The Products of Friedel–Crafts Acetylation of Tricarbonyl(cyclo-octatetraene)chromium

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Reaction of [$Cr(CO)_3(C_8H_8)$] with CH_3COCl–$AlCl_3$ at 0 °C in CH_2Cl_2 yields, after hydrolysis, [$Cr(CO)_3$(*trans*-PhCH=$CHCOCH_3$)]. Hydrogenation of the complex yields tricarbonyl(cyclo-octa-1,3,5-triene)chromium. The variable-temperature ^1H n.m.r. spectra of [$Cr(CO)_3(MeC_8H_7)$] and [$Cr(CO)_3(PhC_8H_7)$] indicate that the substituent is on the unco-ordinated double bond in each case.

In contrast to its lower vinylogue, benzene, cyclo-octatetraene is non-aromatic and its chemical properties resemble those of olefins.[1] However, these properties are altered remarkably on co-ordination of cyclo-octatetraene to tricarbonyliron.[2] Thus, Friedel–Crafts acetylation and Vilsmeir formylation can be performed on [$Fe(CO)_3(C_8H_8)$] (1) to give acetyl- and formyl-(cyclo-octatetraene)iron tricarbonyl respectively,[2] whereas the unco-ordinated hydrocarbon gives only very low yields of styrene derivatives on attempted Friedel–Crafts acetylation, the main product being unidentifiable polymeric material.[3]

While cyclo-octatetraene acts as a bidentate ligand on co-ordination to the tricarbonyliron group, the deep red complex formed with tricarbonylchromium involves cyclo-octatetraene as a tridentate ligand. We have examined some aspects of the chemical reactivity of [$Cr(CO)_3(C_8H_8)$] (2) and compared it to that of [$Fe(CO)_3(C_8H_8)$] (1).

RESULTS AND DISCUSSION

Addition of (2) to a dichloromethane solution of acetyl chloride and aluminium trichloride at 0 °C gave a deep blue solution. After hydrolysis, a 50% yield of [$Cr(CO)_3$(*trans*-PhCH=$CHCOCH_3$)] was isolated. This may be contrasted with the product (*albeit in low yield*) of the attempted Friedel–Crafts acetylation of unco-ordinated cyclo-octatetraene, which was *o*-methylcinnamaldehyde.[3] It is not clear, in the acetylation of (2), whether an unstable complex, [$Cr(CO)_3(MeCOC_8H_7)$], is initially formed which subsequently undergoes decomposition to [$Cr(CO)_3$(*trans*-PhCH=$CHCOCH_3$)] or whether the six-membered ring was formed on the cyclo-octatetraene ring. The latter would appear more likely since decomposition of a monosubstituted eight-membered ring to the co-ordinated benzalacetone would involve a 1,3-hydride shift. The stability of arene(tricarbonyl)chromium derivatives would be expected to provide a considerable driving force for this ring-contraction reaction, which is not without precedent. Thus, Munro and Pauson[4] have shown that treatment of the tricarbonyl(tropylium)chromium cation with sodium cyclopentadienide or with sodium diethylmalonate leads to benzene(tricarbonyl)chromium. However, in these cases the six-membered ring does not contain a substituent and so must be formed by a mechanism different to that involved here. In this work a mechanism is not obvious and must await further more detailed studies. Nevertheless, it is seen that the eight-membered rings in (1), (2), and free cyclo-octatetraene react differently under Friedel–Crafts acetylation conditions.

The reaction of (1) with tertiary phosphines (L) leads to displacement of the ring and formation of [$Fe(CO)_3L_2$].[5] A similar reaction occurs with (2), although much less vigorous conditions are required for the replacement of the cyclo-octatetraene ring. Thus, treatment of a diethyl ether solution of (2) with PEt_2Ph or PMe_2Ph leads to an immediate and quantitative precipitation of *fac*-[$Cr(CO)_3L_3$] (L = PEt_2Ph or PMe_2Ph).[6] The reaction with PPh_3 is slower (1 h at room temperature) but contrasts markedly with the conditions required for the analogous displacement of C_8H_8 from (1) (9 h at 130 °C).[7] Thus, although behaving as a tridentate ligand in (2), cyclo-octatetraene is more easily displaced by tertiary phosphines than as a bidentate ligand in (1). This is similar to the behaviour shown by tricarbonyl(cycloheptatriene)chromium[6] and it would appear that the additional double bond in cyclo-octatetraene contributes little to the overall stability of its complex with tricarbonylchromium.

Although (1) contains two 'free' double bonds in addition to a co-ordinated 1,3-diene unit, it does not undergo catalytic hydrogenation[7] which would be expected to result in the known tricarbonyl(cyclo-octa-1,3-diene)iron.[8] On the other hand, cyclo-octatetraene(cyclopentadienyl)cobalt containing 1,5-bonded cyclo-octatetraene and two free double bonds readily gives cyclo-octa-1,5-diene(cyclopentadienyl)cobalt on treatment with hydrogen in the presence of Raney nickel.[9] We find that (2) in pentane undergoes no hydrogenation when subjected to 1 atm † of hydrogen in the presence of a palladium–charcoal catalyst. However, in ethanol as solvent a 20% yield of tricarbonyl(cyclo-octa-1,3,5-triene)chromium[10] may be isolated after catalytic hydrogenation. We have further established that the low yield of this reduced product is due to the reaction of ethanol with (2), although we have not been able to identify the yellow carbonyl-containing product of this reaction.

Finally, we have examined the variable-temperature

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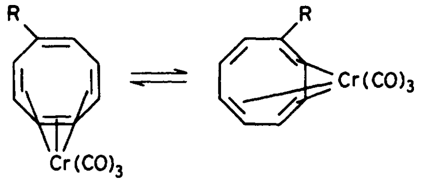
† Throughout this paper: 1 atm = 101 325 Pa; 1 eV ≈ 1.60 × 10^{-19} J.

^{1}H n.m.r. spectra of the monosubstituted cyclo-octatetraene derivatives, [Cr(CO)$_3$(MeC$_8$H$_7$)] (3) and [Cr(CO)$_3$(PhC$_8$H$_7$)] (4). ' Frozen spectra ' of both species have been obtained in [^{2}H$_8$]toluene at −40 °C. Spin-decoupling experiments and comparison with the ^{1}H n.m.r. spectrum of (2) at −40 °C [11] with that of tricarbonyl(cycloheptatriene)chromium have shown unequivocally that the substituent is on the unco-ordinated double bond in both cases. This is in contrast to the behaviour shown by both [Fe(CO)$_3$(MeC$_8$H$_7$)] (5) and [Fe(CO)$_3$(PhC$_8$H$_7$)] (6). At room temperature, (5) involves the tricarbonyliron moiety bound to a 1,3-diene unit in which the methyl substituent is on one of the ' inner ' carbons.[12] In (6) at room temperature, the tricarbonyliron moiety shows no site preference in the ring, but at lower temperatures (−110 °C) the tricarbonyliron group comes to rest on a 1,3-diene unit containing the phenyl substituent.[13] At present we see no obvious reason for this difference in site preference between Fe(CO)$_3$ and Cr(CO)$_3$.

The high-temperature ^{1}H n.m.r. spectra (105 °C in [^{2}H$_8$]toluene) of both (3) and (4) are consistent with species undergoing the fluxional process shown below.



(3; R = Me)
(4; R = Ph)

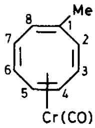
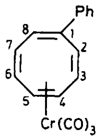
A considerable shift in the weighted average of the chemical shifts in the low- and high-temperature spectra of both (3) and (4) was observed. A similar phenomenon was noted in the variable-temperature spectra of (2) in the same solvent.

Unfortunately, (3) and (4) were somewhat unstable at high temperatures and rather broad peaks were obtained in the high-temperature spectra making it impossible to test the validity of the conclusions by spin-decoupling experiments. It is also noteworthy that simultaneous broadening of all peaks was observed on going from low to high temperatures. Thus, it may be assumed that a ' flat ring ' intermediate is involved as described for [Mo(CO)$_3$(C$_8$H$_8$)].[14]

Because of the complexity of the spectra, rate constants and activation energies for the fluxional processes could not be reliably determined.

It would appear, therefore, that cyclo-octatetraene exhibits a different chemical reactivity when bonded to Cr(CO)$_3$ as opposed to Fe(CO)$_3$. The bond between the C$_8$ ring and the tricarbonylchromium moiety appears to be weaker than that between the ring and the tricarbonyliron moiety in (1). These differences must be associated with the electron-withdrawing capacity of the Cr(CO)$_3$ group which may be compared to the electron-donating effect of the Fe(CO)$_3$ moiety. Such differences have, in fact, been previously observed. Thus, although tricarbonyl(cycloheptatriene)iron readily undergoes Friedel–Crafts acetylation to give (1-acetylcyclohepta-1,3,5-triene)tricarbonyliron and (2—6-η-1-acetylcycloheptadienium)(tricarbonyl)iron hexafluorophosphate,[15] similar treatment of tricarbonyl(cycloheptatriene)chromium gave no isolable products.[16] In view of the reactivity of (2), tricarbonyl(cycloheptatriene)chromium could reasonably be expected to undergo a ring contraction under Friedel–Crafts acetylation conditions to give tricarbonyl(phenylacetone)chromium, but this was not observed. The electron-withdrawing effect of the Cr(CO)$_3$ moiety would tend to destabilise the cationic species formed after electrophilic attack on the olefinic ring leading either to decomposition or to rearrangement as observed with (2). On the other hand, the electron-donating effect of the Fe(CO)$_3$ group would have a stabilising effect on such species. However, it is not clear how the remaining differences in reactivity and bonding

^{1}H N.m.r. spectra at high and low temperatures

Compound and solvent	θ_c/°C	Chemical shift (τ)	Multiplicity	Relative intensity	Assignment	J/Hz
 (3) [^{2}H$_8$]toluene	103	4.81	t	1	H^5	8.0
		5.11	m	2	H^4	
		5.61	m	4	H^2, H^3	
		8.65	s	3	Me	
	−40	4.80	dd	2	H^4, H^5	4.5, 3.5
		5.65	m	2	H^3, H^6	
		5.84	m	1	H^8	
		6.19	m	1	H^7	
		6.35	d	1	H^2	9.5
		9.08	s	3	Me	
 (4) [^{2}H$_8$]toluene	108	3.02	s	5	Ph	
		4.58	t	1	H^5	8.0
		4.81	m	2	H^4	
		5.35	m	4	H^2, H^3	
	−43	3.10	m	5	Ph	5
		4.87	m	2	H^4, H^5	2
		5.25	d	1	H^8	1
		5.52	m	2	H^3, H^6	2
		6.52	m	2	H^3, H^7	2

behaviour come about and an answer must await further studies.

EXPERIMENTAL

Methylcyclo-octatetraene[17] and phenylcyclo-octatetraene[18] were prepared as described. Other chemicals were commercial samples. Hydrogen-1 n.m.r. spectra were obtained using a Varian Associates HA 100 machine, mass spectra on an AEI MS 12 spectrometer, and i.r. spectra on a Perkin-Elmer 257 instrument. All experimental manipulations were carried out under an atmosphere of nitrogen.

$[Cr(CO)_3(RC_8H_7)]$ (R = H, Me, *or* Ph).—The compound $[Cr(CO)_6]$ (5 mmol) was refluxed in acetonitrile (50 cm^3) for 48 h. After removal of the acetonitrile at reduced pressure, the flask was charged with dry tetrahydrofuran (50 cm^3) and RC_8H_7 (R = H, Me, or Ph) (7 mmol). This mixture was refluxed for 30 min and then evaporated to dryness. The residue was extracted with diethyl ether and the red solid remaining after evaporation of the ether was chromatographed on silica gel. A red band, eluted with pentane–4% diethyl ether, gave the *products* in *ca.* 50% yields: $[Cr(CO)_3(C_8H_8)]$, red crystals (m.p. 102—105 °C), mass spectrum (70 eV) 240 $(M)^+$, 184 $(M - 2CO)^+$, and 156 $(M - 3CO)^+$, i.r. (pentane) 1 994, 1 939, and 1 911 cm^{-1}; $[Cr(CO)_3(MeC_8H_7)]$, red solid, mass spectrum (70 eV) 254 $(M)^+$, 198 $(M - 2CO)^+$, and 170 $(M - 2CO)^+$, i.r. (pentane) 1950, 1 939, and 1 912 cm^{-1} (Found: C, 56.4; H, 4.00. Calc. for $C_{12}H_{10}CrO_3$: C, 56.7; H, 3.95%), $[Cr(CO)_3(PhC_8H_7)]$, red oil, mass spectrum (70 eV) 316 $(M)^+$, 260 $(M - 2CO)^+$, and 232 $(M - 3CO)^+$, i.r. (pentane) 1 997, 1 942, and 1 915 cm^{-1} (Found: C, 63.9; H, 3.80. Calc. for $C_{17}H_{12}CrO_3$: C, 64.5; H, 3.80%).

Acetylation of (2).—Compound (2) (1 mmol) in dichloromethane (10 cm^3) was added dropwise to a dichloromethane solution (10 cm^3) containing 2 mmol each of acetyl chloride and aluminium chloride at 0 °C. The resulting deep blue mixture was stirred at this temperature for 5 min and then hydrolysed with ice–water. The organic layer was separated, dried, and evaporated. Chromatography of the residue on silica plates, eluting with benzene, gave a broad orange band which afforded orange crystals of $[Cr(CO)_3$(*trans*-$PhCH=CHCOCH_3)]$ in 50% yield, m.p. 95—98 °C (Found: C, 56.2; H, 3.80. Calc. for $C_{13}H_{10}CrO_4$: C, 55.4; H, 3.55%). Mass spectrum (70 eV): 282 (M^+), 226 $(M - 2CO)^+$, and 198 $(M - 3CO)^+$. I.r. (CCl_4): 1 979, 1 913 (br), and 1 671 cm^{-1}. ^1H N.m.r., $\tau(CDCl_3)$: 2.99 (d, J 16.5 Hz, 1 H), 3.51 (d, J 16.5 Hz, 1 H), 4.58 (m, 5 H), and 7.70 (s, 3 H).

Hydrogenation of (2).—Compound (2) (0.5 mmol) was dissolved in absolute ethanol (15 cm^3) and 10% palladium on charcoal catalyst (50 mg) was added. The mixture was then shaken under 1 atm of hydrogen for 3 h. After filtration, the mixture was poured into water (50 cm^3) and extracted with diethyl ether. After drying ($MgSO_4$) the ether solution, it was evaporated and the residue was taken up in pentane. Evaporation of the pentane solution gave a 20% yield of tricarbonyl(cyclo-octa-1,3,5-triene)chromium which was identified by mass spectrometry and by comparison of its ^1H n.m.r. spectrum with that of an authentic sample.[19]

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