Electrophilic Substitution in (Arene)tricarbonylchromium Complexes. Part 1.

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The Friedel-Crafts acetylation of several (arene)tricarbonylchromium complexes have been investigated. From the results it is concluded that the tricarbonylchromium group deactivates to a small extent towards electrophilic substitution the ring to which it is attached. In the case of tricarbonyl(diphenyl-methane)chromium (**1**; $n = 1$), however, attack occurred on both rings to about an equal extent; possible explanations for this unexpected behaviour are advanced.

Since the discovery of (η^6-arene)tricarbonyl chromium complexes during the period 1957—58,[1-4] a large number have been prepared and the properties and reactions of some of them investigated.[5] The overall picture emerging is that the $Cr(CO)_3$ unit has a significant influence upon the reactivity of the attached arene system. The predominant view seems to be that it has a strong electron-withdrawing effect, similar in magnitude to that of a nitro-group.[2] Observations supporting this view include (i) the weaker basic character[6] of $[Cr(CO)_3(aniline)]$ compared with aniline, (ii) the greater acid strength[2,6] of $[Cr(CO)_3(benzoic acid)]$ compared with benzoic acid (the pK_a of the former is of the same order as that of *p*-nitrobenzoic acid), and (iii) the fact that $[Cr(CO)_3(chlorobenzene)]$ undergoes nucleophilic displacement with sodium methoxide smoothly to yield $[Cr(CO)_3(anisole)]$ in high yield (compare *o*- and *p*-chloronitrobenzenes, and contrast chlorobenzene),[2,7,8] It has also been reported that the $Cr(CO)_3$ complexes of anisole and mesitylene do not undergo electrophilic substitution when subjected to Friedel-Crafts conditions (although we shall report in a forthcoming paper that in our hands these compounds do indeed participate in this reaction), and the conclusion was drawn that 'it is unlikely that electrophilic substitution will prove useful synthetically in this field.'[2] On the other hand Pettit and co-workers[9] have shown that $[Cr(CO)_3(benzyl chloride)]$ suffers S_N1 solvolysis at a rate *ca.* 10^5 times that of benzyl chloride; this suggests that the $Cr(CO)_3$ is functioning as an electron-releasing group capable of stabilizing the benzylic carbocation, the intermediacy of which has been established spectroscopically.[10]

Only sporadic investigations have been carried out on electrophilic substitution.† We describe here some experiments designed to provide more information about the influence of the $Cr(CO)_3$ group on the process, perhaps leading to a less equivocal answer to the question as to whether the group assists or hinders electrophilic attack on a complexed ring.

We selected Friedel-Crafts acetylation as the reaction for study, since it is conducted under mild conditions unlikely to disrupt the molecule seriously in the area of the metal, as do the more vigorous halogenation, sulphonation, nitration, *etc.*[2] Standard conditions for the acetylation were worked out (see below) and adhered to strictly in each case. The substrates chosen for study were the tricarbonyl chromium complexes of benzene, of a series of hydrocarbons of type (**1**) (mono-complexes), and of *trans*-1,4-diphenylcyclohexane (mono-complex) (**2**).

The hydrocarbons were either available commercially or were synthesized. 1,3-Diphenylpropane (**1**; $n = 3$) and 1,4-diphenylbutane (**1**; $n = 4$) were prepared by catalytic


(**1**)

(**2**)
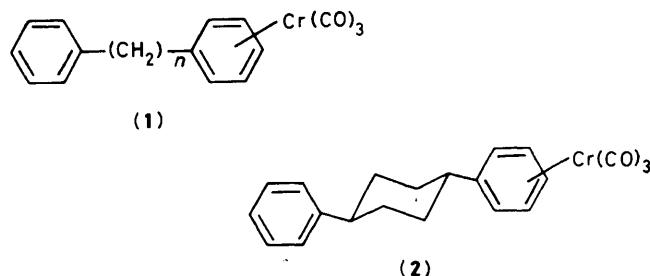
hydrogenation of benzylideneacetophenone[12] and 1,4-diphenylbuta-1,3-diene,[13] respectively. *trans*-1,4-Diphenylcyclohexane was synthesized from commercial 4-phenylcyclohexanone. The complexes were made by thermal reaction between the hydrocarbons and hexacarbonyl chromium. The acetylation of each complex was effected in methylene dichloride as solvent using the standard conditions already referred to. Some acetylations were performed in carbon disulphide, for comparison purposes.

(*Benzene*)*tricarbonylchromium.*—It has been reported[14] that in carbon disulphide benzene is acetylated to give a negligible yield of acetophenone, whereas under these conditions (benzene)tricarbonylchromium affords $[Cr(CO)_3(MeCOPh)]$ in 30% yield; other workers claim considerably higher yields (72%,[15] ~80%[16]). We have repeated these acetylations carefully and found, in the case of benzene, that the yield of acetophenone depends very much on the time allowed for acetylium salt formation before addition of the benenze. If the latter were added to the heterogeneous system immediately after addition of the acetyl chloride, and then the mixture stirred at 0 °C for 3.5 h, the yield of acetophenone was only 4%. On the other hand if the CS_2–$AlCl_3$ MeCOCl mixture was stirred for 30 min at 0 °C and then the benzene added, the yield was 60—71%. Next, when (benzene)tricarbonylchromium was acetylated under the latter conditions the yield of $[Cr(CO)_3(MeCOPh)]$ was 8% consistently, large amounts of unchanged $[Cr(CO)_3-(C_6H_6)]$ being recovered. These results suggested that the $Cr(CO)_3$ unit exerts a deactivating influence towards electrophilic substitution.

It was, however, felt that because of the heterogeneous nature of the reaction medium (the acetylium salt appears to be only sparingly soluble in CS_2) these conditions could make the result an unreliable guide to the influence of the $Cr(CO)_3$ group. Standard conditions were therefore defined, using methylene dichloride as solvent, which yielded a clear solution of the pre-formed acetylium salt. When benzene was acetylated under the new conditions an 82% yield of purified acetophenone resulted. When $[Cr(CO)_3(benzene)]$ was treated in exactly the same manner a 68% yield of $[Cr(CO)_3(acetophenone)]$ resulted.

† For some Friedel-Crafts acylations of substituted arenetricarbonyl-chromium complexes see ref. 11.

These experiments were repeated several times with consistent results; they point to the suspicion that the $Cr(CO)_3$ group exerts a weak deactivating effect on the ring towards electrophilic attack. However, more reliable deductions would be forthcoming from compounds containing two aromatic rings, one complexed and one uncomplexed, as outlined in the sequel.

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(4)
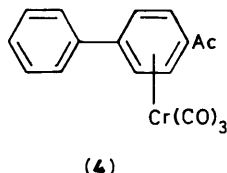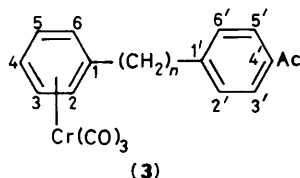
Biphenyltricarbonylchromium (**1**; $n = 0$).—When this compound was acetylated using the standard conditions a quantitative yield of compound (**3**; $n = 0$) was obtained. That the acetyl group had entered the *para* position of the uncomplexed ring regiospecifically was proved by the ^1H n.m.r. spectrum of the product: two multiplets for aromatic protons (ratio 5:4) appeared, centred at δ 5.60 and 7.79 (AB quartet, J 8 Hz), due respectively to 'complexed' and 'uncomplexed' aromatic protons. Also, the COMe protons appeared at 2.61 (s, 3 H) {compare acetophenone (2.59 and $[Cr(CO)_3(MeCOPh)]$ 2.33)}. Finally, the product proved to have a m.p. and ^1H n.m.r. spectrum identical with those obtained by Gubin and co-workers[17] for the product from the reaction of 4'-phenylacetophenone with $[Cr(CO)_6]$. It is noteworthy that these workers obtained both (**3**; $n = 0$) and (**4**) in their synthesis. In spite of a careful search we were unable to detect any (**4**) in our product; the only impurity was a very small amount ($<5\%$) of biphenyl, the result of demetallation. It appears that the $Cr(CO)_3$ group in (**1**; $n = 0$) directs the electrophile into the uncomplexed ring exclusively. This would be in harmony with its electron-withdrawing, deactivating character. Experience shows that in monosubstituted biphenyls substitution occurs only in the unsubstituted ring if the substituent is electron-withdrawing; if it is weakly electron-releasing entry may occur in either ring and if strongly so in the substituted ring.[18]

Tricarbonyl(diphenylmethane)chromium (**1**; $n = 1$).—Subjection of this complex to the standard Friedel–Crafts conditions led to the formation of several products. Minor products resulting from demetallation and acetylation were 4'-benzylacetophenone (**5**) and bis-4-acetylphenylmethane (**6**), identified by mass spectrometry and by comparison with authentic samples.[19,20]

The major product proved to be an orange–red mixture of (**7**) and (**8**), hitherto inseparable, together with a small amount of the diketone (**9**), separated by chromatography and identified by mass spectrometry (M^+ m/z 388, $C_{20}H_{16}CrO_5$ requires M, 388.3) The mixture of (**7**) and (**8**) had M^+ at m/z 346 ($C_{18}H_{14}CrO_4$ requires M, 346.3); in its ^1H n.m.r. spectrum there were discernible AB quartet patterns in both the 5.6 and 7.5 p.p.m. regions, and COMe signals appeared as sharp singlets at 2.36 and 2.51 p.p.m., consistent with the presence of (**8**) and (**7**), respectively. The two benzylic protons appeared at 3.70 and 3.98 p.p.m. There appeared to be an approximate 1:1 ratio of (**7**) and (**8**) in the mixture, t.l.c. of which revealed two components,

(5)

(6)

(7)

(8)

(9)

(**1**; n=1) $\xrightarrow{Ac^+}$ (**10a**)

(**8**) $\xleftarrow{-H^+}$ (**10a**)

(**10b**)
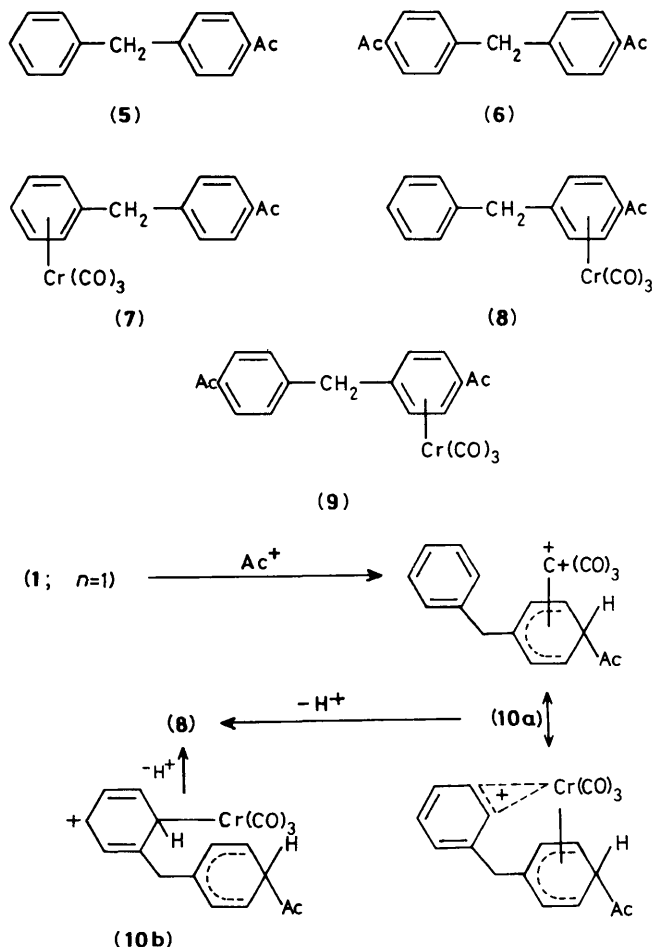
the spots being very close together and discernible without visualisation. Both spots were unstable on silica gel, being decolourised within a few minutes. When the mixture was irradiated at room temperature in methylene dichloride 4'-benzylacetophenone (**5**) was obtained as sole product, by demetallation. Finally, when the latter (**5**) was treated with $[Cr(CO)_6]$ under the usual conditions a mixture of (**7**) and (**8**) was formed; this mixture behaved on t.l.c. and spectroscopically exactly as did the acetylation mixture. It is concluded that in (**1**; $n = 1$) both rings are about equally susceptible to electrophilic attack, in contrast to those in (**1**; $n = 0$). A possible explanation for this behaviour is the participation of the Wheland intermediate (**10a**)*, with an electron-deficient chromium atom stabilised by interaction with the π-system of the uncomplexed ring, or of the related carbocation (**10b**). Another tentative explanation is that the $Cr(CO)_3$ group is in part being transferred from one ring to the other during the reaction, leading to two products. Transfer of the group in an intramolecular sense between aromatic rings is well documented.[21-23]

(Bibenzyl)tricarbonylchromium (**1**; $n = 2$).—Acetylation of (**1**; $n = 2$) under the standard conditions led to a crystalline, single product (**11**), accompanied by a very small amount of the diketone (**12**), which were easily separated chromatographically. The latter was identical with an authentic sample.[20,24,25] The structure (**11**) for the former is indicated unequivocally by its ^1H n.m.r. spectrum (AB quartet at δ 7.55, COMe at 2.58 s), its

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* This possibility was suggested by a referee.

elemental analysis, and its mass spectrum (M^+, 360. $C_{19}H_{16}$-CrO_4 requires M, 360.3). No evidence for the formation of any of the isomeric compound (13) was forthcoming. It is evident that in this reaction the $Cr(CO)_3$ group is deactivating the ring to which it is attached, forcing substitution in the uncomplexed
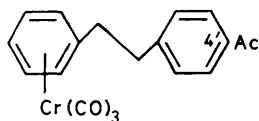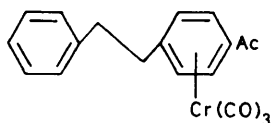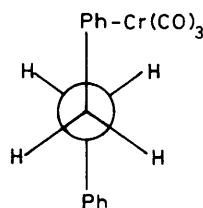

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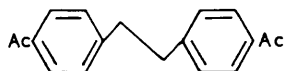
(12)

ring. A possible explanation of this observation might be the preferred, fully staggered conformation (14) adopted by the substrate, in which the phenyl groups are too far apart to permit bridging of the type postulated in the previous section, and thus transfer of the $Cr(CO)_3$ group.


(13)

(14)

Tricarbonyl (1,3-*diphenylpropane*)*chromium* (1; $n = 3$).—The result of acetylation of this complex was formation of (i) a small amount of 1,3-diphenylpropane (the result of demetallation), (ii) starting material (1; $n = 3$), (iii) an orange–red syrup (major product) containing, on ^{1}H n.m.r. evidence, the isomers (15) and (16), the former predominating. The ^{1}H n.m.r. spectrum of the mixture showed COMe signals at 2.56 (major) and 2.40 p.p.m., in agreement with the presence of (15) (major) and (16) respectively, a partly obscured AB quartet centred at 7.57 p.p.m., due to (15), and a partly obscured AB quartet in the 5.5 p.p.m. region due to (16). An attempt to separate these components was partially successful; it yielded reasonably pure (15) (AB quartet at 7.20, 7.30, 7.83, and 7.92 p.p.m., COMe signal at 2.56) with M^+ at 374 ($C_{20}H_{18}CrO_4$ requires M, 374.3) in its mass spectrum. The other fraction was a mixture of (16) and its demetallation product (17), on ^{1}H n.m.r. and mass spectral evidence and by comparison with authentic (17). Evidently in this example the $Cr(CO)_3$ group shields the ring to which it is attached against acetylation to a major extent, not as efficiently as in the cases of (1; $n = 0$ and $n = 2$), but more so than when $n = 1$. Inspection of a model of the starting material shows that in some conformations the phenyl groups are close enough to permit bridging, or easy transfer of the $Cr(CO)_3$ group.
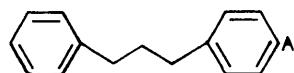
Tricarbonyl(1,4-*diphenylbutane*)*chromium* (1; $n = 4$) *and Tricarbonyl*(*trans*-1,4-*diphenylcyclohexane*)*chromium* (2).—Friedel-
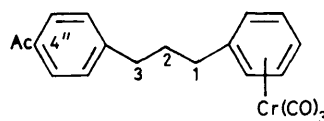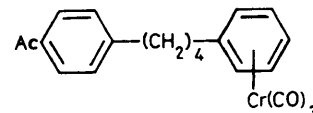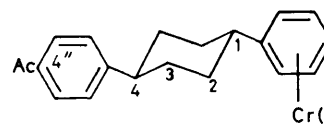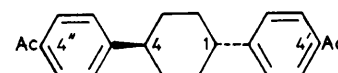

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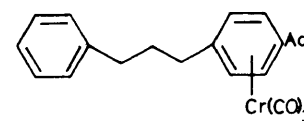
(16)

(17)

(18)

(19)

(20)

Crafts acetylation of these complexes resulted in a regiospecific attack on the *para* position in the uncomplexed ring, to afford (18) and (19) respectively. In both cases the product was accompanied by small amounts of starting material; there was no evidence of attack on the complexed ring. The ^{1}H n.m.r. spectra showed a well-defined AB quartet in the 7.6 p.p.m. region, and a COMe signal at 2.58 p.p.m. Evidently in these examples the $Cr(CO)_3$ group forces a regioselective attack on the other ring; this was to be expected with (2) because the aromatic rings are very remote from each other. In the other case the molecule (1; $n = 4$) is much more flexible, but evidently statistically the chances of the two rings being proximate enough to permit bridging or transfer are remote. In the case of (2) a small amount of the diketone (20) was isolated.

Conclusions

The experiments described indicate that a tricarbonylchromium group attached to an aromatic ring deactivates the ring to a small extent towards electrophilic substitution (Friedel-Crafts acetylation). The extent of this effect is not sufficient to block attack on (benzene)tricarbonylchromium, but the yield is reduced slightly compared with benzene, under identical conditions. In all cases except one where two aromatic rings, one complexed and one uncomplexed, in the same molecule, are available for entry, the $Cr(CO)_3$ causes a regioselective attack on the uncomplexed ring. In the exceptional case there may be a conformational situation in which the metal forms a bridge between the two rings, thereby exerting its influence on both, or a partial transfer of the $Cr(CO)_3$ group between the rings after reaction may be involved. *ortho*-Substitution was not encountered in any of the reactions studied.

Experimental

M.p.s are uncorrected. I.r. spectra were recorded on Perkin-Elmer 1310 and Nicolet 5DX FT-IR instruments, as liquid films or Nujol mulls. ^{1}H N.m.r. spectra were recorded on JEOL FX-90Q and Perkin-Elmer-Hitachi R-24 instruments, in deuteriochloroform. Mass spectra were measured on a Hewlett-

Packard 5985A GC/MS instrument. Elemental analyses are by Atlantic Microlab, Inc., Atlanta, Georgia. All solvents were dried, distilled, and de-aerated with dry nitrogen before use. T.l.c. separations were effected on Merck Kieselgel 60G, and column chromatography on Woelm 63—200 silica gel; all such operations were conducted in the absence of direct light, sometimes in darkness. Light petroleum means the fraction b.p. 60—80 °C. Diglyme refers to bis(2-methoxyethyl) ether.

Preparation of Arenetricarbonylchromiums.—The arenes used were either commercially available or obtainable by published procedures. Their tricarbonylchromium complexes were pre-pared by the well-documented reaction between them and hexacarbonyl chromium in diglyme solution in the presence of 2-methylpyridine, under N_2.[1–4] A carbon monoxide gas trap was used to monitor the reaction. A double-surface reflux condenser was used, from which sublimed $[Cr(CO)_6]$ was periodically dislodged by stopping the flow of water and giving the apparatus two or three sharp jolts. Refluxing was main-tained until the evolution of gas ceased. The cooled solution was filtered with the aid of Celite, freed of solvent, and the residue chromatographed on silica gel. The products formed bright yellow bands, eluted with light petroleum–benzene, from which they were crystallised. M.p.s were sometimes unsharp, owing to partial decomposition prior to melting.

(Benzene)tricarbonylchromium. From benzene (7.8 g, 100 mmol), $[Cr(CO)_6]$ (11.0 g, 50 mmol), 2-methylpyridine (4.65 g, 50 mmol), and dry diglyme (30 ml); period under reflux 9 h; yield 4.0 g (37%); yellow prisms from light petroleum–benzene (1:1), m.p. 161.5—162 °C (lit.,[2] m.p. 165.5—166.5 °C); $v_{max.}$ (Nujol mull) 1 860 and 1 967 cm^{-1} (C≡O); m/z 214 (M^+), 130 ($C_6H_6Cr^+$), and 52 (Cr$^+$, base peak).

(Biphenyl)tricarbonylchromium (**1**; $n = 0$). From biphenyl (11.55 g, 75 mmol), $[Cr(CO)_6]$ (5.55 g, 25 mmol), 2-methyl-pyridine (2.4 g, 26 mmol), and diglyme (70 ml); period under reflux 6.5 h; yield 1.8 g (25%), yellow prisms from light petroleum–benzene (2:1), m.p. 86 °C (lit.,[25] m.p. 87 °C); $v_{max.}$ (Nujol mull) 1 852 and 1 975 cm^{-1} (C≡O); m/z 290 (M^+), 206 (Ph$_2$Cr$^+$), and 52 (Cr$^+$); δ 7.4 (5 H, m) and 5.6 (5 H, m).

Tricarbonyl(diphenylmethane)chromium (**1**; $n = 1$). From diphenylmethane (6.72 g, 40 mmol), $[Cr(CO)_6]$ (2.20 g, 10 mmol), 2-methylpyridine (0.93 g, 10 mmol), and diglyme (40 ml); period under reflux 5.5 h; yield 2.15 g (71%), yellow prisms from light petroleum–benzene (1:1), m.p. 98 °C (lit.,[26] m.p. 97—98 °C); $v_{max.}$ (Nujol mull) 1 860 and 1 950 cm^{-1} (C≡O); m/z 304 (M^+), 220 (Ph$_2$CH$_2$Cr$^+$), and 52 (Cr$^+$); δ 7.3 (5 H, m), 5.25 (5 H, m), and 3.70 (2 H, s).

(Bibenzyl)tricarbonylchromium (**1**; $n = 2$). From bibenzyl (14.5 g, 0.08 mmol), $[Cr(CO)_6]$ (4.40 g, 20 mmol), 2-methylpyridine (1.86 g, 20 mmol), and diglyme (80 ml); period under reflux 5 h; yield 5.1 g (80%), greenish yellow prisms, m.p. 99 °C (lit.,[27] m.p. 98—100 °C); $v_{max.}$ (Nujol mull) 1 893 and 1 958 cm^{-1} (C≡O); m/z 318 (M^+), 234 [(PhCH$_2$)Cr$^+$], 143 ($C_7H_7Cr^+$), 91 ($C_7H_7^+$), and 52 (Cr$^+$); δ 7.2 (5 H, m), 5.2 (5 H, m), and 2.8 (4 H, A$_2$B$_2$q).

Tricarbonyl(1,3-diphenylpropane)chromium (**1**; $n = 3$). From diphenylpropane (7.84 g, 40 mmol), $[Cr(CO)_6]$ (2.2 g, 10 mmol), 2-methylpyridine (0.93 g, 10 mmol), and diglyme (50 ml); period under reflux 5 h; yield 3.3 g (100%), yellow needles from light petroleum, m.p. 74—75 °C (lit.,[26] m.p. 75 °C); $v_{max.}$ (Nujol mull) 1 870 and 1 950 cm^{-1} (C≡O); m/z 332 (M^+), 248 ($C_{15}H_{16}Cr^+$), 196 ($C_{15}H_{16}^+$), and 52 (Cr$^+$); δ 7.21 (5 H, m), 5.2 (5 H, m), 2.3—2.8 (4 H, m), and 1.95 (2 H, m).

Tricarbonyl(1,4-diphenylbutane)chromium (**1**; $n = 4$). From diphenylbutane (5.0 g, 24 mmol), $[Cr(CO)_6]$ (1.75 g, 8 mmol), 2-methylpyridine (0.74 g, 8 mmol), and diglyme (50 ml); period under reflux 5.5 h; yield 1.8 g (65%), yellow needles from light petroleum, m.p. 49—50 °C (lit., m.p. 52 °C[26], 44.5—45 °C[28]);

$v_{max.}$ (Nujol mull) 1 870 and 1 962 cm^{-1} (C≡O); m/z 346 (M^+), 262 ($C_{16}H_{18}Cr^+$), 210 ($C_{16}H_{18}$), and 52 (Cr$^+$); δ 7.20 (5 H, m), 5.20 (5 H, m), 2.3—2.72 (4 H, m), and 1.64 (4 H, m).

Tricarbonyl(trans-1,4-diphenylcyclohexane)chromium (**2**). A Grignard reaction between 4-phenylcyclohexanone and phenyl-magnesium bromide.[29,30] gave a mixture of cis- and trans -1,4-diphenylcyclohexanols (12.5 g), which was dissolved in dry benzene (150) ml and treated with toluene-p-sulphonic acid (monohydrate, 0.5 g) under reflux in a Dean-Stark apparatus until no more water was eliminated (2 h). The benzene solution was cooled, diluted with ether, washed with aqueous NaHCO$_3$ and water, dried (Na$_2$SO$_4$), and concentrated. The residual 1,4-diphenylcyclohexene (11.6 g, 100%) solidified readily and was crystallised from methanol (200 ml), m.p. 99—100 °C (lit.[31] m.p. 102 °C, 101—103 °C[30]) (8.9 g, 77%). This hydrocarbon (3.0 g, 13 mmol) in purified ethyl acetate (50 ml) was shaken in hydrogen under ambient conditions for 2 h in the presence of 10% palladised carbon (0.3 g) (observed H$_2$ uptake 100% of theoretical). The solution was filtered and evaporated to dryness under reduced pressure to yield a semicrystalline product, which was dissolved in absolute ethanol (50 ml), filtered, seeded, and set aside at 0 °C. The crystalline deposit was collected and dried *in vacuo*, to yield trans-1,4-diphenyl-cyclohexane (1.0 g, 33%), plates m.p. 165—166 °C (lit.[32] m.p. 171—172 °C).

The *tricarbonylchromium complex* was prepared from the above hydrocarbon (2.0 g, 8.5 mmol), $[Cr(CO)_6]$ (0.93 g, 4.2 mmol), 2-methylpyridine (0.4 g, 4.2 mol), and diglyme (50 ml); dried under reflux 6 h; yield 0.3 g (20%), pale yellow needles from petroleum–benzene (4:1), m.p. 129—130 °C (decomp.); $v_{max.}$ (Nujol mull) 1 884 and 1 970 cm^{-1} (C≡O); m/z 372 (M^+), 288 ($C_{18}H_{20}Cr^+$), 236 ($C_{18}H_{20}^+$), 91 ($C_7H_7^+$), and 52 (Cr$^+$); δ 7.24 (5 H, m), 5.30 (5 H, m), and 1.49—2.1 (10 H, m) (Found: C, 67.8; H, 5.4. $C_{21}H_{20}CrO_3$ requires C, 67.7; H, 5.4%).

Friedel-Crafts Acetylation of Complexes.—The following standard conditions were used.[33] Finely powdered anhydrous aluminium chloride (1.1 mol) was suspended in methylene dichloride (*ca.* 20 ml per g, distilled over CaH$_2$) and stirred at 0 °C under dry N$_2$. Freshly distilled acetyl chloride (1.1 mol) in methylene dichloride (*ca.* 10 ml g^{-1}) was added during a few min; the resulting clear solution was stirred at 0 °C for 30 min. The complex (1.0 mol) in methylene dichloride (*ca.* 10 ml g^{-1}) was added dropwise during 30 min, with stirring at 0 °C. The mixture was stirred for a further 5 h at room temperature and then poured into ice–water. The layers were separated, and the aqueous layer extracted twice with methylene dichloride. The combined organic layers were washed in turn with water, aqueous sodium hydrogen carbonate, and water, and then dried (Na$_2$SO$_4$) and concentrated under reduced pressure at 40—50 °C. The syrupy residue sometimes solidified readily and was crystallised from benzene–light petroleum. In other cases it was examined by t.l.c. and then subjected to column chromatography on Woelm 63—200 silica gel (*ca.* 25 g per g of product), with elution with light petroleum containing increasing proportions of benzene, in subdued light. The ketonic product formed a bright-red upper band, eluted with benzene. Earlier fractions usually contained small amounts of unchanged complex and demetallated ketone; a later fraction sometimes contained very small amounts of chromium-complexed and demetallated di-ketones. The major product usually solidified readily and was crystallized from benzene–light petroleum.

(Acetophenone)tricarbonylchromium. From benzenetricarb-onylchromium, yield 66%; orange–red prisms from benzene–light petroleum (1:2), m.p. 88 °C (lit.,[3] m.p. 91—92.5 °C); $v_{max.}$ (Nujol mull) 1 901, 1 975 (C≡O), and 1 671 cm^{-1} (C=O); m/z 256 (M^+), 172 (CH$_3$COC$_6$H$_5$Cr$^+$), 77 ($C_6H_5^+$), and 52 (Cr$^+$); δ 5.1—6.0 (5 H, m) and 2.33 (3 H, s).

(4'-Acetylbiphenyl)tricarbonylchromium* (**3**; n = 0). From tricarbonyldiphenylchromium, yield 100%; orange–yellow prisms from benzene–light petroleum (1:1), m.p. 145—146 °C (decomp.) (lit.,[17] m.p. 145—146 °C); $\nu_{max.}$ (Nujol mull) 1 852, 1 975 (C≡O), and 1 675 cm⁻¹ (C=O); m/z 290 (M^+), 206 (Ph_2Cr^+), and 52 (Cr^+); δ 8.04, 7.95, 7.63, 7.54 (4 H, AB quartet, J 8 Hz), 5.44—5.76 (5 H, m), and 2.61 (3 H, s).

[4-Acetylphenyl(phenyl)methane]tricarbonylchromium (**8**) and [4'-Acetylphenyl(phenyl)methane]tricarbonylchromium (**7**). From tricarbonyl(diphenylmethane)chromium (**1**; n = 1). Chromatography of the orange–red syrupy product (3.2 g) yielded starting material [1.05 g, eluted with benzene–light petroleum (1:2)], a small amount of 4'-benzylacetophenone (**5**) [eluted with benzene–light petroleum (1:1)], m.p. and mixed m.p. 40 °C,[19,20] a main fraction (1.25 g, 36%, eluted with benzene), and a final, red fraction [0.4 g, eluted with benzene–ether (1:1)]. The syrupy main fraction on t.l.c. showed two spots of equal intensity with very close R_F values. Attempts to separate these components have not so far been fruitful. The product had $\nu_{max.}$(film) 1 893, 1 971 (C≡O), and 1 683 cm⁻¹ (C=O); m/z 346 (M^+), 262 ($Me_3COC_6H_4CH_2PhCr^+$), 210 ($Me_3COC_6H_4CH_2$-Ph^+), and 52 (Cr^+); δ 7.92, 7.82 (one half of AB quartet, J 9 Hz), 7.24 (containing other half), 5.87, 5.80, 5.52, 5.45 (AB quartet, J 6.3 Hz), 5.20—5.07 (m), 4.01, 3.72 (CH_2), 2.54 (COMe in uncomplexed ring), and 2.39 (COMe in complexed ring). The spectra of this mixture were very closely similar to those of the mixture obtained by reaction of 4'-benzylacetophenone with [Cr(CO)₆] (see below). The last fraction (0.4 g), also a syrup, eventually solidified; it separated from benzene–light petroleum (1:1) as prisms, m.p. 92—92.5 °C, alone or admixed with an authentic sample of bis(4-acetylphenyl)methane (**6**), m.p. 92.5—93 °C;[19,20] $\nu_{max.}$ (Nujol mull) 1 671.5 cm⁻¹; m/z 252 (M^+), 237 ($M - Me^+$), and 43 ($MeCO^+$); δ 7.93, 7.84, 7.30, 7.21 (4 H, AB quartet, J 8 Hz), 4.08 (2 H, s), and 2.56 (6 H, s).

Reaction of 4'-Benzylacetophenone (**5**) *with* [Cr(CO)₆].—The ketone (2.10 g, 10 mmol), [Cr(CO)₆] (2.20 g, 10 mmol), 2-methylpyridine (0.93 g, 10 mmol), and diglyme (20 ml) were refluxed for 6 h. After work-up the syrupy product (2.0 g) was chromatographed on silica gel. The complexed product (0.5 g) was eluted with benzene. Evaporation yielded a syrup which was shown by t.l.c. to contain two products, in the ratio ca. 1:1. The t.l.c. behaviour of this material and its spectral properties were closely similar to those of the mixture of acetylation products described in the previous section.

Demetallation of Major Products in the Foregoing Acetylation.—The syrupy mixture of acetyl derivatives (**7**) and (**8**) described above (1.0 g) in methylene dichloride (20 ml) was stirred and irradiated in a 50 ml Pyrex flask under a nitrogen atmosphere with a 200 W lamp for 1.5 h. The solution was filtered free from inorganic chromium and the solvent evaporated under reduced pressure. The oily residue (0.55 g, 90%) solidified on cooling; t.l.c. showed it to consist of a single product. It separated from a small volume of methanol, m.p. 40 °C, along or mixed with an authentic sample of 4'-benzylacetophenone (**5**).[19,20]

(4'-Acetylbibenzyl)tricarbonylchromium (**11**).—From (bibenzyl)tricarbonylchromium, yield 33%; yellow, elongated prisms from benzene–light petroleum, m.p. 91 °C; $\nu_{max.}$ (Nujol mull) 1 875, 1 954 (C≡O), and 1 674 cm⁻¹ (C=O); m/z 360 (M^+), 276 [$CH_3COC_6H_4(CH_2)_2C_6H_5Cr^+$], and 52 ($Cr^+$); δ 7.92, 7.84, 7.27, 7.19 (4 H, AB quartet, J 7 Hz), 5.35—5.04 (5 H, m), 2.94—

2.65 (4 H, m), and 2.58 (3 H, s) (Found: C, 63.4; H, 4.5; $C_{19}H_{16}CrO_4$ requires C, 63.3; H, 4.4%). Chromatography of the crude product gave small amounts of unchanged complex (eluted with benzene–light petroleum, 1:1), and 4,4'-diacetylbibenzyl (**12**) (eluted with benzene–ether, 4:1), m.p. 167 °C, alone or mixed with an authentic sample.[19,23,24]

[1-(4''-Acetylphenyl)-3-phenylpropane]tricarbonylchromium (**15**). From 1,3-diphenylpropanetricarbonylchromium (**1**; n = 3); the product was a syrup which contained at least four components, partially separable by chromatography: (i) eluted by benzene–light petroleum (1:1): small amount of 1,3-diphenyl-propane; (ii) same eluant: unchanged complex (**1**; n = 3) (33%); (iii) benzene: demetallated ketone 1-(4'-acetylphenyl)-3-phenyl-propane (**17**), m.p. and mixed m.p. 40 °C[19,20] (15%); 2,4-dinitrophenylhydrazone, orange–red prisms from ethyl acetate, m.p. 180 °C (Found: C, 66.1; H, 5.25. $C_{23}H_{22}N_4O_4$ requires C, 66.0; H, 5.3%); (iv) benzene–ether (4:1): above complexed ketone (**15**) (11%); $\nu_{max.}$(film) 1 870, 1 960 cm⁻¹ (C≡O), and 1 670 cm⁻¹ (C=O); m/z 374 (M^+), 290 ($C_{17}H_{18}CrO^+$), 238 ($C_{17}H_{18}O^+$), 91 ($C_7H_7^+$), and 52 (Cr^+); δ 7.92, 7.83, 7.30, 7.20 (4 H, AB quartet, J 10 Hz), 5.35—5.16 (5 H, m), 2.56 (3 H, s), and 2.40—1.93 (6 H, m).

In the ¹H n.m.r. spectrum of the crude product there appeared a discernible AB quartet (δ 6.09, 6.01, 5.10, 5.03, J 7 Hz), which suggests that acetylation has also occurred to a very small extent in the complexed ring, leading to (**16**).

[1-(4''-Acetylphenyl)-4-phenylbutane]tricarbonylchromium (**18**). From 1,4-diphenylbutanetricarbonylchromium, yield 30%; yellow plates from benzene–light petroleum (1:4), m.p. 77.5—78 °C; $\nu_{max.}$ (Nujol mull) 1 973, 1 958, 1 888, 1 886, 1 851 (C≡O), and 1 688 cm⁻¹ (C=O); m/z 388 (M^+), 304 ($C_{18}H_{20}CrO^+$), 252 ($C_{18}H_{20}O^+$), and 52 (Cr^+); δ 7.93, 7.84, 7.29, 7.20 (4 H, AB quartet, J = 8 Hz), 5.17 (5 H, m), 2.58 (3 H, s), 2.70—2.39 (4 H, m), and 1.66 (4 H, poorly resolved t) (Found: C, 64.8; H, 5.2. $C_{21}H_{20}CrO_4$ requires C, 64.95; H, 5.15%). The only other product encountered was unchanged starting material (12%).

[trans-1-(4''-Acetylphenyl)-4-phenylcyclohexane]tricarbonyl-chromium (**19**). From (trans-1,4-diphenylcyclohexane)tricarbonylchromium, yield 32%; yellow prisms from benzene–light petroleum (1:1), m.p. 146—147 °C; $\nu_{max.}$ (Nujol mull) 1 970, 1 890, 1 885 (C≡O), and 1 675 cm⁻¹ (C=O); m/z 414 (M^+), 330 ($C_{20}H_{22}CrO^+$), 278 ($C_{20}H_{22}O^+$), and 52 (Cr^+); δ 7.95, 7.86, 7.35, 7.26 (4 H, AB quartet, J Hz), 5.31 (5 H, br s), 2.57 (3 H, s), 2.00 (2 H, m), and 1.60 (8 H, m) (Found: C, 66.8; H, 5.4. $C_{23}H_{22}CrO_4$ requires C, 66.7; H, 5.3%). Also obtained were unchanged starting material (35%), and (by elution with benzene–ether, 1:1) trans-1,4-bis(4'-acetylphenyl)cyclohexane (**20**) (14%), which separated from cyclohexanone as elongated prisms, m.p. 212 °C, alone or mixed with an authentic sample (see below); $\nu_{max.}$ (Nujol mull) 1 675 cm⁻¹ (C=O); m/z 320 (M^+), and 305 (M—Me^+); δ 7.97, 7.87, 7.38, 7.29 (8 H, AB quartet, J 9 Hz), 2.58 (6 H, s), and 2.11—1.64 (10 H, m) (Found: C, 82.4; H, 7.55. $C_{22}H_{24}O_2$ requires C, 82.5; H, 7.55).

trans-1,4-Bis(4'-acetylphenyl)cyclohexane (**20**). trans-1,4-Diphenylcyclohexane (2.36 g, mmol) in dry methylene dichloride (30 ml) was added gradually (20 min) at 0 °C to a stirred solution of acetyl chloride (1.7 g, 22 mmol) and anhydrous aluminium chloride (3.0 g, 22 mmol) in methylene dichloride (35 ml). The mixture was stirred under N_2 overnight at room temperature and then decomposed with ice–water. The product (2.45 g, 77%) was crystallised from cyclohexanone, m.p. 212 °C (for analysis and spectral properties, see above).

Acknowledgements

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