Chemistry of Methinyltricobalt Enneacarbonyls. Part VIII.† Friedel–Crafts Reactions with Halogeno-clusters

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Friedel–Crafts reactions with halogenomethinyltricobalt enneacarbonyls afford a useful route to a wide range of aryl clusters, $RCCo_3(CO)_9$. The usefulness of g.l.c. in their purification is emphasised. Substitution is predominately in the *para*-position but exceptions occur when the aryl substituent is small (*e.g.* F). In one case ($R = ClC_6H_4$) both *ortho*- and *para*-isomers were isolated. Methods for determining the structure are described and the inductive-mesomeric effects of a Co_3C cluster evaluated.

PREVIOUS studies of methinyltricobalt enneacarbonyls have dealt with their preparation,[1] physical properties,[1] and the co-ordination chemistry of the basal cobalt triangle.[1-4] Another little explored facet is the organic chemistry of the Co_3C core. The Co_3CY unit is truly an organometallic cluster as the apical carbon atom is an integral part of the tetrahedral structure. This four-co-ordinate carbon atom is conventionally aliphatic. Nonetheless, there is a considerable body of experimental evidence to suggest that the apical C–Y bond has properties inconsistent with a saturated (sp^3) carbon atom. For example, a number of C–Y bonds are shorter than 'normal' single bonds,[5-7] C–F, C–Cl, and C–Br stretching frequencies are anomalously high[1,8,9] and the ^1H n.m.r. of $MeCCo_3(CO)_9$ and its derivatives shows that the Me group is strongly deshielded.[10] Moreover, the co-ordination behaviour of the cluster is clearly influenced by the nature of the apical group.[2-4,11] These, and related observations,[2,12] may be explained using the concept of a delocalized polarizable Co_3C core which is electron-withdrawing with respect to the apical group, Y.[2,3,12] Whether inductive ($-I$) or a combination of $-I$ and $-M$ effects operate has not been settled.

The reactivity of a co-ordinated apical group may be altered by these electronic effects and the severe stereochemical constraints imposed on these clusters[13] in the following manner.

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† *Previous Part*: ref. 4.

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(*a*) Cations of the type $^+CCo_3(CO)_9$ should be stabilized, *i.e.* the apical carbon atom should be activated towards nucleophilic attack.

(*b*) The apical bond is sterically protected from 'back-side' attack and dissociative mechanisms will be favoured.

(*c*) Co-ordinated apical groups, including aryls, will be more susceptible to nucleophilic attack irrespective of whether inductive or mesomeric effects dominate.

(*d*) The alcohol $HOCCo_3(CO)_9$ should be an acid and indeed it would appear that the anion $^-OCCo_3(CO)_9$ is capable of independent existence.[14] Boron and silicon derivatives of this base are also known.[15,16]

Aspects of apical group reactivity are currently under investigation; this paper describes some Friedel–Crafts reactions of Cl– and $BrCCo_3(CO)_9$. Preliminary results have been reported.[17]

RESULTS

Both $ClCCo_3(CO)_9$ and $BrCCo_3(CO)_9$ react with arenes in the presence of a Lewis acid such as $AlCl_3$ or BF_3 forming brown volatile aryl clusters, $RCCo_3(CO)_9$, in up to 90% yield (Table 2). Dichloromethane is a convenient solvent and no complications through the solvent acting as the electrophile arose (*cf.* aromatic reactions [18]). The extent of the reaction is governed by the usual restraints in aromatic systems. Deactivated (*e.g.* nitrobenzene), hindered and polysubstituted (*e.g* mesitylene) arenes failed to react or the product yield was low. Purification proved difficult in some cases with conventional organometallic procedures (even sublimation) as it seemed that solvent molecules were trapped within the crystal lattice. However we discovered that purification was simple using g.l.c. although applications of this technique to metal carbonyls have been reported.[19] Retention times for some methinyltricobalt enneacarbonyls are given in Table 1; no trends are recognizable. Broad peaks for the toluene and chlorobenzene derivatives suggested that these compounds were isomeric mixtures and this was subsequently confirmed by the structural studies (see below).

TABLE 1

Retention times for some methinyltricobalt enneacarbonyls [a]

Y	R.T./s	Y	R.T./s
C_6H_4Me	115	o-$C_6H_3Me_2$	250
H	194	m-$C_6H_3Me_2$	370
Ph	195	C_6H_4Br	385
$C_{12}H_{11}$	212	Cl	485
C_6H_4I	213	Me	520
C_6H_4Cl	226	Br	645
p-$C_6H_4Me_2$	249	$C_{10}H_9$	1820

[a] Loenco 160 prep-matic detector. 433 K; injection, 413 K; column, 353 K. 4 ft. coiled steel, 4 mm i.d. column, packed with 100/120 mesh Q coated with 5% SE-30. N_2 gas-flow rate 45 cm^3 min^{-1}. Concentrated solutions in CH_2Cl_2.

A mechanism similar to that assumed for Friedel–Crafts alkylation is proposed. Green compounds which may well be the intermediate carbonium ions (I) have been isolated but their instability has hindered definite characterization.

$$\begin{tikzcd}
(CO)_9Co_3CCl + AlCl_3 \arrow[r, shift left] & (CO)_9Co_3C\text{–}Cl\text{–}AlCl_3 \arrow[l, shift left] \arrow[d, "R\text{–}H"] \\
RCCo_3(CO)_9 + HCl + AlCl_3 & {[HRCCo_3(CO)_9]^+AlCl_4^-(I)} \arrow[l]
\end{tikzcd}$$

A new type of dimeric methinyltricobalt enneacarbonyl was produced with a few arenes (Table 2). Because the co-ordinated aryl is deactivated towards further electrophilic attack (*q.v.*) it is not surprising that yields are low.

$$e.g.\ 2ClCCo_3(CO)_9 + C_6H_6 \xrightarrow{AlCl_3} C_6H_4[CCo_3(CO)_9]_2 + 2HCl$$

In normal Friedel–Crafts reactions of alkylbenzenes and halogenobenzenes for instance dealkylated or rearrangement products are common.[18] This was not the case in these cluster reactions with the exception that traces of $PhCCo_3(CO)_9$ and $C_6H_4CH_3CCo_3(CO)_9$ were detected (g.l.c. and mass spectrum) with toluene and xylene as solvents respectively.

Earlier work [5,6] demonstrated that $ClCCo_3(CO)_9$ decomposes in high boiling arenes to the acetylene derivatives $C_2[CCo_3(CO)_9]_2$ *etc.* but they were not detected in the Friedel–Crafts reactions. Further, there was no evidence to indicate that halogeno analogues of $MeCCo_3(CO)_6$arene [3] were formed although $AlCl_3$ is often used to prepare arene complexes.[20]

Structure.—The possible isomeric structures are shown in the Figure: substitution may be *ortho*, *meta*, or *para* with respect to the cluster.

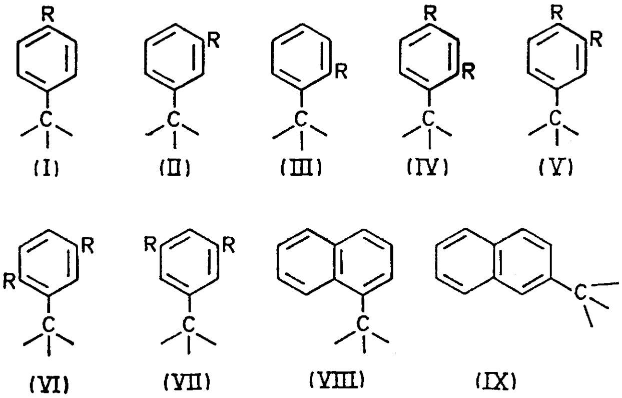

FIGURE Possible structures of arylmethinyltricobalt enneacobalt

Chemical, and i.r., n.m.r., and mass spectral evidence was utilized to deduce the type of substitution as indicated in Table 2. In the majority of reactions with monosubstituted arenes *para* substitution was favoured [structure (I)]. This was also true for disubstituted arenes, and biphenyl. Thus structures (V) and (IV) are adopted by *ortho*- and *meta*-substituted arenes respectively. Exceptions to the general pattern occur when R is a small substituent like fluorine or if *para*-substitution is not possible [structure (VI)], *e.g.* *p*-xylene and *p*-dichlorobenzene. Chlorine and the methyl group occupy an intermediate position

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in that the substitution pattern is kinetically controlled. Thus, for the reaction with toluene, the *ortho-para* ratios are approximately 2 : 1 and 1 : 2 at 320 and 383 K respectively. It proved impossible to separate the isomers but the *o*-toluene (and *m*-toluene) isomer has been prepared by other methods.[21] Pure samples of both the *ortho* and *para* $ClC_6H_4Co_3(CO)_9$ compounds were obtained however.

Certain aspects of the data used for structural assignment will be discussed.

Chemical Degradation.—A number of methods are available for the complete degradation of the cluster but the most satisfactory is oxidation with a Ce^{4+}–acetone mixture.[22] The resulting carboxylic acids are easily characterized.

$$e.g.\ ClC_6H_4CCo_3(CO)_9 \xrightarrow{Ce^{4+}} ClC_6H_4CO_2H + [Co^{II}] + 9CO$$

I.r. Spectra.—Methinyltricobalt enneacarbonyls typically show four strong ν(CO) bands in their i.r. spectra (Table 3) not five as expected from the local C_{3v} symmetry. Bor has recently demonstrated[23] that a weak *E* mode sometimes appears at *ca.* 2020 cm^{-1} and that the broad bands around 2050 cm^{-1} are not accidentally degenerate *E* modes as was originally suggested.[24] Nevertheless, whenever Y is a bulky or asymmetric group the concept of local symmetry no longer applies and this broad band may split, especially if Y has a side chain adjacent (*ortho*) to the cluster (*cf. p*-xylene derivative). Note that this is not a rigorous criterion for *ortho* substitution as small substituents such as chlorine only cause the 2050 cm^{-1} band to become very broad and asymmetric. The diagnostic aromatic δ(C–H) bands in the 900—700 cm^{-1} region in all cases confirmed the postulated mode of substitution. Thus *p*-$ClC_6H_4CCo_3(CO)_9$ had one strong band at 826 cm^{-1} (2 adjacent hydrogens) and the *ortho* isomer two bands, 790 (3 adjacent) and 744 cm^{-1} (4 adjacent hydrogens).

The symmetrical in-phase ν(CO) band around 2100 cm^{-1} is very sensitive to the electronic requirements of the apical group. Since this band is essentially invariant in these aryl clusters the phenyl ring must be buffering any inductive effects brought about by a change in arene substituents.

Mass Spectra.—The fragmentation processes were as described in detail for other methinyltricobalt enneacarbonyls.[25] A high proportion of migration ions are always observed and it was thought their composition depended on the substitution pattern. Ions of the type XCo_3^+ (X = aryl substituent) and HCo_3^+ were believed to be indicative of *ortho* and *para* substitution respectively. There are exceptions to this rule and our conclusion is that XCo_3^+ ions are statistically in higher abundance and HCo_3^+ ions often absent in *ortho*-substituted derivatives.*

^{1}H *N.m.r.*—The most definitive evidence, summarized in Table 4, for the proposed stereochemistry came from the ^{1}H n.m.r. spectra. Assignments were straightforward and will not be discussed further.

The broad structureless resonance observed for the bromobenzene derivative persisted down to 243 K and in a variety of solvents (*cf. p*-dibromobenzene[26]), that is, protons adjacent to a bromine atom and the cluster are magnetically equivalent. A cluster is clearly an electronegative substituent with respect to an aromatic ring, a conclusion in line with other evidence cited earlier. It is tempting to deduce a value for the electronegativity from this fact but although systematic variations with substituent in the resonances of aromatic ring protons have been recognized no single mechanism operates and it is not possible to distinguish between inductive and mesomeric effects.[27] A comparison of the CH_3 resonances for the *para-*, *meta-*, and *ortho*-toluene derivatives reveals that the first two are virtually identical whereas the last is at a higher field as is the case for disubstituted benzenes having electronegative substituents.[28] Again it would seem that a negative inductive effect is operating.

Conclusions.—These Friedel–Crafts reactions provide a useful route to *para-*, and in some cases *ortho-*, substituted arylmethinyltricobalt enneacarbonyls. Other synthetic methods using for example 1,1,1-trihalogenomethanearyls[1,8] or acetylene complexes $[Co_2(CO)_6RC_2H]$[1] are not satisfactory for the reasons mentioned earlier.[17] Other convenient routes utilising diaryl-mercury compounds[29] or Grignard reactions[21] have been discovered recently.

In alkylations of arenes primary *ortho-para* substitution is the rule. The same holds true for the cluster reactions except that steric hindrance generally prevents *ortho*-substitution; the *para*-isomer is thermodynamically more stable. Intramolecular steric interactions obviously play an important role in these reactions and are the reason for the unreactivity of polysubstituted arenes and low yields with hindered arenes. It is interesting that there was no evidence for rearrangement to *meta*-isomers at high temperatures which commonly occurs in aromatic Friedel–Crafts reactions and the cluster reactions do not appear to be reversible.[18] Despite the fact that polysubstitution is usual in aromatic alkylations and the absence of steric strain in *p*-$[Co_3(CO)_9C]_2C_6H_3R$ derivatives, only two of the latter compounds could be isolated. Moreover, $PhCCo_3(CO)_9$ undergoes Friedel–Crafts reactions but yields are low and reactions slow.[21,22] Clearly the cluster is a deactivating substituent with respect to electrophilic substitution as anticipated from the ^{1}H n.m.r. evidence which equated the inductive–mesomeric effects with that of a bromine atom. Physicochemical investigations are underway to separate the $-I$ and $-M$ components.

In general an alkyl group is introduced at the β-position in naphthalene, as in the cluster reactions, but with the former yields are low as binapthyls are obtained.[18] Presumably the bulky cluster prevents binaphthyl formation and the yield of β-naphthylmethinytricobalt enneacarbonyls is high; introduction of the cluster into the α position is unlikely on steric grounds alone.

EXPERIMENTAL

I.r., mass, and ^{1}H n.m.r. spectra were recorded on Perkin-Elmer 225, A.E.I. M.S.9 and Varian HA100 spectrometers

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* Spectra are available from the authors.

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respectively. Reactions and manipulations were carried out under nitrogen using standard equipment. Reactions were monitored by t.l.c. or i.r. All preparations were similar to the one described below; the solvent used for solid arenes was dichloromethane. Yields and analyses are given in Tables 2 and 5 respectively. The clusters $ClCCo_3(CO)_9$ and $BrCCo_3)CO)_9$ were prepared by standard methods.[1]

TABLE 2

Structure of products formed in Friedel–Crafts reaction with $ClCCo_3(CO)_9$

Mono-substituted arenes	Solvent	Temp.(K)/Time (min)	Sub-stitution	Structural assignment	Yield (%)
PhF	PhF	343/45	*o*	i.r., n.m.r.	90
	CH_2Cl_2	315/60	*o*		80
PhCl	PhCl	343/60	*o*	ox, n.m.r.	90
	CH_2Cl_2	315/90	*p*	i.r., n.m.r.	85
PhBr	PhBr	343/45	*p*	ox, i.r.	90
	CH_2Cl_2	315/90	*p*	n.m.r.	85
PhBr	CH_2Cl_2	315/90	*p*	i.r., n.m.r.	90
PhMe	MePh	343/60	*o,p*	i.r., n.m.r.	40
	CH_2Cl_2	315/12	*p,o*		60
Ph	PhH	343/90		i.r., n.m.r.	50
	CH_2Cl_2	315/90		i.r., n.m.r.	50
Ph·Ph	CH_2Cl_2	315/30	*p*	i.r., n.m.r.	75
$C_{10}H_8$	CH_2Cl_2	315/60	β	ox, n.m.r.	80
Di-substituted arenes					
o-$Me_2C_6H_4$	CH_2Cl_2	315/90	*p,m*	i.r., n.m.r.	80
m-$Me_2C_6H_4$	CH_2Cl_2	315/120	*p,o*	i.r., n.m.r.	10
p-$Me_2C_6H_4$	CH_2Cl_2	315/120	*m,o*	i.r., n.m.r.	10
o-$Cl_2C_6H_4$	CH_2Cl_2	315/45	*p,m*	ox, n.m.r.	22
m-$Cl_2C_6H_4$	CH_2Cl_2	315/90	*o,p*	i.r., n.m.r.	15

TABLE 3

Infrared spectra (2200—1700 cm^{-1}) of aryl derivatives [a]

2-FC_6H_4	2102(m)	2056(s)	2039(s)	2024(w)
2-ClC_6H_4	2103	2056 [c]	2043	2025
4-ClC_6H_4	2102	2055	2040	2021
4-BrC_6H_4	2103	2056	2042	2023
4-IC_6H_4	2103	2056	2042	2022
Ph	2101	2056	2040	2021
4-MeC_6H_4 [b]	2102	2055	2040	2021
3,4-$Me_2C_6H_3$	2101	2054	2039	2020
2,4-$Me_2C_6H_3$	2101	2055, 2052	2039	2021
2,5-$Me_2C_6H_3$	2093	2054, 2051	2038	2019
$C_{10}H_7$	2101	2054	2040	2022
$C_{12}H_9$	2101	2054	2040	2022
2,4-$Cl_2C_6H_3$	2102	2057	2040	2027
3,4-$Cl_2C_6H_3$	2104	2057	2042	2024
2,5-$Cl_2C_6H_3$	2103	2056 [c]	2040	2023
2,5-$Br_2C_6H_3$	2102	2055 [c]	2040	2023

[a] Hexane, ±1 cm^{-1}. [b] Mixture of isomers. [c] Broad and asymmetric.

Preparation of Enneacarbonyl chlorophenylmethinyltricobalt. Enneacarbonylchloromethinyltricobalt (0·1 g, 0·21 mmol) and freshly crushed aluminium trichloride (0·04 g, 0·21 mmol) were dissolved in dry chlorobenzene (12 cm^3) and the stirred solution was heated to 333 K for 2 h. The cooled solution was diluted with chloroform, filtered, and the solvent removed *in vacuo*. The residue was extracted with hexane and the products separated on silica t.l.c. plates: (1) purple band, $ClCCo_3(CO)_9$; (2) brown band, $ClC_6H_4CCo_3(CO)_9$. Band (2) was eluted with hexane–$CHCl_3$ and the residue, left after the evaporation of the solvent, was recrystallized from light petroleum at 273 K. Yield of small dark rhombic crystals was 0·105 g (90%).

Like all methinyltricobalt enneacarbonyls the chlorobenzene derivatives were volatile, soluble in all organic solvents without decomposition, and stable in air for several weeks.

TABLE 4

P.m.r. of aryl derivatives [a]

Substituent [b]	τ(ring) [Intensity] [c]	Multiplicity
Ph	2·43	s
	2·69	s
2-$C_6H_4CH_3$	2·77 [2]	s
	2·80 [1]	t $J = 1$
	2·90 [1]	d $J = 1$
4-C_6H_4Me	2·93 [2], 2·90 [4]	
	2·64 [4], 2·57 [2]	AXX′A′
3,4-$C_6H_3Me_2$	2·68 [1]	d $J_{65} = 9$
	2·91 [1]	d $J_{56} = 2$
	2·63 [1]	s
2,4-$C_6H_3Me_2$	2·49 [1]	d,d $J_{65} = 8$, $J_{62} = 3$
	2·68 [1]	s
	2·74 [1]	d,d $J_{56} = 8$, $J_{52} = 3$
2,5-$C_6H_3Me_2$	2·50 [1]	s
	2·89 [2]	d $J_{23} = J_{32} = 17$
2-C_6H_4F	3·37 [2]	s
	3·22 [1]	t $J = 3$
	3·11 [1]	d $J = 3$
2-C_6H_4Cl	2·48 [2]	s
	2·65 [1]	s
	2·33 [1]	d $J = 5$
4-C_6H_4Cl	2·70 [1], 2·46 [2]	
	2·60 [2], 2·40 [1]	AXX′A′
4-C_6H_4Br	2·48	s
4-C_6H_4I	2·70 [1], 2·61 [2]	
	2·43 [2], 2·35 [1]	AXX′A′
3,4-$C_6H_3Cl_2$		
2,4-$C_6H_3Cl_2$	2·65	dd, $J_{65} = 8$, $J_{53} = 2$
	2·46	s
	2·05	d $J_{56} = 9$
β-$C_{10}H_7$	2·46 [2]	t,d $J_{678} = J_{765} = 7$, $J_{68} = J_{75} = 3$
	2·24 [2]	d,d $J_{56} = J_{87} = 11$, $J_{57} = J_{86} = 2$
	2·07 [2]	d,d $J_{43} = J_{34} = 8$, $J_{31} = J_{45} = 2$
	1·84 [1]	s,d $J_{13} = 1$
p-$C_6H_4C_6H_5$	2·64 [2], 2·57 [4]	
	2·42 [4], 2·34 [2]	AXX′A′
	2·64 [10]	s

[a] In acetone. [b] Numbered from cluster. [c] Relative intensity.

TABLE 5

Analytical data for aryl clusters

	Found		Calc.	
	C	H	C	H
C_6H_5 [c]	37·1	1·55	37·0	0·95
2-C_6H_4F [c]	35·85	0·85	35·8	0·75
2-C_6H_4Cl [a,c]	35·7	1·0	34·8	0·75
4-C_6H_4Cl [c]	35·7	1·0	34·8	0·75
4-C_6H_4Br [b,c]	32·85	0·95	32·2	0·65
4-C_6H_4I	29·3	0·85	29·8	0·6
4-C_6H_4Me [c]	38·4	1·4	38·3	1·3
3,4-$C_6H_3Me_2$	39·8	1·8	39·45	1·55
2,4-$C_6H_3Me_2$ [c]	39·55	2·95	39·45	1·65
2,5-$C_6H_3Me_2$	39·9	1·8	38·45	1·65
3,4-$C_6H_3Cl_2$	32·2	0·8	32·7	0·5
2,4-$C_6H_4Cl_2$	32·25	0·8	32·7	0·5
β-$C_{10}H_7$ [c]	43·5	1·7	42·2	1·25
p-$C_{12}H_9$ [c]	42·2 49·5	1·5 3·05	44·5	1·5

[a] Found: Cl = 6·31; Calc.: 6·45. [b] Found: Br = 13·3; Calc.: 13·4. [c] Composition confirmed by mass spectrum; high H analysis due to occluded solvent, see text.

The green product obtained in the filtration of the original chloroform solution was washed thoroughly with hot benzene to remove excess $AlCl_3$. However it was decomposed rapidly by traces of moisture and analytical figures were inconsistent. Broad ν(CO) bands were observed in the i.r. spectrum.

We thank the New Zealand University Grants Committee for financial assistance and Professor A. D. Campbell and the Microanalytical laboratory staff for the analyses.

[2/783 *Received, 5th April,* 1972]