work by Whitesides and Ehmann [with $(C_6H_5)_3Cr(THF)_3$ and $CD_3C\equiv CCH_3$]^{13,14,20} has, however, ruled out the intervention of a symmetrical cyclobutadiene intermediate in the formation of the substituted naphthalenes and hexa-substituted benzenes.

dimethylphenanthrene (eqn. 2) illustrates that the chromocycle (XXI) could be an intermediate in the formation of the hexasubstituted benzenes.



The available chemical evidence concerning the reactions of triarylchromium^{1,2,4,6,8,11,13-15,20} and trivinylchromium^{7,12,20} can therefore be interpreted in terms of either the butadienyl-chromium mechanism or the chromocycle mechanism. The existence of both classes of compounds, namely a σ -bonded butadienyl-ruthenium compound and a rhodium metalocycle, has recently been proved by full X-ray structure analyses^{23,24}.

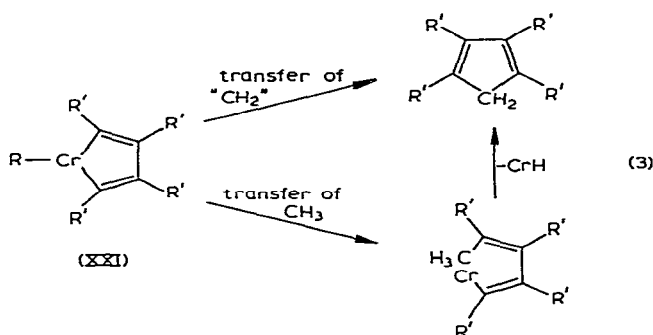
The interpretation of the results from reactions involving the trimethylchromium system^{5,9,10,16-19}, is complicated by the ease with which chromium abstracts hydrogen from an alkyl group bonded to the metal. Thus some of the products (*e.g.*



* Isolated from reaction of methyl-vanadium system and 2-butyne.

1,2,3-triphenyl-4-methylnaphthalene, 1,2,3-triphenylnaphthalene and 1,2,3,4-tetra-phenyl-1,3-cyclopentadiene) correspond to the interaction of two acetylenic units with either one of the organic groups bonded to chromium (CH_3) or with a fragmentation product thereof (H or CH_2). The formation of these compounds can be interpreted in terms of metal hydride elimination in isomeric σ -bonded butadienyl-chromium species, Scheme 5. The latter are, in turn, formed by the interaction of the appropriate isomer of the original vinyl-chromium species with a second molecule of acetylene, Scheme 5.

The tetraphenylcyclopentadiene can also be formed from the chromocycle (XXI) ($\text{R} = \text{CH}_3$). Transfer of a carbenoid unit would give the cyclopentadiene directly^{17,18}, eqn. (3). The transfer of a methyl group results in the σ -bonded butadienyl-chromium species, which upon metal hydride elimination furnishes the cyclopentadiene, eqn. (3) (Cr = chromium and associated ligands, $\text{R} = \text{CH}_3$, $\text{R}' = \text{C}_6\text{H}_5$).



Both the σ -bonded butadienyl-chromium and the chromocycle mechanisms account satisfactorily for the formation of the majority of the products, isolated to date, from the reaction of triorganochromium species with disubstituted acetylenes. A choice between the two mechanisms must therefore await the results of further experiments designed either to prepare authentic specimens of these intermediates, or to establish what relationship if any exists between the rates of formation of the various products. Thus in the butadienyl-chromium mechanism the formation of the vinyl-chromium species and the substituted naphthalenes are related and independent of the formation of the hexasubstituted benzenes. In the chromocycle mechanism the formation of the naphthalenes and R_6C_6 are related and independent of the *cis*-vinyl-chromium species.

EXPERIMENTAL (With Mr. P. Widin)

Experiments with organometallic compounds were carried out under argon. The microanalyses were carried out by Mr. W. Manser of the Eidg. Techn. Hochschule, Zürich.

Tris(2-, 3- and 4-methoxyphenyl)chromium

The title compounds were prepared, in the usual manner², by the interaction of the appropriate anisylmagnesium bromide (160 ml, 120 mmoles) and $\text{CrCl}_3(\text{THF})_3$

(15 g, 40 mmoles) in tetrahydrofuran from -70 to 20° . The tris(3- and 4-methoxyphenyl)chromium compounds were obtained directly from the reaction mixtures, as silky orange-red, air- and moisture-sensitive crystals (ν_{\max} 2837 cm^{-1} , OCH_3). Tris-(2-methoxyphenyl)chromium was obtained as garnet-colored crystals, by the slow concentration (high vacuum) of the total reaction mixture remaining after the removal of the magnesium salts (precipitated with dioxane). The crystalline $(2\text{-An})_3\text{Cr}$, μ_{eff} , 3.9 B.M.* reacted with D_2O to give a quantitative yield of 2-deuterioanisole (isotopic composition, D_0 , 1.2; D_1 , 98.8%)**, identified by IR spectroscopy²⁵.

The individual, crystalline, trianisylchromium compounds reacted with HgCl_2 (in tetrahydrofuran) to give (2-, 3- and 4-methoxyphenyl)mercury chlorides (in 93, 96, 95% yield), m.p. and mixed m.p. 178–179, 163–164 and 252–255°, respectively.

Reaction of tris(2-, 3- and 4-methoxyphenyl)chromium with 2-butyne

In three parallel experiments, solutions of the title compounds (see above) were treated with 2-butyne (20 ml) at 0° . The reaction mixtures were kept at 0° , under argon, for one week***. The total reaction mixtures were hydrolyzed (gas evolution), acidified (dilute HCl), and the organic material extracted with ether. The volatile products, anisole and THF, were removed by distillation (water pump). The remaining organic products were isolated from these residues by a combination of column chromatography, GLC, and derivative formation (picrates).

$(2\text{-An})_3\text{Cr}$. The residue (9.403 g) gave, as hexane eluate, an oily mush (5.6 g) from which the following compounds were isolated: (i) Hexamethylbenzene (2.04 g), m.p. and mixed m.p. $161\text{--}163^\circ$. (ii) *cis*-2-(2-Methoxyphenyl)-2-butene, colorless oil, identified by a direct comparison of its IR and NMR spectra with those of an authentic specimen. (iii) 1,2,3,4-Tetramethylnaphthalene, m.p. and mixed m.p. $102\text{--}105^\circ$, this compound was isolated via its picrate, m.p. and mixed m.p. $178\text{--}180^\circ$. (iv) One of the isomeric 2,3-bis(2-methoxyphenyl)-2-butenes, m.p. $87\text{--}89^\circ$; (Found: C, 80.3; H, 7.6; O, 12.4, mol. wt., 267****. $\text{C}_{18}\text{H}_{20}\text{O}_2$ calcd.: C, 80.6; H, 7.5; O, 11.9%; mol. wt., 268.3.); λ_{\max} (EtOH) 274, 279 (log ϵ , 3.79, 3.78), λ sh. 245 nm (log ϵ , 3.88). ν_{\max} 2837 cm^{-1} (OCH_3). NMR δ_{TMS} (CDCl_3): 2.075 (singlet, 6 protons, 2 C=C-CH₃), 3.71 (singlet, 6 protons, 2 ArOCH₃); 6.35 to 7.2 (multiplet, 8 protons, 2 C₆H₄). Preliminary crystallographic data**** did not show the presence of a center of symmetry in the unit cell. It is therefore probable that the compound is *cis*-2,3-bis(2-methoxyphenyl)-2-butene. (v) 5-Methoxy-1,2,3,4-tetramethylnaphthalene (10 mg), this compound, separated via its crimson picrate, m.p. $170\text{--}172^\circ$, was obtained crystalline (ex MeOH), m.p. $78\text{--}80^\circ$. (Found: C, 84.0; H, 8.5; O, 7.8. $\text{C}_{15}\text{H}_{18}\text{O}$ calcd.: C, 84.1; H, 8.5; O, 7.5%.) NMR δ_{TMS} (CDCl_3): 2.37 (singlet, 6 protons, 2 ArCH₃); 2.56 (singlet, 3 protons, ArCH₃); 2.79 (singlet, 3 protons, ArCH₃); 3.86 (singlet, 3 protons, ArOCH₃); 6.75 (2 doublets *o*- and *m*-coupled, 1 proton, 6-H); 7.3 (multiplet, 1 proton, 7-H); 7.6 (2

* This magnetic moment was kindly determined by Drs. S. and G. Olivé of MRSA, Zürich.

** All isotopic compositions were kindly determined, mass-spectrometrically by Dr. W. E. Koerner and his associates, Research Center, Monsanto Company, St. Louis, U.S.A.

*** Subsequent product distribution studies, with $(2\text{-An})_3\text{Cr}$, showed that there was no change in the relative amounts of products after 80–90 h.

**** Kindly determined, by crystallographic methods, by Drs. J. J. Daly and F. Sanz of MRSA (Zürich), using the measured unit cell volume and the measured density (1.160 gm/cc, by flotation in KBr solution).

doublets *o*- and *m*-coupled, 1 proton, 8-H). (vi) 2,2'-Dimethoxybiphenyl, m.p. and mixed m.p. 151–153°.

(3-*An*)₃Cr. The residue (9.506 g) gave, as hexane eluate, an oily mush (6.50 g) from which the following compounds were isolated: (i) Hexamethylbenzene (2.65 g), m.p. and mixed m.p. 161–163°. (ii) 5-Methoxy-1,2,3,4-tetramethylnaphthalene (0.5 g), isolated by preparative-scale GLC. and identified by NMR spectroscopy and m.p. and mixed m.p. (78–80°). (iii) 6-Methoxy-1,2,3,4-tetramethylnaphthalene (1.4 g), identified by NMR spectroscopy and m.p. and mixed m.p. (114–115°). (iv) Both *cis*- and *trans*-2-(3-methoxyphenyl)-2-butene (minor amounts), identified by a direct comparison of their IR and NMR spectra with those of authentic specimens. (v) 3,3'-Dimethoxybiphenyl, m.p. and mixed m.p. 42–44°. (vi) Two oily fractions (preparative-scale GLC) whose NMR spectra* are in keeping with *cis*- and *trans*-2,3-bis(3-methoxyphenyl)-2-butene; NMR, 1, δ_{TMS} (CCl₄): 2.1 (6 protons, CH₃); 3.47 (6 protons, OCH₃); 6.3 to 7.3 (8 protons, Ar-H); NMR, 2, δ_{TMS} (CCl₄), 1.85 (6 protons, CH₃); 3.75 (6 protons, OCH₃); 6.3 to 7.4 (8 protons, Ar-H).

(4-*An*)₃Cr. The residue (10.307 g) gave, as hexane eluate, an oily mush (7.307 g) from which the following compounds were isolated: (i) Hexamethylbenzene (3.1 g), m.p. and mixed m.p. 161–163°. (ii) 6-Methoxy-1,2,3,4-tetramethylnaphthalene (2.2 g), m.p. 114–115°; (Found: C, 84.0; H, 8.5; O, 7.75. C₁₅H₁₈O calcd.: C, 84.1; H, 8.5; O, 7.5%) NMR, δ_{TMS} (CDCl₃): 2.3 (singlet, 6 protons, Ar-CH₃); 2.45 (singlet, 6 protons, ArCH₃); 3.8 (singlet, 3 protons, ArOCH₃); 6.95 (multiplet, 2 protons, Ar-H); 7.75 (doublet, 1 proton, Ar-H). (iii) Both *cis*- and *trans*-2-(4-methoxyphenyl)-2-butene (minor amounts), identified by a direct comparison of their IR and NMR spectra with those of authentic specimens. (iv) 4,4'-Dimethoxybiphenyl, m.p. and mixed m.p. 172–173°. (v) Two fractions, isolated by GLC, whose NMR spectra were in keeping^{26,27} with those of *cis*- and *trans*-2,3-bis(4-methoxyphenyl)-2-butene: NMR, 1 δ_{TMS} (CCl₄): 2.08 (6 protons CH₃); 3.66 (6 protons OCH₃); 6.35 to 7.00 (8 protons, Ar-H); NMR, 2, δ_{TMS} (CCl₄): 1.86 (6 protons, CH₃); 3.77 (6 protons, OCH₃); 6.80 (m, 4 protons, Ar-H); 7.10 (m, 4 protons, Ar-H). The latter NMR spectrum and the m.p. (131°) of the crystalline material are in accord with those recorded in the literature (NMR²⁷, m.p.²⁸ 131°).

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

(1). *Isolation of organometallic products.* A solution of the title compound [from 2-methoxyphenylmagnesium bromide (50 ml, 43 mmoles) and CrCl₃(THF)₃ (5.35 g, 14.3 mmoles) in tetrahydrofuran] was treated, at 0° with 2-butyne (10 ml). The reaction mixture was kept for one week, at 0–5°, under argon, and then filtered under argon. The *residue* was suspended in dry oxygen-free tetrahydrofuran and treated, under argon, with a solution of 2,2'-bipyridine (4 g) in tetrahydrofuran. The blue-violet material obtained, was suspended in aqueous methanol and treated with KI (4 g) and oxygen. Crystallization of the resulting orange-red solid from methanol gave *cis*-bis(2-methoxyphenyl)bis(2,2'-bipyridine)chromium(III) iodide (0.4517 g)³, characterized by IR spectroscopy and by reaction with HgCl₂ (to give 2-methoxyphenylmercury chloride, m.p. and mixed m.p. 178–179°).

(2). *Deuterolysis.* In two parallel experiments the title compound [from 2-

* For assignment of isomers see ref. 26.

methoxyphenylmagnesium bromide (65 ml, 61.5 mmole) and $\text{CrCl}_3(\text{THF})_3$ (7.6 g, 20.5 mmole)] was allowed to stay in contact with 2-butyne (20 ml) for one week (exp. A) and two weeks (exp. B) respectively. In both cases the total reaction mixture was treated with D_2O (20 ml) for 3 h (gas evolution) and then acidified. The organic material was extracted with ether. The anisole, *cis*-2-(2-methoxyphenyl)-2-butene, and 1,2,3,4-tetramethylnaphthalene were isolated from the concentrated extracts by preparative scale GLC*.

TABLE 1

ANALYTICAL DATA FOR ISOMERIC $\text{CH}_3\text{C}(\text{RC}_6\text{H}_4)=\text{CHCH}_3$

| Isomer | R | C | H | O | |
|--------------|--------------------|------|-----|------|---|
| <i>cis</i> | 2-OCH ₃ | 81.6 | 8.9 | 9.7 | |
| <i>trans</i> | 2-OCH ₃ | 81.5 | 8.8 | 9.8 | |
| <i>cis</i> | 3-OCH ₃ | 81.6 | 8.7 | 10.0 | |
| <i>trans</i> | 3-OCH ₃ | 80.9 | 8.7 | 10.0 | |
| <i>cis</i> | 4-OCH ₃ | 81.0 | 8.7 | 10.0 | |
| <i>trans</i> | 4-OCH ₃ | 81.6 | 8.8 | 10.0 | |
| | | 81.4 | 8.7 | 9.9 | (C ₁₁ H ₁₄ O calc.) |

TABLE 2

| Isomer ^b | NMR SPECTRA ^a OF | | | | AND | | Coupling constants ^c |
|---------------------|-----------------------------|-------------|-------------|-------------|---------------------|--|---------------------------------|
| | $\delta(1)$ | $\delta(2)$ | $\delta(3)$ | $\delta(4)$ | $\delta(\text{Ar})$ | | |
| <i>cis</i> -2 | 1.90(2q) | 5.40(m) | 1.73(2q) | 3.69(s) | 6.55 to 7.25(m) | $J_{1,2}$, 1.45 $J_{1,3}$, 1.08 $J_{2,3}$, 6.9 | |
| <i>trans</i> -2 | 1.92(2q) | 5.45(m) | 1.41(2q) | 3.67(s) | 6.60 to 7.28(m) | $J_{1,2}$, 1.49 $J_{1,3}$, 1.52 $J_{2,3}$, 6.86 | |
| <i>cis</i> -3 | 1.97(2q) | 5.75(m) | 1.75(2q) | 3.70(s) | 6.47 to 7.25(m) | $J_{1,2}$, 1.40 $J_{1,3}$, 1.10 $J_{2,3}$, 7.00 | |
| <i>trans</i> -3 | 1.97(2q) | 5.45(m) | 1.56(2q) | 3.72(s) | 6.55 to 7.30(m) | $J_{1,2}$, 1.40 $J_{1,3}$, 1.60 $J_{2,3}$, 7.10 | |
| <i>cis</i> -4 | 1.94(2q) | 5.65(m) | 1.74(2q) | 3.68(s) | 6.58 to 7.32(m) | $J_{1,2}$, 1.40 $J_{1,3}$, 1.13 $J_{2,3}$, 7.00 | |
| <i>trans</i> -4 | 1.95(2q) | 5.42(m) | 1.56(2q) | 3.72(s) | 6.57 to 7.30(m) | $J_{1,2}$, 1.52 $J_{1,3}$, 1.40 $J_{2,3}$, 7.00 | |

^a The values quoted are δ_{TMS} for CCl_4 solutions. ^b The assignment of the isomers is based upon the chemical shifts of the proton and the methyl group on the second carbon atom, $\delta(2)$ and $\delta(3)$ and on the coupling constants $J_{1,3}$ ³⁰. ^c Coupling constants in Hz.

* The isotopic compositions of the anisole and the anisylbutenes isolated by distillation, were the same as that of those isolated by preparative scale GLC.

The anisoles from experiments (A) and (B) had the isotopic compositions D_0 , 28.6 (33.4); D_1 , 71.1 (66.3); D_2 0.3 (0.3%); ν_{\max} , 2280 and 2267 cm^{-1} (Ar-D) and consisted of mono-Ar-deuterioanisoles.

The 2-(2-methoxyphenyl)-2-butene from exp. (A), consisted of essentially pure *cis*-2-(2-methoxyphenyl)-3-deuterio-2-butene; D_0 , 3.0; D_1 , 97.0; D_2 , 0.0%; ν_{\max} , 2280 (w); 2232 (s) cm^{-1} (C=C-D); band at 827 cm^{-1} missing; δ_{TMS} (CCl_4): 1.71 (singlet, 3 protons, CH_3); 1.89 (4 lines, 3 protons, CH_3); 3.70 (singlet, 3 protons, OCH_3); 5.4 (no signal); 6.8 (multiplet, 4 protons, C_6H_4). The 1,2,3,4-tetramethylnaphthalenes, m.p. 104–105°, from exp. (A) and (B) [D_0 , 100% (100)] were not enriched in deuterium.

Authentic compounds

(1). 1,2,3,4-Tetramethylnaphthalene had previously been prepared [by the interaction of $(\text{C}_6\text{H}_5)_3\text{Cr}(\text{THF})_3$ and 2-butyne⁴]. The pure substance, m.p. 105–106°, had NMR, δ_{TMS} (CCl_4): 2.36 and 2.55 (two singlets, each 6 protons, 4 Ar CH_3); 7.1 to 8.0 (two six-line signals each 2 protons, 4 Ar-H).

(2). *cis*- and *trans*-2-(2-, 3-, and 4-methoxyphenyl)-2-butenes were prepared by the interaction of the appropriate anisylmagnesium bromide and methylethylketone²⁹, and subsequent dehydration (NaHSO_4) of the crude carbinols. The pure compounds, separated by preparative scale GLC, were obtained as colorless oils. The analytical data and NMR spectra are given in Tables 1 and 2.

ACKNOWLEDGEMENT

The authors wish to thank Mr. F. Bangerter (MRSA, Zürich) for all the NMR data.

REFERENCES

- 1 R. P. A. Sneed and H. H. Zeiss, *J. Organometal. Chem.*, 29 (1971) C31.
- 2 R. P. A. Sneed and H. H. Zeiss, *J. Organometal. Chem.*, 20 (1969) 153.
- 3 J. J. Daly, F. Sanz, R. P. A. Sneed and H. H. Zeiss, *J. Chem. Soc. D*, (1971) 243.
- 4 H. H. Zeiss and W. Herwig, *J. Amer. Chem. Soc.*, 80 (1958) 2913.
- 5 M. Tsutsui and H. H. Zeiss, *J. Amer. Chem. Soc.*, 81 (1959) 6090.
- 6 W. Metlesics, W. Herwig and H. H. Zeiss, *J. Amer. Chem. Soc.*, 81 (1959) 6203.
- 7 H. P. Thronsdon, W. Metlesics and H. H. Zeiss, *J. Organometal. Chem.*, 5 (1966) 176.
- 8 Y. T. Huang, H. I. Tai, S. L. Ch'en, K. Y. Hou and T. N. Ni, *Hua Hsueh Hsueh Pao*, 31 (1965) 149; *Chem. Abstr.*, 63 (1965) 5543.
- 9 M. Michman and H. H. Zeiss, *J. Organometal. Chem.*, 15 (1968) 139.
- 10 M. Michman and H. H. Zeiss, *J. Organometal. Chem.*, 13 (1968) P23.
- 11 I. Hashimoto, M. Ryang and S. Tsutsumi, *J. Org. Chem.*, 33 (1968) 3955.
- 12 M. Sato and Y. Ishida, *Bull. Chem. Soc. Jap.*, 41 (1968) 730.
- 13 G. M. Whitesides and W. J. Ehmann, *J. Amer. Chem. Soc.*, 90 (1968) 804.
- 14 G. M. Whitesides and W. J. Ehmann, *J. Amer. Chem. Soc.*, 91 (1969) 3800.
- 15 M. Sato, Y. Ishida, *Nippon Kagaku Zasshi*, 91 (1970) 173; *Chem. Abstr.*, 73 (1970) 25624b.
- 16 J. R. C. Light and H. H. Zeiss, *J. Organometal. Chem.*, 21 (1970) 391.
- 17 J. R. C. Light and H. H. Zeiss, *J. Organometal. Chem.*, 21 (1970) 517.
- 18 M. Michman and H. H. Zeiss, *J. Organometal. Chem.*, 25 (1970) 161.
- 19 M. Michman and H. H. Zeiss, *J. Organometal. Chem.*, 25 (1970) 167.
- 20 G. M. Whitesides and W. J. Ehmann, *J. Amer. Chem. Soc.*, 92 (1970) 5625.

- 21 R. P. A. Sneed and H. H. Zeiss, *J. Organometal. Chem.*, 28 (1971) 259.
- 22 D. J. Cram, in A. T. Blomquist (Ed.), *Organic Chemistry*, Vol. 4, Academic Press, New York, 1965.
- 23 T. Blackmore, M. I. Bruce, F. G. A. Stone, R. E. Davis and A. Garza, *J. Chem. Soc. D*, (1971) 852
- 24 E. Müller, E. Langer, H. Jäkle, H. Muhm, W. Hoppe, R. Graziani, A. Gieren and F. Brandl, *Z. Naturforsch. B*, 26, (1971) 305.
- 25 G. E. Hall, R. Piccolini and J. D. Roberts, *J. Amer. Chem. Soc.*, 77 (1955) 4540.
- 26 N. Inamoto, S. Masuda, Y. Nagai and O. Simamura, *J. Chem. Soc.*, (1963) 1433.
- 27 G. P. Newsoroff and S. Sternhell, *Austr. J. Chem.*, 21 (1968) 747.
- 28 F. Wessely, A. Bauer, Ch. Chwala, I. Plaichinger and R. Schönbeck, *Monatsh. Chem.*, 79 (1948) 596.
- 29 M. J. S. Dewar and N. A. Puttnam, *J. Chem. Soc.*, (1959) 4080.
- 30 M. Barbieux, N. Defay, J. Pecher and R. H. Martin, *Bull. Soc. Chim. Belg.*, 73 (1964) 716.

J. Organometal. Chem., 40 (1972)