# Chemistry of Methylinyltricobalt Enneacarbonyls. Part IX.[1] Reactions with Grignard and Organolithium Reagents

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Aryl Grignard reagents react with halogenomethinyltricobalt enneacarbonyls to give the corresponding aryl-clusters in good yield. Substitution with alkyl Grignard reagents is not possible. Reactions with organolithium and Grignard reagents (under a CO atmosphere) invariably give products formed by CO insertion, principally the acid, $HO_2CCCo_3(CO)_9$. Possible intermediates in these reactions are discussed.

ALTHOUGH the apical substituent (Y) of methinyltricobalt enneacarbonyls, $YCCO_3(CO)_9$, has been shown to be susceptible to electrophilic attack [1-4] there are few reports on the activity of nucleophiles. It is known [5] that strong alkali causes decomposition to $Co(CO)_4^-$ and in the presence of alcohols, the acetylene derivatives $RC_2RCo_2(CO)_6$ [6,7] and $RC_2RCo_4(CO)_{10}$.[8] The esters, $RO_2CCCo_3(CO)_9$, are formed when the halogeno-clusters are treated with boiling alcohols.[9] This paper describes the action of Grignard and organolithium reagents on the halogeno-clusters, Cl- or $Br\text{-}CCo_3(CO)_9$.

*Reactions with Organomagnesium Reagents under Nitrogen.*—Chloro- or bromo-methinyltricobalt enneacarbonyls react smoothly with arylmagnesium bromides in THF to give the corresponding aryl-clusters in good yields.

$$RMgBr + BrCCo_3(CO)_9 \longrightarrow RCCo_3(CO)_9 + MgBr_2$$

It is essential that the Grignard : cluster mole ratio is greater than 9 : 1 and maximum yields are achieved with low reaction temperatures (*ca.* 273 K). Tertiary-alkyl Grignards fail to react under these conditions as do primary and secondary alkyl reagents if the Grignard : cluster ratio is less than 9 : 1.

A variety of aryl-cluster derivatives have been prepared by this route, some of which are listed in Table 1. This method has proved to be superior to that using Friedel–Crafts reagents [1] both for convenience and stereospecificity of synthesis. Thus we have isolated pure samples of the 2-,3- and 4-$C_6H_4(CH_3)$-clusters whereas the Friedel–Crafts reaction with toluene, gave a mixture of isomers. The steric restraints on this method are those noted for the Friedel–Crafts reaction, namely, it is difficult to prepare derivatives with bulky groups on the aryl *ortho* to the cluster.

The spectral properties of the new compounds are compatible with other cluster derivatives [2,10] (Table 2) and fully support the structural assignments. A further examination of the mass spectra appears to confirm the earlier suggestion [11] that the secondary fragmentation pattern can be used to determine the stereochemistry of aryl-derivatives. This is evident from the data in Table 3; the stereochemistry can be deduced from the abundance of migration fragments and the mode of aryl fission.

Phenol derivatives cannot be synthesised directly although an anisole-cluster can be demethylated to the phenol-cluster in high yield by utilising the mild electrophile $BBr_3$.

TABLE 1

Arylmethinyltricobalt enneacarbonyls

| Aryl [a] | Yield | Found [b] (%) C | H | N | Required (%) C | H | N |
|---|---|---|---|---|---|---|---|
| 2-Me [c] | 40 | 38·45 | 1·4 | | 38·3 | 1·3 | |
| 3-Me [c] | 70 | 38·2 | 1·45 | | 38·2 | 1·3 | |
| 4-Me [c] | 60 | 38·5 | 1·45 | | 38·3 | 1·3 | |
| 2-OMe | 30 | 37·3 | 1·5 | | 37·2 | 1·3 | |
| 4-OMe [c] | 40 | 37·6 | 1·55 | | 37·2 | 1·3 | |
| 3-OMe | 35 | 37·4 | 1·45 | | 37·2 | 1·3 | |
| 2-Me,4-OMe | 25 | 38·5 | 1·8 | | 38·45 | 1·6 | |
| 3-Me,5-OMe | 20 | 38·85 | 1·85 | | 38·45 | 1·6 | |
| 2-Cl,4-OMe | 10 | 38·55 | 1·25 | | 35·05 | 1·05 | |
| 3-Cl,4-OMe | 35 | 35·25 | 1·2 | | 35·05 | 1·05 | |
| 2,3-$Me_2$,4-OMe | 23 | 39·95 | 2·1 | | 39·6 | 2·1 | |
| 3,5-$Me_2$,4-OMe | 36 | 39·8 | 2·1 | | 39·6 | 2·1 | |
| 4-$NMe_2$ | 23 | 39·35 | 2·2 | 2·3 | 38·5 | 1·8 | 2·5 |
| 3-Me,4-$NMe_2$ | 25 | 39·85 | 2·25 | 2·3 | 39·65 | 2·1 | 2·45 |
| 2-Me,4-$NMe_2$ | 15 | 40·05 | 2·25 | 2·2 | 39·65 | 2·1 | 2·45 |
| 3-Cl,4-$NMe_2$ | 21 | 36·3 | 1·6 | 2·05 | 36·15 | 1·5 | 2·35 |
| 2,5-$Me_2$,4-$NMe_2$ | 17 | 43·75 | 3·5 | 2·35 | 40·75 | 2·4 | 2·4 |
| 2,3-$Me_2$,4-$NMe_2$ | 21 | 43·4 | 3·1 | 2·35 | 40·75 | 2·4 | 2·4 |
| 3,5-$Me_2$,4-$NMe_2$ | 30 | 41·1 | 2·6 | 2·35 | 40·75 | 2·4 | 2·4 |
| α-$C_{10}H_7$ [c] | 30 | 42·55 | 1·45 | | 42·25 | 1·25 | |

[a] Numbered from cluster. [b] In all cases the composition was confirmed by an analysis of the mass spectrum. [c] Mentioned also in ref. 7.

$$e.g.\ 4\text{-}MeOC_6H_4CCo_3(CO)_9 \xrightarrow[CH_2Cl_2]{BBr_3} 4\text{-}HOC_6H_4CCo_3(CO)_9$$

Demethylation is not possible when the methoxyl group is adjacent (*ortho*) to the cluster as this group prevents the formation of the intermediate boron complex.[12] Likewise, Grignard reactions with aniline itself are unsatisfactory as the basic aniline preferentially co-ordinates to cobalt, but we were unable to find a mild reagent suitable for the demethylation of *N*,*N*′-dimethylaniline clusters.

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[1] Part VIII, R. Dolby and B. H. Robinson, *J.C.S. Dalton*, 1972, 2046.

[2] D. Seyferth and A. T. Wehmann, *J. Amer. Chem. Soc.*, 1970, **92**, 5520.

[3] R. Dolby, T. W. Matheson, B. Nicholson, B. H. Robinson, and J. Simpson, *J. Organometallic Chem.*, 1972, **43**, C13.

[4] D. Seyferth and G. H. Williams, *J. Organometallic Chem.*, 1972, **38**, C11.

[5] R. Ercoli, *Chimica e Industria* (*Milano*), 1962, **44**, 565.

[6] K. Tominga, N. Yamagami, and H. Wakamatsu, *Tetrahedron Letters*, 1970, **25**, 2217.

[7] D. Seyferth, J. E. Hallgren, R. J. Spohm, A. T. Wehman, and G. H. Williams, Special Lectures, XXIII I.U.P.A.C., Boston, 1971.

[8] T. W. Matheson, unpublished work.

[9] G. Bor, L. Marko, and B. Marko, *Chem. Ber.*, 1961, **95**, 333.

[10] G. Bor, Proc. Symp. Coord. Chem. Tihany (Hungary), 1964, 361.

[11] R. Dolby and B. H. Robinson, *Chem. Comm.*, 1970, 1058.

[12] F. L. Benton and T. E. Dillon, *J. Amer. Chem. Soc.*, 1942, **64**, 1128.

TABLE 2

$^1$H N.m.r. and $\nu$(CO) i.r. bands of RCCo$_3$(CO)$_9$ compounds

| | N.m.r. data [a] | | | I.r. data [b] | | | |
|---|---|---|---|---|---|---|---|
| Substituent, R | $\tau$ | | | $A_1$ | $E$ | $E$ | $A_1$ |
| 2-MeC$_6$H$_4$ | 2·77 | | Complex | 2100 | 2053 | 2037 | 2020 |
| | 2·80 | | | | | | |
| | 2·90 | (CH$_3$) | (d) $J = 1$ | | | | |
| | 7·56 | | | | | | |
| 3-MeC$_6$H$_4$ | 2·52 | [1] | (d) $J = 3$ | 2100 | 2052 | 2038 | 2020 |
| | 2·80 | [2] | (d) $J = 3$ | | | | |
| | 2·92 | [3] | (d) $J = 4$ | | | | |
| | 7·65 | (CH$_3$) | | | | | |
| 4-MeC$_6$H$_4$ | 2·63 | [2] | (d) $J_{6,5}$, $J_{2,3} = 14$ | | | | |
| | 2·89 | [2] | (d) $J_{5,6}$, $J_{3,2} = 13$ | | | | |
| | 7·66 | (CH$_3$) | | | | | |
| 2-MeOC$_6$H$_4$ | 2·73 | [1] | (d) $J_{1,2} = 13$ | 2098 | 2051 | 2034 | 2018 |
| | 2·86 | [1] | (d) $J_{3\,4} = 8$ | | | | |
| | 3·19 | [2] | (t) $J_{123} = J_{234} = 5$ | | | | |
| | 6·22 | (CH$_3$O) | | | | | |
| 3-MeOC$_6$H$_4$ | Complex envelope | | | 2101 | 2053 | 2039 | 2020 |
| | 6·28 | | | | | | |
| 4-MeOC$_6$H$_4$ | 2·45 | [2] | (d) $J_{6,5}$ $J_{2,3} = 13$ | 2100 | 2053 | 2036 | 2019 |
| | 3·28 | [2] | (d) $J_{5,6}$ $J_{3,2} = 13$ | | | | |
| | 6·22 | (CH$_3$O) | | | | | |
| 2-Me,4-MeOC$_6$H$_3$ | 2·49 | [1] | (d) $J_{6,5} = 12$ | 2098 | 2050 | 2034 | 2017 |
| | 3·40 | [1] | (s) | | | | |
| | 3·49 | [1] | (d) $J_{5,6} = 13$ | | | | |
| | 6·22 | (CH$_3$O) | | | | | |
| | 7·55 | (CH$_3$) | | | | | |
| 3-Me,4-MeOC$_6$H$_3$ | 2·84 | [1] | (d) $J = 5$ | 2098 | 2050 | 2035 | 2018 |
| | 2·87 | [1] | (s) | | | | |
| | 3·35 | [1] | (d) $J = 5$ | | | | |
| | 6·21 | (CH$_3$O) | | | | | |
| | 7·78 | (CH$_3$) | | | | | |
| 2-Cl,4-MeOC$_6$H$_3$ | 2·44 | [1] | (d) $J_{6,5} = 15$ | 2100 | 2053 | 2036 | 2026 |
| | 3·48 | [1] | (s) | | | | |
| | 3·72 | [1] | (d) $J_{5,6} = 15$ | | | | |
| 3-Cl,4-MeOC$_6$H$_3$ | 2·35 | [1] | (d) $J_{2,5} = 3$ | 2101 | 2053 | 2038 | 2020 |
| | 2·67 | [1] | (d) $J_{6,5} = 16$ | | | | |
| | 2·77 | [1] | (d) $J_{5,6} = 15$ | | | | |
| | 6·15 | (CH$_3$O) | | | | | |
| 2,3-Me$_2$,4-MeOC$_6$H$_2$ | 2·52 | [1] | (d) $J_{6,5} = 14$ | 2097 | 2050 | 2034 | 2017 |
| | 3·55 | [1] | (d) $J_{5,6} = 14$ | | | | |
| | 6·27 | (CH$_3$O) | | | | | |
| | 7·95, 8·18 | (CH$_3$) | | | | | |
| 3,5-Me$_2$,4-MeOC$_6$H$_2$ | 3·00 | [2] | (s) | 2100 | 2051 | 2037 | 2018 |
| | 6·30 | (CH$_3$O) | | | | | |
| | 7·72 | (CH$_3$) | | | | | |
| 4-Me$_2$NC$_6$H$_4$ | 2·61 | [2] | (d) $J_{6,5}$, $J_{2,3} = 14$ | 2096 | 2049 | 2033 | 2014 |
| | 3·42 | [2] | (d) $J_{5,6}$, $J_{3,2} = 14$ | | | | |
| | 7·05 | (CH$_3$) | | | | | |
| 2-Me,4-Me$_2$NC$_6$H$_3$ | 2·56 | [1] | (d) $J_{6,5} = 12$ | 2095 | 2047 | 2032 | 2015 |
| | 2·88 | [1] | (s) | | | | |
| | 3·68 | [1] | (d) $J_{5,6} = 12$ | | | | |
| | 7·18 | (Me$_2$N) | | | | | |
| | 7·55 | (CH$_3$) | | | | | |
| 3-Me,4-Me$_2$NC$_6$H$_3$ | 2·88 | [1] | (d) $J_{6,5} = 12$ | 2099 | 2051 | 2035 | 2017 |
| | 2·90 | [1] | (s) | | | | |
| | 3·12 | [1] | (d) $J_{5,6} = 12$ | | | | |
| | 7·30 | (Me$_2$N) | | | | | |
| | 7·71 | (CH$_3$) | | | | | |
| 3-Cl,4-Me$_2$NC$_6$H$_3$ | 2·77 | [1] | (d) $J_{5,6} = 12$ | 2100 | 2052 | 2039 | 2019 |
| | 2·89 | [1] | (s) | | | | |
| | 3·24 | [1] | (d) $J_{5,6} = 12$ | | | | |
| | 7·18 | | | | | | |
| 2,3-Me$_2$,4-Me$_2$NC$_6$H$_2$ | 2·61 | [1] | (d) $J_{5,6} = 12$ | 2096 | 2049 | 2033 | 2019 |
| | 3·39 | [1] | (d) $J_{5,6} = 12$ | | | | |
| | 7·33 | (Me$_2$N) | | | | | |
| | 7·63, 7·76 | (CH$_3$) | | | | | |
| 2,5-Me$_2$,4-Me$_2$NC$_6$H$_2$ | 2·63 | [1] | (s) | 2097 | 2049 | 2033 | 2017 |
| | 3·42 | [1] | (s) | | | | |
| | 6·97 | (Me$_2$N) | | | | | |
| | 7·31, 7·44 | (CH$_3$) | | | | | |

TABLE 2 (*Continued*)

| Substituent, R | N.m.r. data [a] τ | | | I.r. data [b] $A_1$ | $E$ | $E$ | $A_1$ |
|---|---|---|---|---|---|---|---|
| 3,5-$\mathrm{Me_2}$,4-$\mathrm{Me_2NC_6H_2}$ | 2·86 | [2] | (s) | 2099 | 2051 | 2037 | 2018 |
| | 7·21 | ($\mathrm{Me_2N}$) | | | | | |
| | 7·75 | ($\mathrm{CH_3}$) | | | | | |
| 1-$\mathrm{C_{10}H_7}$ | 2·25 | [1] | (d) | 2099 | 2054 | 2037 | 2023 |
| | 2·34 | [1] | (d) | | | | |
| | 2·63 | [3] | (t) | | | | |
| | 2·76 | [2] | (d) | | | | |

[a] $^1$H N.m.r. spectra taken in $\mathrm{CDCl_3}$, relative to tetramethylsilane, relative intensities in brackets, multiplicity in parentheses, coupling constants *J* in Hz. [b] I.r. spectra taken in hexane solution, in cm$^{-1}$, ±0·5 cm$^{-1}$, relative intensities: *A*, medium, *E*, very strong; assignments follow a personal communication from G. Bor.

The other product in the Grignard reactions is $\mathrm{HCCo_3(CO)_9}$. Its formation most likely results from the transfer reaction:

$$\mathrm{C{-}Cl} + \mathrm{BrMgR} \longrightarrow \geqslant\mathrm{C{-}MgBr} + \mathrm{R{-}Cl}$$
$$\Big\downarrow \mathrm{H_2O}$$
$$\geqslant\mathrm{C{-}H} + \mathrm{MgBr(OH)}$$

This is supported by the fact that yields are proportionally high if the arylmagnesium compound has an *ortho* substituent; for example with *o*-$\mathrm{CH_3C_6H_4MgBr}$ the yield of $\mathrm{HCCo_3(CO)_9}$ is 27%.

TABLE 3

Structurally important fragmentations in the mass spectra of arylmethinyltricobalt enneacarbonyls [a]

*Compounds*: R-$\mathrm{C_6H_5}$–$\mathrm{CCo_3(CO)_9}$

R *ortho* to cluster (2-aryl derivatives):

Migration fragments [b] of the type $\mathrm{RC_nH_mCo_x^+}$ ($x$ = 1—3) are obtained in moderate abundance (10—20%).

The aryl substituent fragments to give ions of the type $\mathrm{RC_nH_mCCo_3^+}$, $n$ = 2—6, in abundance 10—20%.

R *para* to cluster (4-aryl derivatives):

No migration fragments, $\mathrm{RC_nH_mCo_x^+}$, are found.

The aryl fragments to give ions of the type $\mathrm{RC_nH_mCCo_3^+}$ and $n$ = 4—6 only.

R *meta* to cluster.

Migration fragments are in small abundance (*ca.* 5%).

Fragments of the type $\mathrm{RC_nH_mCCo_3^+}$, $n$ = 3—6 are found.

[a] Full mass spectra may be obtained from the authors. [b] Absence of apical carbon atom; see ref. 19.

*Reactions with Organolithium Reagents; Reactions with Grignard Reagents under Carbon Monoxide.*—Organolithium reagents, irrespective of the reagent: cluster ratio, do not undergo the substitution reactions discussed above. The major product with one mole of RLi per mole of halogeno-cluster is the acid, $\mathrm{HO_2CCCo_3(CO)_9}$(I); that is, a product resulting from CO insertion. Minor

$$\mathrm{BrCCo_3(CO)_9} \xrightarrow[\text{(ii) H}_2\text{O}]{\text{(i) RLi}} \mathrm{HO_2CCCo_3(CO)_9}$$

products in these reactions include $\mathrm{HCCo_3(CO)_9}$ (II), $\mathrm{[Co_3(CO)_9C][Co_2(CO)_6C_2H]}$ (III),[13] $\mathrm{[CCo_3(CO)_9]_2C_2}$ (IV),[14] and $\mathrm{[CCo_3(CO)_9]_2C_2[Co_2(CO)_6C_2H]}$ (V),[15,16] but the respective yields depend on the nature of RLi, the apical substituent (Y), working-up temperature and reaction atmosphere (Table 4). Maximum yields are obtained in an atmosphere of carbon monoxide.

TABLE 4

Yields from organolithium reactions with $\mathrm{XCCo_3(CO)_9}$ [a]

| RLi R | $\mathrm{XCCo_3(CO)_9}$ X | (I) | (II) | (III) | (IV) | (V) | Work-up temperature/ K |
|---|---|---|---|---|---|---|---|
| Bu$^n$ | Br | 43 | 2 | 3 | 3 | 4 | 298 |
| | Br [b] | 57 | | | | | 253 |
| | Cl | | 1 | 4 | 2 | | 298 |
| | Br [c] | 10 | | | | | 253 |
| Ph | Br | 27 | 2 | 11 | 2 | 6 | 298 |
| | Br | 52 | 19 | | | | 253 |
| | Cl | 20 | 8 | 14 | 6 | 6 | 298 |
| Me | Br | 36 | 25 | | | | 253 |

[a] The yields are based on the amount of cluster used, not necessarily consumed in the reaction. See Experimental section. [b] Yield, 96%, based on recovered $\mathrm{BrCCo_3(CO)_9}$. [c] $\mathrm{N_2}$ Atmosphere.

The hydrolysis is acid-catalysed; yields are *ca.* 50% of those given in Table 4 if acid is not present during the working-up. If an excess of RLi is used only traces of cluster products can be isolated. Esters are formed in good yield (*ca.* 80%) if the organolithium intermediate is decomposed in the presence of alcohols.

$$\textit{e.g.}\ \mathrm{ClCCo_3(CO)_9} \xrightarrow[\text{(ii) MeOH}]{\text{(i) BuLi}} \mathrm{MeOCCCo_3(CO)_9}\quad(81\%)$$

Similarly deuteriated analogues of (I)—(III) and (V) are produced using $\mathrm{D_2O}$. These facts, together with the absence of (II) ⟶ (V) when low temperatures are employed, strongly suggest that the minor products result from decomposition of an intermediate rather than from the initial reaction with RLi.

Grignard reactions carried out under carbon monoxide also gave (I) in small yield but only traces of the acetylene compounds.

The mass spectrum of (I) is unusual in that *ten* CO groups are lost in the primary fragmentation process;

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[13] R. J. Dellaca, B. R. Penfold, B. H. Robinson, W. T. Robinson, and J. L. Spencer, *Inorg. Chem.*, 1970, **9**, 2197.

[14] R. J. Dellaca, B. R. Penfold, B. H. Robinson, W. T. Robinson, and J. L. Spencer, *Inorg. Chem.*, 1970, **9**, 2204.

[15] B. H. Robinson and J. L. Spencer, *J. Organametallic Chem.*, 1971, **30**, 267.

[16] R. J. Dellaca and B. R. Penfold, *Inorg. Chem.*, 1972, **11**, 1855.

the loss of a ketonic CO has also been noted for the esters.[17] This is contrary to the normal primary fragmentation in metal carbonyls [18] and clearly the number of co-ordinated CO groups in methinyltricobalt enneacarbonyls may not be obvious from their mass spectra. The mechanism proposed by Cetini and co-workers, involving OR migration, is reasonable when it is remembered that migration reactions have been observed in the mass spectra of many other $RCCo_3(CO)_9$ derivatives.[19]

## DISCUSSION

The notable feature of reactions carried out under CO is the dominance of products formed by CO insertion. In fact, facile insertion under the influence of (although not necessarily by reaction with) a nucleophile (*e.g.* $H_2O$, ROH[3]) and also certain electrophiles, *e.g.* $AlCl_3$,[3,4] is a widespread phenomenon in halogenomethinyltricobalt enneacarbonyl chemistry. A structural feature which we believe encourages intramolecular insertion is the close proximity of the equatorial CO groups to the apical substituent which are at an average intramolecular contact distance of 3·1 Å.

Any mechanism proposed for the CO insertion must take into account the following observations; (a) only one mole of RLi is required, (b) the insertion is facilitated by CO, (c) the organic moiety, R, from RLi or RMgX reagents is never incorporated in the products whereas $H_2O$ and alcohols facilitate insertion and determine the nature of the final product,[3] (d) RLi and RMgX reagents differ markedly in their reactivity. The dark brown solutions formed initially in the reactions of both RLi (under $N_2$ or CO) and RMgX with $XCCo_3(CO)_9$ ($X =$ Cl or Br) and $RCCo_3(CO)_9$ ($R =$ Me and Ph) contain the same species [$\nu$(CO) for $X =$ Br; 2108w, 2059vs, 2044vs, 2028s, 2007s, and 1879m $cm^{-1}$]. Moreover the addition of $Et_3O^+BF_4^-$ to these solutions yields the parent clusters. Clearly, nucleophilic attack is not occurring at the apical bond but instead on a co-ordinated equatorial carbonyl to produce an unstable carbene-intermediate (VI),[20,21] and consequently a weakened Co–C bond. It is important to note that a bridged configuration not only reduces the charge on the cluster (*cf.* reactions with Lewis bases [22]) but also places the co-ordinated carbonyl group adjacent to the apical bond; [8] an ideal conformation for subsequent intramolecular insertion. In a basic solvent and under the influence of CO the carbene intermediate could then rearrange to the acylium cluster, $^+OCCo_3(CO)_9$ which reacts with the hydroxylic species, ROH,[3,4,7] to produce the product. The driving force for the insertion must be the thermodynamic stability of the acylium cluster.

With the less-reactive aryl-Grignards it would appear that another pathway is available.

$$XCCo_3(CO)_9 + m\mathrm{RMgX} \rightleftharpoons XCCo_3(CO)_{9-m}[(R)COMgX]_m \ (m = 1?)$$

Another mole of reagent could participate in nucleophilic attack at the apical bond although an intramolecular nucleophilic attack is equally probable. Two moles of a Grignard reagent can attack a ketone [23] and we suggest that this is the preferred reaction with primary- and secondary-alkyl Grignard and the clusters. Complete decomposition of the cluster would occur on hydrolysis, as is observed. The failure of bulkier aryl analogues to react in this way may be due to steric hindrance from the mole of RMgX already co-ordinated; the steric requirements of tertiary alkyl Grignard reagents apparently prevent any reaction whatsoever. Finally, the difference in reactivity between RLi and RMgX reagents could be ascribed to the stronger electrophile, $Li^+$ weakening the Co–C bond to such extent that CO insertion predominates.

## EXPERIMENTAL

All solvents were dried before use. Most reagents were commercial grade and the chloro- and bromo-methinyltricobalt enneacarbonyls and Grignard reagents were prepared by standard procedures.

Mass, i.r., and $^1H$ n.m.r. spectra were taken on Varian CH 7, Perkin-Elmer 225, and Varian HA 100 instruments respectively. Analytical data and yields are given in Table 1.

*A Typical Reaction of an Organomagnesium Halide with a Cluster under Nitrogen.*—A stirred solution of chloromethinyltricobalt enneacarbonyl (0·1 g, 0·21 mmol) in THF (20 ml) was cooled to 203 K under nitrogen and a solution of *m*-toluenemagnesium bromide (2·3 mmol, prepared from *m*-bromotoluene) in THF (20 ml) was added dropwise over a period of 15 min. The solution was then brought to 273 K and poured into ice–water (50 g) containing two drops of conc. $H_2SO_4$. The mixture was shaken and extracted with ether (20 ml), the ether removed from the extract *in vacuo*, and the residue separated on a preparative silica gel plate. In hexane the bands eluted in order, purple [$HCCo_3(CO)_9$] followed by brown, [$CH_3C_6H_4CCo_3(CO)_9$]. The residue from the latter layer was recrystallised from hexane to give the product, 3-methylphenylmethinyltricobalt enneacarbonyl, as fine brown-black crystals.

This was the procedure followed in all the Grignard reactions except that the sulphuric acid was omitted and sodium acetate (1 g) added to the ice–water mixture during the working up of the *N,N'*-dimethylaniline compounds.

All the aryl derivatives had similar chemical and physical properties; *viz.* brown-black crystals that sublime with difficulty at 0·1 mmHg, air-stable and soluble in all common organic solvents. Sublimation is not a satisfactory method of purifying these compounds as there is extensive decomposition.

*Demethylation of Aryl Methyl Ether Derivatives.*—The method used was a modification of that described by Benton

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[17] O. Gambino, G. A. Vaglio, R. P. Ferrari, M, Valle, and G. Ceteni, *Org. Mass Spectrometry*, 1972, **6**, 723.

[18] B. F. G. Johnson and J. Lewis, *Accounts Chem. Res.*, 1968, **1**, 245.

[19] B. H. Robinson and W. S. Tham, *J. Chem. Soc.* (*A*), 1968, 1784.

[20] D. J. Darensbourg and M. Y. Darensbourg, *Inorg. Chim. Acta*, 1971, **5**, 247.

[21] M. Y. Darensbourg, *J. Organometallic Chem.*, 1972, **58**, 133.

[22] T. W. Matheson, B. H. Robinson, and W. S. Tham, *J. Chem. Soc.* (*A*), 1971, 1457.

[23] 'A guidebook to Mechanism in Organic Chemistry,' P. Sykes, Longmans, 1967.

and Dillon.[12] 4-Methoxybenzenemethinyltricobalt enneacarbonyl (0·1 g, 0·18 mmole) was dissolved in dry dichloromethane (5 ml) under nitrogen; boron tribromide (0·18 g, 0·72 mmol) was then added from a syringe. The solution was stirred for 15 min before it was carefully poured into ice–water (50 g containing 1 ml of 0·1M-NaOH). This mixture was extracted with $CHCl_3$ and the combined $CHCl_3$ extracts were reduced and the residue (dissolved in hexane) transferred to a preparative silica gel plate. Elution with hexane removed the unreacted anisole; subsequent elution with ether separated the product, 4-hydroxybenzenemethinyltricobalt enneacarbonyl. The crude product was recrystallized from hexane as fine black needles, yield 47% (based on reacted anisole) (Found: C, 36·45; H, 1·4; *M*, 534 (mass spectrum). $C_{16}H_5Co_3O_{10}$ requires C, 36·0; H, 0·95%; *M*, 534). ν(CO): 2099, 2050, 2036, 2028 cm$^{-1}$. $^1H$ N.m.r.: ($CDCl_3$) 2·65, 2·79, 3·31, 3·46 (AXX′A′), 4·98 (OH). Yields using 0·18, 0·54, 1·62 mmol of $BBr_3$ were respectively, 0, 96, and 51%.

This procedure was used for the 3-OH and 3-Me, 4-OH derivatives with equal success (Found: C, 36·8; H, 1·7%; *M* (mass spectrum), 534. $C_{16}H_{15}Co_3O_{10}$ requires C, 36·0; H, 0·95%, *M*, 534. ν(CO): 2101m, 2053vs, 2037vs, 2020m cm$^{-1}$.

Found: C, 38·1; H, 1·65%; *M* (mass spectrum), 548. $C_{17}H_7Co_3O_{10}$ requires C, 37·35; H, 1·3%; *M*, 548. ν(CO): 2099m, 2051vs, 2036vs, 2017m cm$^{-1}$).

No reaction occurred with $BCl_3$ while $FeCl_3$ and $I_2$ oxidised the cluster.

*Reaction of an Organolithium Reagent with a Halogenomethinyltricobalt Enneacarbonyl.*—A typical procedure was as follows. To a stirred solution of $BrCCo_3(CO)_9$ (0·1 g, 0·19 mmol) in tetrahydrofuran (5 ml), cooled to 203 K in a CO atmosphere, was added 0·1 ml of 1·5 M-BuLi in hexane. The temperature of the solution was brought to 253 K and 1 g of ice added. The temperature was then increased to 293 K and the whole reaction mixture poured into ice–water (50 g containing 0·1 ml of conc. $H_2SO_4$). After extraction of this water mixture with ether the solvent from the combined extracts was removed and the residue separated on a preparative silica gel (solvent hexane) plate. The product (the second band) was eluted with ether and recrystallised from chloroform–hexane as brown-black prisms; yield, 57% [or 94% based on $BrCCo_3(CO)_9$ actually consumed].

As noted in Table 4 and the text, other products separated on the plate if the Bu$^n$Li was added at 293 K. The bands elute in the following order (decreasing $R_F$, solvent hexane), (II), (III), (IV), (V), and (I).

*Preparation of* $MeO_2CCCo_3(CO)_9$ *from* $BrCCo_3(CO)_9$.—Butyl-lithium (1 ml, 0·20 mmol) was added to a solution of $BrCCo_3(CO)_9$ (0·1 g, 0·19 mmol) in tetrahydrofuran (10 ml) at 203 K in a CO atmosphere. The brown solution was stirred for 1 h at 243 K before the methanol (2 ml) was added. Ice–water (50 g) was then added at 298 K and the solution extracted with ether. The residue left after the solvent had been removed from the combined ether extracts was dissolved in hexane and run on a preparative silica gel plate to separate the ester from the acid. The product, $MeO_2CCCo_3(CO)_9$ eluted from hexane as dark purple needles, yield 65%.

Other compounds isolated were $HO_2CCCo_3(CO)_9$ (10%) and unreacted $BrCCo_3(CO)_9$.

*Preparation of* $HO_2CCCo_3(CO)_9$ *using Grignard Reagents.*—The procedure was essentially the same as that used for the organolithium reagents except that the Grignard was stirred with $BrCCo_3(CO)_9$ for at least 1 h before the reaction mixture was quenched.

The yield of acid cluster using *p*-$MeC_6H_4MgBr$ was 21%. Other products isolated, soluble in organic solvents, were $HCCo_3(CO)_9$ (4%) and 4-$MeC_6H_4CCo_3(CO)_9$ (4%). When methanol was added to the quenching mixture $MeO_2CCCo_3(CO)_9$ (26%) and $HO_2CCCo_3(CO)_9$ (21%) were obtained.

*Attempted Isolation of Intermediate in the Grignard and Organolithium Reactions.*—Butyl-lithium in ether (5 ml) was added to a solution of $BrCCo_3(CO)_9$ (1 : 1 mole ratio) in diethyl ether (5 ml) held at 213 K under nitrogen. A deep brown solution formed almost immediately [ν(CO): 2108w, 2059vs, 2044vs, 2028s, 2007s, 1879m cm$^{-1}$]. The solution was brought to 243 K, $Et_3O^+BF_4^-$ added, and the solution was stirred at 293 K for 5 min. The solvent was removed under reduced pressure and the residue was extracted with hexane. A nearly quantitative recovery of $BrCCo_3(CO)_9$ (identified by $R_F$ value; i.r., and mass spectrum) was achieved.

Similar results were obtained using THF as the solvent (the brown solution has an identical i.r. spectrum to that in diethyl ether) and when $CH_3CCo_3(CO)_9$ and $PhCCo_3(CO)_9$ were used as the substrates [ν(CO): 2100w, 2058vs, 2037vs, 2010s, 1880m and 2099w, 2057vs, 2038vs, 2010s, and 1880 cm$^{-1}$ respectively]. Likewise the analogous reaction of *p*-$MeC_6H_4MgBr$ with $BrCCo_3(CO)_9$ and $CH_3CCo_3(CO)_9$ in THF yielded brown solutions [ν(CO): 2106w, 2076w, 2057vs, 2044vs, 2026s, 1884s cm$^{-1}$ for the $BrCCo_3(CO)_9$ reaction] but only the reactants were recovered on the addition of $Et_3O^+BF_4^-$. All attempts to crystallise a compound from the various brown solutions failed.

These reactions show however, that CO insertion occurs after the addition of the hydroxy-species.

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