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REACTIONS OF TETRACARBONYLCOBALTATE(—I) WITH CHLOROSILANES IN ETHER SOLVENTS

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Summary

The reactions of $NaCo(CO)_4$ with Me_nSiCl_{4-n} (n = 0—3) in diethylether (Et_2O) and in tetrahydrofuran (THF) have been studied. Three distinct reaction pathways were recognised which depend on the acidity of the chlorosilane and basicity of solvent. Attack at the silicon centre via the Co atom of $Co(CO)_4^-$ leads to formation of a Si—Co bond; reaction involving a CO ligand of $Co(CO)_4^-$ gives clusters $R_3SiOCCo_3(CO)_9$; and chlorosilane induced attack of $Co(CO)_4^-$ on the solvent gives products derived from THF molecules.

Introduction

The most versatile route to Group IV derivatives of metal carbonyls is the salt-elimination reaction (eq. 1).

$$R_3EX + ML_n^- \rightarrow R_3EML_n + X^- \quad (1)$$

(E = C, Ge, Sn, Pb; ML_n^- = $Co(CO)_4^-$, $Mn(CO)_5^-$, $Fe(CO)_2Cp^-$ etc.; R = alkyl, aryl, halogen) [1]

However, this procedure is generally applicable to silicon derivatives only for ML_n^- = $Fe(CO)_2Cp^-$, although isolated examples from other systems are known [2,3,4]. The reasons for the limited utility of silicon halides in these syntheses remain unclear. Some compounds containing Si—Mn bonds are known to react with the THF solvent normally used [5] or with the halide ion concomitantly produced [6,7] but this cannot explain the lack of success when the expected product is stable under these conditions.

Curtis [4,8] has shown that reactions of Ph_3SiCl with metal carbonyl anions can be best explained in terms of electrophilic attack by silicon at a coordinated carbonyl group, and this at present provides the most reasonable explanation of the observed anomalies.

To determine the effects of solvent basicity and degree of halogen substitution at silicon on the course of reaction, we have studied the reactions of methylchlorosilanes with $NaCo(CO)_4$ in Et_2O and THF solvents. Preliminary results have been published [9].

Results and discussion

Reactions of $NaCo(CO)_4$ with chlorosilanes in Et_2O

The reaction of Me_3SiCl with $NaCo(CO)_4$ in Et_2O gives moderate (~20%) yields of $Me_3SiCo(CO)_4$ together with $Co_2(CO)_8$ and $Co_4(CO)_{12}$. This system is therefore analogous to that of Berry and MacDiarmid [2] who have shown that $Me_3SiMn(CO)_5$ is formed from Me_3SiCl and $NaMn(CO)_5$ in weakly basic solvents but not in THF.

More complex behaviour was found for Me_2SiCl_2 and $NaCo(CO)_4$ in Et_2O; a mixture of products resulted and these defied separation and characterisation;

The reaction of $MeSiCl_3$ or $SiCl_4$ with $NaCo(CO)_4$ in Et_2O follows a different course. Addition of the chlorosilane gives an immediate white precipitate (NaCl) and the solution turns deep purple over 30 min. In each case good yields of the cluster compounds $R_3SiOCCo_3(CO)_9$ (R_3 = $MeCl_2$ or Cl_3) are formed. The $—CCo_3(CO)_9$ core is well-known [10] and similar siloxy clusters have previously been synthesised by other routes (eqs. 2 and 3).

$$Me_3SiCo(CO)_4 \xrightarrow{THF} Me_3SiOCCo_3(CO)_9 \qquad [5] \qquad (2)$$

$$(CO)_9Co_3CO^-Li^+ \xrightarrow{R_3SiCl} R_3SiOCCo_3(CO)_9 \qquad [11,12] \qquad (3)$$

$$[R = Me, Ph]$$

We have extended the method outlined in eq. 3 to provide confirmation of the products obtained in this study. Thus reaction of $(CO)_9Co_3COLi$ with $MeSiCl_3$ or $SiCl_4$ gave identical products to those obtained from $NaCo(CO)_4$ and the corresponding chlorosilane in Et_2O.

The intermediacy of a silicon—cobalt bonded compound in the formation of the cluster products was considered in the light of work by MacDiarmid et al. (cf. eq. 2) [5]. However in contrast to $Me_3SiCo(CO)_4$ it was found that $Cl_3SiCo(CO)_4$ is stable in ether solvents. After refluxing in THF for 24 h 90% of a sample of $Cl_3SiCo(CO)_3$ was recovered, and in a separate experiment no reaction was observed between this compound and $NaCo(CO)_4$. (This latter observation is of interest in view of the recent synthesis of $(CO)_4CoSiCo_3(CO)_9$ from SiI_4 and $NaCo(CO)_4$ in hexane, in which $I_3SiCo(CO)_4$ is a likely intermediate [13]).

The formation of $R_3SiOCCo_3(CO)_9$ from $MeSiCl_3$ or $SiCl_4$ and $NaCo(CO)_4$ in ether can be explained in terms of Curtis' proposal [4,8] that attack by silicon at a coordinated carbonyl ligand is a favoured process. A suggested reaction pathway is outlined in Scheme 1 for $SiCl_4$.

SCHEME 1

$$Co(CO)_4^- + SiCl_4 \rightarrow [(CO)_3CoC{-}O{-}SiCl_4]^- \rightarrow (CO)_3CoC{-}O{-}SiCl_3 + Cl^-$$

$$3(CO)_3CoC{-}O{-}SiCl_3 \rightarrow (CO)_9Co_3COSiCl_3 + Cl_3SiOSiCl_3\ (?) + \ldots$$

Supporting evidence for this scheme can be found in the literature. Thus aluminium [14], boron [14] and titanium [15] halides (all Lewis acids) react with cobalt carbonyl species to give analogous cluster compounds (eqs. 4, 5).

$$Co_2(CO)_8 + Br_3M \cdot NEt_3 \rightarrow (CO)_9Co_3COMBr_2 \cdot NEt_3 \qquad [14] \qquad (4)$$

$(M = B, Al)$

$$Co_2(CO)_8 + Cp_2TiCl_2 \rightarrow (CO)_9Co_3COTi(Cl)Cp_2 \qquad [15] \qquad (5)$$

For the aluminium example direct evidence has been obtained for the initial coordination of a CO oxygen atom to the metal [16,17]. Silicon halides are also known to be Lewis acids [18,19] with diminishing acidity (towards pyridine) in the order

$$SiCl_4 > MeSiCl_3 > Me_2SiCl_2 > Me_3SiCl \qquad [18]$$

Therefore the results obtained in this study can be rationalised as follows. For $Co(CO)_4^-$ there are two potentially reactive sites; one at the metal centre and the other at a carbonyl ligand. With the stronger Lewis acids $MeSiCl_3$ and $SiCl_4$, nucleophilic attack occurs through a carbonyl oxygen atom to give initial Lewis adducts which rearrange to give the siloxy clusters $R_3SiOCCo_3(CO)_9$ (Scheme 1). However, Me_3SiCl is a weak acid and shows little tendency to form an adduct, so nucleophilic attack by the cobalt atom of $Co(CO)_4^-$ at the silicon centre predominates giving the anticipated product, $Me_3SiCo(CO)_4$. The complexity of the reaction with Me_2SiCl_2 may suggest that this chlorosilane is borderline in acidity and so both types of behaviour are occurring.

The new compounds $MeCl_2SiOCCo_3(CO)_9$ and $Cl_3SiOCCo_3(CO)_9$ have similar properties. They form black crystals which are very soluble in organic solvents to give red-purple solutions, although decomposition occurs in EtOH, and more slowly in THF, to give $Co_4(CO)_{12}$. Both compounds are air-sensitive and thermally decompose on attempted sublimation at 50°C/0.1 Torr. Reaction with water gives $Co_4(CO)_{12}$, in contrast to the recently reported $Cl_3SiCCo_3(CO)_9$ which hydrolyses to give the stable trisilanol $(HO)_3SiCCo_3(CO)_9$ [20].

Reactions of $Co(CO)_4^-$ with chlorosilanes in THF

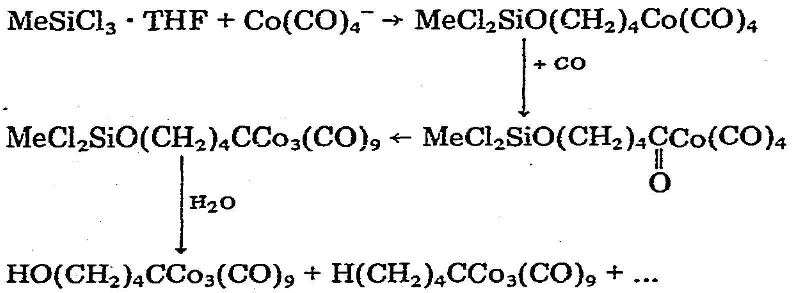
When Me_3SiCl, Me_2SiCl_2 or $MeSiCl_3$ is added to $Co(CO)_4^-$ in THF, reaction occurs over one hour to give a solution with $\nu(CO)$ bands identical to those of $RC(O)Co(CO)_4$ (R = alkyl) in the same solvent. Confirmation that an acyltetracarbonylcobalt derivative is formed was obtained by addition of PPh_3 to give a product with CO bands corresponding to $RC(O)Co(CO)_3PPh_3$ [21]. Attempts to isolate the acyl derivatives failed but indirect evidence (vide infra) suggests that the R group is $Me_nCl_{3-n}SiO(CH_2)_4$ (n = 1, 2, 3 for $MeSiCl_3$, Me_2SiCl_2 or Me_3SiCl respectively).

The THF solutions of $RC(O)Co(CO)_4$ from Me_3SiCl or Me_2SiCl_2 decompose during 24 h to give $Co_4(CO)_{12}$ as the main carbonyl-containing product. In contrast, the solution from $MeSiCl_3$ and $NaCo(CO)_4$ turns purple over 18 h at ambient temperature or over 2 h at gentle reflux. Chromatography of this solution on silica gel gave reasonable yields (~40%) of the cluster compound $HO(CH_2)_4CCo_3(CO)_9$, together with trace amounts of other $R'CCo_3(CO)_9$ clusters including $R' = C_4H_9$, C_4H_9O (two isomers).

To confirm that $RC(O)Co(CO)_4$ derivatives do decompose in THF to give $RCCo_3(CO)_9$ clusters, a THF solution of $EtC(O)Co(CO)_4$ was refluxed for two hours. From the resulting mixture $EtCCo_3(CO)_9$ could be isolated by TLC albeit in low yields (~5%).

The apical substituents of the clusters from the $MeSiCl_3$ reaction have obviou been derived from the solvent and a series of experiments was carried out to determine how THF molecules were incorporated into the product. A reaction sequence which is consistent with the observed results is outlined in Scheme 2.

Scheme 2

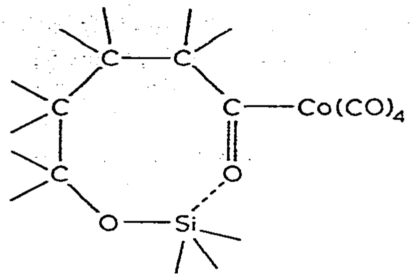


$$\begin{tikzcd}
MeSiCl_3 \cdot THF + Co(CO)_4^- \arrow[r] & MeCl_2SiO(CH_2)_4Co(CO)_4 \arrow[d, "+CO"] \\
MeCl_2SiO(CH_2)_4CCo_3(CO)_9 \arrow[d, "H_2O"] & MeCl_2SiO(CH_2)_4\underset{\underset{O}{\|}}{C}Co(CO)_4 \arrow[l] \\
HO(CH_2)_4CCo_3(CO)_9 + H(CH_2)_4CCo_3(CO)_9 + \ldots &
\end{tikzcd}$$

In THF solution $MeSiCl_3$ is likely to be present as a five- (or six-) coordinate adduct with the solvent [18,19]. Nucleophilic attack by the $Co(CO)_4^-$ occurs at the complexed THF ring to give an alkyl derivative which undergoes carbonyl-insertion, yielding the acyl compound as the initial product. Acyl derivatives of $Co(CO)_4$ are known to be relatively unstable and a variety of isomerisation and elimination processes have been described [21—23]. In particular, thermal decomposition of $RC(O)Co(CO)_4$ in the absence of solvents is reported [23] to follow eq. 6 and it is possible that the acyl compounds derived from Me_3SiCl

$$RC(O)Co(CO)_4 \rightarrow R_2C{=}O + Co_2(CO)_8 + Co_4(CO)_{12} + \ldots \qquad (6)$$

and Me_2SiCl_2 also decompose via this route since an organic oil with $\nu(CO) = 1730\ cm^{-1}$ is obtained. In contrast the acyl intermediate from $MeSiCl_3$ follows a new mode of decomposition in giving $RCCo_3(CO)_9$ clusters in good yields. To account for the effect of the silicon group of $MeCl_2SiO(CH_2)_4C(O)Co(CO)_4$ on the decomposition pathway an interaction between the silicon atom and the acyl oxygen is proposed (see diagram). (Interactions related to this have been encountered in systems pertaining to acyl derivatives of other metal carbonyls [24].) This intramolecular interaction plays a vital role in assisting deoxygenation to the acyl carbon atom and explains why only poor yields of CCo_3



clusters are obtained with $RC(O)Co(CO)_4$ derivatives where similar interactions are likely to be weak ($R = Me_3SiO(CH_2)_4$ or $Me_2ClSiO(CH_2)_4$) or non-existent (R = alkyl). In this context it is interesting to note that alkyltrichlorosilanes form chelated acetylacetonate complexes but the di- and tri-alkyl silicon halides adopt open chain O-silylated structures [25]. That the silicon-assisted deoxygenation process is intra-molecular was shown by the thermal decomposition of $EtC(O)Co(CO)_4$ in THF in the presence of $MeSiCl_3$; yields of $EtCCo_3(CO)_9$ were no different from those obtained in the absence of chlorosilanes.

Other mechanisms leading to acyl derivatives incorporating THF molecules must also be considered. It is known that chlorosilanes cleave THF in the presence of metal salts (Zn^{2+}, Mg^{2+}) [26] and we have found Co^{2+} to be equally effective. Thus refluxing $MeSiCl_3$ and THF in the presence of $CoCl_2$ gave 70% yields of $MeCl_2SiO(CH_2)_4Cl$ and this turn did react with $NaCo(CO)_4$ in THF to give $HO(CH_2)_4CCo_3(CO)_9$ as the main product after hydrolysis. However, the intermediacy of $MeCl_2SiO(CH_2)_4Cl$ in the reaction involving $MeSiCl_3$ can be discounted for two reasons; the Co^{2+} catalysed cleavage of THF proceeds at a negligible rate at room temperature and alkyl chlorides do not alkylate $Co(CO)_4^-$ under the reaction conditions employed [27]. Thus no change was observed in solutions of $NaCo(CO)_4$ in THF containing either $CH_3CH_2CH_2Cl$ or $Me_3SiO(CH_2)_4Cl$ over 12 h. The fact that both $MeSiCl_3$ and $MeCl_2SiO(CH_2)_4Cl$ ultimately yield the same products is apparently a consequence of similar acidity of the silicon centre in both chlorosilanes. Therefore attack by $Co(CO)_4^-$ on $MeCl_2(Cl(CH_2)_4O)Si \cdot THF$ gives initially $Me(Cl)(Cl(CH_2)_4O)SiO(CH_2)_4C(O)Co(CO)_4$ which rearranges as outlined in Scheme 2.

In view of the results obtained in Et_2O, the intermediacy of $MeCl_2SiOCCo_3(CO)_9$ was considered possible in the formation of CCo_3 clusters in THF. However, although this compound slowly decomposes in THF no new CCo_3 compounds were formed; $Co_4(CO)_{12}$ was the main product.

Finally, the reaction of $SiCl_4$ with $NaCo(CO)_4$ in THF gave moderate yields of $Cl_3SiOCCo_3(CO)_9$. This is the same result obtained for reactions in Et_2O and presumably follows the same course. Apparently $SiCl_4$ is a sufficiently strong acid to form a Lewis adduct with $Co(CO)_4^-$ via a carbonyl oxygen (cf. Scheme 1) even in the presence of THF as a competitive base.

Conclusion

A variety of factors determine the course of reactions between chlorosilanes and $Co(CO)_4^-$. The fact that Si—Co bonded compounds are rarely formed can be attributed to alternative reaction pathways. In this respect it appears that the strong affinity of silicon for oxygen favours reactions involving carbonyl ligands of $Co(CO)_4^-$ in contrast to the heavier Group IV congeners where formation of metal—cobalt bonds predominates. Increasing Lewis acidity at the silicon centre enhances this tendency. The use of THF as a solvent for Si—M bond formation via the salt-elimination reaction is to be exercised with care because of the possibility of complicating reactions involving ring cleavage.

Experimental

All reactions were carried out under oxygen-free nitrogen using standard inert-atmosphere techniques. THF and Et_2O were distilled from sodium benzophenone ketyl immediately before use. Solutions of $NaCo(CO)_4$ were obtained by sodium amalgam reduction of $Co_2(CO)_8$ (Pressure Chemical Co.). Chlorosilanes (P.C.R. Chemicals) were redistilled before use. $LiOCCo_3(CO)_9$, $Me_3SiO(CH_2)_4Cl$ and $MeCl_2SiO(CH_2)_4Cl$ were prepared according to literature methods. [12,26]. Infrared spectra were recorded on a Perkin—Elmer Model 180 spectrometer and mass spectra on a Varian CH-7 machine. Identification of products was based mainly on mass spectrometry because of the difficulty in obtaining analytically pure products.

Reaction of $NaCo(CO)_4$ with Me_3SiCl in Et_2O

A solution of $NaCo(CO)_4$ (2 mmol) in Et_2O (12 cm^3) was treated with Me_3SiCl (8 mmol). After 3 h at room temperature the solvent was removed and sublimation of the residue served to separate $Me_3SiCo(CO)_4$ (0.10 g, 20%) from $Co_2(CO)_8$ and $Co_4(CO)_{12}$.

Reaction of $NaCo(CO)_4$ with Me_2SiCl_2 in Et_2O

Me_2SiCl_2 (4 mmol) was added to $NaCo(CO)_4$ (2 mmol) in Et_2O (12 cm^3) and the mixture stirred for 5 h. An infrared spectrum of the resulting solution showed a complex mixture of carbonyl containing products which could not be separated by crystallisation. Attempted chromatography lead to decomposition.

Reaction of $NaCo(CO)_4$ with $MeSiCl_3$ in Et_2O

$MeSiCl_3$ (0.2 g, 1.3 mmol) was added to $NaCo(CO)_4$ (1.6 mmol) in Et_2O (20 cm^3). After 45 min at room temperature volatile components were removed in vacuo and the residue extracted with hexane (15 cm^3). After filtration, the hexane solution was concentrated to ca. 3 cm^3 and cooled to —30°C to give black crystals of $MeCl_2SiOCCo_3(CO)_9$ (0.13 g, 44%) identified by mass spectrometry. ν(CO) 2104w, 2053s, 2039s, 2020w. NMR ($CDCl_3$), 8.62 τ (singlet).

An identical compound was obtained (35% yield) by reaction of $LiOCCo_3(CO)_9$ with $MeSiCl_3$ following the procedure of Fieldhouse et al. [12].

Reaction of $NaCo(CO)_4$ with $SiCl_4$ in Et_2O

Following the method described above, $SiCl_4$ (0.4 g, 2.4 mmol) was reacted with $NaCo(CO)_4$ (2 mmol) in Et_2O (20 cm^3). Recrystallisation from hexane afforded black crystals of $Cl_3SiOCCo_3(CO)_9$ (0.2 g, 52%), ν(CO) 2104w, 2056s, 2040s, 2020w(sh). A mass spectrum gave a weak parent ion and fragments $Cl_2SiOCCo_3(CO)_n^+$ (n = 9—0).

An identical product was obtained from $LiOCCo_3(CO)_9$ and $SiCl_4$.

Reaction of $NaCo(CO)_4$ with $MeSiCl_3$ in THF

A solution of $NaCo(CO)_4$ (3 mmol) in THF (10 cm^3) was treated with $MeSiCl_3$ (0.4 g, 2.7 mmol). After 1 hour a brown solution was formed with $\nu(CO)$ 2104m, 2045s, 2023vs, 2003vs, 1708m (br). After a further 18 h at 25°C (or 2 h at 60°C) a red-purple solution formed. After hydrolysis with saturated NH_4Cl solution the organic layer was separated, dried (Na_2SO_4) and evaporated in vacuo. The residue was chromatographed on silica gel plates, eluting with Et_2O/hexane (1 : 5). The major product ($R_f = 0.2$) was $HO(CH_2)_4CCo_3(CO)_9$ (0.21 g, 40%); $\nu(CO)$ 2099w, 2048s, 2034s, 2015w. The mass spectrum gave all fragments $HO(CH_2)_4CCo_3(CO)_n^+$ (n = 9—0). Other minor products, identified as $RCCo_3(CO)_9$ derivatives by their characteristic colour and IR spectra, were formed. The presence of organic oils together with the low yields made complete identification difficult but derivatives with R = C_4H_9 and C_4H_9O (2 isomers) were indicated by mass spectrometry.

The analogous reaction between $MeCl_2SiO(CH_2)_4Cl$ and $NaCo(CO)_4$ in THF gave a similar range of products.

Reaction of $NaCo(CO)_4$ with Me_3SiCl or Me_2SiCl_2 in THF

The addition of Me_3SiCl or Me_2SiCl_2 (4 mmol) to $NaCo(CO)_4$ (2 mmol) in THF (10 cm^3) gave, after two hours, a brown solution with $\nu(CO)$ 2104w, 2045s, 2023vs, 2003vs, 1708m (br). Further stirring led to decompositions, giving $Co_4(CO)_{12}$ as the only metal carbonyl containing product. An organic oil was also formed, with $\nu(CO)$ 1730s, but this appeared to be a mixture of several components and was not characterised.

Reaction of $NaCo(CO)_4$ with $SiCl_4$ in THF

Addition of $SiCl_4$ (1.6 mmol) to $NaCo(CO)_4$ (2 mmol) in THF (10 cm^3) led, after 30 min, to a red-purple solution. Removal of solvent and recrystallisation of the residue from hexane gave $Cl_3SiOCCo_3(CO)_9$ (0.13 g, 32%), identified by mass and infrared spectroscopy.

Stability of $Cl_3SiCo(CO)_4$ in THF

A solution of $Cl_3SiCo(CO)_4$ (0.3 g) in THF (10 cm^3) was gently refluxed for 24 h. Infrared examination showed no new carbonyl containing products had been formed. Removal of solvent followed by sublimation of the residue gave 90% recovery of starting material.

Stability of $MeCl_2SiOCCo_3(CO)_9$ in THF

A solution of $MeCl_2SiOCCo_3(CO)_9$ (0.2 g) in THF (10 cm^3) was stirred for 12 h by which time all starting material had been consumed. Chromatography of the product gave $Co_4(CO)_{12}$ as the only carbonyl containing product.

Decomposition of $EtC(O)Co(CO)_4$ in THF

A solution of $NaCo(CO)_4$ (2 mmol) in THF (10 cm^3) was cooled to 0°C and EtC(O)Cl (0.28 g, 3 mmol) was added. After one hour an infrared spectrum showed formation of $EtC(O)Co(CO)_4$ to be complete ($\nu(CO)$ 2104m, 2045s, 2023vs, 2003vs, 1702m(br)). The solution was refluxed for 2 h. Solvent was removed in vacuo and a hexane extract of the residue chromatographed on silica-gel plates to give $EtCCo_3(CO)_9$ (identified by mass spectrometry), 0.015 g, 5%, together with $Co_4(CO)_{12}$ as the only other carbonyl-containing product.

Reaction of $Me_3SiO(CH_2)_4Cl$ with $NaCo(CO)_4$ in THF

A solution of $NaCo(CO)_4$ (2 mmol) in THF (10 cm^3) was treated with $Me_3SiO(CH_2)_4Cl$ (0.36 g, 2 mmol). After 8 h at 25°C infrared examination showed undiminished peaks due to $Co(CO)_4^-$ and no indication that alkylation had occurred.

Preparation of $MeCl_2SiO(CH_2)_4Cl$ catalysed by Co^{2+}

A mixture of $MeSiCl_3$ (20 cm^3, 25 g, 0.17 mol) and THF (12 cm^3, 10.7 g, 0.15 mol) and anhydrous $CoCl_2$ (1 g) were heated at 70°C for 8 h. Fractionation of the resulting liquid at 48—50°C/1 Torr gave $MeCl_2SiO(CH_2)_4Cl$ (24 g, 70%) (cf. ref. 26a). Purity was checked by NMR spectroscopy.

Acknowledgements

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