

TRICARBONYL(PHENYLACETYLENE)CHROMIUM AND TRICARBONYL(STYRENE)CHROMIUM

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SUMMARY

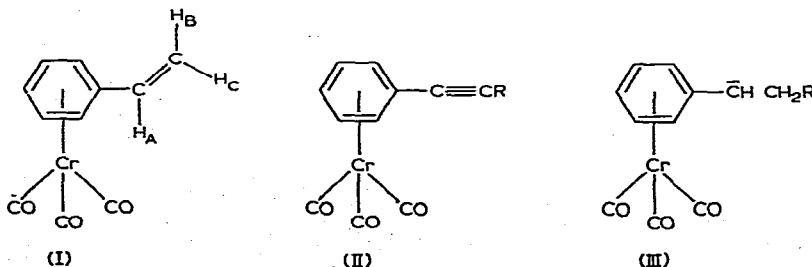
The preparation and several reactions of tricarbonyl(phenylacetylene)-chromium and tricarbonyl(styrene)chromium are described.

INTRODUCTION

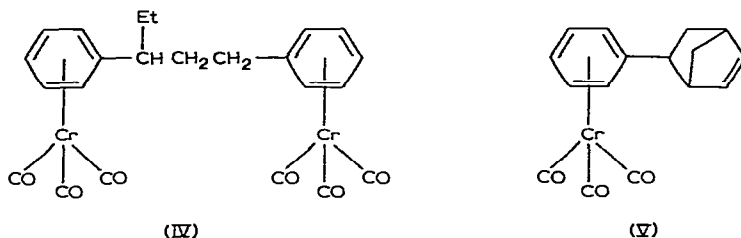
Recent interest in tricarbonyl(styrene)chromium^{1,2*} prompts us to record our own experiences with this complex (I) and the acetylene analogue [(II); R=H]. We undertook this study in order to determine to what extent the tricarbonylchromium group affects the behaviour of the $-\text{CH}=\text{CH}_2$ and $-\text{C}\equiv\text{CH}$ groups towards electrophiles, nucleophiles or radicals.

DISCUSSION

Our preparation of the styrene complex (I) involved the use of tris(acetonitrile)-tricarbonylchromium and the properties of our product correspond with those reported by Rausch *et al.*¹ who used tris(ammonia)tricarbonylchromium. The acetylene complex [(II); R=H] was prepared via the trimethylsilyl derivative [(II); R=SiMe₃] which could be hydrolysed smoothly with alkali. The silane [(II); R=SiMe₃] itself was however only obtained in low yield both from the trisacetonitrile complex and from tris(ammonia)tricarbonylchromium.



* An independent synthesis has been carried out by Dr. W. R. Jackson (personal communication) who has also made a preliminary study of the reactivity of this styrene complex towards nucleophiles.



In agreement with the American workers¹ we find that the styrene complex shows little tendency to polymerise. Its instability towards acids precluded attempts to effect cationic polymerisation, but it was largely recovered after heating with the free-radical initiators, benzoyl peroxide or azobis(isobutyronitrile). Even refluxing in benzene with a large excess of the latter catalyst gave only some three per cent of polymer.

Polymerisation was again slight with organolithium compounds as potential initiators. At low temperatures, these added reasonably smoothly to the β -carbon of the styrene complex, the product [(III); R = Ph] being isolated after hydrolysis as the tricarbonyl complex of bibenzyl, identical with an authentic sample. Methyl-lithium gave less of the 1/1-adduct [(III); R = Me], but after hydrolysis the main product was that (IV) formed from the latter and a further molecule of the styrene complex (I). But although much unchanged styrene complex was recovered and although the initial adduct was warmed to room temperature in the presence of this excess of starting material (I), very little higher molecular weight product resulted.

Diels-Alder addition of cyclopentadiene to the styrene complex (I) took place in refluxing *m*-xylene and gave the expected adduct (V) (of uncertain stereochemistry). As a byproduct tricarbonyl(*m*-xylene)chromium was formed under these conditions by ligand exchange. Attempted hydroboration of the complex (I) followed by peroxide oxidation led unexpectedly to tricarbonyl(ethylbenzene)chromium and this complex was also readily obtained by catalytic reduction of either the styrene (I) or acetylene [(II); R = H] complexes. The latter could also be converted to tricarbonyl(acetophenone)chromium by hydration, showing that electrophiles which do not destroy the complex can add to it in the normal fashion, without reversal of the direction of addition due to the electron-withdrawing effect of the tricarbonylchromium group.

EXPERIMENTAL

All reactions were conducted under nitrogen. Light petroleum refers to the solvent of b.p. 40–60° unless otherwise stated.

Tricarbonyl(styrene)chromium (I)

Tris(acetonitrile)tricarbonylchromium was prepared by refluxing freshly sublimed hexacarbonylchromium (5.0 g, 0.023 mole) with dry acetonitrile (50 ml) for 18 h in the apparatus designed by Strohmeier³ and then removing the solvent under reduced pressure. Styrene (1.5 g, 0.014 mole) and catechol (0.1 g) in tetrahydrofuran (50 ml) were added and the mixture refluxed for 2 h in the dark. After filtration through

kieselguhr and removal of solvent under reduced pressure, unreacted hexacarbonylchromium was sublimed off at 60°/0.2 mm and the residue extracted with ether. The extract was filtered, evaporated under reduced pressure and the product chromatographed on neutral alumina using light petroleum/ether (9/1) as solvent. Crystallisation of the eluate from light petroleum (b.p. 30–40°) and sublimation at 75°/0.2 mm gave the product (I) (1.2 g, 35%) as yellow crystals, m.p. 78–80° (lit.^{1,2} m.p. 80–81°); $\nu_{\max}(\text{CCl}_4)$ 1981, 1912 and 1630 cm^{-1} ; NMR(CS_2): $\tau(\text{H}_A)$ 3.65 (1H, dd, J_{AB} 18 Hz, J_{AC} 11 Hz), $\tau(\text{H}_B)$ 4.35 (1H, dd, J_{BC} 1 Hz), $\tau(\text{H}_C)$ 4.65 (1H, dd) and $\tau(\text{C}_6\text{H}_5)$ 4.6–4.8 (5H, m). (Found: C, 54.9; H, 3.3. $\text{C}_{11}\text{H}_8\text{CrO}_3$ calcd.: C, 55.0; H, 3.3%.)

Polymerisation of tricarbonyl(styrene)chromium (I). A mixture of the complex (I) (0.12 g) and azobis(isobutyronitrile) (0.10 g) was refluxed in benzene (15 ml) for 12 h. The filtered solution was evaporated and chromatographed as above, giving unchanged styrene complex (I) (0.08 g). A yellow band was firmly retained at the top of the column; this zone was removed and extracted with ether. Evaporation left a yellow gum (10 mg), ν_{\max} (film) 1962 and 1875 cm^{-1} . Heating the styrene complex (I) with benzoyl peroxide or with triphenylmethyl fluoroborate as initiators caused no polymerisation (the former caused slight decomposition).

Reaction of complex (I) with phenyllithium. Tricarbonyl(styrene)chromium (I) (0.10 g, 0.4 mmole) in dry ether (50 ml) was treated at 0° with excess of phenyllithium (6 mmole) and the mixture was stirred at 0° for 5 h. Water (100 ml) was carefully added and then more ether (50 ml). The ether layer was separated, washed with water (2 × 50 ml), dried and evaporated. The residual orange oil was chromatographed on alumina; light petroleum/ether (4/1) eluted starting material (I) (10 mg, 10%) followed by tricarbonyl(bibenzyl)chromium (40 mg, 30%), yellow crystals from ether/light petroleum, m.p. 96–98° (lit.⁴ m.p. 100°); $\nu(\text{CO})(\text{CCl}_4)$ 1968, 1895 cm^{-1} , ν_{\max} (Nujol) 1600, 1500, 1150, 815, 742 and 696 cm^{-1} ; NMR(CDCl_3): $\tau(\text{C}_6\text{H}_5$ uncomplexed) 2.6–3.0 (5H, m), $\tau(\text{C}_6\text{H}_5$ complexed) 4.6–5.05 (5H, m) and $\tau(\text{CH}_2)$ 7.25 (4H, dd); identical (m.p., IR and NMR) to an authentic sample prepared by hydrogenation of tricarbonyl(*trans*-stilbene)chromium⁴ over Raney nickel catalyst. A further yellow band, moving only slowly in methanol gave a yellow oil (10 mg), $\nu(\text{CO})(\text{CCl}_4)$ 1966 and 1895 cm^{-1} .

Reaction of complex (I) with methyllithium. Tricarbonyl(styrene)chromium (I) (0.20 g) in dry ether (50 ml) was treated at 0° with a large excess of methyllithium. After 3 h little reaction had occurred and the mixture was allowed to warm to room temperature and stirring continued for a further 6 h. Methanol (5 ml) was carefully added and the mixture then poured into water (100 ml). The ether layer was separated, washed with water (2 × 50 ml), dried and evaporated. The yellow oily residue was chromatographed on neutral alumina; light petroleum/ether (9/1) eluted tricarbonyl(*n*-propylbenzene)chromium (15 mg, 7%), yellow crystals, m.p. 40–41.5° (from ether/light petroleum); $\nu(\text{CO})(\text{CCl}_4)$ 1970, 1890 cm^{-1} , ν_{\max} (Nujol) 1150, 1090, 997 and 825 cm^{-1} ; NMR(CDCl_3): $\tau(\text{C}_6\text{H}_5)$ 4.5–5.0 (5H, m, C_6H_5), $\tau(\text{PhCH}_2)$ 7.65 (2H, t, J 7 Hz), $\tau(\text{CH}_2\text{C}\equiv)$ 8.4 (2H, sextet) and $\tau(\text{CH}_3)$ 9.04 (3H, t, J 7 Hz). Next, light petroleum/ether (4/1) eluted starting material (I) (20 mg, 10%). The same solvents (1/1) then eluted an unstable red compound {possibly $\text{CH}_2=\text{CHC}_6\text{H}_5\text{Cr}(\text{CO})_2[\text{C}(\text{OH})\text{Me}]$ } followed by compound (IV) (32 mg, 16%), a yellow oil; $\nu(\text{CO})(\text{CCl}_4)$ 1966, 1895 cm^{-1} , ν_{\max} (Nujol) 1525, 1150 and 810 cm^{-1} ; NMR(CDCl_3): $\tau(\text{C}_6\text{H}_5)$ 4.6–5.0 (10H, m), $\tau(\text{benzylic CH}_2$ and CH) 7.4–7.9 (3H, m), $\tau(\text{other CH}_2)$ 8.0–8.6 (4H, m) and $\tau(\text{CH}_3)$ 9.1 (3H, t, J 7 Hz).

A further fraction eluted similarly gave a yellow oil (20 mg) $\nu(\text{CO})(\text{CCl}_4)$ 1968 and 1895 cm^{-1} believed to contain higher oligomers.

Diels–Alder reaction. A solution of tricarbonyl(styrene)chromium (0.50 g) and a large excess of freshly distilled cyclopentadiene in xylene was refluxed for 18 h. The resulting solution was filtered through kieselguhr, then evaporated and the residue chromatographed on neutral alumina using light petroleum/ether (9/1) as solvent. The first fraction gave a yellow solid (6 mg), m.p. $69.5\text{--}70^\circ$ (from light petroleum/ether); $\nu_{\text{max}}(\text{CCl}_4)$ 1940, 1874, 825, 660 and 625 cm^{-1} whose NMR spectrum showed no vinylic hydrogens. This was followed by tricarbonyl(*m*-xylene)chromium (99 mg), m.p. $103\text{--}105^\circ$ (lit.⁵ m.p. $105\text{--}106^\circ$); $\nu_{\text{max}}(\text{CCl}_4)$ 1975, 1903, 1540, 1035, 832, 720, 660 and 625 cm^{-1} , NMR(CS_2): $\tau(\text{H}_5)$ 4.65 (1H, t, J 6 Hz), $\tau(\text{H}_2)$ 4.85 (1H, s), $\tau(\text{H}_{4,6})$ 5.10 (2H, d, J 6 Hz) and $\tau(\text{CH}_3)$ 7.82 (6H, s). The third fraction gave the adduct (V) (0.235 g, 37%), as a yellow oil, which solidified on standing at 0° to yellow crystals, m.p. $42\text{--}44^\circ$ (from light petroleum); $\nu_{\text{max}}(\text{CCl}_4)$ 1978, 1905, 1530, 810, 750, 720, 685, 660 and 625 cm^{-1} ; NMR(CS_2): $\tau(\text{CH}=\text{CH})$ 3.70 and 4.20 (each: 1H, q), $\tau(\text{C}_6\text{H}_5)$ 4.60–5.20 (5H, m), $\tau(\text{allylic and benzylic H})$ 6.80–7.20 (3H, m) and $\tau(\text{CH}_2)$ 7.70–9.10 (4H, m). Fraction four yielded starting material (I) (60 mg) and was followed by polymerised complex (15 mg).

Hydroboration. Excess of sodium borohydride (1.5 g) in diglyme (20 ml) was added to a solution of tricarbonyl(styrene)chromium (I) (0.20 g) in diglyme (20 ml) and the mixture stirred magnetically at ambient temperature while adding a solution of boron trifluoride etherate (2 ml) in diglyme (10 ml) over 30 min. Stirring was continued for $1\frac{1}{2}$ h. Water (20 ml) was then carefully added followed by hydrogen peroxide (10 ml, 100 vol) and sufficient 0.5 *M* sodium hydroxide solution to maintain approximately pH 8. The mixture was then extracted with ether (800 ml), the extract washed thoroughly with water to remove diglyme, dried and evaporated. The yellow solid residue (0.12 g) was chromatographed on neutral alumina using light petroleum/ether (4/1) as solvent to elute tricarbonyl(ethylbenzene)chromium (40 mg), m.p. $44\text{--}45^\circ$ (lit.⁵ m.p. $48\text{--}49^\circ$); $\nu(\text{CO})(\text{CCl}_4)$ 1980 and 1906 cm^{-1} ; NMR(CS_2): $\tau(\text{C}_6\text{H}_5)$ 4.6–5.1 (5H, m), $\tau(\text{CH}_2)$ 7.6 (2H, q, J 8 Hz) and $\tau(\text{CH}_3)$ 8.8 (3H, t).

Tricarbonyl[(trimethylsilyl)phenylacetylene]chromium [(II), $R = \text{SiMe}_3$]

(a). (Trimethylsilyl)phenylacetylene (6.0 g) and tris(acetonitrile)tricarbonylchromium, prepared as before from hexacarbonylchromium (5 g) were refluxed for 2 h in tetrahydrofuran (25 ml). The product, after removal of solvent under reduced pressure, was dissolved in ether, filtered through kieselguhr, and again evaporated. Recovered hexacarbonylchromium was sublimed off ($60^\circ/0.01\text{ mm}$) and the residue chromatographed on neutral alumina using light petroleum/ether (4/1) as solvent.

(Trimethylsilyl)phenylacetylene (1.2 g) was followed by the complex [(II); $R = \text{SiMe}_3$] (0.1 g, 1%), golden plates, m.p. $75\text{--}76^\circ$ (from light petroleum/ether), $\nu_{\text{max}}(\text{CCl}_4)$ 2160, 1985, 1920, 1600, 1250, 1220, 1070, 1025, 850, 700, 690 and 640 cm^{-1} ; NMR(CS_2): $\tau(\text{C}_6\text{H}_5)$ 4.60–4.90 (5H, m) and $\tau(\text{CH}_3)$ 9.80 (9H, s). (Found: C, 54.4; H, 4.7. $\text{C}_{14}\text{H}_{14}\text{CrO}_3\text{Si}$ calcd.: C, 54.2; H, 4.55%) A final fraction (0.5 g) probably consisted of (acetonitrile)pentacarbonylchromium.

(b). (Trimethylsilyl)phenylacetylene (1.67 g) and tris(ammonia)tricarbonylchromium (1.91 g) were refluxed for 4 h in tetrahydrofuran (100 ml). The mixture was cooled, filtered and evaporated to give a yellow oil. The oil was treated with light

petroleum/ether (9/1, 6.0 ml). Some tris(ammonia)tricarbonylchromium precipitated out and was filtered off (0.3 g). The filtrate was chromatographed over neutral alumina using light petroleum/ether (9/1) as eluant. (Trimethylsilyl)phenylacetylene (0.05 g) eluted first, followed by tricarbonyl[(trimethylsilyl)phenylacetylene]chromium [(II), R = SiMe₃] (0.13 g, 4.2%).

A third fraction (0.12 g) consisting of the tris(ammonia)tricarbonylchromium was eluted with light petroleum/ether (1/1).

Tricarbonyl(phenylacetylene)chromium [(II); R = H]

Sodium hydroxide (3 ml, 2 M) was added to the silyl derivative [(II); R = SiMe₃] (0.2 g) in methanol (10 ml). Evolution of a gas occurred and the solution became warm; it was allowed to stand for 15 min, then poured into water (100 ml) extracted with ether, dried and evaporated. The product [(II); R = H] (0.15 g) crystallised from light petroleum as yellow needles, m.p. 70–71°; ν_{\max} (CCl₄) 3290, 2120, 1989, 1923, 1145, 818, 675, 650 and 620 cm⁻¹; NMR (CS₂): τ (C₆H₅) 4.5–5.0 (5H, m) and τ (C≡CH) 7.15 (1H, s).

This compound was not formed directly from phenylacetylene with tris(acetonitrile)tricarbonylchromium.

Hydration of the acetylene complex [(II); R = H]. The complex [(II); R = H] (0.11 g) was dissolved in methanol (20 ml) containing aqueous sulphuric acid (1 ml, 2 M) and mercuric sulphate (~1 g) and the mixture stirred at 60° for 1.5 h, then poured into water (150 ml) and extracted with ether (4 × 100 ml). The combined extracts were washed with water, dried and evaporated to leave tricarbonyl(acetophenone)chromium (85 mg) which formed orange-yellow crystals, m.p. 83.5–84.5° (lit.⁶ m.p. 91–92.5°; m.p. 87–88°) (from light petroleum); ν_{\max} (CCl₄) 1992, 1925, 1694, 1360, 1290, 1255, 950, 820, 680, 650 and 620 cm⁻¹; NMR (CS₂): τ (H_{2,6}) 4.05 (2H, d, *J* 6 Hz), τ (H₄) 4.45 (1H, t, *J* 8 Hz), τ (H_{3,5}) 4.80 (2H, dd) and τ (CH₃) 7.63 (3H, s).

Catalytic hydrogenations

The acetylene complex [(II); R = H] (15 mg) was hydrogenated in cyclohexane (40 ml) using "Lindlar" catalyst (30 mg). After 20 min, the solution was filtered and evaporated and the residue identified as tricarbonyl(ethylbenzene)chromium by its m.p. 42–44°, and its IR spectrum.

Tricarbonyl(styrene)chromium (I) (0.2 g) was similarly hydrogenated (18 h) in cyclohexane (70 ml) over the same catalyst (0.2 g) and the same product (0.198 g, 98%) isolated after chromatography.

Styrene itself was also readily hydrogenated to ethylbenzene under the same conditions.

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